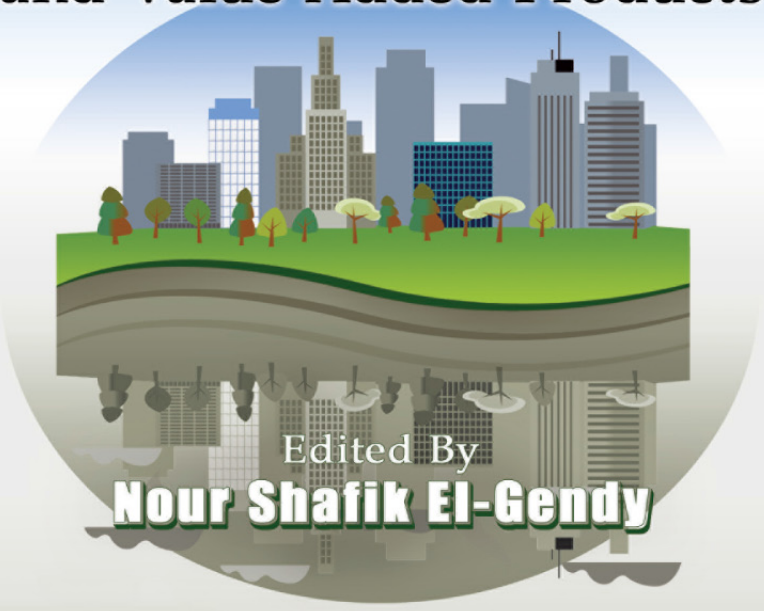
SUSTAINABLE SOLUTIONS FOR ENVIRONMENTAL POLLUTION

VOLUME 1

Waste Management and Value-Added Products



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Nour Shafik El-Gendy

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Sustainable Solutions for Environmental Pollution

Volume 1

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Library of Congress Cataloging-in-Publication Data

ISBN 9781119785354

Cover image: Stockvault.com
Cover design by Russell Richardson

Set in size of 11pt and Minion Pro by Manila Typesetting Company, Makati, Philippines

Printed in the USA

10 9 8 7 6 5 4 3 2 1

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Preface

There is a continuous worldwide growth in population which consequently leads to a proliferation of industrial and agricultural activities and a growth in the annual consumption of energy, food, water and different agricultural crops, as well as an upturn of global warming and the produced solid wastes. These come with the depletion of fossil fuel reserves, in addition to the worldwide massive water scarcity problem and issues related to climate change, besides the enormous air, soil and water pollution. Further, solid waste management (SWM) is considered nowadays as a critical public issue because of the negative impact of such wastes on the environment, climate, ecosystem, biodiversity and human health.

The main concern worldwide nowadays is how to achieve the seventeen goals of sustainable development (SDGs) for: (1) attaining water and food security for all, (2) saving life on land and under water, (3) assuring the presence of clean and renewable energy, (4) overcoming poverty, (5) securing decent work as much as it could be for all, (6) diminishing the problem of climate change, (7) guaranteeing growth in innovation, the economy and different industrial sectors, (8) increasing awareness of the concept of a circular economy for ensuring responsible sustainable consumption and production patterns.

This book reports some of the global researchers' activities on the nexus of biofuels, biorefineries, sustainable energy, environment, climate change, water, health, and the economy. It focuses on the occurred positive impacts on air, water, land use, food, society, and economy via the valorization of different available resources into sustainable biofuels and bio-products.

The chapters are: Chapter 1-An Overview of Electro-Fermentation as a Platform for Future Biorefineries; Chapter 2-Biodiesel Sustainability: Challenges and Perspectives; Chapter 3-Multidisciplinary Sides of Environmental Engineering and Sustainability; Chapter 4-Biofuels; Chapter 5-Sustainable Valorization of Waste Cooking Oil into Biofuels and Green Chemicals: Recent Trends, Opportunities and Challenges; Chapter 6-Waste Valorization: Physical, Chemical, and Biological Routes;

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Chapter 7-Electrocoagulation Process in the Treatment of Landfill Leachate; Chapter 8-Sustainable Solutions for Environmental Pollutants from Solid Waste Landfills; Chapter 9-Progress on Ionic Liquid Pre-Treatment for Lignocellulosic Biomass Valorization into Biofuels and Bio-Products; Chapter 10-Septage Characterization and Sustainable Fecal Sludge Management in Rural Nablus, Palestine; Chapter 11-Lipase Catalyzed Reactions: A Promising Approach for Clean Synthesis of Oleochemicals; Chapter 12-Seaweeds for Sustainable Development.

Thus, this book addresses the different multidisciplinary sides of environmental and sustainable development engineering which is a subsystem of sustainable development using system theory and its related integrated system approach. It provides a state-of-the-art presentation on how to reach a sustainable and clean environment via waste management and valorization of different readily available resources into biofuels, biorefineries and different value-added products. It discusses the challenges and opportunities for enlarging the world markets of biofuels, biorefineries and bio-products and how countries can set up policies to decrease fossil fuel dependency and petro-based synthesis of commodity chemicals and move steadily towards the bio-based economy. The utilization of renewable resources such as seaweeds and waste biomass is often considered as an attractive candidate for biofuels and different bioproducts. However, limitations regarding the robustness of process and selectivity of target products are often considered bottlenecks to their sustainable commercialization. This book discusses such bottlenecks and suggests many feasible applicable techniques to increase the yield of the targeted bioproducts. For achieving the circular economy with the concept of zero-wastes, this book discusses the production of bioethanol from different lignocellulosic wastes and seaweeds and also the production of biodiesel from waste oils and fats using sustainable heterogeneous catalysts. Further, it explains how to reach for a feasible transesterification process that produces high yield of qualified biodiesel to be successfully used as alternative and/or complementary for the conventional petro-diesel without affecting the engine performance. The book also debates how the applications of heterogeneous catalysts valorized from different readily available natural resources would be very beneficial in the production of biodiesel and bioglycerol. It also states the applicability of lipases in production of biodiesel and oleochemicals. The use of ionic liquids (ILs) in the lignocellulosic wastes pretreatment for further use in bioethanol and other biorefineries production has gained considerable attention in this book.

It also clarifies how solid waste management can in general open a new sustainable revolution in different sectors which would indeed lead

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to the successful achievement of the three pillars of sustainability, social, environment and economic. Special attention is given to valorization as a technical route adopted for the recycling of waste into desirable products having non-toxic economic worth. Moreover, the valorization of different available bio-wastes into different biofuels and value-added products, for example, glycerol, oleochemicals, bioplastics, biopolymers, biofertilizers, animal feed, etc., with the concept of reaching zero-waste is discussed from the perspective of achieving the seventeen goals of sustainability, and overcoming the problems of water scarcity, waste management and climate change.

One of the most important sectors this book covers is the main environmental problems related to landfills including soil, water and air contamination, and it also highlights and discusses some of the sustainable solutions and management for such problems including landfill design and location, leachate management and treatment, gas and emission control. Moreover, the effect of unsuitable locations of landfills on the environment is discussed and evaluated. This book also goes through optimizing the treatment of landfill leachate for minimizing its adverse impacts on the natural ecosystem as it is an urgent concern with the increased municipal solid wastes. It emphasizes on the promising electrocoagulation process for its outstanding ability in decontaminating leachate pollution in an economic, viabile, and green approach. A case study for septage characterization and sustainable fecal sludge management has been also reported in this book.

The multidisciplinary approach discussed in this book extends the different scientific and engineering disciplines to reach all other disciplines including economics, politics and other social sciences. Thus, it is time for engineers, scientists, medical doctors, economists, politicians, military officers and specialists, etc., to join forces in multidisciplinary research and development projects to achieve sustainability for better, stable, peaceful, non-sectarian, prosperous and more clean and sustainable societies.

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1

An Overview of Electro-Fermentation as a Platform for Future Biorefineries

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Abstract

Many countries have set up policies to decrease fossil fuel dependency and petro-based synthesis of commodity chemicals. Fermentative biofuels and bioresource recovery processes are expected to assist considerably in this context of sustainable transition to a bio-based economy. The utilization of renewable resources such as waste biomass is often considered an attractive feature of fermentative bioprocesses. However, limitations regarding the robustness of process and selectivity of target products are often considered bottlenecks to their sustainable commercialization. Particularly, in conventional fermentation processes, microorganisms produce undesired by-products to attain intracellular redox balance, which leads to a low yield of target products. Recently, electro-fermentation has emerged as an innovative approach for changing metabolic pathways of fermentative microorganisms towards target products with higher yields and productivities by changing intracellular redox potential. Lab-scale EF studies have successfully demonstrated superior performance over conventional fermentation to produce a wide variety of biofuels and commodity chemicals. This book chapter provides an overview of fundamental and applied aspects of various value-added products synthesis with the EF process and identifies research gaps for future development.

***Keywords*:** Electro-fermentation, electro-selective fermentation, fermentation, value-added products, biofuel, biorefinery

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Nour Shafik El-Gendy (ed.) Sustainable Solutions for Environmental Pollution Volume 1: Waste Management and Value-Added Products, (1–40) © 2021 Scrivener Publishing LLC

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1.1 Introduction

Microbial electrochemical cell (MXC) is a unique type of bioreactor, which integrates biological processes (e.g., utilizing electroactive bacteria as biocatalyst) with electrochemistry (e.g., introducing electrodes, potentials) to convert the chemical energy in organic matter into bioenergy. To differentiate the various types of MXCs, different names have been assigned based on the products or their provided services. Over the decades, the MXCs were largely focused to generate bio-electricity in microbial fuel cells (MFCs) (Logan, 2008). More recently, MXCs were engineered to produce various biogas, such as bio-hydrogen in microbial electrolysis cell (MEC) (Logan *et al.*, 2008; Wagner *et al.*, 2009) and bio-methane in microbial electrolysis cell assisted anaerobic digester (MEC-AD) (Huang *et al.*, 2020; Zakaria and Dhar, 2019). Nonetheless, the MXCs were also implemented for many other applications, such as water desalination in microbial desalination cell (MDC) (Al-Mamun *et al.*, 2018; Jafary *et al.*, 2020), nutrient recovery (Barua *et al.*, 2019; Qin *et al.*, 2016; Zou *et al.*, 2017), CO_2-reduction-to-value-added-products in microbial electrosynthesis (MES) (Lovley and Nevin, 2013; Rabaey and Rozendal, 2010; Zhang and Angelidaki, 2014) and production of chemicals, such as hydrogen peroxide in microbial peroxide producing cells (MPPCs) (Chung *et al.*, 2020b; Rozendal *et al.*, 2009). Due to the extensive studies since the early 2000s, several studies have been dedicated to scaling-up the MXCs (Dhar *et al.*, 2016; Heidrich *et al.*, 2014; Hiegemann *et al.*, 2016; Liang *et al.*, 2018; Sim *et al.*, 2018). However, the main bottleneck of the aforementioned MXC applications was the requirement of high energy input or output, whether the electrons are the main driving force in MECs, MDCs, MES, and MPPCs, or they are the desired product (e.g., in MFCs). Often, challenges in achieving high current density from MXCs was the main argument against further development and scaling-up (Feng *et al.*, 2014; Heidrich *et al.*, 2014; Sim *et al.*, 2018; Zakaria and Dhar, 2019). On the other hand, the MXCs have gained interest for further development when utilized as a biosensor, where they mainly focus on changes in electrical energy (e.g., signal output), not necessarily required to produce high electrical energy output (Chung *et al.*, 2020a; Do *et al.*, 2020; Jiang *et al.*, 2018). Hence, proposing a new application of MXC focusing on using low energy input can also be a novel means.

Fermentation process is one of the bioprocesses that converts complex organics to various types of soluble molecules, such as alcohols and carboxylates, and sometimes, along with some energy-rich biogases (e.g., hydrogen and methane) (Dhar *et al.*, 2015; Elbeshbishy *et al.*, 2017; Ghimire *et al.*, 2015; Guo *et al.*, 2010; Moscoviz *et al.*, 2016). The process of fermentation is carried

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out by a large diversity of microorganisms (e.g., pure or mixed cultures), which can utilize different types of substrates and organic wastes (Ghimire *et al*., 2015; Guo *et al*., 2010). There are many different environmental parameters, such as the inoculum type, medium composition, pH, temperature, hydraulic retention time, and accumulation of bi- and end-products that can affect alter the fermentative pathways (Moscoviz *et al*., 2016). Despite the extensive studies conducted for controlling of aforementioned environmental parameters for the fermentation processes, targeting a specific end product is still challenging, especially concerning mixed cultures (Moscoviz *et al*., 2016). Hence, instead, engineering the oxidation-reduction potential (ORP) of the fermentation medium (e.g., also known as the extracellular ORP) can be an alternative to control the microbial metabolism to generate a target product (Wong *et al*., 2014; Zhu *et al*., 2014). The extracellular ORP corresponds to the activity of electrons in the medium (e.g., in this case, substrates or organic wastes during fermentation), where it is mainly influenced by the chemical composition of the medium, the degree of reduction of the metabolites produced by fermentation, and the temperature (Moscoviz *et al*., 2016). Particularly, the extracellular ORP is critical as it substantially impacts the intracellular ORP via NADH and NAD^+ (e.g., reduced/oxidized form of NAD) balance (Liu *et al*., 2013). The intracellular ORP represents the redox state inside a cell, which can control enzyme synthesis and gene expression; hence, it ultimately affects the entire metabolic process and it can modify the metabolic pathways during fermentation (Liu *et al*., 2013). Previously, studies have successfully demonstrated the chemical control of using extracellular ORP to enhance the production of succinate (Chen *et al*., 2012; Li *et al*., 2010) and 1,3-propanediol (Du *et al*., 2006) during fermentation, in which, the MXCs can also potentially be implemented to modify the extracellular ORP via supplying or collecting electrical energy (e.g., electrons, current) using electrodes. This process of combining the fermentation process with an MXC was named "electro-fermentation".

Electro-fermentation (EF) is a unique process, which introduces electrical energy to microbial fermentative metabolism (Moscoviz *et al*., 2016). The electrical energy in the EF system can control and stabilize the fermentation process, overcoming the metabolic limitations of balanced reactions (Moscoviz *et al*., 2016). Nonetheless, the EF system requires lower electrical energy compared with other aforementioned applications of MXCs, where high electrical energy (e.g., high current densities) can result in reduced performance or system failure due to the inhibition of fermentative bacteria (Lai and Lan, 2020). More importantly, even small applied current densities can affect both extracellular and intracellular ORP (e.g., overall biological regulation) through the changes in NADH/NAD+ ratio, which can substantially affect the final

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fermentation products (Moscoviz *et al*., 2016; Speers *et al*., 2014; Sturm-Richter *et al*., 2015; Zhou *et al*., 2015). In this context, the electrical energy (e.g., current) in the EF system is not the product of interest nor the main driving energy source, but it is a trigger that allows the fermentation to occur under unbalanced conditions (Moscoviz *et al*., 2016). Furthermore, the features of EF can significantly overcome the problems of the conventional fermentation process. For instance, using electroactive bacteria (e.g., capable of converting volatile fatty acids to electrons, protons, and carbon dioxide) and electrodes in the EF system can alleviate the challenges, such as accumulation of short-chain volatile fatty acids (SCVFAs) (Lai *et al*., 2016b) and toxicants (e.g., nitrite, if nitrate is used as an electron acceptor) (Takeno *et al*., 2007), which are experienced by the conventional fermentation. With such advantages, EF systems

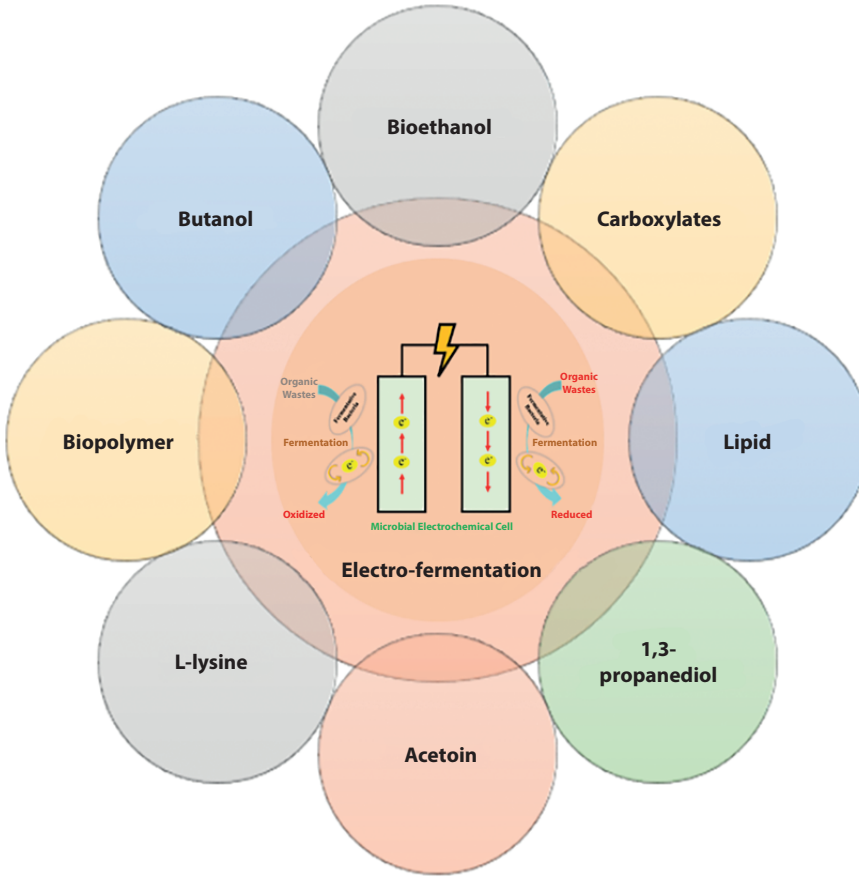

Figure 1.1 Overview of various value-added products produced via electro-fermentation.

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present an emerging platform for future biorefinery for the synthesis of various value-added products from organic feedstocks. To date, the EF systems have been implemented for enhancing various biofuels and chemical productions, such as carboxylates, alcohols, solvents, lipids, acetoin, biopolymer, and many more (see Figure 1.1) (Bursac *et al*., 2017; Choi *et al*., 2014; Jiang *et al*., 2020; Lai and Lan, 2020; Liu *et al*., 2019; Mostafazadeh *et al*., 2016; Vassilev *et al*., 2018; Villano *et al*., 2017). This book chapter presents fundamental mechanisms, applied and scientific aspects of EF to produce different value-added products, and finally, perspectives for future development.

1.2 Fundamental Mechanisms

A system for EF consists of an anode and a cathode, and the chambers can be separated by an ion-exchange membrane (see Figure 1.2). The use of a membrane is optional; used when preventing product crossover is critical. Briefly describing the entire process, the EF comprises the fermentation of an energy-rich substrate, where the solid electrodes present in the EF system serves as inexhaustible electron donors or acceptors that does not limit the entire fermentation process (Jiang *et al*., 2019; Moscoviz *et al*., 2016). The EF system is generally connected with power sources (e.g., power supply, potentiostat, etc.), where the externally poised potential/voltage is utilized to regulate the fermentation pathways for pure and mixed cultures (Jiang *et al*., 2019; Moscoviz *et al*., 2016; Schievano *et al*., 2016). Briefly speaking, the electrons are transferred between the fermentation medium and the bacteria (e.g., fermentative and/or electroactive), and between the bacteria and the electrodes (e.g., anode or cathode). The electron transfer process between bacteria and electrodes are known as extracellular electron transfer (EET). Depending on the type of fermentation, the EET can be outward (during anodic EF) and inward (during cathodic EF) (Gong *et al*., 2020; Kracke *et al*., 2018). Although EET mechanisms have not been studied exclusively for various EF processes, literature suggests that bi-directional EET can occur via multiple mechanisms, including direct electron transport via extracellular redox co-factors (e.g., cytochromes, and other redox proteins), nanowires, and mediators (Gong *et al*., 2020; Kracke *et al*., 2018).

Depending on the target product (e.g., final product more oxidized vs. reduced form than the initial substrate), the EF can be classified into two main types: (i) anodic electro-fermentation (AEF); and (ii) cathodic electro-fermentation (CEF). When the final product of EF is more oxidized form than the substrate (e.g., ethanol from glycerol), the working electrode acts as an anode and is used to dissipate the excess electrons, known as the

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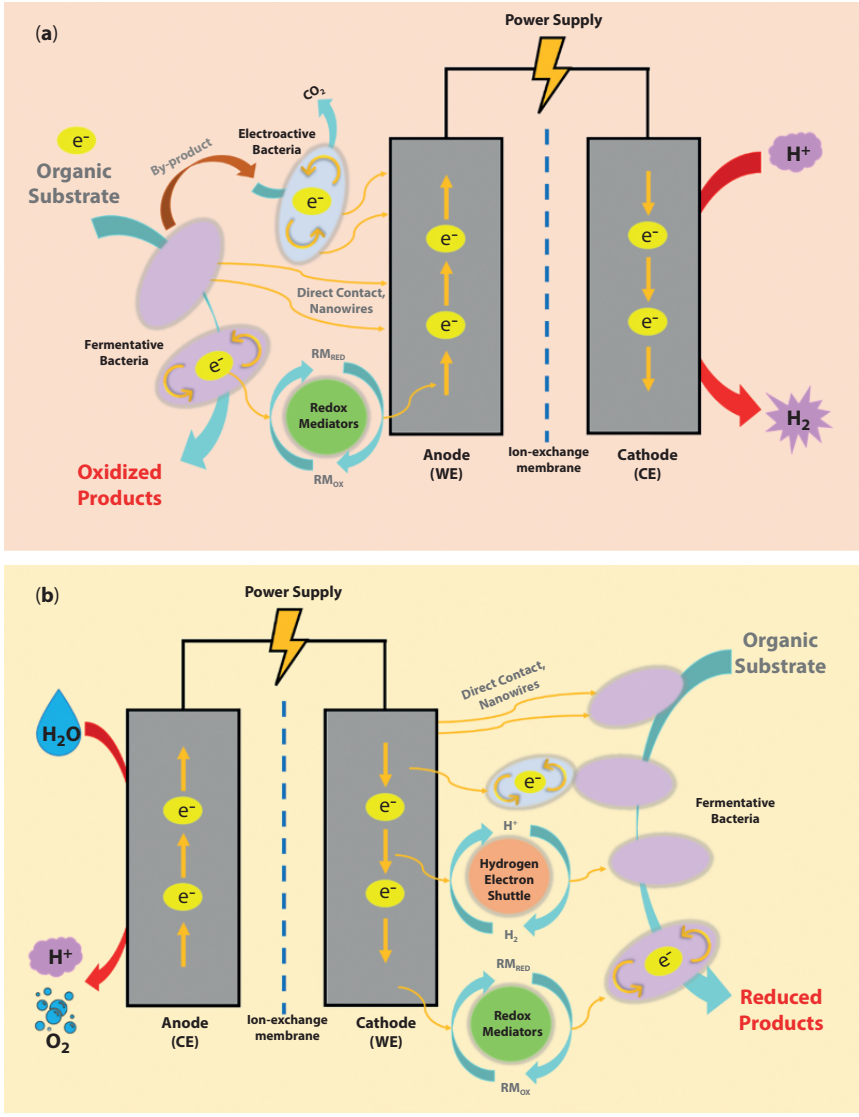

Figure 1.2 Mechanisms of electro-fermentation: (a) anodic electro-fermentation; (b) cathodic electro-fermentation.

AEF. On the other hand, if the final product is in a more reduced form than the substrate (e.g., butanol from glucose), then the working electrode acts as an electron donor, known as the CEF. The electron sinks during AEF are known to synthesize more adenisine triphospates (ATPs) through creating a proton gradient, while the electron sources during CEF have impacts on

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the generation of more reduced redox cofactors, such as NADH (Kracke and Krömer, 2014). Hence, both AEF and CEF can significantly enhance the entire fermentation performance (e.g., product selectivity, production rate and yield) (Xafenias *et al*., 2017). Detail descriptions of underlying mechanisms or EF mechanisms can be found elsewhere (Gong *et al*., 2020; Jiang *et al*., 2019; Moscoviz *et al*., 2016).

As discussed earlier, in most cases, the reactions and electron transfers associated with EF are usually performed via syntrophic interactions between the fermentative bacteria and electroactive bacteria (Jiang *et al*., 2019; Moscoviz *et al*., 2016). However, sometimes, none of the fermentative bacteria are electroactive (e.g., *Clostridium* species), in which, the redox mediators, such as neutral red (Choi *et al*., 2012), methyl viologen (Kim and Kim, 1988), or ferricyanide (Xafenias *et al*., 2017) are required during the fermentation to impact the extracellular ORP (Choi *et al*., 2012; Kim and Kim, 1988; Sturm-Richter *et al*., 2015). When the redox mediators are introduced, they can first, be oxidized or reduced by the fermentative bacteria, then they are recycled or recovered electrochemically by the anode or cathode electrodes (Moscoviz *et al*., 2016). In this context, the redox mediators are used as electron shuttles, and this process is known as the mediated electron transfer (Gong *et al*., 2020; Rabaey and Rozendal, 2010; Thrash and Coates, 2008). Furthermore, other studies demonstrated another way to add a redox mediator in CEF, such as using produced H_2 at the cathode that can be further used as a one-way electron shuttle (Gong *et al*., 2020; Xafenias *et al*., 2015; Zhou *et al*., 2013; Zhou *et al*., 2015).

On the other hand, metabolically engineered fermentative bacterial strains are another feasible option, for instance, by adding the property of electroactivity (Moscoviz *et al*., 2016). This approach has been confirmed by adopting the strains (e.g., *c*-type cytochromes CymA, MtrA, STC) from electroactive bacteria (*Shewanella oneidensis*) to fermentative bacteria (*Escherichia coli*), where the electron transfer process can be greatly improved (e.g., by 183%) (Sturm-Richter *et al*., 2015). Alternatively, electroactive bacterial species (e.g., *Shewanella oneidensis*) can also be engineered to utilize a variety range of substrates and organic wastes to further aid the whole EF processes (Flynn *et al*., 2010).

1.3 Value-Added Products from Electro-Fermentation

To date, electro-fermentation has been investigated for a wide variety of value-added products, including carboxylates, alcohols, biopolymers, and

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Table 1.1 Summary of electro-fermentation and electro-selective fermentation for value-added bioproducts.

Product	Feedstock	Inoculum	System configuration	Total working volume (L)	Temperature (°C)/ initial pH	Applied voltage/ potential	Working electrode	Reference
Butanol	Glucose	*C. pasteurianum*	Dual chamber	900	37/6.7	0-2.6 V	Cathode	(Mostafazadeh *et al.*, 2016)
Butanol	Glucose	*Clostridium pasteurianum* DSM 525	Dual chamber	900	37/6.5	+0.045 V vs. SHE	Cathode	(Choi *et al.*, 2014)
Ethanol	Glycerol	*Clostridium cellobioparum*, + *G. sulfurreducens*	Dual chamber	190	30/6	0.24 V vs. Ag/AgCl	Anode	(Speers *et al.*, 2014)
Ethanol	Glycerol	*Escherichia coli*	Dual chamber	50	37/7.4	−44 mV vs. SCE	Anode	(Sturm-Richter *et al.*, 2015)
Ethanol	Cellobiose	*G. sulfurreducens*+ *Cellulomonas uda*	Single chamber	1000	30/6.97	0.24 V vs. Ag/AgCl	Anode	(Awate *et al.*, 2017)
Ethanol	Food waste	Mixed culture	Single chamber	400	30/6.8	-	-	(Chandrasekhar *et al.*, 2015)
Acetone-Butanol-Ethanol (ABE)	Glucose	*C. acetobutylicum*	Dual chamber	240	37/6.8	-600 mV vs. Ag/AgCl	Anode	(Engel *et al.*, 2019)
1,3-propanediol	Glycerol	Mixed-culture + *G. sulfurreducens* pre-colonized cathode.	Dual chamber	900	37/7	-900 mV vs. SCE	Cathode	(Moscoviz *et al.*, 2018)

(*Continued*)

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Table 1.1 Summary of electro-fermentation and electro-selective fermentation for value-added bioproducts. (*Continued*)

Product	Feedstock	Inoculum	System configuration	Total working volume (L)	Temperature (°C)/ initial pH	Applied voltage/ potential	Working electrode	Reference
1,3-propanediol	Glycerol	Mixed culture	Dual chamber	520	21/6.9	−0.80 V to −1.10 V vs. SHE	Cathode	(Xafenias *et al.*, 2015)
1,3-propanediol	Glycerol	*Clostridium pasteurianum* DSM 525	Dual chamber	900	37/6.5	+0.045 V vs. SHE	Cathode	(Choi *et al.*, 2014)
Butyric acid	Glucose	Mixed culture	Dual chamber	540	25/5.5	-700 mV vs. SHE	Cathode	(Paiano *et al.*, 2019)
3-hydroxypropionic acid	Glycerol	Recombinant *Klebsiella pneumoniae* L17	Dual chamber	620	37/6	+0.5 V vs. Ag/AgCl	Anode	(Kim *et al.*, 2017)
Mixed VFAs	Off gases from fermentation (CO_2+H_2)	Mixed culture acclimatized homoacetogens	Dual chamber	400	37/6.5	-1.0 V vs. SHE	Cathode	(Zhou *et al.*, 2019)
Caproate	Ethanol, acetate	Mixed culture	Dual chamber	240	37/7.2	−0.8 V and −1.1 V vs. Ag/AgCl	Cathode	(Jiang *et al.*, 2020)

(*Continued*)

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Table 1.1 Summary of electro-fermentation and electro-selective fermentation for value-added bioproducts. (*Continued*)

Product	Feedstock	Inoculum	System configuration	Total working volume (L)	Temperature (°C)/ initial pH	Applied voltage/ potential	Working electrode	Reference
Iso-butyrate	Glucose, ethanol, and acetate	Mixed culture	Dual chamber	540	-/5.6	-700 mV vs. SHE	Cathode	(Villano *et al.*, 2017)
Lipid	Microalgae biomass	Scenedesmus acutus	Dual chamber	340	30/7.5	-0.3 V vs. Ag/AgCl	Anode	(Liu *et al.*, 2019)
Lipid	Microalgae biomass	Scenedesmus acutus	Dual chamber	200	25/7.0	-0.3 V vs. Ag/AgCl	Anode	(Liu *et al.*, 2020c)
Lipid	Microalgae biomass	Scenedesmus acutus	Dual chamber	200	-/-	-	Anode	(Liu *et al.*, 2020b)
Acetoin	Lactate	*Shewanella oneidensis*	-	270	-/-	0 mV vs. NHE	Anode	(Bursac *et al.*, 2017)
Acetoin	Glucose	Escherichia coli	Dual chamber	23	/-/	0.2 mV vs. NHE	-	(Förster *et al.*, 2017)
Polyhydroxybutyrate (PHB)	Glycerol	*Ralstonia eutropha* H16	Single chamber	500	-/-	10 mA	Anode	(Lai & Lan, 2020)
L-lysine	Glucose	Corynebacterium glutamicum	Dual chamber	360	20/7.0	-1.25 V	Cathode	(Xafenias *et al.*, 2017)
L-lysine	Glucose	Corynebacterium glutamicum	Dual chamber	350	30/7.2	0.697 V vs. SHE	Anode	(Vassilev *et al.*, 2018)

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other platform chemicals (see Table 1.1). This section reviews the studies related to EF for producing different value-added products.

1.3.1 Carboxylates

Carboxylates (organic acids having a carboxyl group) are primarily categorized as (1) short-chain carboxylates, containing 2–5 carbon atoms, such as acetate, propionate, butyrate, valerate, and (2) medium-chain carboxylates, containing 6–12 carbon atoms, such as caproate, heptanoate, caprylate (Nzeteu *et al*., 2018). They can be used as valuable platform chemicals and as precursors for the synthesis of a wide variety of marketable products, including fertilizers, pharmaceuticals, polymers, and personal care products (Mohan *et al*., 2016). The synthesis of these chemicals via microbial fermentation of organic waste and waste biomass provides a biorefinery framework for sustainable waste management for a greener future. However, a high-rate and robust fermentation processes must be achieved to ensure the same and lower prices of these chemicals, as compared to their petroleum-based production pathways. Recent studies have shown that EF could be a potential approach to achieve this goal.

1.3.1.1 Short-Chain Carboxylates

Various short-chain carboxylates, such as acetate, propionate, butyrate, etc., can be produced via microbial fermentation of organic feedstocks, including waste biomass. The acidogenic fermentation of complex organic substrates with mixed consortia can produce a mixture of various short-chain carboxylates (also called volatile fatty acids) in the fermentation broth (Paiano *et al*., 2019). These short-chain carboxylates can be either extracted or incorporated within other bioprocesses. However, a stand-alone acidogenic fermentation process is yet to be developed for industrial-scale synthesis of short-chain carboxylates (Paiano *et al*., 2019). Over the past few decades, significant research efforts have been dedicated towards developing strategies for long-term operation of acidogenic fermentation, optimization of process parameters (e.g., retention time, pH, temperature, substrate concentration, etc.), tuning the product spectrum (i.e., composition of carboxylates) (Arslan *et al*., 2016; Paiano *et al*., 2019).

Recently, EF has been investigated for various short-chain carboxylates production (see Table 1.1). These studies showed promising results in enhancing the yield and productivity of short-chain carboxylates with pure and mixed-culture. For example, Villano *et al*. (2017) studied cathodic EF of single and mixtures of substrates (glucose, ethanol, and acetate)

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with undefined mixed culture. Their results showed an applied potential of -700 mV vs. SHE could increase iso-butyrate production over the control (open-circuit reactor) by 20-fold (0.43 vs. 0.02 mol/mol glucose) for a mixture of glucose, ethanol, and acetate. Interestingly, iso-butyrate yields were quite comparable for both reactors when operated with glucose as a sole substrate and a combination of glucose plus ethanol or glucose plus ethanol. Thus, their results suggested that in the presence of applied potential and mixture of substrates could stimulate the growth of iso-butyrate producing microbial population. Although no exogenous redox mediator was provided in the fermenter, cyclic voltammetry (CV) of microbial culture showed a reduction peak at -700 mV vs. SHE (same as operating working electrode potential of EF system). Thus, the authors concluded that applied potential altered the redox status of the cells by shifting intracellular NADH/NAD^+ ratio, which subsequently redirected their metabolic pathway towards iso-butyrate production. Recently, another study by Paiano

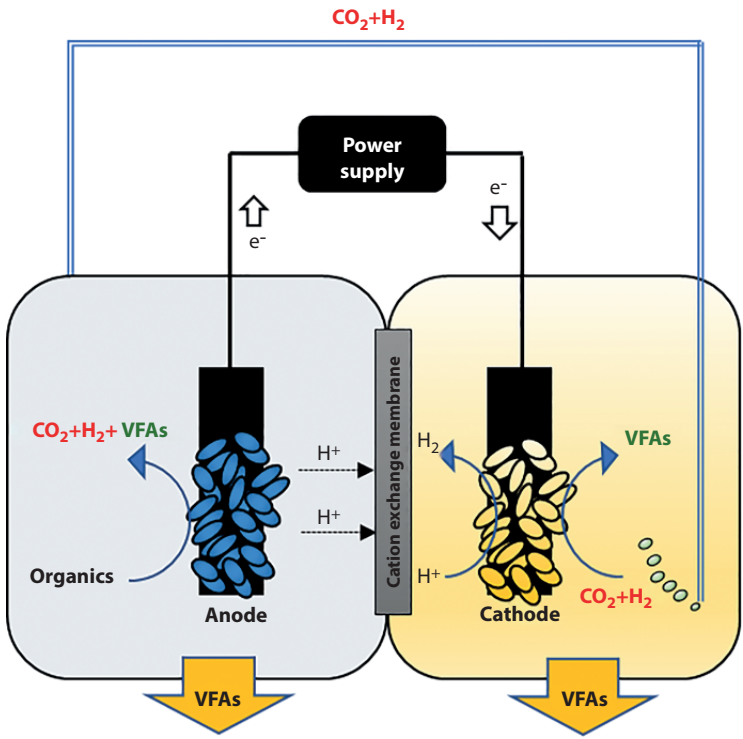

Figure 1.3 A conceptual schematic showing combined anodic acidogenic EF coupled with cathodic EF of off-gases produced during anodic EF. The figure drawn with modification after Zhou *et al.* (2019).

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et al. (2019) also reported a 4-fold higher n-butyrate yield with unmediated mixed-culture cathodic EF at an applied potential of -700 mV vs. SHE. The authors found that iso-butyrate yield could reach up to 0.6 mol/mol glucose when the system was operated with glucose along with its fermentation products. Furthermore, the authors performed mediated EF tests using Neutral Red and AQDS as exogenous mediators. Only the n-isomer of butyrate was produced in the presence of these mediators, suggesting mediators could introduce a high selectivity towards specific compounds.

Recently, a study by Zhou *et al.* (2019) combined anodic acidogenic EF of glucose coupled with cathodic EF of off-gases produced during anodic EF to improve the yield of mixed volatile fatty acids (see Figure 1.3). Their results suggested that the conversion of off-gases (mainly CO_2+H_2) to mixed volatile fatty acids on the cathode enriched with homoacetogens could contribute to ~14% of the overall VFAs recovery from the integrated process. to improve the product and carbon conversion. Thus, the development of such engineering strategies could further improve product yield from EF.

1.3.1.2 Medium-Chain Carboxylates

Due to low values of short-chain carboxylates, there has been significant interest in upgrading short-chain carboxylates to high-value chemicals, such as medium-chain carboxylates (C6-C12; caproate, heptanoate, caprylate, etc.). Particularly, chain elongation has emerged as an innovative approach for manipulating carbon chain length of the products. The biological upgrading of short-chain carboxylates (e.g., acetate, propionate, butyrate) and alcohols (e.g., ethanol) via chain elongation can be used to synthesize medium-chain carboxylates. Chain elongation can be defined as an anaerobic open-culture secondary fermentation process that converts short-chain volatile fatty acids and an electron donor into medium-chain carboxylates (Angenent *et al.*, 2016). The chain elongating microbes, such as *Clostridium kluyveri* can use the reverse β-oxidation pathway to convert short-chain volatile fatty acids to medium-chain carboxylates with ethanol as an electron donor (Roghair *et al.*, 2018). For every five chain elongation reactions, one additional mole of ethanol is oxidized into acetate (Roghair *et al.*, 2018; Seedorf *et al.*, 2008).

$$5C_xH_{2x-1}O_2^- + 6C_2H_6O \rightarrow 5C_{x+2}H_{2x+3}O_2^- + C_2H_3O_2^- + 4H_2O + H^+ + 2H_2$$

Among various medium-chain carboxylates, caproate (C6) has received increasing interest due to its application as a precursor for aviation fuels and various commodity chemicals (Roghair *et al.*, 2018). Jiang *et al.* (2020)

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studied the impact of cathodic EF on the mixed culture chain elongation for caproate production from acetate+ethanol. Integrating EF with the chain elongation process could increase the caproate specificity by ~28% with a fresh carbon felt cathode compared to a control reactor (open circuit without electrodes). However, EF with an acclimated cathode failed to increase the caproate specificity; caproate specificity was highly varied with the substrate concentrations. Thus, their results suggested a direct interaction between chain elongating microbes and the fresh electrode. Overall, their results suggested that deploying EF can provide an excellent opportunity to tune the chain elongation process for achieving higher efficiency.

1.3.2 Bioethanol

Over the past few decades, there has been a growing interest worldwide to cut transport emissions. Given the rapidly increasing demand for transport fuels, many countries worldwide are now investing in alternative fuels from bio-sources. At present, ethanol (E10, 10% ethanol mixed with 90% gasoline) is the most widely used transport biofuel with potential as a valuable gasoline replacement to reduce transport emissions (Daylan and Ciliz, 2016). Hence, over the last decade, the global bioethanol market has seen rapid growth. Currently, most bioethanol is produced through the fermentation of corn grain using industrial yeast strains (Gomez-Flores *et al*., 2018). However, pH imbalances introduced by the formation of unwanted metabolites and subsequent inhibition, batch-to-batch inconsistency, decreasing product yield, and product quality have been identified as major bottlenecks in ethanol fermentation complex feedstocks (Awate *et al*., 2017). Anaerobic fermentation of glucose may produce a wide variety of by-products, including formate, acetoin, glycerol, acetate, and lactate (Awate *et al*., 2017; Speers *et al*., 2014). To address these challenges, genetically modified microorganisms have been implemented to redirect the fermentation pathways towards the target product (i.e., ethanol) (Awate *et al*., 2017). Recently, a few studies investigated EF as a strategy for alleviating these bottlenecks in fermentative ethanol production from different complex feedstocks, including glycerol, food waste, etc. (Table 1.1).

Speers *et al*. (2014) studied anodic EF of glycerol with a customized co-culture of electro-active *Geobacter sulfurreducens* and glycerol-fermenting *Clostridium cellobioparum*. For industrially relevant loadings of glycerol, the system was able to provide ethanol concentration up to 10 g/L with 90% yield (glycerol-to-ethanol). In their dual-chamber system, anodic *Geobacter sulfurreducens* played a key role in this process by utilizing by-products of glycerol fermentation for the current generation.

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The electrons transferred to the anode were utilized for electrochemical hydrogen production on the cathode, which could provide an added-value-product from the process.

In another study, Awate *et al.* (2017) investigated EF of cellobiose with a bioanode comprised of cellulose-degrading fermentative bacteria

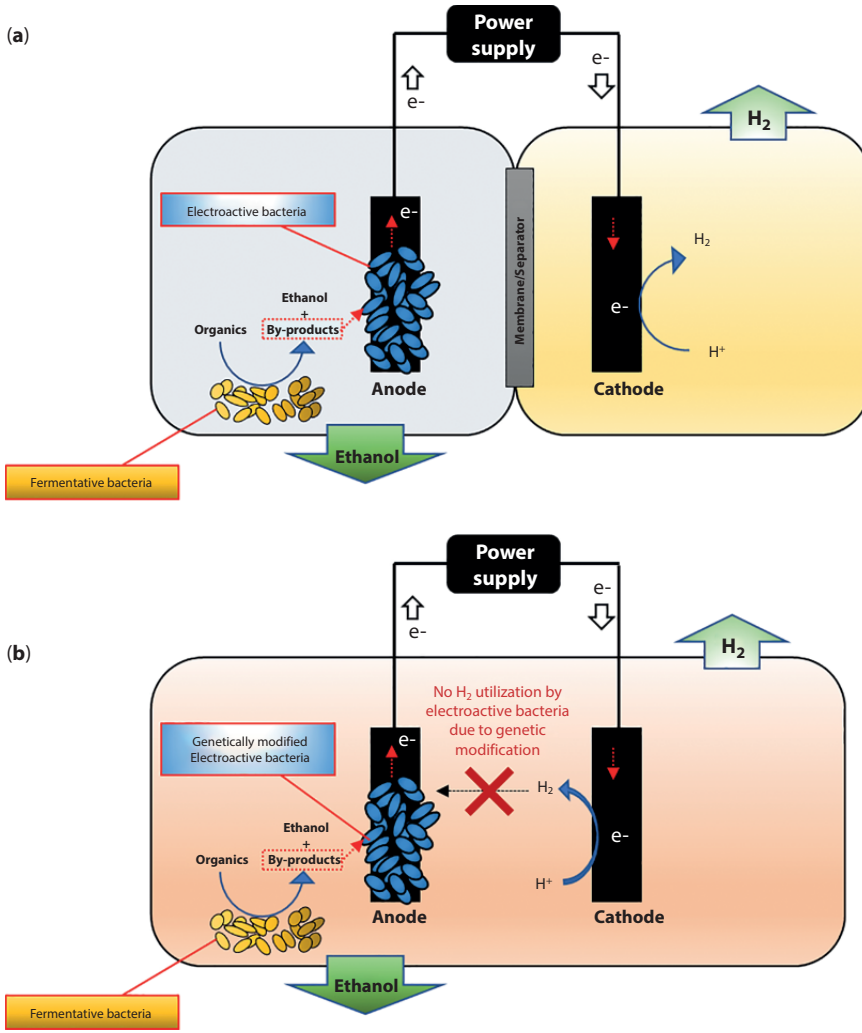

Figure 1.4 A conceptual schematic showing anodic ethanol-fermentation using customized co-culture of fermentative and electroactive bacteria using (a) dual-chamber, (b) single-chamber electro-fermentation systems. The figures draw on concepts proposed by Awate *et al.* (2017) and Speers *et al.* (2014).

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Cellulomonas uda and a genetically engineered *Geobacter sulfurreducens*. In their single chamber reactor, *Cellulomonas uda* efficiently hydrolyzed and fermented cellobiose to ethanol, while *Geobacter sulfurreducens* rapidly utilized non-ethanol by-products and prevented feedback inhibition of ethanol fermentation. The electron captured by *Geobacter sulfurreducens* then converted to hydrogen gas on the cathode. Furthermore, genetic modification of *Geobacter sulfurreducens* provided improve lactate (a fermentation by-product) oxidation, while preventing the oxidation of hydrogen produced on the cathode. Overall, their single-chamber EF demonstrated higher ethanol concentration (0.332 vs. 1.226 g/L), yield (0.103 vs. 0.275 g/g cellobiose), and productivity (0.015 vs. 0.056 g/L/h) over conventional fermentation. Studies by Awate *et al.* (2017) and Speers *et al.* (2014) suggested that anodic EF with designer bioanode combing electroactive and fermentative bacteria could efficiently remove fermentation by-products in both single and dual-chamber systems (see Figure 1.4). Thus, EF can potentially reduce downstream purification costs, which can be as high as 80% of the total cost (Schievano *et al.*, 2016).

Chandrasekhar *et al.* (2015) demonstrated a solid-state EF for simultaneous biohydrogen and bioethanol generation from food waste. The authors reported a maximum hydrogen production rate of 21.9 ml/h and maximum ethanol production of 4.85% (w/v). Although the authors did not compare the performance with a control reactor, their study demonstrated the possibility of valorization of real organic waste (i.e., food waste) for bioethanol production via EF. As shown in Table 1.1, the majority of EF studies were conducted with synthetic substrates. Therefore, future EF should consider utilizing real waste biomass to demonstrate the feasibility of EF for practical application.

1.3.3 Bio-Butanol

Bio-butanol is another increasingly popular platform chemical that can also be used as liquid biofuel or additive to fossil fuel due to high energy content (27.08 MJ/l) and compatibility with combustion engines (Kumar and Gayen, 2011). The fermentation process driven by solventogenic *Clostridia* has been widely used for biobutanol production from carbohydrates-rich feedstock due to its low capital cost compared to the petrochemical butanol production process (Elbeshbishy *et al.*, 2015). Before 2005, butanol was mainly used for the synthesis of other industrial chemicals. After being recognized as a biofuel, the demand for butanol has considerably increased in the last 15 years (Kumar and Gayen, 2011). The global market

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of biobutanol is now expected to reach USD 17.78 billion by 2022 (Grand View Research, 2020).

Low biobutanol yield, as well as production rate, have been identified as major bottlenecks for wide-scale application of fermentative biobutanol production (Elbeshbishy *et al.*, 2015). Over the years, various strategies, including the deployment of genetically modified Clostridia and non-Clostridia organisms as well as designing novel fermentation systems, have been considered for alleviating these bottlenecks. In recent years, a few studies investigated biobutanol production via EF of glucose with pure-culture *Clostridium* species (Choi *et al.*, 2014; Engel *et al.*, 2019; Mostafazadeh *et al.*, 2016). Choi *et al.* (2014) studied cathodic EF of glucose with pure culture *Clostridium pasteurianum* DSM 525 in a dual-chamber EF system. The authors found that *C. pasteurianum* could produce butanol by utilizing electrons from both cathode and substrate (glucose). Although NADH generation from electricity was trivial as compared to that generated from glucose, EF could increase butanol production by 2.5 times over the control fermenter. Thus, their results suggested a metabolic shift in reduction pathways in *C. pasteurianum* due to the applied potential.

A study by Mostafazadeh *et al.* (2016) also reported enhanced biobutanol yield (g butanol/g consumed glucose) and productivity (g butanol/L-h) in cathodic EF using pure-culture *C. pasteurianum*. Compared to the control (i.e., conventional fermentation), butanol yield and productivity increased by 29% and 30%, respectively. Furthermore, their study highlighted the importance of process optimization of EF for biobutanol production. The authors investigated the effects of various process parameters, including glucose concentration (86.3-153.6 g/L), temperature (27.6-39.4°C), and applied voltage (0-2.6 V) using statistical design of experiment in cathodic EF of glucose to biobutanol using pure-culture *C. pasteurianum*. The maximum biobutanol concentration of 13.31 g/L butanol was achieved at an applied voltage of 1.32 V under an operating temperature of 33.51°C and at a glucose concentration of 120 g/L. The glucose concentration ≥140 g/L introduced inhibition and led to a decrease in butanol yield. Furthermore, the authors also compared the impact of cathode electrode materials on butanol production. The results showed that up to an applied voltage of 1.5, graphite felt as cathode could provide higher butanol concentration as compared to the stainless-steel electrode. However, with the applied voltage >1.5 V, the performance of both electrodes declined. With an increase in applied voltages, hydrogen production on the cathode linearly increased in both reactors. Moreover, the stainless-steel electrode led to higher hydrogen production as compared to the graphite, which is consistent with some of the reports on superior hydrogen evolution reaction (HER)

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with the metal electrode (Cheng *et al*., 2009). Thus, superior HER on the stainless surface could introduce instability of cathode biofilms. Overall, this study demonstrated considerable scope to optimize process parameters and design of EF systems to maximize productivity and yield of target value-added products.

1.3.4 Microalgae Derived Lipids

Up to date, fossil fuels have been widely adopted as energy sources across the world. However, there is a great need to significantly develop the renewable fuels (e.g., non-fossil fuel) as energy sources on a large scale to outcompete the fossil fuels, eliminating the issues of aggravating CO_2 concentrations and global warming (IPCC, 2018; Liu *et al*., 2019; Liu *et al*., 2020c). Out of many renewable fuels, microalgae-derived biofuels have demonstrated to be highly promising due to their advantages, such as high biomass production per unit area, a high weight ratio of lipids and ability to accumulate lipids in oleosomes, and no competition for arable land usage (Adeniyi *et al*., 2018; Chisti, 2007; Hallenbeck *et al*., 2016; Hu *et al*., 2008; Rittmann, 2008). Despite these attracting features, several drawbacks for the microalgae biofuel generation have been reported, emphasizing their high costs, and environmental concerns associated with algae harvesting and lipids extraction (Markou and Nerantzis, 2013; Pierobon *et al*., 2018; Rittmann, 2008; Sills *et al*., 2013). For instance, the requirement of pre-treatment (e.g., acid/alkaline hydrolysis, pulsed electric fields, ultrasound (Sheng *et al*., 2011; Zbinden *et al*., 2013)) for microalgae processing are generally highly energy intensive (e.g., in terms of both capital and operational costs), which was one of the arguments against further development and scaling-up. Lipid extraction is a critical step prior to the microalgal biodiesel production process. However, highly toxic chloroform-methanol solvents have been widely adopted for lipid extractions due to their effective performance (e.g., the ability to penetrate cell wall and membrane) (Bligh and Dyer, 1959; Folch *et al*., 1957). However, they must be replaced by other non-toxic solvents (e.g., hexane-isopropanol) due to the environmental and public health concerns (Lai *et al*., 2016a; Lai *et al*., 2014). Hence, a greener approach is required to address the challenges associated with microalgae-derived lipids extraction.

In response, selective fermentation (SF) has been implemented as a new approach for enhancing lipid extraction for microalgae biofuel generation (i.e., biodiesel) (Lai *et al*., 2016b). SF utilizes the fact that lipids are generally biodegraded more slowly than carbohydrates and proteins under an anaerobic environment (Lai *et al*., 2016b; Rittmann and McCarty,

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2001; Siegert and Banks, 2005), in which, the lipid fermenters, known as the slow-growing microbes (Christ *et al*., 2000; Rittmann and McCarty, 2001), can be washed out of the system with a relatively short solids retention time (SRT) (Lai *et al*., 2016b). Hence, the SF solely allows the removal of carbohydrates and proteins in microalgae cells, leaving the lipids intact, providing a state much easier to extract lipids (Lai *et al*., 2016b). More importantly, the SF process can significantly promote the lipid extraction process (e.g., >5000-fold increase vs. untreated biomass) when using the hexane-isopropanol solvents (Lai *et al*., 2016a). Moreover, the lipid extraction is also benefitted by SF due to biohydrogenation, where the dominant lipid groups on long-chain fatty acids (LCFAs) are converted to saturated forms (e.g., C18:1 to C18:0) (Liu *et al*., 2019); the SF process can increase the saturation ratio of extracted lipids by up to 80% (Liu *et al*., 2020c). This saturating process via SF for the LCFAs is highly desirable as they can aid the transportation fuel generation due to more energy value, higher octane number (e.g., better combustion efficiency), and greater resistance to oxidation (Knothe, 2011). Also, SF biohydrogenation is superior to the catalytic hydrogenation (e.g., requires high temperature and metal catalysts to operate) due to significantly less or no energy/catalyst demand (McArdle *et al*., 2011; Plourde *et al*., 2004; Wang *et al*., 2017). Figure 1.5 shows a conceptual schematic of lipid extraction from microalgae using electro-selective fermentation.

However, the SF itself can suffer from the fact that the protein fermentation is slower than the carbohydrate fermentation (Lu *et al*., 2010). Furthermore, accumulation of short-chain carboxylates (e.g., high COD in the system) is another challenge (Lai *et al*., 2016b), resulting in the following two cases: (1) wasting the electrons from the feed biomass (e.g., not all the electrons are used up or recovered as value-added products); and (2) lowering pH, which inhibits the fermentation process (Siegert and Banks, 2005). Hence, stimulating the protein and SCFAs biodegradation is of great interest to assist lipid extractions. Previous studies have reported that MECs have the potential to accelerate the fermentation of protein along with other complex organics, such as SCFAs (Lu *et al*., 2012; Velasquez-Orta *et al*., 2009). Furthermore, with the increased removal of protein, hydrogen bonds between membrane proteins and lipids can be disrupted, rupturing the cell membrane and exposing intracellular lipids for much simpler extraction (Cooney *et al*., 2009; Sheng *et al*., 2011). Hence, this was the main motivation behind coupling MEC with SF, also known as the electro-selective fermentation (ESF), to significantly enhance lipid wet-extractions (Liu *et al*., 2019; Liu *et al*., 2020b; Liu *et al*., 2020c).

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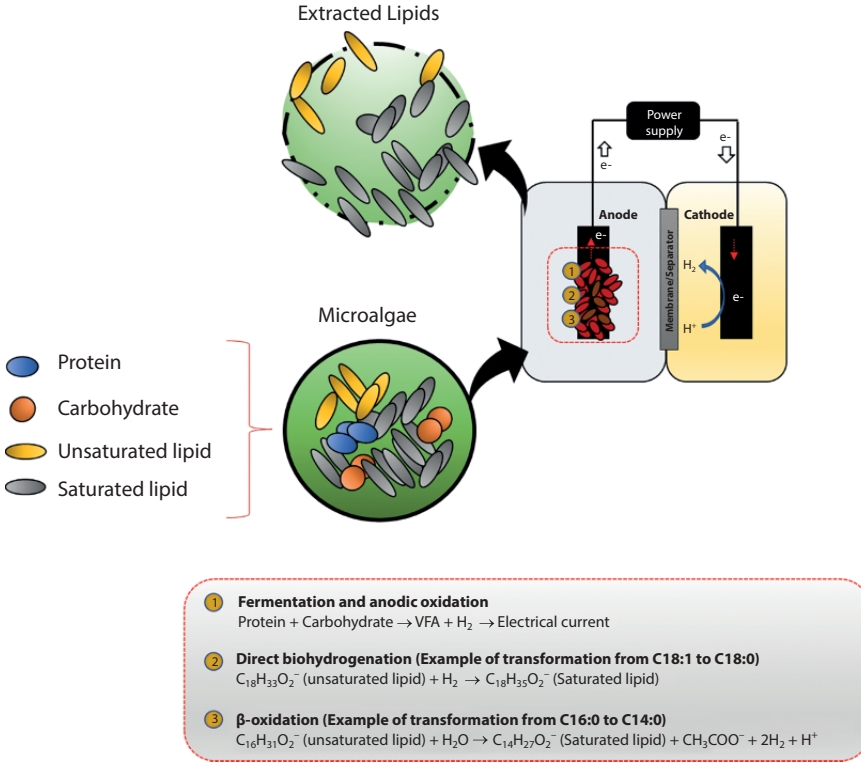

Figure 1.5 A conceptual schematic showing lipid extraction from microalgae using electro-selective fermentation. The figure is drawn with modification after Liu *et al.* (2019).

Recently, several studies have successfully demonstrated superior lipid extraction from microalgae using the ESF (Liu *et al.*, 2019; Liu *et al.*, 2020b; Liu *et al.*, 2020c). Liu *et al.* (2019) first investigated the relative performance of ESF compared to SF, in terms of protein and COD removal. When the ESF and SF (Control) reactors were fed with microalgae biomass (*Scenedesmus acutus*), significant differences were found in TCOD removal (12% vs. 2%), TCOD-to-SCOD conversion (17% vs. 11%), and protein biodegradation (42% vs. 10%) for ESF and SF, respectively. Interestingly, although the anodic respiration only contributed to < 1% of the total electron input, the ESF system yielded much higher protein and COD degradations. More importantly, even with the greater loss of total lipids due to β-oxidation-linked-to-biohydrogenation (e.g., shifting LCFAs from C18:1 to C16:0 or C14:0) in the ESF system, it still demonstrated significantly higher lipid yields (37%) compared with the SF (12%) and the lipid

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extractions with hexane-isopropanol solvents (~4%). In summary, despite currently being a small component of overall COD balance, ESF exhibited superior hydrolysis of protein of microalgae biomass (*Scenedesmus acutus*), a higher saturation ratio of LCFA, and higher lipid yields (~3 folds) over SF (Liu *et al*., 2019). On the other hand, Liu *et al*. (2020c) have introduced a flat-plate MEC based ESF to observe the performance in lipid extraction by having a large anode surface area for electroactive bacteria biofilm. The benefit was in the enhanced electron consumptions, where the electrons in the microalgae biomass were greatly scavenged by electroactive bacteria in the anode biofilm. Furthermore, the SCFAs were also efficiently converted to current (e.g., preventing the accumulation of SCFAs), maintaining the optimal working environment (e.g., preventing pH drop) for the fermentation process. Compared with Liu *et al*. (2019), the ESF significantly improved in microalgae lipid extraction, achieving 56% (vs. 37%) extraction from the total lipids.

Finally, Liu *et al*. (2020b) have compared various SRTs on the ESF performance. In their study, ESF systems with different SRTs were compared (System A: start with a 6 d SRT, then switch to 2 d SRT vs. System B: start with a 2 d SRT, then switch to 6 d SRT). The ESF system A exhibited the highest lipid extractability (25%) when operated with a 6 d SRT, and gave the highest lipid productivity (450 mg/L/d) when switched to a 2 d SRT. This was attributed to establishing the microbial community containing protein fermenters at a 6 d SRT and washing out of lipid fermenters when the system A was switched to the 2 d SRT. Opposingly, the system B failed to enhance the lipid extractability. It initially (e.g., at a 2 d SRT) washed out the lipid fermenters, but it was unable to recover them when the system switched to a 6 d SRT. Ultimately, demonstrated by multiple studies, the further studies are warranted to bring this technology forward towards further development, scaling-up and potential commercialization.

1.3.5 Acetoin

Acetoin is known to be a volatile compound, which is widely utilized in chemical synthesis, cigarettes, cleaning products, food, personal care products, plant growth, pest controls, wine, etc. (Cheynier *et al*., 2010; Förster *et al*., 2017; Xiao and Lu, 2014). Especially, acetoin has been largely applied as food flavoring (e.g., has an intense butter flavor) and fragrance manufacturing (Xiao and Lu, 2014). Moreover, acetoin is also highly promising, ranking in the top 30 for its potential applications as the bio-based building block precursors (Werpy and Petersen, 2004), which can embrace a green environment (e.g., petro-free economy). Due to these several industrial applications, in recent

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years, the production of acetoin became highly desirable due to a significantly large annual consumption across the globe (e.g., 2-4 mg per day per person, equal to several thousand tons per year worldwide) (Xiao and Lu, 2014).

In general, acetoin is a substance that cannot be generated as the sole end product during the anaerobic fermentation due to being more oxidized form than other typical substrates, such as glucose (Förster *et al*., 2017). Hence, the acetoin is generated under a specific condition during fermentation by *Bacillus subtilis* and serval *Enterobacteria* species, for instance: (1) occurs as an intermediate in the formation of 2,3-butanediol in butanediol fermentation; (2) produced in a two-step process from pyruvate (Cheynier *et al*., 2010; Förster *et al*., 2017; Härtig and Jahn, 2012; Krieg and Padgett, 2011). Briefly describing the two-step process, the acetolactate synthase (AlsS) first catalyzes the condensation of two molecules of pyruvate to acetolactate, where one molecule of CO_2 is released during this reaction. Then, acetolactate is decarboxylated by the acetolactate decarboxylase to produce acetoin (Nicholson, 2008; Ramos *et al*., 2000).

To date, several limitations in acetoin synthesis have been reported. For instance, only low acetoin yields can be achieved using wild-type strains because the majority of other products are transformed to 2,3-butanediol (Förster *et al*., 2017). Hence, significant efforts have been dedicated to engineering the strains (e.g., *Bacillus subtilis*, *Serratia marcescens*, *Clostridium acetobutylicum*, *Candida glabrata*) to maximize acetoin output (Bai *et al*., 2015; Li *et al*., 2015; Liu *et al*., 2015; Zhang *et al*., 2016). However, despite the high acetoin yields (e.g., ~70-96% of maximum theoretical), acetoin-producing strains can be pathogenic, which may limit their use in the markets without appropriate post-treatment (Bursac *et al*., 2017; Förster *et al*., 2017; Xiao & Lu, 2014). Moreover, the related studies were performed using oxic (either anoxic or aerobic) processes, which are highly unfavorable for the biosynthesis of value-added products due to the requirement of aeration and a higher ratio of anabolism over catabolism (Weusthuis *et al*., 2011). Therefore, a more suitable approach that is capable of producing a high amount of environmental-friendly acetoin is greatly needed.

In response, studies have been implemented to produce acetoin using EF systems (Bursac *et al*., 2017; Förster *et al*., 2017) (see Table 1.1). Bursac *et al*. (2017) studied *Shewanella oneidensis* to produce acetoin from lactate in an EF system. In their study, first, the *Shewanella* strains were engineered for the acetoin synthesis, where the *Bacillus subtilis* genes, capable of acetolactate synthase and acetolactate decarboxylase, were codon-optimized and integrated into pBAD202 plasmid, and then the plasmid was transformed into different *Shewanella* stains. Using the engineered strains, acetoin production of 40% of the theoretical maximum was achieved by

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complete degradation of lactate (50 mM) after 48 hours of fermentation. To further exhibit higher acetoin production, their study developed the strains again (e.g., deleting the -prophage to increase cell adhesion on the anode) and introduced an EF system. Hence, the EF system with engineered strains demonstrated higher acetoin yield (78% of the maximum theoretical vs. 40% in conventional fermentation) (Bursac *et al.*, 2017). On the other hand, Förster *et al.* (2017) investigated acetoin production in an EF system operated with glucose. Their study chose *Escherichia coli* because it was found to be the most suitable host organism, due to its versatile metabolism and genetic tractability (Nielsen *et al.*, 2010; Xu *et al.*, 2015; Xu *et al.*, 2014). Similar to Bursac *et al.* (2017), Förster *et al.* (2017) engineered the strain, such as the quadruple mutant JG806 (Δ*frd* Δ*adhE* Δ*ldhA* Δ*pta-ack*) to achieve high pyruvate production, for the optimal production of acetoin. First, Förster *et al.* (2017) initiated their using nitrate as an electron acceptor (e.g., anoxic fermentation) for the production of acetoin and achieved a yield of 90% of maximum theoretical. However, the anoxic fermentation led to the accumulation of pyruvate and acetate. On the other hand, when the EF system was introduced, an acetoin yield of 79% of maximum theoretical was observed, and more importantly, there were no other end products besides acetoin with such high columbic efficiency (93.4%). Despite lower acetoin yield demonstrated by the EF system e.g., (79% vs. 90% - anoxic fermentation), Förster *et al.* (2017) have clearly demonstrated that the EF system can still provide an efficient acetoin generation along with the elimination of aeration and volatile fatty acids accumulations.

1.3.6 Biopolymer

Polymers have been recognized as one of the versatile class of materials due to their enormous contributions to our standard of living, quality of life, and human well-being across the globe (Rajan *et al.*, 2018). However, the extensive usage of polymers has challenged solid waste management, concerning the adverse impact of plastic wastes on the ecosystem (Rajan *et al.*, 2018; Urbanek *et al.*, 2018). Specifically, for instance, the petrochemical-derived plastics have been extensively generated over the last decades, where their recalcitrance (e.g., strong resistance to biodegradation) posed significant threats to both environment and human health (Mostafa *et al.*, 2020; Rajan *et al.*, 2018). Hence, the production of environmental-benign polymers is highly necessary in order to address the challenges associated with solid waste management (Mostafa *et al.*, 2020). Recently, renewable bio-based plastics, such as polyhydroxyalkanoate (PHAs) have received

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significant attention due to their potential application as a green alternative over other types of polymers (Liu *et al*., 2020a; Mostafa *et al*., 2020; Myung *et al*., 2017; Rajan *et al*., 2018). PHAs are non-toxic, biocompatible, and biodegradable, which have similar properties to conventional plastics (Kourmentza *et al*., 2017; Myung *et al*., 2014). The accumulation of PHA inside the bacterial cells provides a defense mechanism, when the bacterial growth is limited due to the stress conditions, such as nutrient imbalance (Chien *et al*., 2007; Myung *et al*., 2017). To date, many different variations in functional groups (e.g., methyl to tridecyl, unsaturated bonds, chain length, etc.) make PHA suitable biopolymers for various applications (Verlinden *et al*., 2007). The most common form of PHA is known as poly-3-hydroxybutyrate (PHB), which accumulates in various types of microbes by binding the -hydroxybutyrate monomers with ester bonds (Juengert *et al*., 2018).

Different fermentation methods can be utilized for the production of bio-based plastics like PHA. First, a sugar-based fermentation, which was the conventional method, has been implemented for the production of bioplastics (Jabeen *et al*., 2015; Rossell *et al*., 2002), but this conventional approach was not favorable due to reasons such as accumulation of short-chain volatile fatty acids (discussed in the previous sections) and the redox imbalance (e.g., restraining the product selectivity) (Lai and Lan, 2020). A newer fermentation approach using methanotrophs has been developed recently (Liu *et al*., 2020a; Myung *et al*., 2017). However, the major challenge of using methanotrophic fermentation for the production of bioplastics was the high production costs (e.g., feedstock, aeration), low yields, and mass transfer limitations (e.g., oxygen transfer, low methane solubility in water) (Liu *et al*., 2020a). To address such challenges, Myung *et al*. (2016) grew methanotrophs in water-in-oil emulsions (e.g., using the fact that methane was more soluble in oil than water) and increased the mass transfer efficiency, yielding higher production of bioplastics. However, utilizing oil may not be environmental-friendly and the high costs triggered by the aeration requirement and feedstock must still be considered (Liu *et al*., 2020a).

On the other hand, the EF system showed a high potential to greatly assist the production of bioplastics. To the best of the author's knowledge, Lai and Lan (2020) were the only studies that investigated the application of the EF system on bioplastic production. In their study, *Ralstonia eutropha* H16 species went under growth-suppressing conditions (e.g., nitrogen starvation) for the production of PHB in two different bioreactor setups, a control (e.g., without any electrical energy input) and a test reactor (e.g., EF system). When the electrical current (10 mA) was applied along

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with a redox mediator (methyl blue), the PHB productivity remarkably increased by 30% (e.g., after 60 h of operation) along with higher final biomass residual (13.6 g/L vs. 11.8 g/L), higher maximum specific growth rate (m_{max} = 0.133/h vs. 0.127/h), and higher specific substrate utilization rate (q_s = 0.187 g/g vs. 0.169 g/g) compared with the control. The enhancement of the PHB accumulation was due to the additionally supplied electrons and redox mediators accelerated the glycolytic pathway and redox cycling of NADH/NAD^+, which boosted the adenosine triphosphate (ATP) generation, facilitating the biosynthesis of PHB (Lai & Lan, 2020).

1.3.7 L-lysine

The market of amino acid, which is known to be a key sector of industrial biotechnology, has been rapidly growing recently (Vassilev *et al*., 2018; Xafenias *et al*., 2017). Specifically, such a high production rate for L-lysine, an amino acid (e.g., 2.2 million tons per year with 7% increase per year) has been reported due to the growing demand for meat because the L-lysine was extensively used as an additive in animal nutrition (Ajinomoto Co., 2013; Eggeling and Bott, 2015; Xafenias *et al*., 2017). Over the decades, various industrial biotechnologies, based on Gram-positive soil bacteria (e.g., *Corynebacterium glutamicum*), have been utilized for the production of lysine due to their advantages (e.g., a safe production host) (Eggeling and Bott, 2005; Tatsumi and Inui, 2012; Vassilev *et al*., 2018; Wittmann and Becker, 2007). To begin with, using *C. glutamicum* in aerobic bioreactors (e.g., using oxygen as a terminal electron acceptor) was the initial attempt to produce L-lysine, but low product yields via substrate loss and oxygen mass transfer were the limitations for further development and scaling-up (Gill *et al*., 2008; Hannon *et al*., 2007; Takeno *et al*., 2007). In fact, aerobic bioreactors will result in higher capital costs compared to anaerobic systems (Garcia-Ochoa and Gomez, 2009). Alternatively, a study in 2004 revealed that *C. glutamicum* was capable of performing fermentation of glucose to organic acids, such as lactate and acetate under oxygen deprivation conditions (Inui *et al*., 2004), which demonstrated another pathway for L-lysine production. Despite the advantages of the anaerobic process (e.g., low cost), due to the low yield, efforts (e.g., the introduction of nitrate, anoxic condition) have been made to promote the growth of *C. glutamicum*, but the growth was inhibited due to the production of toxicants (e.g., nitrite) in the bioreactor (Takeno *et al*., 2007).

To enhance the growth of *C. glutamicum* and to increase the production of L-lysine, studies have utilized the EF system (Vassilev *et al*., 2018;

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Xafenias *et al*., 2017). The production of lysine using the EF system was first investigated by Xafenias *et al*. (2017). In their study, glucose, *C. glutamicum*, and nitrate were selected as substrate, bacterial type, and additional electron acceptor, respectively, and the EF system was performed in reductive mode. This study had three highlighted features, which were: (1) the performance of the EF system, in terms of lysine production; (2) effects and comparison of different environmental conditions (e.g., CO_2- vs. N_2-gas environment); and (3) impact of exogenous redox mediators. The lysine generation was comparable between the open circuit control (e.g., ~75 g/L) and the EF system under reductive conditions of -1.25 V (e.g., ~154 g/L). The maximum lysine production significantly increased by ~10-folds when the EF system was switched from the N_2-gas environment (e.g., ~12 g/L) to the CO_2-gas environment (e.g., ~112 g/L). Especially, under the reductive condition (EF system), the maximum lysine production can further be increased by >3-folds (e.g., from ~112 g/L to ~357 g/L) by adding redox mediators, such as anthraquinone-2-sulfonate. Furthermore, the values for lysine yields relative to glucose consumed were significantly varying (e.g., 5 – 40 mol-lysine/mol-glucose) with each environmental condition, highlighting the importance of electrochemical parameters, N_2 vs. CO_2-gas, and presence of additional redox mediators (Xafenias *et al*., 2017). Next, Vassilev *et al*. (2018) also supported the application of the EF system on lysine production using similar conditions (e.g., glucose and *C. glutamicum*) as Xafenias *et al*. (2017). Their study identified that the microbial interaction (*C. glutamicum*) with the anode was very limited as illustrated by a low current output (e.g., 0.022 mA/cm^2). Hence, their study first focused on enhancing the electron transfer by introducing an additional redox mediator, ferricyanide to support the oxidation of the metabolic substrate (fermentation process), which can potentially increase the lysine production. When the ferricyanide was introduced, it was reduced to ferrocyanide by *C. glutamicum*, then, reoxidized by the anode, where this resulted in transfer of electrons to the anode and development in current output (e.g., 0.022 mA/cm^2 to ~0.090 mA/cm^2). Similar to a previous study (Xafenias *et al*., 2017), their EF system showed a higher volumetric production rate of lysine (e.g., 35 μmol/L/hr vs. 24 μmol/L/hr) compared with the open circuit control. Additionally, when higher biomass inoculum of *C. glutamicum* (e.g., 6.6 times higher, 0.42 g/L vs. 2.8 g/L) was used, the volumetric production rate of lysine significantly increased from 35 μmol/L/hr to 202 μmol/L/hr due to higher glucose consumption (e.g., > 97% glucose was consumed in 13.4 h compared to 78 h in lower biomass inoculum), achieving the total lysine concentration of 2.94 mM.

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1.3.8 1,3-propanediol

1,3-propanediol is an important industrial chemical widely used as a monomer to synthesize various commercial products, including cosmetics, plastics, foods, and medicines (Yang *et al*., 2018). The global market size for1,3-propanediol is expected to reach ~690 million USD by the year 2025 (www.marketsandmarkets.com). Although 1,3-propanediol can be produced chemically through two methods (hydroformylation of ethylene and the hydration of acrolein), these traditional chemical synthesis methods are not considered sustainable due to high energy consumption, the requirement of expensive catalysts, and the generation of hazardous intermediates (Yang *et al*., 2018). Therefore, the biological production of 1,3-propanediol from waste biomass (e.g., glycerol waste from the biodiesel production process) is considered as a greener and safer approach (Vivek *et al*., 2017; Yang *et al*., 2018). Particularly, microbial conversion of glycerol with various fermentative bacteria (e.g., *Citrobacter, Klebsiella, Lactobacillus, Enterobacter, and Clostridium*) has been extensively investigated (Drozdzynska *et al*., 2011; Vivek *et al*., 2017; Yang *et al*., 2018). Crude glycerol, a major by-product from biodiesel production process can serve as a feedstock for 1,3-propanediol synthesis via fermentation. Typically, 1 L of crude glycerol is generated per 10 L of biodiesel production via transesterification of triglycerides (vegetable oil or animal fats), in the presence of primary alcohol (e.g., methanol) and a catalyst (Sarma *et al*., 2012). However, low yield, product inhibition, etc., have been identified as the major bottlenecks in the fermentation of glycerol to 1,3-propanediol (Vivek *et al*., 2017; Yang *et al*., 2018).

Various approaches proposed by researchers for enhancing biosynthesis of 1,3-propanediol from glycerol include the customization of metabolic pathways of fermentative bacteria by genetic engineering (Yang *et al*., 2018). As demonstrated by a few studies, cathodic EF appeared to be a promising method for enhancing the biosynthesis of 1,3-propanediol from glycerol (Choi *et al*., 2014; Moscoviz *et al*., 2018; Xafenias *et al*., 2015; Zhou *et al*., 2013; Zhou *et al*., 2015). Notably, for 10% increase in 1,3-propanediol yield, the required energy for EF operation was <1% of the total electron equivalents of a substrate (e.g., glycerol) (Moscoviz *et al*., 2018). Choi *et al*. (2014) studied 1,3-propanediol production via cathodic EF of glycerol (~300 mM) with pure culture *Clostridium pasteurianum* DSM 525 in a dual-chamber bioreactor. Their study showed that *Clostridium pasteurianum* could directly accept electrons from the cathode electrode. Electrochemically induced reducing power could considerably influence intracellular redox condition and accelerate the synthesis of NADH-consuming compounds

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like 1,3-propanediol. Notably, as compared to the control (i.e., conventional fermentation), EF could increase NADH consumption towards 1,3-propanediol synthesis by 3.5 times; other by-products were butanol and butyrate. Nonetheless, NADH generation from electricity was very minimal as compared to the NADH generated from substrate. Thus, EF could provide a shift in metabolic pathways in *Clostridium pasteurianum* to provide a higher 1,3-propanediol yield from glycerol.

A few studies also investigated mixed-culture EF of glycerol for improving 1,3-propanediol yield (Xafenias *et al*., 2015; Zhou *et al*., 2013). Xafenias *et al*. (2015) studied mixed-culture cathodic EF of glycerol in a dual-chamber bioreactor operated under different cathode potential ranged from −0.80 V to −1.10 V vs. SHE (Standard hydrogen electrode). Compared to the conventional fermentation, EF could increase 1,3-propanediol production rate up to 6 times. Moreover, 1,3-propanediol concentration was considerably higher in the EF fermentation (EF: 42 g/L; Control: 18 g/L), suggesting microbial consortia in EF had a higher tolerance to product inhibition. As mentioned earlier, product inhibition is a commonly identified phenomenon in fermentative 1,3-propanediol production. The authors hypothesized that the higher local pH near the cathode could provide a favorable metabolic condition for microbial consortia in the cathode biofilms by decreasing concentrations of undissociated acids. This study also demonstrated the importance of cathode potential optimization for improving EF performance. Notably, known 1,3- propanediol-producing microbes (*Clostridiaceae*) were enriched at an applied cathode potential of −1.1 V vs. SHE, while unfavorable applied potential led to the enrichment of propionate-producing microbes (e.g., *Veillonellaceae*), which also corroborated with propionate accumulation. Moreover, after replacing the biocathode with an electrode lacking biofilms, glycerol consumption considerably decreased with a lower yield of 1,3- propanediol. The absence of EF stimulated the growth of *Lactobacillaceae* followed by the production of lactate.

A recent study by Moscoviz *et al*. (2018) demonstrated biocathode pre-enriched with *G. sulfurreducens*, a known electroactive bacterial species, could improve mixed-culture glycerol EF with considerably shortened lag time and enhanced 1,3- propanediol production by up to 10%. The authors suggested that *G. sulfurreducens,* pre-enriched on the cathode, could serve as a living mediator between the electrode and fermentative bacteria and promote the selection of kinetically efficient 1,3- propanediol producers. Based on these studies, EF opens up promising opportunities for increasing glycerol fermentation rates and 1,3- propanediol yields.

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1.4 Challenges and Future Outlook

Still, several challenges must be addressed before further development or scaling-up of the EF system for biofuel and value-added chemical synthesis (e.g., lipids, acetoin, PHB, L-lysine). To start with, more explorations of different working conditions, such as temperature, pH, and working electrode potentials are required for the commercialization of the EF system. General mechanism and fundamental knowledge on bacterial strains and their impact on the EF performance are still lacking. For instance, Bursac *et al.* (2017) were not able to identify the reasons behind the positive impact on anode cell densities in their EF system due to -prophage deletion during acetoin production. Furthermore, Lai and Lan (2020) stated that an optimal energy input should be evaluated in EF, where their EF performance was reduced due to higher current input inhibiting their bacteria (e.g., *Ralstonia eutropha* H16). High electrical current supply can cause direct cell damage (sometimes resulting in cell death) via electroporation, production of reactive oxygen species, or generation of other toxic substances (Lai & Lan, 2020). Hence, more experimental evidence is needed for the selection of optimal energy input for the EF system. Particularly, minimal information is available on the complex interactions among electrode polarization, substrate composition, and microbial consortia.

Also, fundamental understandings, such as (1) interactions between fermentative bacteria; (2) dissolved redox couples of the medium; and (3) interactions between fermentative bacteria and the surface of the electrodes via different electron transfer mechanisms, remains as insufficient to clearly describe the effectiveness of the EF system (Lai and Lan, 2020; Moscoviz *et al.*, 2016; Xafenias *et al.*, 2017). The interactions between microbial cells and electrodes, particularly EET mechanisms for electron transfer from bacteria to electrode, have been extensively studied for various MXCs, while electron transport from the electrode to microbial cells is relatively unexplored (Gong *et al.*, 2020; Kracke *et al.*, 2018). For EF-based production of some specific value-added products (Table 1.1), an in-depth understanding of cathodic EET mechanisms (e.g., electron uptake) should be further investigated for successful engineering cathodic EF process.

In recent years, the utilization of waste feedstocks for biofuels productions (e.g., bioethanol, biodiesel, etc.) has received significant attention worldwide. Electro-fermentation carries an excellent potential for regulating fermentation pathways and enhancing productivity and yield of target value-added products. However, except for a few studies, most of the EF studies utilized synthetic model compounds rather than real feedstocks.

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For instance, further research would be needed for developing a sustainable crude glycerol-based EF process. Crude glycerol from the biodiesel production process may contain a considerable amount of impurities (e.g., metals and residual alcohols) (Xafenias *et al*., 2015); the biodiesel process uses excess methanol to promote product yields (Dhar and Kirtania, 2009). Therefore, the effects of those impurities on EF should be further studied for practical application. Thus, the feasibility of utilizing waste biomass has yet to be demonstrated on a lab-scale to reach a considerable state for further pilot, scale-up, and commercialization. With more future experimental evidence, the EF system can demonstrate such high potential to facilitate the field-scale productions of biofuels and chemicals with only small electrical energy input.

1.5 Acknowledgements

We gratefully acknowledge support from Natural Sciences and Engineering Research Council of Canada (NSERC) Discovery Grant for this research. Tae Hyun Chung acknowledges support from Alberta Innovates Graduate Student Scholarship and NSERC Alexander Graham Bell Canada Graduate Scholarship-Doctoral programs.

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2

Biodiesel Sustainability: Challenges and Perspectives

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Abstract

The worldwide depletion of high-quality oil reserves and the immense stringent environmental regulations force decision makers towards alternative biofuels. However, that comes in parallel with the worldwide water scarcity and food versus fuel problems. So for achieving secured economy, sustainable clean energy, overcoming the problem of climate change, ensuring safe lands for food, and preserving oil crops for humans, it is important to produce such biofuels using non-edible feedstock. This chapter discusses in brief the history of biodiesel development as an example of ecofriendly, biodegradable, non-toxic and sustainable biofuels. It emphasizes the production of biodiesel from waste oils and fats using sustainable heterogeneous catalysts. It ends with the challenges and opportunities for reaching a feasible transesterification process producing high yield of qualified biodiesel suitable to be used as alternative and/or complementary to the conventional petro-diesel without affecting engine performance.

***Keywords*:** Biodiesel production routes, sustainable feedstock, transesterification, sustainable heterogeneous catalysts, challenges and opportunities

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Nour Shafik El-Gendy (ed.) Sustainable Solutions for Environmental Pollution Volume 1: Waste Management and Value-Added Products, (41–122) © 2021 Scrivener Publishing LLC

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Abbreviations

American Society for Testing and Materials	ASTM
Angle Wing Shells	AWS
Biomass Support Particles	BSPs
Box-Behnken Design	BBD
Calorific Value	CV
Carbon Dioxide	CO_2
Carbon Mono-oxide	CO
Central Composite Design	CCD
Central Composite Face Centered Design	CCFCD
Central Composite Rotatable Design	CCRD
Cetane Number	CN
Chicken Eggshells	CES
Cloud Point	CP
Deodorization of Palm Oil	DDPO
Design of Experiments	DOE
Diesel Index	DI
Diglyceride	DG
Dimethyl Sulfoxide	DMSO
D-Optimal Design	DOD
Fatty Acid Methyl Ester	FAME
Fatty Acids	FAs
Flash Point	FP
Fluorapatite	$Ca_5(PO_4)_3F$
Free Fatty Acids	FFAs

(*Continued*)

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French Institute of Petroleum	FIP
Full Factorial Design	FFD
Greenhouse Gas	GHG
Heteropoly Acids	HPAs
Hydroxyapatite	$Ca_5(PO_4)_3OH$
Jatropha Curcas-Biodiesel	JCB
Jatropha Curcas-Oil	JCO
Methanol:Oil	M:O
Monoglyceride	MG
Multiple Linear Regression	MLR
National Renewable Energy Laboratory	NREL
Nitrogen Oxides	NOx
Non-edible Spent Waste Vegetable Oils	NSWVO
Orthogonal Arrays	OA
Palm Fatty Acid Distillate	PFAD
Particulate Matter	PM
Pour Point	PP
Quail Eggshells	Qes
Response Surface Methodology	RSM
Rice Husk Ash	RHA
Rice Husk Char	RHC
Sulfated Zirconia	SZ
Sulfur Oxides	SOx
Temperature Programmed Desorption	TPD
Tetrahydrofuran	THF

(*Continued*)

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(*Continued*)

Total Acid Number	TAN
Tri-calcium Phosphate	β-$Ca_3(PO_4)_2$
Triglycerides	TG
US Department of Energy	US-DOE
Used Cooking Oil	UCO
Used Vegetable Oil	UVO
Waste Cooking Oil	WCO
Waste Frying Oil	WFO
Waste Vegetable Oil	WVO

2.1 Introduction

Due to the worldwide decrease of high-quality low-sulfur content petroleum reserves and the fluctuations of crude oil prices, as well as the increase of environmental concerns over the greenhouse gas (GHG) emissions, searching for alternative fuels is a mandatory concern. Rudolph Diesel developed a diesel engine in 1893 that used vegetable oils, for example, peanut oil (Cheng and Timilsina, 2011; Boro *et al*., 2012; Changmai *et al*., 2020). However, this was found unsatisfactory even if it is used as blends with petro-diesel, due to its acid composition, and high viscosity and free fatty acids (FFAs) content. Not only this, but lubricating oil thickening, carbon deposits and gum formation caused by oxidation and polymerization during the storage and combustion, withdraw this application in both direct and indirect injections diesel engines (Verma and Sharma, 2016). The National Soy Diesel Development Board in the US (presently, National Biodiesel Board) introduced the term "biodiesel" in 1992 and pioneered its commercialization (Ramadhas *et al*., 2004). Biodiesel has cardinal potential as an alternative/complementary fuel for petro-diesel for diesel engines (Sahu *et al*., 2018). Germany is the world's leader in biodiesel production (Thanh *et al*., 2012). It is defined as simple alkyl esters of fatty acids produced from renewable sources such as vegetable oils (edible and non-edible oils), animal oil/fats, tallow and waste frying oil (WFO) (Maddikeri *et al*., 2012; Diamantopoulos *et al*., 2015; Gholami *et al*., 2020). Biodiesel has higher combustion efficiency, flash point, lubricating efficiency and cetane

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number than conventional petro-diesel. Biodiesel has approximately 95% energy content of petro-diesel and it has a positive net energy gain of approximately 3-4:1 (Jairam *et al*., 2012). Biodiesel is a clean, renewable, sustainable, biodegradable, and non-toxic, and it reduces global hygiene and health problems. It is characterized by better lubricity and thus, enhanced engine longevity, extremely low sulfur and aromatic contents fuel and the lack of metals and tiny particles of solid (Jeswani *et al*., 2020). Biodiesel returns about 90% more energy than that used in its production (Semwal *et al*., 2011; Farooq *et al*., 2015). It has similar physicochemical properties to those of petro-diesel fuel (Li *et al*., 2014). Thus, biodiesel is a realistic fuel alternative for diesel engines (Vashist and Ahmad, 2014). The standards for bio- and petro-diesel fuels are provided in Table 2.1. It can be used in any compression ignition engine

Table 2.1 Standard properties of bio- and petro-diesel.

	Petro-diesel	**Bio-diesel**	
Fuel standard / **Fuel property**	**ASTM D975**	**ASTM D6751**	**EN14214**
Kinematic viscosity cSt at 40°C	1.9 – 4.1	1.9 – 6.0	3.5–5
Density at 15.56°C	----	----	0.86–0.9
API gravity at 15.56°C	35-38	----	----
Pour point °C	Depends on the location	----	----
Cloud point °C*	Depends on the location	Report*	-4
Total acid number mg KOH/g	----	<0.5	<0.5
Total S wt.%	<0.5	<0.05	<0.01
Water content ppm	<500	<500	<500
Flash point °C	>52	>130	>101
Calorific value MJ/kg	>44		32.9
Cetane number	>40	>47	>51
Iodine number mg I_2/100 g	----	----	<120

(*Continued*)

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Table 2.1 Standard properties of bio- and petro-diesel. (*Continued*)

Fuel property \ Fuel standard	Petro-diesel	Bio-diesel	
	ASTM D975	ASTM D6751	EN14214
Calcium and Magnesium, combined ppm	----	<5	<5
Cold soak filterability s	----	<360	----
Methanol content wt.%	----	<0.2	<0.2
Sulfated ash wt.%	<0.01	<0.02	<0.02
Copper strip corrosion	No.3	No. 3	Class 1
Carbon residue wt.%	<0.1	<0.05	----
Free glycerin wt.%	----	<0.02	<0.02
Total glycerin wt.%	----	<0.240	<0.25
Phosphorus content wt.%	----	<0.001	<0.001
Distillation temperature** °C	282-338	<360	----
Sodium and potassium, combined ppm	----	<5	<5
Oxidation stability hrs	----	>3	>8

* The cloud point of biodiesel is generally higher than petroleum based diesel fuel and should be taken into consideration when blending.
** Atmospheric equivalent temperature, 90% recovered.

without any required modifications. Its higher flash point gives it better and safer performance during its handling and storage. Moreover, its high oxygen content (approximately 10-12%) improves the combustion efficiency and reduces the greenhouse gases emissions, carbon mono- and di- oxides (CO and CO_2), soot, unburned hydrocarbons and particulate matter (PM) (Gorji, and Ghanei, 2014). Biodiesel affords a sustainable reduction in SO_x emissions. The CO_2 is continuously cycled and reused for growing plants instead of being released in the atmosphere, since the plants help in CO_2 fixation during the photosynthesis process. The National Renewable Energy (NREL) and US Department of Energy (US-DOE) reported that the overall life cycle emissions

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of CO_2 from 100% biodiesel (i.e., B100) are approximately 78.45% lower than those of 100% petro-diesel (i.e., B0) (Luque *et al*., 2010). The blend with 20% biodiesel (i.e., B20) would reduce the net CO_2 emissions by approximately 15.66%. The substitution of B0 by B100 in buses would reduce the life cycle consumption of petro-diesel by 95%, while applying B20 would drop the life cycle consumption of petro-diesel by approximately 19%.

Helwani *et al*. (2009) reported that the combustion of B100 decreases the CO, PM and unburned hydrocarbons by approximately 46.7, 66.7 and 45.2, respectively. The suppression in soot formation is attributed to the biodiesel composition, since it is an oxygenated fuel having an oxygen mass fraction of approximately 10-12%. One of the most important advantages of biofuels in general, is a political one: producing biofuels would make nations totally or partially independent of other oil-producing countries. Thus, it would consequently save foreign currency. Besides reducing global warming, it has additional benefits for society, such as rural revitalization and creation of new job opportunities (Sulaiman and Amin, 2016). But biodiesel may cause a slight increase in the NO_x, which can be positively influenced by delaying the injection timing in engines (Liaquata *et al*., 2012). It has also, some technical problems, including the low-temperature properties, lower oxtidation and storage stability (Kumar *et al*., 2015). Antioxidant additives can be added to improve the oxidation and storage stability (Sorate and Bhale, 2015), while oxygenates and cetane-improving additives can be added to reduce the NOx emissions and increase the cetane number, respectively (Silitonga *et al*., 2013; Tan *et al*., 2015a).

Most of the biodiesel produced worldwide comes from edible oils (Khan *et al*., 2014). That causes competition with the edible oil market, which consequently increases the cost of edible oils and biodiesel. In some countries, that causes deforestation, since forests have been felled for oil crops plantation. The cost of the feedstock accounts for about 60-95% of the overall cost of biodiesel production (Taher *et al*., 2011; Niju *et al*., 2014). Nowadays, production of biodiesel from non-edible oil crops like castor, jatropha, jojoba, neem, polanga, rubber seed, cotton seed, *Karanja*, linseed, etc., is of great interest, since these crops can be cultivated in waste lands that are not suitable for food crops, using low-quality water. Cultivation of these crops is of a lower cost, and sustains reasonably high yield without intensive care (Takase *et al*., 2015; Meira *et al*., 2016). However, compared to edible-oils; non-edible oils contain high FFAs. That requires pretreatment process before the transesterification process, which increases the overall production cost and may lower the ester yield of biodiesel below the standards (Atabani *et al*., 2013). Moreover, although, the non-edible oil crops solve the problem of direct competition with food oils, they do

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not overcome the problem of requirement of large plantation land area (Gui *et al*., 2008) and also produce a lot of solid wastes (for example, the pressed seed cake) which causes a new disposal and waste management problem (Nunes *et al*., 2009). Animal fats cost is higher than that of vegetable oils. It usually contains higher concentration of saturated fatty acids; thus, it normally exists in solid form at room temperature that consequently would cause many problems in biodiesel production process. It is desirable to use WFO, due to its economic and environmental benefits; its low price, approximately two to three cheaper than fresh vegetable oils (Zhang *et al*., 2003; El-Gendy *et al*., 2014) and the recycling of the WFO would reduce waste management problems (Banerjee and Chakraborty, 2009; Niju *et al*., 2014). However, the quality of WFO is very important, as its physicochemical properties depends on the composition of the fresh cooking oil. Not only this, but the WFO would contain undesirable impurities, water and high concentration of FFAs (El-Gendy and Deriase, 2015; El-Gendy *et al*., 2015a).

This chapter gives a background about the progress of the biodiesel production routes and the different available sustainable feedstock for its production. Then it discusses the main factors affecting the success of the most applied biodiesel production technique, which is the transesterification process. It also gives an introduction to the importance of choosing the suitable catalyst and how the type of feedstock affects that. Also, it emphasizes the different possible catalytic transesterification mechanisms. This chapter also discusses in brief how to achieve the biodiesel sustainability via the usage of waste cooking oils as a feedstock and heterogeneous catalysts prepared from natural resources. Then it ends with the challenges and opportunities for enlarging the worldwide biodiesel markets.

2.2 Biodiesel Production

There are mainly four routes for production of biodiesel: direct use of vegetable oils and its blends with petro-diesel, micro-emulsions, thermal cracking and transesterification (Thanh *et al*., 2012; Dwivedi *et al*., 2013; Tan *et al*., 2015a; Verma and Sharma, 2016).

Blending petro-diesel with vegetable oil (i.e., dilution of vegetable oil with petro-diesel) this can improve the viscosity, decrease the injector coking and carbon deposition and enhance the engine performance. However, it is not recommendable for long-term usage in direct-injection engine due to its lower volatility, higher viscosity and reactivity of unsaturated hydrocarbons (Tan *et al*., 2015a).

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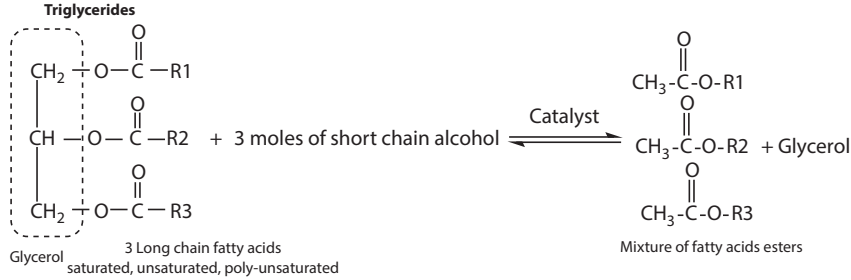
Thermal-cracking or pyrolysis of vegetable oils in the presence of nitrogen and absence of air or oxygen breaks the chemical bonds and procures alkanes, alkenes, alkadyns, aromatics and carboxylic acid. The produced fuel has low viscosity, and high cetane number, with appropriate amount of sulfur, water, deposits and corrosion rate of copper. However, has improper amount of ash, carbon residue and cloud point and the eco-friendly advantage of oxygenated oils vanishes (Srivastava and Prasad, 2000; Helwani *et al*., 2009). Catalytic cracking of triglycerides (TG) using Al_2O_3, MgO, SiO_2/Al_2O_3, NiMo/g-Al_2O_3, $NiSiO_2$, zeolites composites and others have been reported. However, a gasoline-like fuel is mainly formed rather than a diesel-like fuel (Fréty *et al*., 2011; Xu *et al*., 2013; Vu., 2014; Vu *et al*., 2015).

***Micro-emulsions*,** using solvents; methanol, ethanol or butanol and co-surfactant, decrease the viscosity of vegetable oils. But the produced fuel has low cetane number, low calorific value and its combustion would be incomplete, thus, it leads to formation of carbon deposits (Boro *et al*., 2012; Tan *et al*., 2015a).

Generally, the most common process to produce biodiesel is through a transesterification or alcoholysis reaction of TG with a short chain alcohol (such as methanol, ethanol and butanol) in the presence of homogeneous or heterogeneous catalyst to form mono-alkyl esters of long chain fatty acids (i.e., biodiesel) and glycerol as a by-product (Scheme 2.1).

However, the produced biodiesel by this method has high cetane number, low pollutants emissions, high combustion efficiency and the main advantage of the transesterification process is that it saves the oxygen atoms in the produced biodiesel molecule The produced glycerol should be completely removed from the produced biodiesel, otherwise, it would produce formaldehyde or acetaldehyde on fuel combustion. Glycerol is characterized by higher density than biodiesel, so the glycerol phase would be settled at the bottom of the reaction vessel. Phase separation can be



Scheme 2.1 General transesterification reaction.

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performed by settlement which would take several hours or by centrifugation. The produced biodiesel and glycerol should be further purified from unreacted catalyst, alcohol and oil and soap that may have been produced during the reaction. The transesterification process is widely used to reduce the viscosity of TG that consequently would enhance the physicochemical properties of the renewable fuels which would improve the engine performance. The purified glycerol can be used in numerous applications; in industries of moisturizers, soaps, cosmetics, medicines, exclusives, heavy duty detergents and degreaser. Glycerol can be fermented to produce ethanol, i.e., another kind of biofuel. Distillation step is important for removing and recovery of excess alcohol from the produced biodiesel, before the warm water washing step (if homogeneous catalysts are used), which is very effective for removing soap, glycerol and unreacted catalyst and prevents the precipitation of saturated fatty acid esters and retards the formation of emulsions. The excess water after washing can be removed by centrifugation or separation funnels, and then filtered over heated anhydrous Na_2SO_4. However, this has many drawbacks, including the increased overall cost, production time, polluting wastewater effluents, and product loss. Moreover, emulsion due to the soap formation can occur during the wet-washing step of biodiesel, especially if the feedstock was waste cooking oil (WCO) or high FFAs content (Gomes *et al*., 2015). Dry washing is a promising technique for the selectivity of adsorbents, due to its low cost and simple operational design (Atadashi *et al*., 2011a). Membrane extraction is a promising method for purifying biodiesel (Atadashi *et al*., 2011b). Gomes *et al*. (2015) reported the purification of biodiesel by dry cold washing using the cheap, abundant, biodegradable, non-toxic, biocompatible and renewable starch and cellulose natural adsorbents.

The feedstock should be characterized to choose the optimum pretreatment method. Generally, the raw materials would contain TG, FFAs, water and other impurities. For example, vegetable oil contains phospholipids that can be removed in a degumming step, where the phospholipids can produce a commercial emulsifier; lecithin. The excess FFAs can be removed as soaps. Deodorization is an important step, where a steam at 1-6 mm Hg pressure is purged into the oil at 490-550 K to eliminate FFAs, aldehydes, unsaturated hydrocarbons and ketones, those which cause undesirable odors and flavors in the oils. If the FFAs content is higher than 2.5 wt.%, a neutralization step using caustic soda is required. The pretreatment of high FFAs feedstock is preferable to be done through esterification step using acid catalyst (Santacesaria *et al*., 2012), instead of steam distillation or extraction by alcohol methods, since steam distillation needs high temperature and pressure and has low efficiency. Because of the low solubility

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of FFAs in alcohol, extraction by alcohol would need a larger amount of solvent and it is a very complicated process. Solid-acid catalyst is preferable although of its lower rate, as it eliminates the separation, corrosion, toxicity and environmental problems. The main drawback in acid pretreatment is that a huge amount of water is produced that should be removed before the transesterification process. Strong acidic ion-exchange resins can be used for the esterification of FFAs. However, the loss of the catalytic activity is another problem (Leung *et al*., 2010). Iodine can be used as a catalyst to decrease the FFAs content to less than 2% (Li *et al*., 2008). Glycerol in presence of $ZnCl_2$ at high temperature about 200°C can decrease the FFAs producing mon- and di- glycerides. Thus, can be further transesterified using the alkaline catalysts. The advantage of this process is that there is no need of alcohol and the produced water can be vaporized and vented from the mixture, but the main drawbacks are the requirement of high temperature and the relatively slow reaction rate (Van Gerpen *et al*., 2004). The pretreatment step increases the overall cost of biodiesel production, thus there is an increase in the research field to establish catalysts tolerable to high concentrations of FFA. Bi-functional solid acid catalysts can perform simultaneously the esterification and transesterification reactions. The bi-functional catalyst is inorganically and organically functionalized. The inorganic catalyst contains neither the Bronsted nor the Lewis acid sites, unlike the organic ones, which predominate in the transesterification reaction (Diamantopoulos *et al*., 2015).

2.3 Factors Affecting Biodiesel Production Process

2.3.1 The Type of Feedstock

Depending on the feedstock, the biodiesel can be classified into two categories (Gnanaprakasam *et al*., 2013). The first generation is where the biodiesel is derived from edible vegetable oils (e.g. soybean, palm, rapeseed, sunflower, corn, etc.). The second generation, which is considered as one of the advanced biofuels, can be obtained from non-edible oils (e.g., castor, jatropha, jojoba, neem, waste cooking oil, etc.), microalgae, animal fats (e.g., tallow and yellow grease). Europe employs sunflower and rapeseed oils, tropical countries use palm oil, the United States mainly uses soybean oil, while Canada uses canola oil (Singh and Singh, 2010; Diya'uddeen *et al*., 2012). Choosing the right feedstock is very important, since its cost accounts for about 80% of the overall production cost (Demirbas, 2009) and it has also a statistical significant effect on the catalyst activity and

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consequently on the biodiesel yield (El-Gendy and Deriase, 2013). Also, the yield and physicochemical properties of the produced biodiesel are strongly dependent on the used feedstock (El-Gendy and Deriase, 2015). For example, vegetable oils are mainly consisting of TG, approximately 98% and small amounts of mono- and di- glycerides (Koohikamali *et al*., 2012). The TG are esters of three long chain fatty acids (FAs) and one glycerol that contains considerable amounts of oxygen in its structure. The FAs differ in their carbon chain length and number of double bonds. However, the volatility and reactivity of unsaturated hydrocarbon chains are low. Table 2.2 summarizes the empirical formula and structure of the most popular FAs present in vegetable oils (Banerjee *et al*., 2014; Carlini *et al*., 2014).

The FFAs content in the WCO strongly affect the transesterification reaction and the type of catalyst to be used and it should be within a certain limit; otherwise it would cause a lot of operational problems and decrease the biodiesel yield. High FFAs and water contents would lead to soap formation and hydrolysis, respectively, and both reactions result in low biodiesel yield and high catalyst consumption (Banerjee and Chakraborty, 2009;

Table 2.2 Empirical formula and structure of popular FAs present in vegetable oil feedstock.

FAs	Chemical name	Chemical structure	Chemical formula
Lauric	Dodecanoic	C12:0	$C_{12}H_{24}O_2$
Myristic	Tetradecanoic	C14:0	$C_{14}H_{28}O_2$
Palmitic	Hexadecanoic	C16:0	$C_{16}H_{32}O_2$
Stearic	Octadecanoic	C18:0	$C_{18}H_{36}O_2$
Oleic	cis-9-Octadecanoic	C18:1	$C_{18}H_{34}O_2$
Linoleic	cis-9,cis-12-Octadecadienoic	C18:2	$C_{18}H_{32}O_2$
Linoleic	cis-9,cis-12,cis-15-Octadecatrienoic	C18:3	$C_{18}H_{30}O_2$
Arachidic	Eicosanoic	C20:0	$C_{20}H_{40}O_2$
Behemic	Docosanoic	C22:0	$C_{22}H_{44}O_2$
Erucle	cis-13-Docosanoic	C22:1	$C_{22}H_{42}O_2$
Lignoceric	Tetracosanoic	C24:0	$C_{24}H_{48}O_2$

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Suryaputra *et al*., 2013). It has been reported to grant a yield of approximately 90%, water content should not exceed 0.5% (Arun *et al*., 2011). According to Diamantopoulos *et al*. (2015); as low as the cost of the feedstock is as high as the FFAs content will be. A mixture of *Karanja* and *Mahua* (50;50 v/v) was reported to produce under optimum conditions high yield of biodiesel (approximately 95%) with good quality that meets the ASTM standards. The advantages of using the mixed feedstock are: higher biodiesel yield with lower viscosity and higher flash point than that of *Karanja* biodiesel. Moreover, the cost of mixed biodiesel was estimated to be 60-70% lower than that produced from edible or non-edible fats and oils (Yathish *et al*., 2013). Mixtures of rapeseed, soybean and sunflower have been reported as feedstocks for biodiesel production. It was found that oil mixture content affects the FAME distribution (Martinez *et al*., 2014) and the produced biodiesel qualifications (Jurac and Zlatar, 2013). Costa *et al*. (2013) have also studied the production of biodiesel from a mixture of waste fish and olive oils. Galvan *et al*. (2013) have studied the effect of different ratios of soybean oil, beef tallow and poultry fat on the oxidation stability of the produced biodiesel. Then evaluated the kinetics and thermodynamics parameters of the biodiesel oxidation reaction from the optimized mixture of 50, 20 and 30 wt.%, respectively. de Almeida *et al*. (2015) studied the effect of different ratio of waste fish oil, palm oil and WCO mixtures as a feedstock on the viscosity, oxidation stability and cold flow properties on the produced biodiesel.

Several techniques can be applied to reduce the high FFAs content; for example, acid esterification with methanol and sulfuric acid, neutralization with alkalis followed by soap separation by decanter, esterification of FFAs with ion exchange resins or extraction with polar liquids along with acid esterification and distillation of FFAs. Water content is reported to be usually eliminated by heating the waste vegetable oil (WVO) above 100°C (Gnanaprakasam *et al*., 2013), alternatively, by vacuum distillation at 0.05 bar pressure. The suspended solids, food debris, phospholipids and any other impurities can be removed by centrifugation or filtration (Mazubert *et al*., 2013). Usually, methanol or ethanol is applied for the esterification of FFAs. However, Gomes and Vergueiro (2011) reported the glycerolysis of high FFAs oils to be used as a feedstock for biodiesel production. The main advantage of this technique is that the FFA levels are reduced using glycerol, which is a by-product of the transesterification (i.e., biodiesel) reaction. Hydro-esterification is another technique, in which the tri-, di- and mono- glycerides are hydrolyzed to glycerol and concentrated FFAs that transformed to FAME through an esterification reaction. This technique is commercially applied in biodiesel plants in Brazil (Machado *et al*., 2011).

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The viscosity and oxidation stability of the produced biodiesel mainly depends on the type of oil feedstock. The high viscosity biodiesel would deteriorate the atomization, evaporation and air-fuel mixture formation characteristics. That led to improper combustion and higher smoke emission. Not only this, but high viscosity biodiesel would generate some other operational problems, such as difficulty in engine starting, unreliable ignition and deterioration in thermal efficiency. It creates problems in the atomization of the fuel spray and function of the fuel injectors. The cetane number depends on the proportion and location of the double bonds. The higher the iodine number, the higher is the number of double bonds (Pullen and Saeed, 2012). Oil feedstock riches in unsaturated fatty acids, e.g., linoleic and linolenic acids, tends to give biodiesel with low oxidation stability (Ramos *et al*., 2009). The overall characteristics of biodiesel are nearly similar to petro-diesel. Thus, the former is considered as a reliable fuel to replace and/or complement petro-diesel if the need arises. However, biodiesel has a little lower volumetric heating values than petro-diesel (El-Gendy *et al*., 2016).

2.3.2 The Type of Alcohol

The transesterification reaction is also called alcoholysis, in which an alcohol displaces another alcohol in an ester (here; TG), to produce a new monoester and alcohol. This process is similar to hydrolysis, except that a short chain alcohol is employed instead of water. The type of alcohol and its molar ratio relative to the feedstock affect the reaction kinetics and biodiesel yield and characteristics (Koohikamali *et al*., 2012; Verma and Shrma, 2016). Alcohols such as methanol, ethanol, propanol, butanol, and amyl alcohol can be applied in the transesterification reaction. However, methanol is the most widely used, due to its availability, low price, its polarity, its physical and chemical advantages and its low boiling point (65°C), thus excess methanol can be easily separated and recovered. Moreover, it produces higher biodiesel yield (Koohikamali *et al*., 2012). However, in Brazil, since ethanol is more abundant and cheaper than methanol, it is the one used for biodiesel production (Thanh *et al*., 2012; Haigh *et al*., 2014; Ullah *et al*., 2015). Ethanol is more soluble in oil; thus this would decrease the mass transfer limitations and it is less toxic than methanol; also, it can be obtained from renewable sources and is biologically more environmentally benign (Gnanaprakasam *et al*., 2013). However, ethanol or isoproponal would form azeotrope with water, thus it would be difficult to recover excess alcohol or separate it from water during the distillation process (Van Gerpen, 2005). Moreover, glycerol and alkyl-monoesters would

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form stable emulsions during the ethanolysis (Zhou *et al*., 2003; Hossain *et al*., 2010). So, methanol/ethanol mixture is proposed to gain the advantages of both. It has been reported that the type of alcohol affects the reaction conversion rate and the physical properties of the produced biodiesel (Gorji and Ghanei, 2014). For example, using ethanol instead of methanol would produce biodiesel yield with better cold flow properties and higher biodegradability. Longer chain alcohols would produce fuels with better cold flow properties (Canakci, 2007; McNeff *et al*., 2008). However, using methanol will produce higher biodiesel yield from WCO with lower viscosity than biodiesel produced from other alcohols (Hossain *et al*., 2010). Ethanol is recommended in enzymatic reactions (Kumari *et al*., 2009) and butanol can be added as a solvent to avoid the inhibition effect of methanol and glycerol on lipase (Royon *et al*., 2007). The green biomass-derived alcohols; bioethanol and biobutanol as less toxic alcohols compared to methanol with a less negative impact on human health and environment have been reported for the biodiesel production (Brunschwig *et al*., 2012; Abderrahim *et al*., 2014). However, their use in industrial scale is limited due to their higher production cost than that of methanol.

2.3.3 Effect of Alcohol to Oil Molar Ratio

The transesterification process is a three-step reversible reaction. Excess alcohol is needed to shift the equilibrium to the forward direction, i.e., biodiesel production and 1 mole of glycerol, although higher molar ratios are required to move the reaction in the forward direction and yield greater ester conversion in a shorter time (Highina *et al*., 2011). However, excess alcohol over the optimum ratio would decrease the biodiesel yield and increase the recovery cost of the glycerol and the excess alcohol (Knothe and Steidley, 2009). The alcohol oil molar ratio is dependent on the type of the catalyst. A molar ratio of 6:1 is usually used in the industrial alkaline processes to obtain biodiesel yield higher than 98% on a weight basis. But when applying acid catalysts, more alcohol/oil molar ratio is required.

2.3.4 Catalyst Concentration

Catalyst concentration affects the biodiesel yield and it depends on the type of the applied catalyst. As the catalyst concentration increases, the conversion of TG and biodiesel yield increases. Insufficient concentration of catalyst would result in an incomplete conversion of the TG into fatty acid esters (Gnanaprakasam *et al*., 2013). But excess catalyst concentration beyond the optimum value, especially for homogeneous-base catalysts,

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would lower the biodiesel yield due to the formation of soap, while in the case of heterogeneous catalyzed system, excess catalyst concentration would decrease the conversion rate due to the increase of the reaction mixture viscosity and the mass transfer limitation (Kiakalaieh *et al*., 2013a,b; El-Gendy *et al*., 2015b). Also, in enzyme-catalyzed transesterification reaction, increase of enzyme concentration will increase the biodiesel yield but to a certain limit. With the excess enzyme concentration, agglomeration of enzyme would occur and consequently a decrease in the available active sites occurs (Kumari *et al*., 2009).

2.3.5 Catalysts Type

Generally, there are three types of catalyst used in the transesterification reaction: homogeneous, heterogeneous and enzymes (Thangaraj *et al*., 2019). Even the enzymes can be either homogeneous or heterogeneous depending on its mobility. The catalyst type has main effect on the reaction time (Gorji and Ghanei, 2014).

2.3.5.1 Lipases

Both extracellular and intracellular lipases can effectively catalyze the transesterification of TG, either in aqueous or non-aqueous systems. It is highly specific, non-polluting, and chemically clean, it also overcomes most of the alkaline-transesterification problems (Table 2.3); tolerates high FFAs and water contents in the oil feedstock, avoiding the soap formation. Thus, the purification of biodiesel and glycerol is much easier. But enzymes are expensive to be used on commercial scale. The production cost of a lipase catalyst is significantly greater than that of acid or alkaline ones. High concentrations of FFAs and short chain alcohols (methanol and ethanol) would denature the enzyme and glycerol, the main by-product of the transesterification reaction, has a serious negative effect on lipase. Lipases are known to have a propensity to act on long-chain fatty alcohols better than on short-chain ones. To overcome the lipase inactivation; stepwise methanol addition is recommended in industrial process, usually, three steps of 1:1 mole ratio each, and excess dispersed methanol droplets in oil should be avoided. However, reaction system containing approximately 1.5 molar equivalents of methanol against oil, in which, methanol is completely dissolved is mandatory for lipase-catalyzed methanolysis of oils, to increase its stability reaching more than 50 cycles. Enzymes need more stringent control on the reaction conditions, for example; the reaction alcohol/oil molar ratio, temperature pH and the co-solvent type, otherwise

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Table 2.3 A comparable summary for homogeneous alkaline- and lipase-catalyzed transesterification reactions.

Parameter	Homogeneous alkaline catalyst	Lipase
Reaction Temperature (°C)	60-70 depending on the alcohol	30-40
FFA fate	saponification	Esters
Water effect	Interfere with the reaction	No influence
Glycerol recovery	Difficult	Easy
Biodiesel purification	Several times washing	None
Catalyst cost	Relatively cheap	Relatively expensive

the deactivation of the enzyme would occur (Kiakalaieh *et al*., 2013b; El-Gendy *et al*., 2015b). Enzymes require limited amount of water to be active, which should be lower than the monolayer amount of water molecules around the enzyme molecules. If the water content in the feedstock exceeds this limit, it will deactivate lipase and consequently will decrease the conversion and biodiesel yield (Shah *et al*., 2003; Kumari *et al*., 2009).

Different types of lipases have been reported for high yield of biodiesel (> 80%); *Candida rugose* lipase powder, immobilized *Mucor miehei* lipase (Liposzyme IM-20), immobilized *Rhizomucor miehei* (Liposzyme IM-77), *Rhizopus oryzae* lipase, immobilized *Candida antractica* lipase (Novozyme 435), *Pseudomonas cepacia*, *Pseudomonas fluorescens*, *Burkholderia cepacia* and *Penicillium camembertii* (Iso *et al*., 2001; Devanesan *et al*., 2007; Yagiz *et al*., 2007; Yan *et al*., 2011; Balasubramaniam *et al*., 2012; El-Gendy *et al*., 2015b).

Pseudomonas cepacia lipase is reported to have substantial methanol tolerance, producing high biodiesel yield in reaction mixture with up to 2 or 3 molar equivalents of methanol to oil (M:O). Novozyme 435 is reported to be the most effective for methanolysis among lipases (El-Gendy *et al*., 2015b).

Application of magnetic Fe_3O_4 nano-particles for immobilization of *Thermomyces lanuginose* lipase to enhance the transesterification of soybean oil has been reported (Xie and Ma, 2010). Li and Dong (2016) reported the application of the RSM based on three-level-four-factor

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D-optimal design to optimize the transesterification of cotton seed oil with methanol in presence of *Pichia guilliermondii* lipase immobilized on hydrophobic magnetic particles. Where, approximately 89% biodiesel yield was obtained at optimum operating conditions of 4.715:1 M:O molar ratio, 38.76°C, 31.3% immobilized lipase and 10.4% water content.

To overcome the expensive and complex process of purification of enzymes, there are considerable researches for direct use of whole cells as biocatalyst, i.e., immobilized cells. For example, using particles (BSPs) has several advantages; lower cost as no chemical additives, no need for cell reproduction, aseptic handling of particles is unnecessary, prevent cell contamination, there is a large mass transfer rate of substrate and production within the BSPs, reusability, stability of lipase activity over a long period, durability against mechanical shear, easy handling and bioreactor scale-up in batch and continuous processes.

2.3.5.2 Acid Catalysts

Acid catalyst can be applied simultaneously for both esterification and transesterification reactions (Lotero *et al.*, 2005).

Homogeneous acid catalysts (such as, sulfuric, phosphoric, hydrochloric and organic sulfonic acids) can tolerate high concentrations of FFAs. It is more suitable for feedstock with high water content, low-grade feedstock like sulfur olive oil and such oils with 160 mg KOH/g (Boey *et al.*, 2011a). The extraction and transesterification can be performed simultaneously, avoiding the pre-extraction of the seed oil. Also, it has the advantage of the simultaneous esterification along with the transesterification and it prevents the soap formation. Acid-catalyzed transesterification reaction is an energy-intensive process and operates at high temperature and pressure, needs high alcohol/oil molar ratio and high catalyst concentration. The rate of acid-catalyzed transesterification reaction is much lower than the alkali-catalyzed ones and requires a higher alcohol/oil molar ratio. It is difficult to recycle the catalyst and causes serious environmental and corrosion problems. So, equipment needs to withstand this acidic environment.

The solid acid-catalysts—zirconium oxide, titanium oxide and zinc oxide—are transition metal oxides with good acidic properties to be applied in biodiesel production. They have good potential in eliminating the corrosion and environmental hazard problems associated with the liquid acid catalysts. Moreover, it is recyclable. The main disadvantages of acid-heterogeneous catalysts are: limited density of acid sites, low catalyst porosity, penetration limitations and the catalyst high price (Leung *et al.*, 2010; Chouhan and Sarma, 2011). There are several factors that should be

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controlled to achieve the maximum catalytic efficiency in solid acid catalysts; the higher the acidity of the catalyst, the better its activity is, the catalyst should be porous, with interconnecting pores, thus, the entire surface of the catalyst would be available for promoting the transesterification reaction. The more hydrophobic the surface of the catalyst is, the more the promotion of preferential adsorption of oily hydrophobic species on the catalyst surface is. Thus, this would avoid the deactivation of the catalytic sites by the strong adsorption of polar by-products, i.e. glycerol or water. It is important to measure the hydrophobicity of the solid-catalyst to appropriately correlate this with its activity. Zeolite has been reported for biodiesel production, because of its uniform pore structure (Damyanova *et al*., 2008). However, Zeolites β are reported not to exhibit high activity in the transesterification reaction, but it has a selective removal of the FFAs in waste oils (Diamantopoulos *et al*., 2015). The Y-type zeolite, which is a weak solid acid catalyst, has been reported for its good reactivity in a continuous tubular reactor at atmospheric pressure (Wang *et al*., 2012). Zeolites have the ability to be modulated to exhibit hydrophobic characteristics without altering its functionalized acidic sites. This can be done by incorporation of heteropoly acids (HPAs) in their pore structures. The HPAs have the advantage of water tolerance. The heteropoly tungstate CsHPW catalyst has been reported for its high activity, water tolerance, stability, reusability and environmentally benign nature, during its application in biodiesel production, due to its porous structure and high surface acidity (Chai *et al*., 2007; Diamantopoulos *et al*., 2015). Singh and Patel (2014) reported the active acid catalyst; heteropoly tungstate ($H_3PW_{12}O_{40}$) for simultaneous esterification and transesterification of waste oils. Mono lacunary phosphotungstates $PW_{11}O_{39}^{7-}$ (PW_{11}) can be formed by creating a defect in its structure, i.e., by the removal of one W-O octahedral from the fully occupied phosphotungstate ($PW_{12}O_{40}^{3-}$). Singh and Patel (2015) reported the application of a series of acidic solid catalyst containing 10-40 wt.% PW_{11} anchored to MCM-41 and their application in the transesterification of WCO. Where, 90% conversion occurred at 30% PW_{11}, 8:1 M:O w/w ratio, 7 wt.% catalyst concentration, 65°C, 16 h and 800 rpm. There are several reports about ZrO and its application in transesterification reaction rather than other transition metal oxides due to its relatively strong acidity and its large pores size that would minimizes the diffusional limitations as it can accommodate the large free acids molecules. Its acidity can be also enhanced by anions like sulfate and tungstate (Ardizzone *et al*., 2004). Where, presence of SO_4^{2-} anions, promotes the Bronsted acid sites on the catalyst surfaces (He *et al*., 2007). Lopez *et al*. (2007) reported that calcination at 800°C increases the catalytic activity of the strong acid catalyst

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ZrO_2/WO_3^{2-}, with the formation of 161 μmol/g Bronsted acid sites. Ramu *et al.* (2004) reported that the amount of loaded WO_3 and calcination temperature strongly affect the catalytic activity of ZrO_2/WO_3^{2-}. The highest activity was achieved with 5 wt.% loading of WO_3 and 500°C calcination temperature. The activity is attributed to the formation of tetragonal phase of ZrO_2, which would be transferred to the monoclinic phase at temperature beyond 500°C. The excess coverage of WO_3 on ZrO_2 would decrease the acidity of the catalyst. Owing to the extreme thermal and mechanical stability of alumina and its high specific surface area, large pore size and pore volume, it is widely used as a support in catalysis process (Zabeti *et al.*, 2009). $Al_2O_3/ZrO_2/WO_3$ solid acid catalyst was prepared by co-precipitation method and applied for transesterification reaction (Furuta *et al.*, 2006). The RSM has been reported to optimize biodiesel production from waste cooking palm oil using Sr/ZrO_2 mixed heterogeneous catalyst, that yielded approximately 80% FAME at 29:1 M:O, 2.7 wt.% catalyst concentration and 115.5°C within 87 min (Omar and Amin, 2011). Hillion *et al.* (2003) have reported a continuous process for biodiesel production from rapeseed and soy oils applying a mixed metal oxide catalyst of zinc and aluminum. Mixed metal oxides of alumina, titanium, zirconium and antimony oxides reported high oil conversion of approximately 99% (Su and Guo, 2014). The impregnation of alumina-silicates with sulfuric acid is reported to increase the catalyst activity (Mittelbach *et al.*, 1995). Aluminum phosphate solid acid catalyst was patented by Kaita *et al.* (2002) and the catalyst shape, found to be highly affects the methyl ester yield. Sulfonic acid supported by mesoporous silica was patented by Lin and Radu (2006) as a strong solid acid catalyst for transesterification reactions. Di Serio *et al.* (2007) reported the good activity of vanadium phosphate solid acid catalyst for the transesterification reaction of soybean oil with methanol at 150°C, low catalyst concentration; 0.2 wt.% and alcohol/oil molar ratio; 1:1, within a short time; 1 h. The catalyst could be readily regenerated. However, relatively low catalyst deactivation would occur at higher temperature, due to the reduction of V^{5+} to V^{3+} with methanol. The catalyst activity of Fe-Zn double metal cyanide complex is attributed to the Lewis acid active sites of Zn^{+2} on the catalyst surface. It is also characterized with good hydrophobicity, that it shows good transesterification efficiency for oils with up to 20% water content (Sreeprasanth *et al.*, 2006). Sunita *et al.* (2007) reported that zirconia-supported isopoly tungsten is more active than that of heterpoly tungsten, since isopoly tungsten has more Bronsted acid sites. Ion-exchange resins such as Amberlyst-15 and Nafion-NR50 with abundant sulfonic acid groups are reported to be effective in the biodiesel production process (Zuo *et al.*, 2013). However, the

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swelling of organic resins is the main drawback, as it affects the accessibility of the acidic sites and consequently its activity. Not only this, but it is expensive and most of the ion exchange resins are not thermally stable at high temperatures, which is required for the completion of the acid-transesterification reaction (Kiss *et al*., 2006). Thus, these mentioned drawbacks limit their industrial applications. The sulfated zirconia (SZ) and the more modified ones with sulfate ions are well known for industrial applications, as they are characterized by being super-acidic, high activity, very selective and thermally stable catalysts. Moreover, it can restore its original activity by a simple calcination process (Kiss *et al*., 2008; Patel *et al*., 2013). But, it is expensive, since the zirconium itself is a rare and costly metal. Not only this, but high temperature is required for calcination and reactivation of these catalysts.

There are a few reports about a new strategy of preparing carbohydrate-based solid acid catalysts from various cheap and readily available starting materials, including; cellulose, bagasse, D-glucose, starch and sucrose and their activity has been examined for the production of biodiesel from high FFAs content WCO (Toda *et al*., 2005; Takagaki *et al*., 2006; Lou *et al*., 2008; Konwar *et al*., 2014; Zhang *et al*., 2015). These green-catalysts are characterized by being non-toxic, inexpensive, recyclable and eco-friendly, have high stability, numerous strong acid sites, large pores and hydrophobic surface. They can be produced from agricultural wastes, that not only reduce the cost of procuring and preparation of the catalyst, but it would also open additional revenue for farmers. Moreover, the use of agricultural wastes for catalyst preparation will solve one of the major waste management problems. They are expected to display much higher activity than the expensive inorganic-oxide solid acids such as zeolite, zirconia and niobic acid. Since, inorganic-oxide solid acids have lower densities of effective acid sites, readily lose their activities under harsh conditions, and have small pores, thus are not suitable for biodiesel productions because of the diffusion limitation of the large fatty acids molecules. Not only this, but as aforementioned, high temperatures are also required for calcination and reactivation of these expensive catalysts (Sani *et al*., 2014). Okamura *et al*. (2006) reported that the incomplete carbonization of d-glucose produces a rigid carbon material composed of small polycyclic aromatic carbon sheets in a three-dimensional sp^3-bonded structure. The sulfonation of this carbonized material produces a highly stable solid acid catalyst that can be applied in the esterification of high FFAs as it is characterized by high concentration of active SO_3H sites, that is physically robust and not leached during its use. Zong *et al*. (2007) reported the good esterification of oleic, palmitic and stearic acids with methanol

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using a D-glucose-derived catalyst. Lou *et al.* (2008) reported the preparation of a strong acid starch-derived solid catalyst which is insoluble in the tested solvents and liquid reactants (water, methanol, n-hexane, t-butanol, oleic acid, triolein and WCO). Moreover, it has excellent operational stability and showed higher activities than the typical sulfated zirconia and niobic acid for converting high FFA-containing WCO (27.8 wt.% FFA) to biodiesel by simultaneous esterification and transesterification reactions. That produced about 92% biodiesel yield after 8h. Dehkhoda *et al.* (2010) reported a simultaneous catalyzed esterification and transesterification reactions of canola oil with high concentration of FFAs using a biochar sulfonated acid solid catalyst. That consisted of a flexible carbon-based framework with highly dispersed polycyclic aromatic hydrocarbons containing sulfonic acid groups. The high activity and catalytic stability is attributed to the high acid size density, large pores size which provides more acidic sites for the reactants, the hydrophobicity which prevents the hydration of –OH species and finally, the hydrophilic functional groups (-SO_3H) which can improve the accessibility of methanol to the TG and the FFAs. Hara (2010) reported the high transesterification activity and reusability of solid sulphonated carbon catalysts produced from sugars, starch and cellulose. Chen and Fang (2011) reported FAME yield of approximately 90% from waste cottonseed oil (FFA 55.2 wt.%) using acid sulfonated glucose/starch carbon based catalyst at 20:1 M:O molar ratio, 5 wt.% catalyst loading, 80°C and 600 rpm, within 12 h reaction time. The non-edible and low-cost palm fatty acid distillate (PFAD) is a by-product produced during the refining of palm oil within the fatty acid stripping and deodorization stages. It can be used as a fuel for power plants and industrial boilers and as a source for fatty acids for some non-food industrial applications (Cheah *et al.*, 2010). Chen *et al.* (2012) reported the preparation of solid acid catalyst throughout the sulfonation of partially carbonized sugarcane bagasse. It was applied for the esterification of high acid value PFAD (195–215 mg KOH/g), that produced 80% FAM yield within 30 min, methanol and catalyst weight ratios of 20 and 11.5 wt.% of PFAD, respectively at 170°C. Lou *et al.* (2012) reported that the bagasse derived solid acid catalyst can be reused for eight successive esterification cycles of oleic acid with methanol, retaining approximately 90% of its original activity. Ezebor *et al.* (2014) reported the transesterification of high FFA content WCO by solid acid derived catalyst; of sugarcane bagasse and oil palm trunk; yielding 83.2 and 80.6%, respectively, under a pseudo-infinite methanol state. Li *et al.* (2013) reported the preparation of sulfonated carbon-based solid acid catalyst by the sulfonation of rice husk char (RHC) with concentrated sulfuric acid at 90°C and 0.25 h. That yielded 98.7% conversion of oleic acid at 4:1 M:oleic

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acid molar ratio, 5 wt.% catalyst concentration, 110°C and 2 h. Moreover, the prepared catalyst retained its esterification activity for seven successive cycles. Li *et al.* (2014) have also reported the production of biodiesel from WCO using the solid acid catalyst RHC-SO_3 in a continuous reaction apparatus with a rectifying column, at 20:1 M:O molar ratio, 350 rpm, 5 wt.% catalyst concentration and 110°C to instantaneously remove the produced water. That yielded 87.57% FAME yield compared to 45.17% applying the commercial Amberlyst-15 catalyst with 15 h reaction time. The catalyst retained most of its activity after five successive cycles, recoding 80.20% FAME yield, due to the loss of approximately 19.32% of the $-SO_3$ group, relative to the fresh catalyst. Dawodu *et al.* (2014) reported a sulphonated acid solid catalyst derived from the non-edible seed *Calophyllum inophyllum* which expressed high biodiesel production from non-edible oil at low M:O 4:1 molar ratio, 110°C and 2 h reaction time and can be reused for seven successive cycles despite of the leaching of 23% of its active sites, recording approximately 84% biodiesel yield. Prabhavathi Devi *et al.* (2014) reported the reparation of a green recyclable SO_3H-carbon catalyst from glycerol and studied its application in the transesterification of *Karanja* oil with high FFA content (7.5%) in a single step. That yielded more than 99% biodiesel at 160°C, 45:1 M:O molar ratio, 20 wt.% catalyst concentration and 4 h reaction time. Zeng *et al.* (2014) reported a strong Bronsted solid acid catalyst derived from waste peanut shells that produced high biodiesel yield (approximately 90%) from cottonseed oil at 9:1 M:O ratio. Diamantopoulos *et al.* (2015) reported that the higher activity of sugar-derived acid catalysts in oleic acid esterification reactions is attributed to the higher acid sites concentrations on the catalyst surface relative to other acid solid catalysts. Shang *et al.* (2015) reported the preparation of an active biodegradable peanut shell-derived solid acid of amorphous carbon bearing SO_3H, COOH, and phenolic OH groups by a one-step process to simplify the operational process and reduce the catalyst cost. That yielded approximately 98% biodiesel from oleic acid at 10:1 M:O molar ratio, 4 wt.% catalyst loading, 3h and 85°C. Moreover, the catalyst was used for six successive cycles without losing its activity.

2.3.5.3 Alkaline Catalysts

Nowadays, alkali-catalyzed transesterification reaction is the most widely applied process for biodiesel production. However, the maximum amount of FFA content is below 2.5 wt.%, and pretreatment step is required for feedstock with higher FFA content. Figure 2.1 summarizes the process of alkali-catalyzed biodiesel production.

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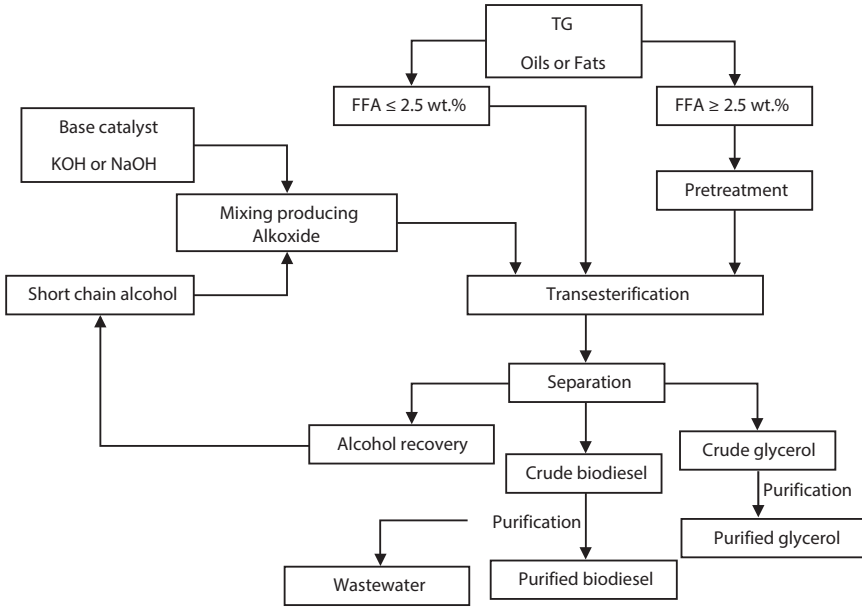

Figure 2.1 Simplified flow chart of base-catalyzed biodiesel production.

Homogeneous alkaline catalysts used for transesterification reaction are; NaOH, KOH and alkoxides, such as sodium and potassium methoxides. The alkali-catalyzed transesterification proceeds approximately 4000 times faster than that of acid-catalyzed ones and can be performed in relatively modest operating conditions (Wen *et al*., 2010a). Thus, the alkali-catalyzed process is the most commercially applied. The methoxides are found to be more effective than the hydroxides. Presumably, this might be because a small amount of water is produced upon mixing NaOH or KOH with methanol. The methoxides can give relatively higher yields (>98%), in a short time (reaching to 30 min) at low molar concentration (0.5 mole%). Sodium methoxide has been reported for being the most active basic catalyst, with good phase separation, without formation of water and soap (Bacovsky *et al*., 2007). However, due to the cheapness of NaOH and KOH, they are widely used in industrial biodiesel production. But it requires higher catalyst concentration 1 – 2 mole% to achieve high biodiesel yield. Moreover, KOH catalyst is less effective than the sodium based catalysts (Atapour *et al*., 2014). Arquiza *et al*. (2000) reported 94% biodiesel yield through the transesterification of used coconut oil with methanol at 6:1 M:O molar ratio, 60-65°C and 0.5 wt.% NaOH catalyst. Behzadi and Farid (2009) reported the biodiesel production from soybean oil using a

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continuous gas-liquid reactor, producing high biodiesel yield 94-96% within the optimal conditions; NaOH 5-7 g/L of methanol, methanol flow rate of 17.2 L/h, 100-120°C. Sunflower (*Helianthus annus*) oil is one of the leading oils that mainly used for human consumption. Thus a large amount of sunflower WCO is produced annually all-over the world. Hossain and Boyce (2009) have reported that NaOH produces more emulsion than KOH and causes problems during product separation and upon optimization of biodiesel production of sunflower waste cooking using KOH the yield reached 99.5% at 6:1 M:O, 1 wt.% catalyst loading, 40°C and 320 rpm stirring speed. Castor oil as a non-edible is a promising source for biodiesel production, despite having high viscosity. Since it has no sulfur, high oxygen content and high cetane number thus promotes more combustion completion and better ignition, respectively (Conceicao *et al*., 2007). Moreover, the presence of high content of ricinoleic acid, the hydroxylated fatty acid, in castor oil improves its lubricity over other vegetable oils (Ramezani *et al*., 2010). Castor oil biodiesel is characterized with better clod flow properties, where the cloud and pour points could reach -23 and -45, respectively (Ismail *et al*., 2016). Jeong and Park (2009) applied RSM to optimize the transesterification of castor oil with methanol in presence of KOH catalyst. That yielded 92% biodiesel at 8.24:1 M: molar ratio, 1.45 wt.% catalyst concentration, 35.5°C and 40 min reaction time. Tiwari *et al*. (2007) applied RSM based on central composite rotatable design (CCRD) to optimize a two-step-acid-base catalyzed transesterification process of *Jatropha curcas* oil with 14% FFA. That reached to less than 1% FFA at optimum operating conditions of; 1.43% (v/v) H_2SO_4 catalyst concentration, 0.28 M:O (v/v), and 88 min reaction time at a constant reaction temperature of 60°C. Then reached to biodiesel yield of more than 99% at optimum conditions of KOH–transesterification of the pretreated oil; 0.16 M:O (v/v) and 24 min of reaction time at constant catalyst concentration, reaction time and temperature of 0.55 wt.%, 90 min and 60°C, respectively. Boonmee *et al*. (2010) reported the application of RSM based on CCD to optimize the biodiesel production from the *Jatropha curcas* L. oil using NaOH homogeneous catalyst. That yielded 99.87% FAME at optimum conditions of 6 M:O molar ratio, 1 wt.% catalyst concentration and 90 min reaction time, at a fixed reaction temperature (60°C) and mixing speed (400 rpm). Shalaby and El-Gendy (2012) reported a two-step alkaline transesterification process of high acid value WCO (5.1 mg KOH/g) with methanol using KOH. That yielded 85 wt.% purified biodiesel yield. Thirumarimurugan *et al*. (2012) reported 80% biodiesel yield from WCO at 6:1 M:O, 1 wt.% NaOH loading, 60°C, 300 rpm and 3 h. Cunha Jr. *et al*. (2013) reported the application of RSM based on 3^3 full factorial design (FFD) to optimize the

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ethanolysis of a mixture of chicken and swine waste fats with KOH at 2000 rpm in a 10 L tubular glass reactor. Where the optimum condition; 30°C, 0.96 wt.% catalyst, 7:1 ethanol:fat produced approximately 83% fatty acid ethyl ester and the obtained biodiesel was purified by elution through a silica-gel column under vacuum. Goyal *et al.* (2013) reported the application of RSM based on CCD to optimize the transesterification of acid pretreated *Jatropha curcas* oil. That yielded 98.3% biodiesel at optimum operating conditions; 11:1 M:O molar ratio, 1 wt.% NaOH concentration, 110 min, 55°C. The WCO coming out from restaurants can be re-used by street sellers to fry their food producing what is called second-used cooking oils. Kawentar and Budiman (2013) reported 92.76% biodiesel yield from a second-used cooking oil at 6.18:1 M:O, 1 wt.% KOH loading, 65°C and 60 min. Veličkovic *et al.* (2013) applied RSM based on 3^3 FFD of experiments to optimize a base-catalyzed ethanolysis process of sunflower oil in presence of NaOH. Where, 97.6% fatty acid ethyl ester was obtained at optimum conditions of; 12:1 ethanol:oil molar ratio and 75°C, 1.25% catalyst concentration. Mostafa and El-Gendy (2013) reported the transesterification of lipid extract from *Spirulina platensis* with methanol in presence of NaOH catalyst. That yielded 16 and 3.45 wt.% biodiesel and crude glycerol relative to the weight of obtained microalga biomass. Banerjee *et al.* (2014) reported 94% biodiesel yield from used vegetable oil (UVO) at 15:1 M:O, 0.69 wt.% NaOH loading, 55°C, 1000 rpm and 90 min. El-Gendy *et al.* (2014a) reported the application of RSM based on CCD of experiments to optimize the biodiesel production from WFO collected from different local restaurants using methanol and KOH, where nearly a complete conversion occurred at 9:1 M:O, 0.6% KOH wt.%, 1 h at 60°C and 300 rpm. many used cooking oils from restaurants were re-used by street sellers to fry their food. Aniya *et al.* (2015) studied the kinetics of batch biodiesel production from *Karanja* oil using methanol (6:1) and KOH (1 wt.%) at 600 rpm at different temperatures 35-55°C. Where, the ester content increased with time until attaining equilibrium and then remained in a steady state. The overall transesterification reaction is modeled based on three control mechanisms, an initial mass transfer regime followed by irreversible pseudo-second-order and finally a reversible second-order equilibrium reaction. It was noticed that at high temperatures equilibrium reaction rate was more dominant than the irreversible pseudo-homogeneous reaction, thus the reaction becomes initially irreversible reaction controlled. de Almeida *et al.* (2015) reported the production of biodiesel from a mixture of waste fish oil with palm oil that characterized by high oxidation stability due to its significant content of saturated fatty acids. Since the cheap and sustainable WCO has better oxidation stability

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than that of waste fish oil, it has been also used in that study. The biodiesel production was performed in two-step processes; firstly by acid esterification using 6:1 M:O molar ratio, 1 wt.% sulfuric acid, 60°C and 1 h. Then, secondly followed by basic homogeneous transesterification reaction using 9:1 M:O molar ratio, 0.5 wt.% NaOH, 60°C and 1 h. El-Gendy *et al.* (2015c) reported the application of RSM based on CCRD of experiments with three levels (coded by -1, 0, and +1) and ± α of ± 1.82116, to study the significance and interactive effects of five variables; M:O molar ratio, catalyst concentration, operating temperature, reaction time and mixing rate on KOH catalyzed transesterification reaction of WCO to maximize the biodiesel yield. Approximately 99 wt.% biodiesel yield was obtained at optimum operating conditions of; 7.54:1 M:O, 0.875 wt.% KOH concentration, 52.7°C, 1.17 h and 266 rpm. Kumar *et al.* (2015) used Taguchi experimental design to optimize the transesterification of *Manilkara zapota* (L.) seed oil with methanol in presence of KOH homogeneous catalyst. That yielded 94.83% biodiesel yield at 6:1 M:O molar ratio, 50°C, 90 min and 1 wt.% catalyst concentration. Betiku *et al.* (2015) reported the methanolysis of acid pretreated shea butter oi in presence of KOH. Onukwuli *et al.* (2016) employed a two-level-four-factor CCD of experiments and RSM to optimize the transesterification of cotton seed oil with methanol in presence of KOH basic homogeneous catalyst. That yielded approximately 96% biodiesel at the following optimal conditions; 6:1 M:O molar ratio, 0.6 wt.% catalyst concentration, 55°C and 60 min at constant mixing speed of 300 rpm. Stamenković *et al.* (2015) reported also the methanolysis of hempseed oil in presence of KOH. Verma and Sharma (2016) reported that ethanolysis yielded lower biodiesel yield than that of methanolysis and needs longer time for reaction completion, since ethanol acts as an acyl acceptor in the transesterification reaction. Thus, the separation of fatty acid ethyl ester from glycerol is more difficult than that of FAME. The RSM based on a Box-Behnken experimental design of four variables and three levels was employed to optimize the KOH- methanolysis and ethanolysis reaction of acid pretreated *Karanja* oil. The methanolysis yielded 91.05% biodiesel at optimum conditions of; 10.44:1 M:O molar ratio, 1.22 wt.% catalyst concentration, 66.8°C and 90.78 min, while the ethanolysis process yielded a lower maximum biodiesel yield of 77.4% at 8.42:1 ethanol:oil molar ratio, 1.22 wt.% catalyst concentration, 61.3°C and 120 min (Verma and Sharma, 2016).

Alkaline-homogeneous catalysts are hygroscopic and absorb water from air during storage. The use of alkaline catalysts has also some drawbacks; the alkali reacts with the FFAs producing large amounts of unwanted soap (Scheme 2.2), creating serious problems; consumes the catalyst, reduces

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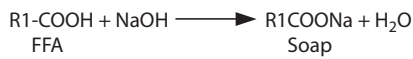
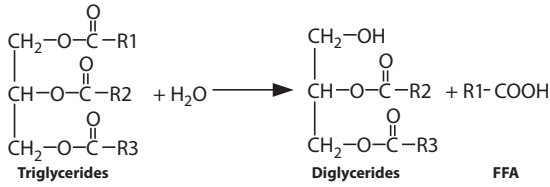


Scheme 2.2 Saponification reaction.

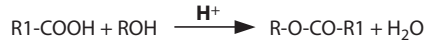
the catalyst efficiency, thus, more catalyst will be needed and it also causes an increase in viscosity and formation of gels.

It also causes difficulties in glycerol and biodiesel separation that lower the biodiesel yield and increase the overall production cost. It is generally recommended that the acidity of the oil feedstock should be less than 1 mg KOH/g oil (Mazubert *et al.*, 2013). Usually the reaction requires high alcohol/oil molar ratio (such as 6:1 or higher) instead the stoichiometric 3:1 ratio to achieve high biodiesel yield. Also, the removal of unreacted catalysts is a technical challenge and brings extra cost to the final product. A large amount of water is required for the washing step to neutralize the produced biodiesel and remove the unreacted catalyst. Thus, a huge amount of very toxic wastewater from the transesterification process is produced which produces a new waste management problem. One of the main problems is the presence of water in the feedstock or its production throughout the saponification reaction, as it retards the transesterification reaction through a hydrolysis reaction. Thus, hydrolysis the TG to diglyceride and forms more FFA (Scheme 2.3). However, the FFA can be reacted with alcohol in presence of acid catalyst to produce biodiesel (Scheme 2.4).

The basic heterogeneous catalysts can be classified into four groups: a single component metal oxide, zeolites, supported alkali metal and clay minerals (Kumar *et al.*, 2014). Using heterogeneous solid catalysts; such as metal hydroxides and alkali earth metal oxides; such as calcium oxide,



Scheme 2.3 Hydrolysis reaction.



Scheme 2.4 Acid-catalyzed esterification of FFA.

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magnesium oxide and strontium oxide overcomes most of the drawbacks of the homogeneous catalysts. It is more environmentally friendly. Solid catalysts are not consumed or dissolved in the reaction mixture, can be easily separated from the products, can be regenerated and reused. No washing step for the product is required, where biodiesel and glycerol with high purity would be obtained. It can be applied in batch and continuous processes, which improves the economy of biodiesel production. It can catalyze the esterification and transesterification reactions, thus, the pre-esterification step in high FFAs feedstock would be eliminated. One of the major drawbacks of heterogeneous catalysts is that it is a three-phase system: catalyst, alcohol and oil. That leads to diffusion limitations, which consequently lower the reaction rate. To overcome these mass transfer limitations; co-solvents such as tetrahydrofuran (THF) and dimethyl sulfoxide (DMSO) can be applied to promote miscibility of oil and alcohol. Thus, accelerate the reaction rate. The use of structure promoters or catalyst supports which would increase the specific surface area and pores for active species that can anchor and react with large TG molecules, would also overcome the mass transfer limitations. However, active species of heterogeneous base-catalysts can be leached out into the reaction mixture, which consequently would react with FFAs in vegetable oils producing soap.

MgO has the weakest base strength and solubility in methanol. However, its activity is high under supercritical temperatures and high pressure (Wang and Yang, 2007). Although SrO is characterized by high stability and can be reused for more than 10 cycles without losing its activity, not many works have reported about this catalyst (Liu *et al*., 2007). Although the basicity of the metal oxides can be ranked as follow; CaO < SrO < BaO, which thus affect their catalytic activity (Mootabadi *et al*., 2010). However, among alkali earth metal oxides, CaO has attracted many researchers, due to its relatively high basic strength, high activity, low cost, low solubility in methanol, it is considered as environmentally benign catalyst, readily available, can be prepared from cheap sources (e.g., calcium hydroxide) and natural ones (e.g., limestone, dolomite, and natural waste shells), can be applied successfully in the transesterification of low-quality oils, as it can tolerate high FFAs and moisture contents, it is characterized by long life activity and can be reused for approximately eight cycles with minimum loss of its activity. Kouzu *et al*. (2008) reported maximum biodiesel production from soybean oil and WCO, using 12:1 M:O molar ratio at 65°C. Son *et al*. (2010) reported 92 and 84% biodiesel yield from sunflower oil and WCO, respectively, at 12:1 M:O molar ratio, 80°C, 120 min, 3 wt.% CaO loading. Avramović *et al*. (2015) reported the application of RSM to optimize the ethanolysis of sunflower oil using CaO.

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Where the maximum fatty acid ethyl ester content (98%) was optioned at optimal conditions of 14:1 M:O molar ratio, 17 wt.% catalyst concentration, 72°C, 440 min. El-Gendy *et al.* (2014b) used the RSM based on face centered design (FCCD) of experiments to statistically evaluate and optimize the conditions for maximum production of biodiesel from waste frying sunflower oil using CaO and to study the significance and interaction effects of M:O molar ratio, catalyst concentration, and reaction time on the yield. Based on an estimated quadratic model, the optimum operating conditions; 7.05:1 M:O, 8.21 CaO wt.% and 1.5 h at 60°C reaction temperature and 300 rpm mixing rate yielded 93 wt.% biodiesel.

The main drawback of CaO is that it easily loses its catalytic activity when exposed to air. This is due to its reaction with humidity and CO_2, producing CaOH and CaO_3, respectively (Scheme 2.5).

In order to overcome this problem, it is recommendable to thermally pretreat the catalyst at 700°C before its application in the transesterification reaction (Granados *et al.*, 2007). However, it was reported by Liu *et al.* (2008a,b) that small amounts of water would improve CaO activity and increase the biodiesel yield. Kesic *et al.* (2012) reported that mixed metal oxides catalysts like CaO-ZnO reduces the required temperature for decomposition of $CaCO_3$ and activation of CaO catalyst. The mixed oxides of CaO-NiO and CaO-Nd_2O_3 reported to exhibit higher basicity, activity, stability reusability and ease of separation than each metal oxide alone (Teo *et al.*, 2014a).

Mg-Al hydrotalcite for biodiesel production was patented by Siano *et al.* (2006), its activity depends on the ratio of Mg/Al, the highest activity occurs with 3:1 Mg/Al ratio. It is suitable for oils with high water content with up to 10,000 ppm and low alcohol/oil ratio as low as 0.45. Di Serio *et al.* (2006) reported the temperature programmed desorption (TPD) analysis of Mg-Al hydrotalcite calcined at 500°C and attributed its high basicity and consequently its high catalytic activity to four basic sites; weak basic sites related to OH^- surface groups, medium basic sites of oxygen atoms in both Mg^{2+}-O^{2-} and Al^{3+}- O^{2-}, strong basic sites and super-basic sites attributed to isolated O^{2-} anions. Not only this, but its high activity is related to its high porosity and large pore size. Thus it would show higher activity than the

$$CaO + H_2O \longrightarrow Ca(OH)_2$$
$$CaO + CO_2 \longrightarrow CaCO_3$$
$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

Scheme 2.5 Poisoning of CaO surface basic sites.

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microporous MgO. The higher basicity of Mg-Al hydrotalcite with specific surface area 82 m^2/g promotes the transesterification efficiency of soybean oil with methanol over that of MgO supported on MCM-41, although of its higher specific surface area of 1289 m^2/g (Georgogianni *et al*., 2009). Potassium supported by alumina is a solid base catalyst that can be prepared by impregnation of aqueous solution of potassium nitrate on alumina, and then calcined at 500°C, and expresses good transesterification activity, due to the basic sites on the surface of the catalyst' K_2O and Al-O-K (Xie *et al*., 2006). The precursor type would affect the catalytic activity, Xie and Li (2006) reported that although the basicity of Al_2O_3/KI is less than that of Al_2O_3/KNO_3, but more biodiesel yield would obtain using Al_2O_3/KI. Jacobson *et al*. (2008) reported the high activity, thermal stability and reusability of zinc stearate supported on silica (ZS/Si) catalyst for transesterification of WCO, yielding 98 wt.% of FAME at 18:1 M:O molar ratio, 3 wt.% catalyst concentration, 600 rpm mixing rate and 200°C. The mixed oxide CaO-MgO supported on alumina reported to express high FAME yield from *Nannochloropis oculata* algal oil, due to the higher active sites on the catalyst surface (Teo *et al*., 2014b). The doping of lithium on CaO, was reported to increase the basicity of the catalyst (Alonso *et al*., 2009). Puna *et al*. (2014) reported the preparation of nano-crystalline Li/CaO catalyst using the wet impregnation method, followed by calcination and then applied for transesterification of soybean oil. Boey *et al*. (2011a) reported approximately 93% methanolysis of soybean oil by 15 wt.% CaO loaded onto mesoporous silica at 5 wt.% catalyst loading within 8h reaction time at 60°C. CaO/Al_2O_3 which was prepared by sol-gel method reported higher activity than MgO/Al_2O_3 (Umdu *et al*., 2009). The basic site density and basic strength are the factors governing the catalytic activity, thus, the Mg/Ca is more active than Mg/Al (Albuquerque *et al*., 2008). The CaO-MgO has higher basic strength, thus, higher catalytic activity in the transesterification of *Jatropha curcas* oil than that of CaO-ZnO and both mixed oxide catalysts have been reported to express higher catalytic activity than that of the single metal oxides; CaO, MgO and ZnO (Taufiq-Yap *et al*., 2011). The mixed oxides showed also better resistance to deactivation by atmospheric CO_2 relative to CaO alone (Wilson and Lee, 2012). The nature of the support plays an important role on the catalyst activity. Pasupulety *et al*. (2013) used different alumina; acidic, basic and neutral for impregnation of CaO. The highest transesterification activity was for CaO supported on neutral Al_2O_3. Wen *et al*. (2010b) reported the preparation of mixed oxide TiO_2-MgO catalyst by sol-gel method in the ratio of 1:1 and then calcination at 650°C. The catalyst showed FAME yield of 92.3% from WCO at a molar ratio of 50:1 M:O, 10 wt.% catalyst loading, 6 h reaction time and 160°C.

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However, the catalyst lost its activity in the recycling process. But its catalytic activity increased reaching 93.8% FAME yield on its regeneration, throughout four times washing with methanol and then once with hexane and finally dried at 120°C. The recorded increase in activity is attributed to the increase in the specific surface area and average pore diameter of the catalyst during the regeneration process. CaO/SiO_2 prepared by the sol-gel technique showed a high performance for transesterification of corn oil (Moradi *et al*., 2014). The mixed metal oxides of; Ca-La, Ca-Zn and Ca-Zr express better catalytic activity. It can be prepared through ammonia-ethanol-carbon dioxide precipitation, physical mixing, impregnation, co-precipitation, mechano-chemical treatment. However, the preparation method, calcination temperature, molar ratio of the metals and the storage conditions of the prepared catalyst affect its basicity and thus its activity (Yan *et al*., 2011; Kesic *et al*., 2012; Xia *et al*., 2014). Mechno-chemical synthesis of the mixed metal oxide catalyst; CaO-ZnO, using the ball milling, reported to produce more active catalyst compared to that prepared by the co-precipitation technique (Kesic *et al*., 2012). Gel-combustion technique was reported as an effective method for preparation of CaO, using $Ca(NO_3)_2$ as the calcium precursor and citric acid as the gelling agent, where the obtained Ca-complex was heated at 420°C, to obtain a fine powder, then it was calcined at 800°C for 4 h to obtain an activated catalyst (Nualpaeng *et al*., 2014). The gel-combusted CaO is characterized by high surface area, porosity and basic sites, thus higher catalytic activity. Urea-nitrate combustion method is reported to be a simple, fast and effective method for preparation of $CaO\text{-}ZrO_2$ without the need for further calcination (Xia *et al*., 2014). The birch template method is reported to improve the pore structure and dispersion of basic sites of Ca-Zr oxide (Liu *et al*., 2015). The ratio of metals in the metal oxide catalysts has a great influence on the basicity of the prepared catalyst, and consequently on its activity. Dehkordi and Ghasemi (2012) reported that the activity of the catalyst $CaO\text{-}ZrO_2$ increases as the Ca/Zr molar ratio increases; however, its stability decreases. Where, a maximum biodiesel yield of approximately 92% was achieved at 65°C, 10 wt.% catalyst loading, 30:1 M:O molar ratio, 2 h reaction time, and 0.5 Ca:Zr molar ratio. The effect of molar ratio of Ca:Mg:Zn, was also investigated and the reported optimum ratio was 3:1:1 for preparation of palm kernel oil methyl esters, at 20:1 M:O molar ratio, 60°C and catalyst loading of 6 wt.% (Limmanee *et al*., 2013). The effect of different calcium/lanthanum molar ratio on the surface are acidity/basicity and catalyst activity on the transesterification of *J. curcas* oil with methanol was reported. The best ratio in $CaO\text{-}La_2O_3$ is reported to be 1:8 La:CO atomic ratio, with approximately 99% biodiesel yield at 160°C, 3h, 25;1

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M:O molar ratio and 3 wt.% catalyst concentration (Lee *et al*., 2015). The application of CaO in the supercritical transesterification process has been reported to decrease the catalyst concentration, reaction temperature and time, thus making the process more energy efficient. CaO showed also better performance in subcritical or supercritical transesterification than those of other metal oxides; SrO, ZnO, TiO_2 and ZrO_2 (Jin Yoo *et al*., 2010). Hwa Teo *et al*. (2015) has reported the good efficiency of Ca/La mixed oxide in the subcritical and supercritical methanolysis of *J. curcas* oil, that yielded approximately 93% FAME at 240°C, 8.2 MPa, 12:1 M:O molar ratio, 1 wt.% catalyst concentration and 10 min reaction time. Guan *et al*. (2009a) has reported the good alkaline properties of the tri-potsaaium phosphate (K_3PO_4) catalyst, as it hydrolyzes in presence of water producing HPO_4^{2-}, $H_2PO_4^-$ and OH^- ions. That produced high biodiesel yield of 97.3% from waste cooking oil (WCO) at 60°C, 4 wt.% catalyst loading and 2 h reaction time. The catalyst can be easily regenerated by aqueous KOH solution without sharp decrease in its activity. Microwave irradiation has been reported in the preparation of CaO supported with zeolites (NaY, KL and ZSM-5) and CaO/NaY has exhibited the best activity on the transesterification of soybean oil (Wu *et al*., 2013). Rice is the main source of food for people all over the world and covers approximately 1% of the earth's surface (Memon *et al*., 2011). The rice husk represents approximately 20 wt.% of the rice crop, upon burning, it produces approximately 40 kg rice husk ash (RHA) from each ton of rice (Zerbino *et al*., 2011). The annual worldwide production of such waste reaches approximately 70 million tons. Chen *et al*. (2013) reported the preparation of active solid base catalyst; Li-modified RHA, using simple mixing and well grinding of RHA with Li_2CO_3 that calcined at 900°C for 4 h. That produced high biodiesel yield 99.5% from soybean oil at 24:1 M:O molar ratio, 4 wt.% catalyst concentration, 65°C and 3 h. Mahesh *et al*. (2015) reported the preparation of KBr impregnated CaO catalyst by wet impregnation method, followed by calcination at 900°C. The RSM using CCD of experiments were applied to study the effects of process variables on biodiesel yield from WCO and optimize the process. The maximum biodiesel yield of approximately 84% was obtained at 12:1 M:O ratio, 3 wt.% catalyst loading and 1.8 h reaction time.

2.3.6 Effect of Reaction Temperature

It is recommendable to heat the oil before mixing with alcohol and catalyst, to decrease the mass transfer limitation and increase the reaction rate that would, consequently, shorten the reaction time (Jiang *et al*., 2010).

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But the oil should be heated to below the boiling point of the alcohol to avoid the alcohol vaporization (for example 64.5°C for methanol). Reaction temperature is important and strongly affects the reaction kinetics, at low temperature; viscosity increases and longer reaction time and higher alcohol/oil molar ratio are required. The increase in temperature can decrease the viscosity of the feedstock, and thus results in an increased reaction rate and shortening of the reaction time (Gnanaprakasam *et al*., 2013). Transesterification can be performed at different temperatures, and the biodiesel yield increases with the increase of the reaction temperature, but to a certain limit. If the reaction temperature increased beyond the optimum level, the biodiesel yield decreased due to the acceleration of saponification reaction of TG at higher temperature (El-Gendy *et al*., 2015c). Moreover, if the temperature increases, reaching the boiling point of the alcohol used in the transesterification reaction, a lot of alcohol bubbles would be formed that would inhibit the mass transfer on the phase's interface, which would lower the reaction rate. In case of enzymes, the conversion reaction increases over the temperature range 30-55°C. Kumari *et al*. (2009) reported maximum conversion of *jatropha* oil using lipase at 55°C, while 50°C for cotton seed oil (Royon *et al*., 2007). Refaat *et al*. (2008) reported highest biodiesel yield at 65°C from different oil feedstock using KOH.

2.3.7 Effect of Reaction Time

Generally, the conversion rate increases with time, since at the beginning the reaction rate is slow for mixing and dispersing the alcohol and the catalyst into the oil. Then the reaction rate increases for maximum biodiesel production, where it remains relatively constant with further increase in the reaction time. However, extra increase in reaction time would reduce the biodiesel yield, due to the drawback reaction, producing more fatty acids and soap (Refaat, 2010; Mazubert *et al*., 2013). Hence, the reaction time should be optimized to reduce the production cost. Thus the reaction rate seems to be sigmoidal, i.e., slow at both, the beginning (to overcome the mass transfer limitation) and at the end of the reaction (since, the glycerol phase separates out taking most of the catalyst with it, as the reaction proceeds) but the rate is fast at the intermediate stage (Slinn and Kendall, 2009). The initial immiscibility between the reactants rapidly disappears through the formation of di- and mono- glycerides which act as emulsifier and the size of the dispersed phase droplets decreases. However, it increases again with the glycerol production (Guan *et al*., 2009b; Slinn and Kendall, 2009). The size of the droplets and the interfacial area directly influence

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the reaction rate (Mazubert *et al*., 2013). Chen *et al*. (2012) enhanced the biodiesel yield from WCO using sodium methoxide and the microwave heating system reduced significantly the reaction time.

2.3.8 Mixing Efficiency

The transesterification reaction is ether two phase in homogeneous catalyzed process or three phase in heterogeneous catalyzed process. So it proceeds, as mentioned before, in three stages; mass transfer between the reactants, the transesterification reaction, then the establishment of equilibrium. Mixing rate and efficiency are very important factors to overcome the mass transfer problem and improve the reaction rate, thus, consequently increase the biodiesel yield and decrease the overall production cost as it would save time and energy consumption (Adeyemi *et al*., 2011; Mathiyazhagan *et al*., 2011; El-Gendy *et al*., 2015c; El-Gendy *et al*., 2016). However, beyond a certain limit of stirring there would be no significant increase in the biodiesel yield, especially when applying enzymes or heterogeneous solid porous catalysts (Gnanaprakasam *et al*., 2013; El-Gendy *et al*., 2015b). Kumari *et al*. (2009) reported that in case of enzyme or heterogeneous porous solid catalysts, the reactants have to diffuse from the bulk liquid to the catalyst surface and then further into the interior surface of the catalyst. For example, increasing the stirring rate from 100 to 200 rpm increased the conversion rate; however, further increase to 250 rpm showed no significant change in the biodiesel yield. That was attributed to the shearing of the enzyme molecules.

Mechanical stirring is the most popular method on the industrial scale. However, under ultrasonic waves, a number of cavitation bubbles would be formed in the liquids. The formation and collapse of these bubbles would consequently disrupt the phase boundary in the two-phase immiscible liquid system (i.e., oil and alcohol phases). That would form a fine emulsion and the droplet size of methanol and oil is in micrometers. Thus, the interface area of alcohol and oil would increase. That consequently would increase the rate of the transesterification reaction. The main advantages of low frequency ultra-sonication transesterification process (20 – 40 kHz) are the requirement of lower temperature process, smaller amount catalyst (it can be lowered by 50%) and methanol, due to the increased chemical activity in the presence of cavitation, relative to the conventional mechanical stirring method (Thanh *et al*., 2008; Tan *et al*., 2015a). It can be applied in batch and continuous reactors. However, ultrasonic small horn transducers and water bath ones can be applied on low volume batch reactors up to 1 L. But it cannot be applied on a large industrial scale. Thanh *et al*. (2012) reported the

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continuous reactor with high power horn type transducer of 1 kW capacity and 20 kHz frequency with a two-step transesterification process.

2.3.9 Effect of pH

The effect of pH is not critical in acid- or base- catalyzed transesterification reactions. However, when applying enzymes, for example; lipase, the pH needs to be considered as enzymes would decompose at lower or high pH values (Gnanaprakasam *et al*., 2013). Devanesan *et al*. (2007) reported the optimum pH for the transesterification of *jatropha* oil by immobilized *Pseudomonas fluorescence* is pH7.

2.4 Transesterification Mechanisms

The important factor that promotes the catalytic effect in acid or base catalyzed transesterification reactions is the protonation of the carbonyl group in the TG molecule. The catalyst-reactants interaction increases the electrophilicity of the adjacent carbonyl carbon atom, making it more susceptible to the nucleophilic attack. Comparing the electrophilic species (in acid-catalysis) to the stronger nucleophile (in base-catalysis), the base catalyst appears to take on a more direct route to activate the reaction of RO^- catalytically active species. Thus, it results in a faster catalytic activity.

Usually the kinetics of the homogeneous catalyzed transesterification reaction can be summarized in three regimes, describing the overall reaction process with the rate-limiting step which is changing over time according to the observed reaction rate. At first, the reaction is mass transfer limited, because of the low miscibility of the reactants, i.e., the non-polar oil phase is immiscible with the polar alcohol-catalyst phase. Thus, this would slow down the reaction rate. With the production of esters, these species would act as an emulsifying agent that consequently gives rise to a second-rate regime that is kinetically controlled and characterized by a sudden increase in biodiesel formation. Finally, a third regime would occur within the last stages of the reaction that is characterized by a slower reaction rate.

2.4.1 Homogeneous Acid-Catalyzed Transesterification Reaction

The acid catalyst firstly protonates the carbonyl group of the TG, and then a nucleophilic attack occurs between the activated carbonyl group in the TG and the alcohol molecule, forming an unstable tetrahedral intermediate.

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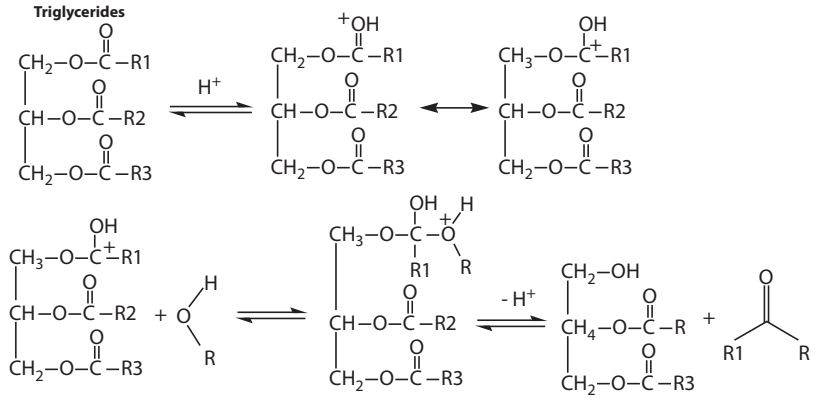

Scheme 2.6 Mechanism of acid-catalyzed transesterification reaction.

That rearranged and broken down, yielding a diglyceride molecule and an alkyl monoester, this sequence is then repeated twice more to yield three alkyl monoesters and glycerol (Scheme 2.6).

2.4.2 Lipase-Catalyzed Transesterification Reaction

The mechanism of transesterification process with lipase appears to be a successive reaction mechanism. The TG and partial glycerides are first hydrolyzed by lipase to partial glycerides and FFAs, respectively, after which, methyl esters are synthesized from FFAs and methanol. This would suggest the benefits of enzymes over chemical catalysts, where the FFAs in feedstock can be easily converted to methyl esters.

2.4.3 CaO-Catalyzed Transesterification Reaction

The structure of CaO is made up of positive CaO ion (cation) which possesses Lewis acid and negative oxygen ion (anion) which possesses Bronsted base. During the methanolysis of oils, CaO provides sufficient adsorptive sites for methanol, in which the O-H bonds would readily break into methoxide anions and hydrogen cations (Figure 2.2). Thus, the presence of a small amount of water would enhance the catalytic activity of CaO. Since, O^{2-} on the surface catalyst would extract H^+ from H_2O molecules producing OH^-, which subsequently would extract H^+ from methanol to form the methoxide anions (Liu *et al.*, 2008a,b). However, excess amount of water would hydrolyze the FAME, generating fatty acids that react with CaO, producing soap. The reactivity of different calcium-based catalysts is

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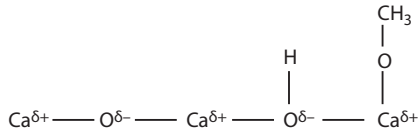


Figure 2.2 Surface structure of CaO.

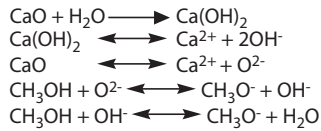
reported to be $Ca(CH_3O)_2$ > CaO > $Ca(OH)_2$ and CaO-methoxide can be reused for 20 successive cycles (Liu *et al*., 2008a).

Sharma *et al*. (2010) has reported another scheme depending on the small extent of CaO solubility in methanol (0.035 wt.%) and the presence $Ca(OH)_2$ due to the reaction of CaO with atmospheric humidity or water content in the feedstock. Where, the produced O^{2-} and OH^- from the dissolution reactions (Scheme 2.7) are responsible for the methoxide anions that act as the catalyst.

Leon-Reina *et al*. (2013) reported that the activity of calcium glyceroxide is higher than that of CaO. However, Sirisomboonchai *et al*. (2015) reported that the activity of calcium glyceroxide prepared from calcined scallop shell is lower than that of CaO prepared from the source. But its formation on CaO surface protects it from CO_2 and H_2O. Lukic *et al*. (2016) reported the preparation of $Ca(C_3H_7O_3)_2$ applying the mechno-chemical method. The main advantage of the prepared glyceroxide is the increase and enhancement of the initial rate of the transesterification reaction. This is due to the elimination of the mass transfer resistance which usually controls the overall rate of methanolysis in case of CaO. This is attributed to the nature of calcium diglycroxide, as it is adsorbed at the droplet interfaces between methanol and oil. Thus, this would lead to the formation of fine dispersion of these two immiscible liquids.

As mentioned above, the real catalyst of the transesterification reaction is the methoxide anions which would consequently react with triglyceride molecules (Scheme 2.8).

That produces an unstable tetrahedral intermediate, which is then rearranged and broken down to form a diglyceride anion and a mole of fatty acid methyl ester. The charged diglyceride is then stabilized by a proton



Scheme 2.7 Methoxide formation applying CaO catalyst.

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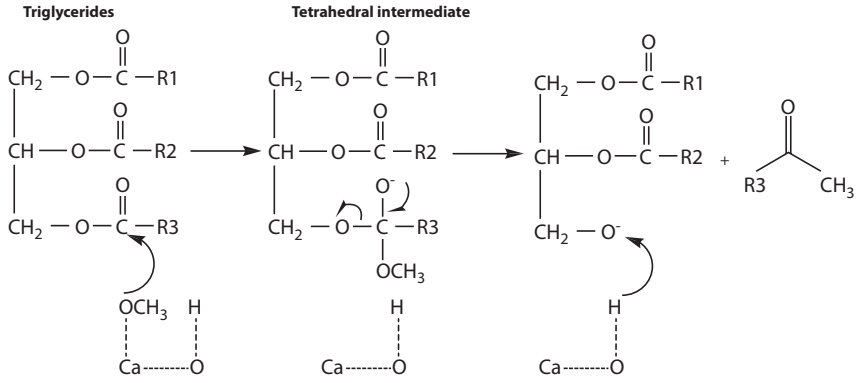

Scheme 2.8 Mechanism of CaO-catalyzed transesterification reaction.

from the catalyst surface to form a diglyceride and regenerates the active sites on the catalyst surface. The aforementioned three steps are then repeated two times in succession to produce 3 moles of methyl esters and one mole of glycerol (Marinkovic *et al*., 2016). The first and second steps, i.e., the reaction of TG with alcohol and formation of diglyceride (DG) and the first FAME and then the reaction of DG with the short chain alcohol to form monoglyceride (MG) and the second FAME are always much faster than the last step, which is the reaction of (MG) with alcohol producing the third FAM and glycerol. Boey *et al*. (2011a) has reported that during this transesterification reaction, calcium oxide can react with glycerol producing calcium diglyceroxide, which can act as a catalyst and has the advantage of tolerance to air exposure (Scheme 2.9). Ferrero *et al*. (2015) reported the preparation of active catalyst, calcium glyceroxide using CaO, glycerol and methanol at a mass ratio of 1:1.6:13.4. that showed good transesterification activity on soybean oil and WCO with 7:1 MO molar ratio, 60°C, 2 h and 0.4 wt.% catalyst loading. The calcium glyceroxide reported to be used for four successive times without losing its activity.

CaO can tolerate high concentration of FFAs content oils. However, calcium soap can be also produced as a side reaction, which would deactivate the catalyst. The low CaO-active species leaching and low methanol solubility (0.035%), promote its reusability, thus promote its further future industrial applicability. However, its solubility in glycerol is very high, so it

$$CaO + 2C_3H_8O_3 \longrightarrow Ca(C_3H_7O_3)_2 + H_2O$$

Scheme 2.9 Reaction of calcium oxide with glycerol.

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should be separated directly after the completion of the reaction. Granados *et al.* (2007) reported that, the presence of approximately 3 wt.% biodiesel, in the initial methanol-TG mixture, enhances the CaO-catalyzed transesterification batch process. Ultra-sonication has been reported to increase the rate of CaO-catalyzed transesterification reaction. Since it overcomes the mass transfer resistance problems, as it produces finer emulsion than the conventional mechanical mixing (Choudhury *et al.*, 2014). Hsiao *et al.* (2011) reported that microwave irradiation enhances the catalytic activity of CaO nanoparticles. That led to approximately complete conversion of soybean oil to FAME at 6:1 M:O molar ratio, 1 wt.% catalyst concentration, 60°C within only 30 min reaction time. The kinetic of CaO-catalyzed transesterification reaction in a batch reactor is usually in the form of S-shape; the initial TG mass transfer controlled phase, followed by a chemical reaction controlled region (Veljkovic *et al.*, 2009). Kouzu *et al.* (2008) reported that the kinetics change with the progress of the transesterification from the zero-order to the first order. However, many researchers used the pseudo-first order kinetic rate equation to describe the heterogeneous-base-catalyzed transesterification process (Birla *et al.*, 2012; Jairam *et al.*, 2012; Pasupulety *et al.*, 2013; Moradi *et al.*, 2014; Hindryawati and Maniam, 2015; Moradi *et al.*, 2015).

2.4.4 Other Calcium Derived-Catalyzed Transesterification Reaction

El-Gendy *et al.* (2015b) reported the preparation basic heterogeneous fluorapatite ($Ca_5(PO_4)_3F$) catalyst from waste animal bones and elucidated the possible mechanism in the transesterification reaction of WCO, where the reaction would start with the dissociation of $Ca_5(PO_4)_3F$ or hydroxyapatite $Ca_5(PO_4)_3OH$ and methanol and formation of methoxide anion from the reaction between methanol and a F^- or OH^- ion. In the first step, surface O_2^- of $Ca_5(PO_4)_3$ extracts H^+ from methanol to form the methoxide anion on the surface of $Ca_5(PO_4)_3$, which attacks the carbonyl carbon of the triglyceride to form a tetrahedral intermediate. The rearrangement of the intermediate molecule results in the formation of a mole of methylester and diglyceride. In the former step, H^+ from the surface of $Ca_5(PO_4)_3$ attacks O^- of the diglyceride anion for the formation of diglyceride molecule along with the regeneration of $Ca_5(PO_4)_3$. A new methoxide anion attacks the formed diglyceride, producing another mole of methylester and monoglyceride. Finally, another methoxide attacks the monoglyceride producing a total of three moles of methylester and a mole of glycerol. A similar mechanism was elucidated by Chakraborty *et al.* (2011) for the tri-calcium phosphate

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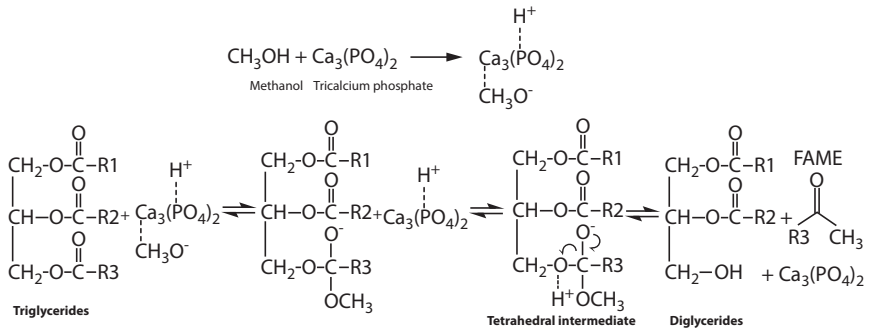
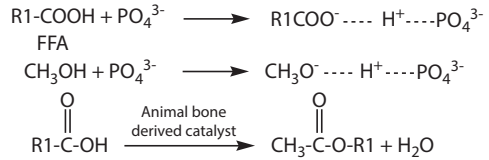


Scheme 2.10 Mechanism of tricalcium phosphate-catalyzed transesterification reaction.



Scheme 2.11 Mechanism of hydroxyapatite-catalyzed transesterification reaction.

(β-$Ca_3(PO_4)_2$) prepared from calcination of fish scales at 900°C as a low-cost heterogeneous catalyst for biodiesel production (Scheme 2.10).

Corro *et al.* (2016) attributed the high basic sites specific density on the calcined animal bones to the oxygen atoms that surround the phosphorous atom in the PO_4^{3-} moiety in $Ca_5(PO_4)_3OH$. The PO_4^{3-} ions can act as a Lewis basic site, i.e., an electron donor species during the FFA esterification with methanol, throughout the adsorption of FFA and methanol on two neighboring free surface Lewis basic sites. Then the two adsorbed reactants interact, producing a surface intermediate. That finally produces methylester and water molecule (Scheme 2.11).

2.5 Production of Biodiesel Using Heterogeneous Catalyst Prepared from Natural Sources

It has been estimated that the cost of raw materials represents approximately 70-95% of the total production cost. Applying WCO instead of fresh oils as a feedstock will reduce the feedstock cost by 60-70%. The cost of the applied catalyst affects the overall production cost as well. Thus, applying catalysts prepared from waste materials will decrease the cost and

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enhance the development of a sustainable biodiesel production process (Zhang *et al*., 2012; Farooq *et al*., 2015).

The natural waste sources that can be used to prepare the basic heterogeneous catalysts can be categorized into shells, ashes, bones and finally rocks and clay (Nurfitri *et al*., 2013). The use of CaO started in the 1980s, and Peterson and Scarrah (1984) first reported the use of CaO for transesterification of rapeseed oil. CaO should be thermally activated at approximately 700°C for 2-3 h before its application in the transesterification reaction to remove the unwanted $Ca(OH)_2$ and $CaCO_3$, as they have low to no transesterification activity, respectively. The pretreatment of CaO with methanol to produce $Ca(OCH_3)_2$ initiate the transesterification reaction and Liu *et al*. (2008a) reported that it can be used for 20 cycles without losing its activity. Adding water to about 2% in methanol enhances also the transesterification reaction, as water enhances the production of more methoxide anions that, consequently, elevates the catalyst activity (Liu *et al*., 2008b). However, the atmospheric water and carbon dioxide poison CaO catalyst (Boey *et al*., 2011a). Although the reaction time of CaO-catalyzed transesterification reaction is longer by 2-4 fold, relative to homogeneous NaOH-catalyzed ones, the low cost of CaO, its preparation from readily available natural sources and the simpler biodiesel production process, make CaO such a promising candidate in biodiesel production. Co-solvent such as tetrahydrofuran, can accelerate the transesterification reaction, as it increases the miscibility of alcohol and oil. Cho *et al*. (2009) reported that the basicity of CaO catalyst mainly depends on the precursors. The CaO crystalline size and its preparation source affect the transesterification reaction. Viriya-empikul *et al*. (2010) reported that the catalyst surface area and Ca content highly affect the catalytic activity. Calcination temperature and duration are very critical and important in preparation of active CaO, as they have a great influence on the catalyst basicity. Even in the loaded CaO-catalysts, the calcination temperature of CaO before the metal loading is very crucial in determining the final activity of the prepared catalyst (Ngamcharussrivichai *et al*., 2007 and 2008).

Ngamcharussrivichai *et al*. (2007) reported the calcination of dolomite at 600°C was much better than that at 800°C as it produces more active basic sites, and the $Ca(NO_3)_2$ loaded on the dolomites calcined at 600°C that was re-calcined again at 800°C generates nearly complete conversion of palm kernel oil at 60°C to FAME in presence of 15 M:O and 10 wt.% catalyst. Ngamcharussrivichai *et al*. (2008) reported also that the mixing of CaO with ZnO, in a ratio of 0.25 Ca/Zn, enhanced the transesterification of palm kernel oil, and the prepared catalyst was used for three times without losing its activity. Ngamcharussrivichai *et al*. (2010) reported the

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calcination of dolomite that consists mainly of $CaCO_3$ and $MgCO_3$ at 800°C for 2 h produced a mixed metal oxide catalyst of CaO-MgO which showed good transesterification efficiency of palm kernel oil of approximately 98% biodiesel yield at catalyst loading of 6 wt.%, 30:1 M:O molar ratio, 60°C and 3 h reaction time. The catalyst was used for seven successive cycles without losing its activity. Do Nascimento *et al.* (2011) reported the preparation of a catalyst from a waste material; Amazon *flint* kaolin, that was used for the transesterification of the distillate produced by deodorization of palm oil (DDPO) producing maximum biodiesel yield of 92.8% at 160°C with 60:1 M:DDPO molar ratio and 4 h reaction time. Ngamcharussrivichai *et al.* (2011) prepared a series of catalysts using a wet mixing of ground limestone with different divalent and trivalent metal precursors (e.g., sodium salt of Al), as good binders in the catalyst shaping, then followed by drying and calcination. The catalyst prepared using combination of the hydroxide precursors of both Mg and Al (CMA-333N) expressed the highest activity and can be reused for 10 times without losing its activity. Sanchez-Cantu *et al.* (2013) reported 100% biodiesel yield from the transesterification of castor oil with methanol using hydrated lime. Borges and Diaz (2013) reported approximately 99.5% FAME from WCO using potassium-loaded pumice material (K-Pumice) as a heterogeneous base catalyst at 55°C, 20:1 M:O, 2 h at a catalytic packed-bed reactor configuration (with 8.2 cm length). Zhang *et al.* (2014) reported a novel catalyst prepared from the calcination of wastewater scale. The derived catalyst is a complex mixture of CaO-MgO-Fe_2O_3-Al_2O_3-SiO_2 and it showed good transesterification activity on soybean oil, producing biodiesel yield of approximately 93% at 12:1 M:O molar ratio, 1 wt.% catalyst, 70°C within 5 h. Melero *et al.* (2014) reported the highly active catalyst Zr-SBA-15/bentonite, prepared by agglomeration of Zr-SBA-15 material with bentonite clay to form a macroscopic structured catalyst of 1.5 mm particle sizes. It has been applied in a continuous process for biodiesel production from WCO on a packed-bed reactor, producing 96% FAME yield at 210°C, 70 bar, 50:1 M:O and 30 min.

The preparation of inexpensive heterogeneous catalysts with high activity is very important to produce biodiesel with competitive cost and quality with petro-diesel. Moreover, waste shells cause a lot of waste management problems and environmental pollution (such as nasty smells) as they are usually disposed in landfills without any pretreatments. The CaO prepared from such natural waste shells (for example; crabs shells, eggshells, etc.) have the advantages of abundance, low cost, porous structure, no-toxic, high basicity, low solubility in biodiesel. To increase the activity of CaO prepared from waste shells, several reports have been published dealing with inexpensive treatments of such catalyst to make its activity more

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competitive with that of conventional homogeneous ones. The hydration-dehydration method is an option to enhance the activity of CaO (Yoosuk *et al*., 2010). The preparation of CaO in the nano-scale increases the surface area of the catalyst and basic sites, thus, increases its activity (Boey *et al*., 2011a).

Xie *et al*. (2008) reported the utilization of a biont shell catalyst in production of biodiesel. That was prepared by the incomplete carbonization of the chitin in the shells followed by impregnation with KF. The weak polarity of the prepared catalyst prevents the reverse glycerolysis reaction, thus increasing the biodiesel yield. Boey *et al*. (2009) reported the preparation of a basic mixed oxide catalyst CaO/MgO from mud crab (*Scylla serrata*) shells by heat treatment in a furnace at 1173 K for 2 h. It is also known as mangrove crab or black crab, which is very abundant in Malaysia. The activity of the prepared catalyst was nearly the same as that of lab-CaO, producing approximately > 95% biodiesel yield from palm olein oil at 12:1 M:O molar ratio, 4 wt.% catalyst loading, 338 K within 2.5 h. It can be reused for 11 successive cycles without losing its activity. The oyster farming is one of the major marine aquacultures in Korea and Japan. That produced huge amounts of unwanted oyster shell wastes, which causes a major waste management problem and affecting the ecosystem on the microbial decay of the flesh remnant causing the production of NH_3, H_2S and amine gases (Boro *et al*., 2012). Nakatani *et al*. (2009) used combusted oyster shell waste at 1000°C as a catalyst for production of biodiesel from soybean oil. It produced 73.8% biodiesel yield that was comparable with lab CaO (72.5%) and high biodiesel purity (98.4 wt.%) at 25 wt.% catalyst concentration, 5 h, 6:1 M:O and 65°C. The activity of CaO produced from oyster shell has been reported to be enhanced by impregnating additional basic sites for example KI on the surface of the shells, due to the synergistic effect of the deposited basic elements and the natural basic solid support (Jairam *et al*., 2012). Yang *et al*. (2009) reported that the major component of shrimp shells is chitin. On its incomplete carbonization, a stereo polymer composed of quasiaromatic compounds, which are six-member heterocylic compounds, are formed, with increased surface area. An active catalyst can be prepared by the impregnation of incompletely carbonized shrimp shells with KF and its activity mainly depends on the carbonization temperature, KF loading and activation temperature. The conversion of rapeseed oil to biodiesel reached approximately 89% at 9:1 M:O molar ratio, 2.5 wt.% catalyst concentration, 65°C reaction temperature and 3 h reaction time, using a catalyst prepared by incomplete carbonization at 450°C, then loaded by 25 wt.% KF and finally, activated at 250°C. Olivera *et al*. (2013) reported that according to FAO (2009); the world egg

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production in 2008 was approximately 62 million tons, and the eggshells represents 11% of its total weight. Thus, approximately 6.82 million tons of waste eggshells would be annually produced. Cho and Seo (2010) have reported that, eggshells composed of three layers; a thin non-porous cuticle outer layer, a thick palisade middle layer with large pores and finally, a non-porous thin mammillary inner layer. Thus, the removal of such dense cuticle layer would enhance the catalytic activity, by accelerating the diffusion of large oil molecules into the porous palisade layer. Moreover, the increase of porosity of palisade layer would further improve the catalytic activity. For example, the low-temperature removal of CO_2 from such layer would suppress the surface rearrangement which causes the disappearance of the strong basic sites (Cho *et al*., 2009). The dilute acid-treatment of eggshells removes the dense cuticle layer (Cho and Seo, 2010). Wei *et al*. (2009) reported that the calcination temperature of the waste shells is a very important factor affecting the biodiesel yield. Where, eggshells calcined at temperatures < 600°C produced biodiesel yield < 30%, while calcination at temperatures > 800°C produced biodiesel yield > 97%. Since the maximum conversion of $CaCO_3$ the main component of eggshells to CaO, which is the active phase of eggshells derived catalyst, occurs at temperatures > 800°C and attributed this also to the decrease of the particle size and increase of the regularity of particles shape at calcination temperatures > 800°C. Cho and Seo (2010) reported that the activity of CaO prepared from quail eggshells (Qes) is higher than that prepared from chicken eggshells (Ces) and attributed this to the more closely dispersed micron-sized pores of the palisade layer of Qes than those of the Ces. Which provide a large amount of strong basic sites for the transesterification and efficient channels for the rapid diffusion of large oil molecules. Sharma *et al*. (2010) reported the biodiesel production from the high FFA content non-edible *Pongamia pinnata* oil (19.88 mg KOH/g) using CaO prepared by calcination of eggshells at 900°C after oil esterification by H_2SO_4 to lower the FFA content to 1.86 mg KOH/g. The prepared eggshells-CaO produced approximately 95% biodiesel yield with high conversion percentage (97.43%) at 8:1 M:O molar ratio, 2.5 wt.% catalyst lading, 600 rpm agitation speed, 65°C and 2.5 h. Boey *et al*. (2011b) reported the use of a mixture of CaO prepared from waste crab and cockle shells for transesterification of chicken oil. Boro *et al*. (2011) reported the preparation of CaO from waste shells of *Turbonilla striatula*, which is widely available and distributed in swamps, rivers and agricultural fields in Chirang, Assam district in India. That yielded > 93% biodiesel from mustard oil at 9:1 M:O molar ratio, 65°C, within 6 h reaction time and 3 wt.% catalyst concentration that was calcined at 900°C for 3 h. Hu *et al*. (2011) reported the preparation of active

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CaO catalyst from freshwater mussel shell by calcination at 900°C then impregnation by deionized water followed by activation at 600°C. That was characterized with good catalytic properties producing 90% biodiesel yield from the Chinese tallow oil at 70°C, 1.5 h, 12:1 M:O molar ratio 5 wt.% catalyst concentration and it was active for seven successive cycles. Singh *et al.* (2011) compared the activity of CaO derived by calcination of eggshells at 900°C for 2 h and conventional homogeneous KOH for transesterification of *Madhuca indica* oil. Where, maximum biodiesel yield of 98 and 95% with high percent conversion of > 96.5% was obtained using KOH and CaO, respectively, using the following optimum conditions: 6:1 M:O molar ratio, 0.75 wt.% KOH catalyst loading, 55°C within 1 h, while for CaO, the optimum conditions recorded; 8:1 M:O molar ratio, 2.5 wt.% CaO loading, 65°C within 2.5h. However, CaO was used for ten successive cycles without losing its activity. The oil feedstock was first esterified using H_2SO_4 to decrease the FFA content from 22.9 mg KOH/g to 2.07 mg KOH/g. Birla *et al.* (2012) reported the transesterification of WFO by CaO prapred from the calcination of snail shells. Konwar *et al.* (2012) reported the support of CaO prepared by calcination of *Turbonilla striatula* shells on a biochar produced by the pyrolysis of *Mesuaferrea Linn* deoiled cakes. The biochar-supported CaO was prepared by wet impregnation method followed by calcination at 600°C. The produced catalyst showed good transesterification activity for the transesterification of *Mesuaferrea Linn* oil of approximately 96% biodiesel yield at 12:1 M:O molar ratio, 65°C and 3 wt.% catalyst loading within 6 h reaction time. Margaretha *et al.* (2012) reported the production of biodiesel from palm oil using CaO prepared by calcination of golden snails (*Pomacea* sp.) shells at 900°C for 2 h. where, 95.61% FAME yield was obtained at 60°C, 7:1 M:O molar ratio, 4 wt.% catalyst concentration and within 4 h reaction time. Obadiah *et al.* (2012) reported the preparation of hydroxyapatite as an active catalyst by the calcination of the milled sheep bones at 800°C. That produced 96.78% biodiesel yield from palm oil at 18:1 M:O molar ratio, 65°C, 200 rpm and 20 wt.% catalyst loading within 4 h reaction time. Roschat *et al.* (2012) reported the high activity of CaO, a bulk solid catalyst (size 0.5 – 1 cm^3) prepared from the calcination of waste coral fragments at 700°C for 1 h. where it produced 98% FAME yield from different types of feedstock; palm oil, soybean oil, rice bran oil or WCO at 15:1 M:O molar ratio, 100 wt.% catalyst concentration, 2 h and 65°C reaction temperature. However, the initial reaction rate decreases as the FFA content in the feedstock increases. The high catalyst loading is required since the surface area is significantly lower than that of the powder catalyst. The catalyst can be used for five successive times without losing its activity. This high activity and reusability of this catalyst

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recommend its application in both slurry and fixed-bed configuration reactors. Moreover, no soap formation occurred even in high FFA content WCO (1.15 mg KOH/g oil). Viriya-empikul *et al.* (2012) reported the applicability of different waste shells; golden apple snail shell, meretrix venus shell and waste eggshell for production of CaO by simple calcination at 800°C. However, the basicity, surface morphology, surface area and particle size of the catalyst depend on the shell source and thus the catalyst activity and consequently the biodiesel yield. Not only have this, but Viriya-empikul *et al.* (2012) also reported that the calcination temperature and time strongly affect the FAME yield. The low biodiesel yield using catalyst calcined at < 700°C was attributed to the presence of a mixture of CaO and $CaCO_3$. While the lower yield at > 800°C was attributed to the lower specific surface area of the prepared catalyst and the sever sintering of the catalyst particles. That also occurred at prolonged calcination time. However, Jazie *et al.* (2013) reported that eggshells calcined at 900°C produced CaO with better porosity, higher specific surface area and higher catalytic activity than that produced by calcination at 800 or 1000°C. Buasri *et al.* (2013) reported the production of 92.92 and 94.49% FAME yield from palm oil using duck and chicken eggshells calcined at 900°C for 4 h, respectively, at optimum conditions of 9:1 M:O molar ratio, 4 h, 65°C and 20 wt.% catalyst concentration. Navajas *et al.* (2013) reported the production of 100% biodiesel yield from WCO using 4 wt.% calcined waste eggshells in a reaction of 5 h. Khemthong *et al.* (2012) reported that eggshell-derived catalysts express the highest catalytic activity relative to the other natural waste shells–derived catalysts. Applying microwave irradiation enhanced the biodiesel production from palm olein oil, recording 96.7% FAME yield within 4 min reaction time 18:1 M:O molar ratio, 15 wt.% eggshell-CaO derived catalyst and 900 watt microwave power. Smith *et al.* (2013) reported the calcination of bovine bone as a waste product from meat production for 6 h at 750°C produces a basic catalyst composed mainly of CaO and to a minor extent; hydroxyapatite. That yielded 97% FAME from soybean oil in a closed transesterification system at optimum conditions of; 6:1 M:O molar ratio, 8 wt.% catalyst concentration, 65°C and 3 h. The waste capiz (*Amusium cristatum*) shells are very abundant in Indonesia as an archipelago country. Suryaputra *et al.* (2013) reported the preparation of CaO by calcination of such waste at 900°C for 2 h. That yielded 93% biodiesel from palm oil at 8:1 M:O molar ratio, 6 h, 3 wt.% catalyst concentration, 60°C and 700 rpm stirring speed. El-Gendy and Hamdy (2014) studied the efficiency of different biocatalysts; Novozyme 435, calcined animal bones at 700°C, calcined eggshells and mollusks shells at 800°C for biodiesel production from WCO and compared their activity

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with that of chemical commercial CaO. Those yielded 87, 90, 94, 93 and 95 wt.% biodiesel yields, respectively in batch transesterification reactions at 60°C, 300 rpm, 60 min, 9:1 M:O molar ratio and 9 wt.% catalyst loading. All the tested catalyst kept their catalytic activity up to five successive transesterification processes except the Novozyme which has been only used once. Lithium incorporated eggshell-derived CaO was reported as an active basic catalyst for the transesterification of the non-edible high acid value Nahor oil (Mesua ferrea Linn), where the basicity affects the catalytic activity more than the surface area. The catalyst produced 94% biodiesel yield at 2% Li loading, 5 wt.% catalyst concentration, 10:1 M:O molar ratio, 65°C, 4 h, 900 rpm. However, there was a drop in catalyst activity throughout its reusability, due to the pore blockage with excess reactants and products, but it can be reactivated at appropriate temperature and reloaded with lithium (Boro *et al*., 2014). Niju *et al*. (2014) reported the production of highly active CaO throughout the calcination-hydration-dehydration treatment of eggshells (denoted as eggshell-CaO-900-600). The specific surface area of eggshell-CaO calcined at 900°C and basic strength were lower than that of eggshell-CaO-900-600, thus the catalytic activity of the former was lower, since the hydration-dehydration treatment increases the surface area of the catalyst (Yoosuk *et al*., 2010). Eggshell-CaO-900-600 catalyst was used for 6 successive cycle wit high biodiesel conversion (> 90 %) from WFO at 12:1 M:O, 5 wt.% catalyst concentration, 1 h and 65°C. Asikin-Mijan *et al*. (2015) reported the preparation of a modified CaO catalyst by hydration-dehydration treatment of waste clamshell (*Meretrix meretrix*), the aforementioned treatment improved the surface area, basicity and textural properties of the catalyst, thus increased its activity and reusability. The hydration duration was found to have a great effect on the catalyst basicity and consequently its activity. The prolonged water treatment process allows more formation of $Ca(OH)_2$ which would promote the formation of Bronsted base sites leading to higher basicity. The catalyst prepared from prolonged hydration duration CS-CaO_{12h} expressed the highest activity and produced high biodiesel yield (> 98%), with 9:1 M:O molar ratio, 1 wt.% catalyst concentration and 2 h reaction time. Ostrich eggs are approximately 18 – 24 times bigger than chicken eggs. Thus it consequently produces larger amounts of eggshells and hence $CaCO_3$, that upon calcination would produce larger amount of CaO catalyst (Tan *et al*., 2015a). Chen *et al*. (2014) reported ultrasonic assisted transesterification of palm oil using ostrich eggshell-derived CaO catalyst. However, applying this technique on a large scale is estimated to have higher production cost, since a large amount of ultrasound probes are required to reach every part of the reactants mixture. Tan *et al*. (2015b) reported the preparation of

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CaO by calcination of grinded ostrich and chicken eggshells at 1000°C, and then applied the prepared catalysts for biodiesel production from acid esterified WCO. That produced 96 and 94% biodiesel yield, respectively, at optimum conditions of 12:1 M:O molar ratio, 65°C, 1.5 wt.% catalyst concentration, 250 rpm and 2 h reaction time. The higher activity of ostrich eggshells-derived catalyst was attributed to its higher basicity, surface area, pore volume, pore diameter and basicity and lower particles size. Moreover, the derived catalysts were reported to be used for 5 successive cycles maintaining their activities. Farooq *et al.* (2015) reported the preparation of basic heterogeneous catalyst, tricaclium phosphate (β-$Ca_3(PO_4)_2$), from chicken bones by simple calcination at 900°C and its application in biodiesel production from WCO, producing maximum yield of 89.33% at 5 wt.% catalyst loading, 15:1 M:O molar ratio, 65°C within 4 h. The prepared catalyst tolerates moisture and high FFA content in the WCO, it can be easily separated from the reaction mixture and reactivated by simple washing with n-hexane to remove the adsorbed materials and calcined at 400°C for 2 h and reused for four successive cycles without losing its activity. The marine gastropod mollusk *Cerithidea obtusa* the "mud creeper" or the "obtuse horn" is from the family *Potamididae* and is used as food in Southeast Asia. Lee *et al.* (2015) reported the preparation of CaO from the calcination of obtuse horn shells at 800°C for 3 h and 5 wt.% of these catalyst performed 86.75% palm oil conversion within 6 h and 12:1 M:O molar ratio. Daily, a large amount of waste scallop shells (*Patinopecten yessoensis*) are produced in the North Japan area. Moradi *et al.* (2015) reported the preparation of CaO and MgO by calcination of demineralized water treatment precipitates at 900°C. That produced higher biodiesel yield compared to that produced using CaO prepared by calcination of waste mussel shells at 1050°C. Nurdin *et al.* (2015) reported the transesterification of castor oil with methanol using calcined mussel shell. That yielded 9.17% biodiesel at 6:1 M:O molar ratio, 60°C, 2 wt.% catalyst concentration and 3 h reaction time. Nur Syazwani *et al.* (2015) reported the shells of *Cyrtopleura costata* (Angle Wing Shells, AWS) to be widely distributed in swamp areas, rivers and agricultural fields in the north part of the west coast of peninsular Malaysia. The CaO prepared by calcination of AWS at 900°C showed good transesterification of 84.11% FAME yield from microalgae *Nannochloropsis ocualata* oil at 1:150 g/g M:O, 9 wt.% catalyst concentration, 1 h, 65°C and 300 rpm. Sirisomboonchai *et al.* (2015) reported the application of the calcined waste scallop shells (at 1000°C) in the transesterification of WCO in a closed reactor (> 1 atm) instead of the conventional reflux reactor, to keep the methanol in the liquid phase and increase the contact between oil and methanol. Where, approximately 85% biodiesel yield was obtained at

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500 rpm, 65°C, 120 min, 6:1 M:O molar ratio and 5 wt.% catalyst concentration and the catalyst can be used for three successive cycles retaining its initial activity. Ismail *et al.* (2016) reported that the transesterification of castor oil by CaO derived from mud clam shell produced higher biodiesel yield than that transesterified by chemical CaO. That produced 96.7 and 93% biodiesel yield, respectively, at 14:1 M:O molar ratio, 3 wt.% catalyst concentration, 60°C and 2 h. Kostic *et al.* (2016) reported the production of CaO from palm kernel shell biochar by calcination at 800°C for 2 h. That showed a good transesterification activity on sunflower oil of about 99% FAME yield at 3 wt.%, temperature of 65 °C, methanol-to-oil molar ratio of 9:1 within 4 h and 900 rpm stirring speed. The catalyst is reported to have been used for three consecutive cycles without losing its activity. But a purification step of the produced biodiesel was recommended since the calcium content in the final yield was higher than the recommendable standard limit. Corro *et al.* (2016) reported that calcined cow bones at 800°C can be used for esterification of FFA with methanol at moderate temperature, followed by a transesterification step in presence of NaOH, applying solar energy as the heat source, in a simple home-made hermetically sealed stainless steel reactor. A 96% FFA conversion has been attained in that reactor applying the optimum conditions; 12:1 M:O molar ratio, 10 wt.% animal bone-derived catalyst, 70°C, 4 h and 40 rpm mixing speed and the catalyst can be used for ten successive cycles retaining its activity. Moreover, applying direct transesterification of WCO by 1 wt.% NaOH and 6:1 M:O molar ratio, using solar energy as a heating source, the percent conversion reached 64% within 20 min, at 60°C and 400 rpm stirring speed. But, nearly complete conversion occurred when applying the aforementioned transesterification parameters onto the esterified WCO. Sulaiman and Amin (2016) reported 86% biodiesel yield from WCO using 6 wt.% fish bone-derived catalyst (calcined at 900°C for 3.5 h) and 18:1 M:O molar ratio within 2 h reaction time at 65°C and 300 rpm mixing speed.

The coal fly ash as a major inorganic waste obtained from the coal combustion process in coal-based thermal power plants, has high concentrations of SiO_2 and Al_2O_3 (approximately 55 and 30%, respectively) (Ojha *et al.*, 2005). That makes it a potential candidate as a low-cost catalyst support. Chakraborty *et al.* (2010) reported the preparation of fly ash supported heterogeneous CaO catalyst using waste eggshells by applying the wet impregnation method and then calcination at 1000°C. The well dispersed presence of CaO over the fly ash frame work and the good basicity (1.6 mmol HCl/g catalyst), high specific surface area (0.701 m^2/g), pore volume (0.0044 cm^3/g) and pore diameter (5.2 nm) of the catalyst promoted its

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catalytic activity. Activated carbon can be also used to support CaO, for its high porous structure, as well as its lower cost relative to the other conventional supports alumina and silica (Wan and Hameed, 2011). Sheng Ho *et al*. (2014) used a palm oil mill fly ash as a support for CaO. The prepared catalyst expressed approximately 76% biodiesel yield, in the transesterification of palm oil under the conditions of 12:1 methanol:oil molar ratio, 6 wt.% catalyst loading, 3 h and 45°C. A large amount of banana stems is produced annually in tropical region, for example, it exceeds 112,98 tons/year in the East Kalimantan Province, Indonesia. Banana stems contain approximately 11.6% carbohydrates and 33.4% potassium based ash. Banana stem ash and coal fly ash as sources for alkali and alkaline earth elements have been reported to be activated by KOH solution and impregnated with KNO_3, then burned at 550°C for 3 h. Those produced 93.26 and 57% biodiesel yield from WCO, respectively, in an ultrasonic reactor (2.5 L capacity and 40 kHz frequency) within 30 min, using 9:1 M:O molar ratio (Marlinda *et al*., 2015). Semwal *et al*. (2011) reported the preparation of Ti based perovskite type catalyst ($CaTiO_3$) using dried sea and egg shells and γ-aluminum oxyhydroxide (AlO.OH) as a binder, followed by calcination at high temperature (1050°C). The catalyst produced 95% biodiesel yield from *Jatropha* oil at 20:1 M:O molar ratio, 10 wt.% catalyst loading, 170°C, 80 bar and 3 h. It can be used for four successive cycles without losing its activity and tolerate feedstock with high acidity (25 mg KOH/g). Hindryawati *et al*. (2014) reported the preparation of three alkali metals (Li, Na, and K) supported by rice husk silica basic heterogeneous catalysts using the wet impregnation method followed by calcination at 500°C for 3h. The reported maximum biodiesel yield of the three prepared catalysts from used cooking oil (UCO) were 96.6, 98.2 and 97.6% for Li_2SiO_3, Na_2SiO_3 and K_2SiO_3 at 3 wt.% catalyst loading, 30 min, 9:1 M:O molar ratio and 65°C. The catalysts tolerate high concentrations of FFAs and water content and can be reused for six successive times. Chen *et al*. (2015) use the biomimetic silicification technique for the preparation of CaO/SiO_2 catalyst using waste eggshells and Na_2SiO_3 and the prepared catalyst showed high transesterification efficiency of palm oil. Hindryawati and Maniam (2015) reported the transesterification of WCO applying ultrasonic in presence of low-cost Na-loaded SiO_2 prepared from waste marine sponge (*Demospongiae*). That was tolerable to 6% and 8% FFA and moisture contents, respectively, and can be used for seven successive cycles retaining its high catalytic activity. Where, approximately 98% FAME yield was obtained at 55°C, 30 min, 9: 1 M:O molar ratio, 3 wt.% catalyst concentration and 300 rpm, using ultrasonic bath (42 kHz) with 100 W power dissipation and 40 W exact power dissipation.

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Statistical techniques have been applied to investigate the effects of various parameters affecting the transesterification reaction using catalysts derived from waste biomass and determine their optimal combination. The RSM based on central composite face centered design (CCFCD) of experiments was applied to optimize the transesterification reaction of soybean oil using fly ash supported heterogeneous CaO catalyst prepared from waste eggshells. The maximum reported biodiesel yield was 96.97% at 30 wt.% CaO, 1 wt.% catalyst concentration, 6.9:1 M:O molar ratio and the catalyst has been used for sixteen successive cycles without major lose in its activity (Chakraborty *et al*., 2010). RSM based on CCD of experiments was applied to optimize and study the effect of catalyst loading and M:O mass ratio on transesterification of palm olein oil using CaO prepared by calcination of waste cockle shell (*Anadara granosa*) at 900°C for 2 h. The catalyst loading was found to express positive impact on purity but negative impact on the biodiesel yield, while M:O mass ratio had positive impact on both the biodiesel purity and yield. The optimum conditions, 4.9 wt.% catalyst concentration and 0.54:1 M:O mass ratio, produced approximately 98% biodiesel yield with percent purity of approximately 99% within 3 h reaction time (Boey *et al*., 2011c). The tricalcium phosphate which has both acidic and basic properties is reported to be prepared by calcination of waste *Labeo rohita* fish scales at 900°C for 2 h (Chakraborty *et al*., 2011). The RSM based on CCD of experiments was also applied to optimize the parametric conditions; 6.27:1 M:O molar ratio, 997.42°C calcination temperature and 1.01 wt.% β-$Ca_3(PO_4)_2$ catalyst concentration, that yielded 97.73% FAME from soybean oil at 70°C and 5 h reaction time. Hu *et al*. (2011) used RSM based on CCD to optimize the transesterification of Chinese tallow oil by CaO prepared from freshwater mussel shells that was prepared by simple calcination-impregnation-activation method. The biodiesel yield reached 97.5% at 5.3 wt.% catalyst, 13.4 M:O molar ratio, 70°C within 1.5 h reaction time. Boey *et al.* (2012) used RSM-based CCD of experiments to optimize the transesterification reaction of WCO by a new catalyst system prepared from the high basic boiler ash as an agricultural waste and mixed CaO prepared by calcination of mud crab shells and cockleshells at 900°C for 2 h, with an aim to decrease the reaction time of CaO-catalyzed reaction and increase the conversion efficiency for boiler ash-catalyzed reaction. Where, approximately a complete conversion was recorded with 3 wt.% boiler ash and reaction time of 30 min at a fixed mixed CaO concentration of 5 wt.%. The RSM based on the Box-Behnken design of experiments was applied to optimize three important parameters for biodiesel production from soybean oil; the calcination temperature for CaO preparation from mussel shell, catalyst concentration, and

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M:O molar ratio. That led to 99.68% purity and 94.17% biodiesel yield at 1050°C calcination temperature, 12 wt.% catalyst concentration and 24:1 M:O molar ratio (Rezaei *et al*., 2013). Taguchi L9 (3^4) orthogonal array was used to evaluate the factors (methanol/oil molar ratio, catalyst concentration, reaction temperature and time) affecting the transesterification reaction of palm oil using CaO prepared from scallop waste shells (that prepared by calcination at 1000°C for 4 h). Where, with the lowest number of experiments, the FAME conversion reached 95.44% at 9:1 M:O, 65°C, 10 wt.% catalyst loading within 3 h (Buasri *et al*., 2014). In order to study the applicability of using different wastes produced from seafood restaurants; El-Gendy *et al*. (2014c) employed RSM based on D-optimal design (DOD) of experiments to study the significance and interactive effects of M:O molar ratio, catalyst loading, reaction time and mixing rate on biodiesel yield, and to optimize the transesterification reaction of WCO with methanol using calcined waste mollusks and crabs shells at 800°C and 700°C, respectively. The prepared green catalysts yielded 96 and 98 wt.% biodiesel yields at optimum operating conditions of 6:1 and 12:1 M:O molar ratio, 4.5 and 7.3 wt.% catalyst loading, 82 and 30 min reaction time, and 220 and 214 rpm, respectively. Moreover, the activities of the produced green catalysts were higher than those of commercial chemical CaO and Novozym 435. El-Gendy *et al*. (2015b) have also employed RSM based on DOD design of experiments to study the significance and interactive effects of the aforementioned important parameters on the biodiesel yield, and to optimize the transesterification reaction of WCO with methanol using calcined waste animal bones at 700°C and Novozym 435. The maximum biodiesel yields of 96 and 62 wt.% were obtained at optimum operating conditions of; 7.35:1 and 6:1 M:O molar ratio, 4.35 and 8.8 wt.% catalyst loading, 91and 96 min reaction time, and 331 and 394 rpm, respectively at 60°C reaction temperature. The process optimization based on the DOD of experiments was found to be capable and reliable to optimize biodiesel production from WCO using natural CaO prepared by calcination of waste eggshells at 800°C and chemical CaO (El-Gendy *et al*., 2016). Where, the activity of the produced green catalyst was comparable to that of chemical CaO, producing high yield of biodiesel ≈ 91 and 98%, respectively, at 8.57:1 M:O molar ratio, 3.99 wt.% catalyst concentration, 31 min reaction time, and 398.88 rpm mixing rate at 60°C. EL-Gendy *et al*. (2016) attributed the recorded higher activity of chemical CaO relative to that of natural CaO prepared from eggshells to the higher basicity of chemical CaO (42.4 and 25.3 and mmol CO_2/g, respectively), with its lower crystalline size (35.52 and 47.39 nm, respectively) and higher; specific surface area (106.37 and 56.82 m^2/g, respectively), average pore size

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(4.12 and 2.89 nm, respectively), and pore volume (0.303 and 0.058 cm^3/g, respectively).

2.6 Challenges and Perspectives

By the early 2000s, the European Union was the dominant player in the biodiesel industry, but nowadays the United States, Asia and Brazil have leveled out the global biodiesel market share. The worldwide annual rate of biodiesel consumption is approximately 5%. The cost of biodiesel is still high but governments worldwide are mandating pollution control. The usage of biodiesel in the short and long term, and collaboration between developing and developed countries in realizing green targets and application of biodiesel in real field, are critical needs. By focusing on these scenarios, research on biodiesel is going to be more and more intense to lower its cost and increase its quality as much as can be.

Producing biodiesel from edible crops is unethical. Growing oil crops requires land for cultivation, water for irrigation and fertilizers that would increase the overall cost of biodiesel production. These croplands and water should instead go towards feeding and satisfying the water needs of animals and humans. Food-biodiesel demand competition results in dramatic increase in some food items. The conventional homogeneous catalytic process results in corrosion problems, non-reusability of the catalyst and multiple processing steps; two-step reaction (esterification of the high FFA concentration and then transesterification), unreacted catalyst removal and neutralization of the produced biodiesel, and finally product separation. A lot of water is currently used in the washing step to purify the final product. That leads to new environmental and waste management problems. Moreover, glycerol as a by-product of this process is of very low quality, due to its high impurities content from unreacted catalyst and methanol, water and produced soap. The purification of such glycerol throughout—filtration, chemical additives, ion exchange resins, fractional vacuum distillation, bleaching or deodoring—is costly, especially for medium- and small-scale biodiesel producers (Jazie *et al.*, 2013). Heterogeneous catalyzed process has the significant advantages of lower amounts of wastewater, catalyst reusability, milder, environmentally friendly, cost-efficient and integrated process, that produces high-quality biodiesel and glycerol (Khemthong *et al.*, 2012).

There are no technical limitations on the replacement of petro-diesel with biodiesel. However, nowadays there is a lot of concern and limitations on the feedstock, and the use of arable farm-land for cultivation of

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oil crops. The use of edible oil or oil crops for production of biodiesel is a point of concern, as it will not mitigate global warming, but on the contrary, it might increase it, because it would be cultivated at tropical forest area which consequently would lead to deforestation. Thus, the advantage of carbon neutrality of biomass would occur on the use of waste frying or cooking oils and animal fats, instead of fresh edible or non-edible oils. Not only this, but applying non-edible oil crops for biodiesel production also produces a lot of solid wastes (for example, the pressed seed cake) which causes a new disposal and waste management problem. To overcome such drawbacks, recently, research is ongoing towards the use of blends of different non-edible oils and non-edible biomass feedstock including algae for producing biodiesel on the commercial scale, with the recommended quality according to the ASTM and European standards (Mohapatra *et al*., 2016). Although micro-algae can be easily cultivated, up till now, it has not been economically viable for production of biodiesel since the processes of cultivation, harvesting, lipid extraction and transesterification are still very expensive (Lee and Steven, 2010). The main problem of applying waste oils is the difficulty of its collection as it is normally scattered. However, to increase the sustainable biodiesel production and decrease its production cost, the enhancement of the collection of the spent waste vegetable oils and the household, resorts, hotels, restaurants and food processing industries' used cooking oils and their transformation should be mandatory at a national level. Promotional campaigns and communication tasks should be developed to motivate a behavioral change among citizens and increase the public interest about the recycling of UCO and the non-edible spent waste vegetable oils (NSWVO). Establish centralized depots for the collected UCO and WVO, to make it easier for direct collection by the biodiesel companies and producers. But the quality of the collected WVO as a feedstock for biodiesel production is very critical as it has a great impact on all the sequential stages and the final product. The main drawbacks of WVO, especially the WCO as resources for biodiesel productions, are their impurities, FFA and water contents, due to their significant adverse effects on the biodiesel processing. That consequently necessitates pretreatment steps before the transesterification process. For example, if the FFA content is above 3 wt.%, significant problems would occur in the transesterification process (Wen *et al*., 2010a,b). Thus, there should be regulations and international standards for the specifications of the WVO, their storage and transportation. Generally, the quality and the price of WVO are determined by their acid and saponification values.

The main processes for the biodiesel industrial production are batch, continuous, supercritical, enzymatic, multi-step and reactive separations.

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Heterogeneous solid catalysts can be applied in the reactive separation processes such as catalytic reactive distillation (Refaat, 2011).

The use of acid or base heterogeneous catalyst prepared from natural sources would lower the overall cost of biodiesel. However, solid acid catalysts have lower activity which can be overcome by operating at higher temperatures (120-450°C), thus higher energy is in demand. Much more research must be done to increase its catalytic efficiency at lower operational temperatures. The application of the bi-functional catalysts can overcome the problems of high FFAs and water contents and can act as acid and base catalyst at the same time (Endalew *et al*., 2011; Farooq *et al.*, 2013; Ani and Bakheit Elhameed, 2014). The use of CaO prepared from different natural waste sources would imply a positive impact on the catalyst cost. The advantages of using these catalysts are availability, low cost, large number of resources, good catalytic activity, renewability, sustainability, and overcoming waste management problems.

It has been reported that, typically, glycerol as a by-product of the transesterification is produced by approximately 10 wt.% of the total amount of produced FAME (Santaceasatia *et al*., 2012). The utilization of the obtained glycerol and its transformation into useful chemicals is another route to decrease the overall cost of biodiesel and the glycerol waste disposal problem. Glycerol can be used for production of biofuels, oxygenated additives for fuels (e.g., ethers, esters, acetals and ketals), cosmetics, detergents, etc. The use of industrial processing wastes such as the defective coffee beans for production of biodiesel (Oliveria *et al*., 2008), would add an advantage for the industries to produce their own fuel. Moreover, as previously mentioned, on the use of non-edible vegetable oils for production of biodiesel, a huge amount of solid residues (such as the pressed seed cakes) are generated, causing a lot of environmental and waste management problems. As an environmentally friendly way to overcome such problems, achieve the concept of circular economy via reaching to zero-waste, is the valorization of such spent waste biomass throughout its thermo-chemical conversion to activated carbon (Nunes *et al*., 2009; Tongpoothorn *et al*., 2011). Activated carbons have a lot of applications, for example, treatment of polluted water, including the removal of heavy metals, organic pollutants, pesticides, dyes, etc. Feng *et al*. (2011) have also reported that the wastes generated from the biodiesel production process can be used for power production.

Briefly, to overcome the drawback of total high cost of biodiesel production, that is one-half higher than that of petro-diesel (Sulaiman and Amin, 2016), it is mandatory that future work should focus on the application of renewable, economic and environmentally friendly heterogeneous sustainable catalysts in the biodiesel production from animal fats and waste oils

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as feedstock to make the process economic and fully ecologically friendly. Moreover, it is very important to study the mass transfer, reaction kinetics and chemical equilibrium and subsequent modelling to optimize the biodiesel production process in laboratory scale before the up-scaling to the industrial scale.

The reaction time can be shortened by increasing the liquid-liquid interfacial area. This can be done by applying different techniques: static mixers, micro-channels reactors, microwave irradiation, ultrasonic waves, rotating/spinning tube reactors, and centrifugal reactors. The process time can be also shortened throughout the integration of the reaction and separation steps to push the equilibrium in a forward direction, i.e., full conversion by applying the catalytic reactive distillation (Minami and Saka, 2006; Kiss, 2011). Hindryawati and Maniam (2015) reported that using the conventional hot plates in the transesterification reaction requires more energy than the ultrasonic process. Thus, applying a low-cost heterogeneous catalyst for biodiesel production from WCO using low energy consumption for processing, such as microwave irradiation or ultrasound waves would lower the reaction time, temperature, required energy, thus, the overall production cost and moreover, increase the biodiesel yield and its purity (Khemthong *et al.*, 2012; Motasemi and Ani, 2012; Hindryawati and Maniam, 2015). Moreover, Corro *et al.* (2016) reported the application of solar energy as a heating source for the transesterification of WFO using waste animal bones.

The base homogeneous catalyzed process faces a major challenge in terms of the FFA and water content. The multi-step process is a promising industrial technique to overcome this challenge; where the TG is first hydrolyzed to FFAs and pure glycerol. Then the FFAs are subsequently esterified to the corresponding fatty esters in a second step in conventional reactors or by solid acid catalysts in various integrated reactive-separation units (Kiakalaieh *et al.*, 2013a,b; Yaakob *et al.*, 2013). Applying solid-acid catalysts deletes the neutralization and washing steps, thus lowers the overall cost and makes the process more efficient and simpler and can be applied directly, in a single esterification step, if the feedstock is mainly FFAs. Reactive-separation processes can be applied in esterification or transesterification reactions, using homogeneous or heterogeneous catalysts. It can be integrated with reactive distillation, reactive absorption, reactive extraction, membrane reactors and centrifugal separators. That leads to high conversion yield, selectivity and energy efficiency (Kiss and Bildea, 2012). These two aforementioned processes would eliminate the drawbacks of the conventional batch processes which are not practically suitable for large industrial scale. Helwani *et al.* (2009) reported that the

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batch biodiesel reactor plants can produce from 500 to 10,000 tons/year. However, this volume can be increased on applying the continuous process technology, whatever; continuous stirred tank reactors, tubular reactors or plug flow reactors. Ho *et al.* (2014) reported two steps catalytic conversion of WCO, by esterification of FFAs with the solid acid catalyst $SrFe_2O_4/SiO_2$-SO_3H followed by transesterification step using KOH. This process showed better activity than using H_2SO_4 in the esterification step; not only this but the solid catalyst can be easily separated by applying a magnetic field and be reused many times without losing its activity, thus, having the potential to be commercialized. ESTERFIP-H^{TM}, a commercial gas-phase process developed by French Institute of Petroleum (FIP) that uses a Zn/Al oxides catalyst. However, its major drawbacks are the requirement of high-quality refined feedstock and high temperature (210-250^{o}C) and pressure (30-50 bar) (Bournay *et al.*, 2005). FIP has also developed both discontinuous and continuous reactors for homogeneous-base-catalyzed-transesterification reaction, with capacity of 80,000 and 100,000 tons FAME/year, respectively, and a yield of approximately 99% (Ballerini *et al.*, 2011). Roschat *et al.* (2012) reported that the scaling up of biodiesel production using heterogeneous solid catalysts, applying the fixed-based reactors, is impossible, due to the high pressure drop that would occur within the reactor. Moreover, the removal of the heterogeneous solid catalyst at the end of the batch process is difficult. However, the continuous process using heterogeneous catalysts solved most of the drawbacks of homogeneous ones and enzymatic processes (Sharma *et al.*, 2011). Brazil has a significant number of biodiesel plants, for example, the Biobrax plant (Bahia, Brazil) with capacity of 60,000 ton biodiesel/year, via the hydro-esterification technique (Aranda *et al.*, 2009). Another plant has been started working since April 2005 in Belem-PA-Brazil with capacity of 12,000 ton biodiesel/year applying the hydro-esterification technique, using a heterogeneous catalytic esterification of fatty acid in a fixed-bed reactor (Machado *et al.*, 2011). The supercritical processes using solid heterogeneous catalysts reduces the reaction time, temperature, and solves the mass transfer problem by increasing the alcohol/oil miscibility. Thus, this technology is more economically attractive (Gomez-Castro *et al.*, 2011).

As mentioned before, one of the main drawbacks of biodiesel is its high price. Blending biodiesel with petro-diesel is a way to overcome the problem of its high price. The blended product is designated as Bxx (e.g., B5 is 5% biodiesel and 95% petro-diesel) (Ullah *et al.*, 2015). Sulfur is known to provide diesel fuels with the required lubricity for engine performance, thus upon applying the stringent regulations towards ultra-low

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sulfur diesel oils, the lubricity would decrease. Thus, upon blending of 1 – 2% of biodiesel to conventional petro-diesel, this would retain the beneficial impact of restoring lubricity throughout an anti-wear action on the engine injection system (Hillion *et al*., 2003). Moreover, applying micro-emulsion of biodiesel with water in diesel engine would enhance its engine performance and reduce greenhouse gases emissions, including the NOx (Tan *et al*., 2015a). The waste fish oil is known to have a high concentration of eicosapentaenoic and docasahexaenoic acids and high content of polyunsaturated fatty acids. Thus the biodiesel produced from such feedstock would be characterized by low oxidation stability. This would produce insoluble deposits that would clog the fuel pumps and lines (Garcia-Moreno *et al*., 2014). This can be solved by the addition of some antioxidants to the produced biodiesel or use a mixture of oils as a feedstock.

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3

Multidisciplinary Sides of Environmental Engineering and Sustainability

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Abstract

This chapter addresses the different multidisciplinary (MD) sides of environmental engineering (EE) and sustainable development engineering (SDE) which is a subsystem of sustainable development (SD) using system theory (ST) and its related integrated system approach (ISA). Special attention is given to bio-fuels (BFs) and integrated bio-refineries (IBRs). This chapter addresses the coupling of endothermic (endo), e.g., dehydrogenation (dehydro) and exothermic (exo), e.g., hydrogenation (hydro) reactions in order to achieve auto-thermal behavior (autotherm) or at least minimize the external heat needed in an industrial complex. This chapter also presents another type of autotherm based on reactor-regenerator (react-regener) catalyst recycling units; the most popular is the different types of fluid catalytic cracking (FCC) units in petroleum refining industry. The principle is applicable to other reactions. The chapter addresses the technical, social and educational aspects of these MD systems. Chemical and biological engineering (CBE) is the heart of analysis and discussion. Development of societies, depletion of classical energy sources, global warming, etc., dictates an MD approach to deal with recent challenges. The MD approach extends the different scientific and engineering disciplines to reach all other disciplines, including economics, politics and other social sciences. It is time for engineers, scientists, medical doctors, economists, politicians, military officers and specialists, etc., to join arms in MD projects to achieve sustainability for better, stable, peaceful, non-sectarian, prosperous and more just societies. The main aim is to introduce a common basis for these disciplines toward these human aims.

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Nour Shafik El-Gendy (ed.) Sustainable Solutions for Environmental Pollution Volume 1: Waste Management and Value-Added Products, (123–162) © 2021 Scrivener Publishing LLC

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***Keywords*:** Dehydrogenation (dehydro), hydrogenation (hydro), integrated bio-refineries (IBRs), renewable raw materials (RRMs), mathematical modeling (MM)

3.1 Introduction

Chemical engineering has witnessed considerable expansion in the last three decades, which is consistent with the Amundson report (Amundson, 1988; Elnashaie *et al*., 1993). The most successful departments in the USA and Canada as well as most of the rest of the world have been those that expanded in the direction of becoming CBE departments and other directions (e.g., Delft, 2003; Fiksel, 2006).

All the Engineering Disciplines (EDs) are strongly linked to the social challenges associated with the subjects and are using the new approach that make them all fall well under the same umbrella. The MD approach extends to include not only EDs but also scientific disciplines such as chemistry, physics, mathematics, microbiology, etc., as well other non-engineering/non-scientific disciplines such as economics, politics, sociology, etc., in addition to newcomers discussed below that make the graduates truly ready for MD jobs in industry as well as for research work in different research establishments. It is also important to emphasise the fact that the new engineering era requires graduates to be prepared for innovation; they should not be taught to learn only while in school and university but should also be taught the culture, ideology and philosophy of Long Life Learning (L3 according to the ABET terminology). With this branching, interaction and synergy between disciplines and these new requirements of modern industry and the healthy forms of globalization, a new approach based on ST and which may be called ISA should be adopted both in undergraduate and postgraduate teaching and research in academia and spread to industry and governmental research centers (Bertalanffy, 1976; Dewulf and Langenhove, 2006; Hens, 2005; Horbach, 2005; IChemE, 2002).

The above is well defined and discussed in the literature and the reader can be referred to excellent references for this purpose, for example, Wei, 1988; Amundson, 1988; Elnashaie *et al*., 1991; Aris, 1991). The last word has not been said with regard to these subjects, but they are matured enough to be considered.

The relative newcomers are: SDE, which is a subsystem of SD as a whole (Elnashaie, 2008). In terms of ST and the ISA, SD itself can be considered as a system formed of technical and non-technical subsystems and

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SDE is a subsystem of the technical subsystem as shown in some details later. SDE is an extension of EE, which is itself an extension of Efficient Engineering (EE' to distinguish it from EE). In other words if SDE (which is a subsystem of the technical subsystem of SD) is a system then EE is a subsystem of it and EE' is a subsystem of EE. In terms of stability theorem terminology EE' can be considered necessary but not sufficient for EE; what makes it sufficient is the introduction of environmental regulations (ERs) which came into the picture in the last four decades only in some countries. Similarly EE is necessary but not sufficient for SDE (which is itself necessary but not sufficient for SD); what makes it sufficient is the introduction of RRMs to replace the Non-RRMs (FAO, 1992). This brings into the picture not only BFs from wastes and energy crops (and not from food) and micro-algae, but also IBRs since societies do not live only on fuels.

Another relatively new and very important arrival is nano-technology (NT) [or nano-engineering (NE)]. Again using ISA, NT is an advanced part of materials science/engineering, but NT cannot develop without MD research including physicists, chemists, electrochemists, etc.; it is actually an advanced system formed of many subsystems and a discipline strongly cross-linked to many other disciplines (Wei, 1988; Amundson, 1988; Elnashaie, *et al*., 1993; Aris, 1991). Another relative newcomer is the practical implications of non-linear dynamics (NLDs), bifurcation (B) and chaos (C). These are actually very old disciplines, and some philosophers will consider them as old as the great French mathematician Poincaré (Smith, 1974; Stewart, 1989; Hawking, 1989) or even older, while other philosophers consider them as old as the great Persian poet Omar-El-Khiam (Elnashaie and Elshishini, 1996). NLD, B and C are new and challenging, especially their practical implications in CBE systems (Iscol, 1970; Elnashaie and El-Henawi, 1979; Elshishini and Elnashaie, 1992; Elshishini *et al*., 1992; Edwards, and Kim, 1998; Elnashaie and Garhyan, 2004; Garhyan and Elnashaie, 2004a-c; Chen and Elnashaie, 2004a,b; Mahecha-Botero *et al*., 2006 and Elnashaie *et al*., 2006).

Complexity (COMP) is also quite important, e.g.: simple configurations having COMP behavior and COMP configurations having simple behavior (Elnashaie and Grace, 2007). It is also important to realize that COMP is strongly related to NLD, B and C and will be kept under this category.

Different types of autotherm are also considered; they may have positive effects on minimizing the consumption of energy, achieving MPMP and help to approach sustainability.

This chapter will address a part of the tip of this iceberg, in an organized manner to be as useful as possible for other researchers of different

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disciplines to develop the ideas much further. The tools are from ISA based on ST. The objective is a systematic organized framework relating CBE, IBRs and EE together with the relative newcomers of SDE, NT and practical implications of NLD, B and C (Smith, 1974; Stewart, 1989; Hawking, 1989; Elnashaie and Elshishini, 1996; Iscol, 1970; Elnashaie and El-Hennawi, 1979; Edwards and Kim, 1998; Elnashaie *et al*., 1993; Elshishini and Elnashaie, 1990; Elnashaie and Garhyan, 2004; Garhyan and Elnashaie, 2004a-c; Chen and Elnashaie, 2004a,b; Mahecha-Botero *et al*., 2006; Elnashaie *et al*., 2006).

3.2 System Theory and Integrated System Approach

The main tools are ST and ISA; the first is the basis of the second and together they form the most efficient methodology for classification, organization and transfer of knowledge (Smith, 1974; Stewart, 1989; Aris, 1991; Elnashaie and Garhyan, 2003; Elnashaie and Uhlig, 2007). The ST approach is very valuable in both research and education. In research, it is one of the most important components for the development of new knowledge and novel processes, especially in areas where MD research and development is a must for innovative solutions. SD is one of those areas which are MD by their very nature. The theme of this part is not to stress only the importance of the ST when dealing with the issue of SD, BFs and IBRs but also to use it in developing the ISA as a tool for investigating and discussing all issues mentioned above including the MD educational methodology. It is also related to Mathematical Modeling (MM), the main tool for computer simulation (CS) and the maximum exploitation of digital computers (DCs) in education, research, innovation and optimal operation and control. ST is the best approach to organize knowledge and transfer it in an organized and easy manner. By this we believe that ST is the basic tool for dealing not only with SD but also to be widely used in engineering education, research and industry in relation to society. A definition of some important terms in ST is essential to build on towards ISA (Elnashaie and Garhyan, 2003; Elnashaie and Uhlig, 2007).

3.2.1 System Theory

The main difference between ST and Set Theory (ST' to distinguish it from ST) is that in ST there is synergy between the subsystems while in ST' we are dealing with "dead" sets formed of "dead" subsets where the set is simply the addition of the subsets with no synergy or in other words no new

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characteristics which do not belong to the subsets. This is not the case with regard to systems and subsystems.

A simpler, more pragmatic description regarding systems includes:

- A system is a whole composed of parts (subsystems or elements).
- The concepts of a system, subsystems and elements are relative and depend upon the degree of analysis. For example, we can take the entire human body as a system, while the heart, arms, liver, etc., are elements. Or we can consider any of these elements as the system and analyze it in terms of smaller elements (or subsystems) and so on.
- The parts of the system can be parts in the physical sense or they can be processes. In the physical sense the parts of the human/animal body or of a chair form a system. On the other hand, for chemical equipment performing a certain function, we can consider the various processes inside (within the boundary) of the system as elements which are almost always interacting with each other in a complex manner to fulfill the functions of the system. A simple chemical engineering example is a chemical/biochemical reactor in which processes like reactions, mixing, heat evolution/absorption, heat transfer, mass transfer, etc., take place to achieve the goal of the reactor, which is to convert reactants/substrates to products. A system can be formed of both, i.e., different parts of the system (a reactor and a regenerator) combined to form an FCC unit, each part having a number of processes taking place within its boundaries, with the different parts interacting through catalyst circulation, and in each vessel the different processes are interacting and all types of interaction are giving the overall characteristics of the FCC unit.
- The properties of the system are not the sum of the properties of its components (elements or subsystems), although they are, of course, affected by those components. Instead, the properties of the system result from non-linear interaction (synergy) between components (elements or subsystems). For example, humans have consciousness, which is not a property of any of its components (elements or subsystems) separated alone. Also, mass transfer with chemical reaction has certain properties, which are not properties of

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chemical reaction or mass transfer alone (for example, multiplicity of steady states, as discussed below). This shows the great difference between ST and ST' as mentioned above.

3.2.2 The State of the System and State Variables

The term "state of the system", rigorously defined through the state variables of the system, is used extensively. These state variables are chosen according to the nature of the system and the utilization and/or manipulation of it. The state of a boiler can be described by temperature and pressure, a heat exchanger by temperature, a non-isothermal reactor by the concentration of the different components and temperature, an isothermal absorption tower by the concentration of different components on different plates, a human body by blood pressure and temperature, flow through a pipe by the axial and lateral profiles of local velocity and pressure. Thus state variables are variables that describe the state of the system.

3.2.3 Input Variables (Parameters)

They are not state variables. Instead, they are external to the system but affect the system, i.e., "work on the system". For example, the temperature and composition of the feed stream to a distillation tower or a chemical reactor or the feed temperature to a heat exchanger are input variables. They affect the state of the system, but are not affected by the state of the system (except when there is a feedback control or a recycle, in which case we distinguish between control variables and disturbances or input variables). Of course, this again depends upon the level of analysis, or the boundary of the system (subsystem), for in many cases these input variables to the system are outputs (or state variables) of a previous system (subsystem).

3.2.4 Design Variables (Parameters)

They are associated with the design of the system and are usually fixed. Examples are the diameter and height of a continuous stirred tank reactor (CSTR) or of a tubular reactor.

3.2.5 Physico-Chemical Variables (Parameters)

They are the physical and chemical parameters of the system, e.g., viscosity, mass and heat transfer coefficients, equilibrium constants, reaction rate constants, etc.

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3.2.6 Boundaries of System

As encountered above, a system has boundaries distinguishing it from the surroundings or environment. The relation between the system and its environment leads to one of the most important and fundamental classifications of systems:

3.2.6.1 Isolated System

It does not exchange matter or energy with the surroundings. It tends to the state of thermodynamic equilibrium (maximum entropy). An example is a batch adiabatic reactor.

3.2.6.2 Closed System

It does not exchange matter with the surroundings, but it does exchange energy. Such a system, again, tends to thermodynamic equilibrium (maximum entropy). A batch non-adiabatic reactor is a typical example.

3.2.6.3 Open System

It exchanges matter and energy with the surroundings. (Notice that exchange of matter automatically implies exchange of energy.) It does not tend to thermodynamic equilibrium but to steady state or what should better be called a "stationary non-equilibrium state", characterized by minimum entropy generation. A CSTR is a lumped example (state variable are not changing with the space dimension(s)), whereas a Tubular Continuous Flow Reactor (TCFR) is a distributed example (state variable are changing with the space dimension(s)). It is important to notice that open systems belong to the category of dissipative systems discussed below.

Flow systems are usually open, with one or more fluid streams entering and discharging from the boundaries. However, mixing vessels and flow loops can be closed systems, with energy transferred across their boundaries (e.g., by impellers of pumps) to provide the energy needed to initiate and maintain the motion, most or all of this energy ultimately being dissipated due to viscosity.

The above shows that the term "steady state" commonly used in CBE is not really very accurate, or at least it is not precise enough. A more accurate phrase should be "stationary non-equilibrium state", which is a

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characteristic of open systems, distinguishing it from "stationary equilibrium state", associated with isolated and closed systems.

3.2.7 Steady, Unsteady States and Thermodynamic Equilibrium of Systems

As briefly stated above, the steady state (stationary non-equilibrium state) is a concept related to open systems (all continuous CBE processes are open systems). Steady state occurs when the state of the system stops changing with time, but the system is not at thermodynamic equilibrium, i.e., the processes inside the system do not stop and the stationary behavior with time is due to a balance between input, output and processes taking place within the boundaries of the system. This steady state of lumped systems is a point in a space having the same dimensions as the problem (number of components + temperature + pressure, etc.), whereas that for distributed systems, it is a profile in the space co-ordinate(s) as additional dimension(s). Unsteady state of an open system starts at an initial condition and tends with time towards a steady state when the system is stable (a point for lumped system and profile for distributed systems). What if the system is unstable? This is addressed in a later section about NLD, B, C and COMP. On the other hand, for isolated and closed systems the unsteady state changes with time, tending towards thermodynamic equilibrium, which is stationary with time because all processes have stopped (the process is "dead").

For flowing systems (leaving aside ideal, i.e., in viscid, fluids and fluid static), energy is required to actuate fluid motion and maintain steady flow and transport processes. If the source of energy (e.g., a pump, potential energy, or a heat source) is terminated or exhausted, then the system asymptotically approaches the thermodynamic equilibrium state of a static isothermal system.

3.3 Sustainable Development, Sustainable Development Engineering and Environmental Engineering

Many SD definitions are "catchphrases" and not real ones reflecting the intimacy of the term. The definition should be formed of a number of components and not a catchphrase.

We would rather then put the SD description definition to be covering the following:

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- Develop novel clean technologies capable of achieving (MPMP).
- Develop technologies capable of using RRMs to achieve sustainability (and may be growth) of raw materials rather than the present situation associated with the continuous and critical depletion of raw materials.
- The use of natural distributed RRMs in contradistinction to the present depleting raw materials concentrated in certain parts of the world causing continuous conflicts and wars.
- Produce environmentally friendly products easy to degrade and/or reuse.
- Develop clean and environmentally friendly housing, office buildings and shopping centers.
- Develop efficient technologies for waste treatment and recycle.
- Build a socioeconomic and political framework to apply the above (including the necessary non-profit tendencies and change of consumer habits, etc.).
- Develop efficient IBRs.

In the light of the ISA discussed below (Section 4), one can stress again the view of SDE as a subsystem of SD. This SDE subsystem will definitely lie among the technological subsystems of SD; the latter at the same time includes non-technological subsystems like socioeconomic, political ethical/moral, etc. Thus EE is a subsystem of SDE. Our technological target therefore is to achieve sustainability, while EE' and EE are subsystems of this sustainability, i.e., necessary but not sufficient for sustainability. The focus of this paper is more on SD with respect to production while the relation with consumption will lie in the background. It is very important to stress that RRMs constitute a crucial component of SDE and thus SD. It is also important to stress the fact that other non-fuel sustainable products are essential for SD, leading us to the very important concept of IBRs. BFs represent a subsystem of IBRs and also a subsystem for other renewable sources of energy, such as wind, hydro, nuclear, solar, etc., which are outside the scope of this paper. Also, improving the efficiency of fossil fuels' use will contribute to sustainability but is outside the scope of this paper. The simplest classification of SD to its subsystems is given in Figure 3.1 and a more condensed one is given in Figure 3.2. More details are given in Figure 3.3 and further details suitable for industries and education are given in Figure 3.4.

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Main Components of SD
1-Political: e.g., legislations And strategic decisions….
2-Economical: e.g., investment in novel new technologies
3-Social, Ethical/Moral: e.g., consumption trends, acceptance of novel clean technologies and products, moral/ethical factors
4-Technological: e.g., novel Efficient clean technologies, clean fuels, efficient utilization of renewable Feed-stocks, new environmentally friendly products, In-process Modification for Minimum Pollution Maximum Production (MPMP), efficient waste treatment.

Figure 3.1 SD is MD by its very nature. Technology is a subsystem of SD.

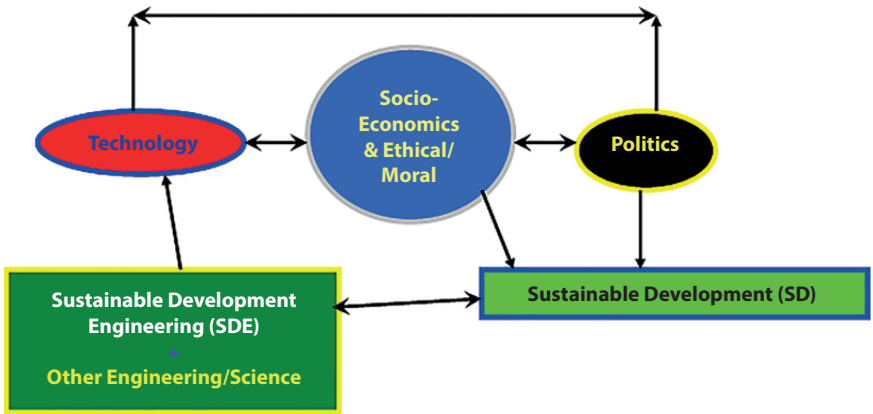

Figure 3.2 SDE is a subsystem of technology which is a subsystem of SD. Technology-Politics, e.g., DOE Extensive Hydrogen/Cellulosic Ethanol Research and Support to Hydrogen Economy by USA.

3.3.1 Bio-Fuels and Integrated Bio-Refineries

An IBR is a complex facility that integrates biomass conversion processes and equipment to produce fuel, power, and chemicals/bio-chemicals from the biomass. It is analogous to today's petroleum refineries and their integrated petrochemical complexes that produce multiple fuels and products from petroleum. IBRs have been identified as the most promising route to

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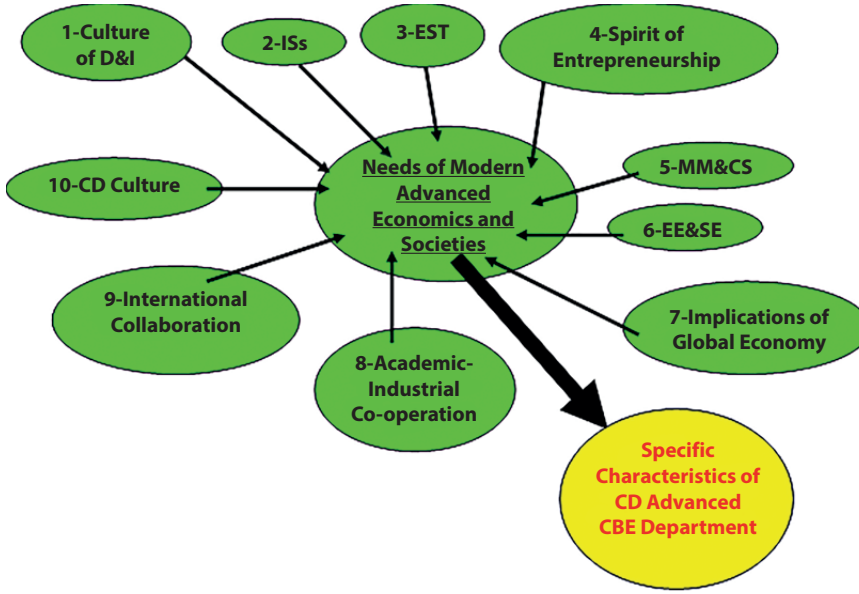

Figure 3.3 Main 10 needs of modern advanced economies and societies and output to Figure 3.4 given below.

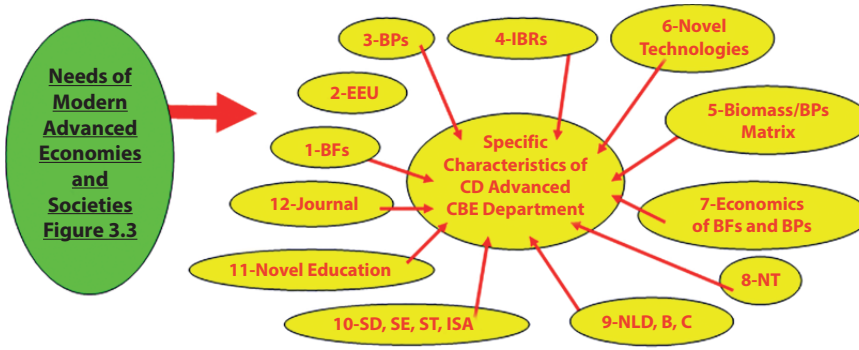

Figure 3.4 More detailed subsystems of SD.

the creation of a new domestic and distributed bio-based industry (Kamm, 2010; Alvarado, 2007; International First Refinery Workshop, 2007; NREL, 2007). Sustainability depends upon BFs and also on other commodities for modern societies (Biofuels Journal, 2007). This important simple fact leads to the important concept of IBRs producing not only sustainable fuels but also other sustainable commodities and energy. The National Renewable Energy Laboratory (NREL) which is a part of the US Department of

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Energy (DOE), defines bio-refinery as "a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass". The present view about IBRs is based on two platforms, the sugar and syngas platforms as discussed later. This paper concentrates on sustainable fuels and IBRs. Production facilities for sustainable BFs are a subsystem of IBRs; the implications of this are (Clean Fuel Summit, 2007):

- A sustainable BFs facility built today should be planned with its growth into an IBR in mind.
- Sustainable fuels production will almost always be a part of IBRs.
- An advanced definition of IBRs and their subsystems including BFs should be developed together with a clear definition of BFs and Bio-products (BPs).
- A clear definition of sustainability and quantification of these definitions into suitable metrics should be developed.

Both National Science Foundation (NSF) and DOE are putting large research funds into development of IBR (Bohlmann, 2005; Chen *et al*., 2005; Christensen and Nielsen, 2005; "Governmental and Industry Partnerships for Developing Biorefineries", 2004; "Integrated bio-refineries", 2007; Clark *et al*., 2006; Kochergin and Kearney, 2006; Realff and Abbas, 2004).

The present few bio-refineries are still very limited because of many factors including a limited understanding of BPs. There are a number of basic principles that need to be very clear from the beginning to well define IBRs and the position within them of their important subsystem BFs. IBRs represent an integral critical subsystem of SD, which is a CD system by its very nature, as discussed earlier. It is best to use ISA to study this complex CD system and its subsystems. Engineers are most interested in the technology part (subsystem of the SD system), but with a background understanding of other subsystems and collaboration with other disciplines, as discussed earlier. As discussed earlier, SDE is the most important subsystem of the technology part which is itself a subsystem of the SD system, and the efficient utilization of RRMs is at the heart of sustainability. RRMs should be defined very clearly, for it is strongly related to the cycle of renewability, i.e., fossil fuels are renewable, but over a cycle of hundreds of thousands of years. RRMs should be renewable over a period of 6-18 months. RRMs can be any kind of renewable waste, e.g., agricultural waste, municipal waste, etc., or special (energy) crops produced specifically to be used for this purpose, e.g., switch-grass cultivated and produced specially for BFs production. On the other hand, useful agricultural products used today for BFs, e.g., corn

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for ethanol; vegetable oil for trans-esterification bio-diesel, etc., are not strategic solutions as RRMs and for sustainability because of the consumption of important edible products at a time of food shortage everywhere, especially in developing nations. As discussed above, bio-diesel can also be produced from the growth of Algae under favorable conditions for it which are not favorable for agriculture. The main RRMs are a storage tank for solar energy through biosynthesis; CO_2 and other nutrients. The ultimate aim for BFs is to produce as much CO_2 as consumed in the biosynthesis of the biomass that produced it. This, with maximum efficiency, may lead to the approach of zero net CO_2 emission. We cannot really dispose of any CO_2 resulting from fossil fuel, it only keeps circulating from one form/place to the other, except with sequestration by injection under the bottom of the oceans, which is expensive; its side effects are not known and can only be practiced by very large companies. All other techniques just move the CO_2 from one location/form to the other without reducing the earth CO_2 added inventory from the carbon source that came from under the ground. Hydrogen is a good clean fuel and will occupy its part in the clean fuels matrix and is therefore one of the potential products of IBRs. However, although the claim that it is 100% clean is locally true, it is actually not globally true if its source is fossil fuel, whether directly through catalytic steam reforming (95% of hydrogen produced in USA is through catalytic steam reforming) or indirectly through production of electricity (90% of electricity in the USA is from coal) followed by electrolysis. It can be globally clean only if the source is bio, wind, hydro, nuclear, etc. The range of fermentable sugars is expanding due to the development in microbiology and the discovery of efficient mutated microorganisms capable of fermenting the wide range of sugars produced from cellulose/hemi-cellulose hydrolysis. A strong challenge with lots of intensive research nowadays is in the field of efficient and clean hydrolysis of cellulose/hemi-cellulose; important improvements are achieved in the enzymatic hydrolysis of cellulose/hemi-cellulose. The process of fermentation is improving continuously using novel membrane immobilized fermenters and novel modes of operation. Lignin from Lingo-cellulose is used as a cheap fuel to improve the energy efficiency of the IBRs; however, the future potential is to use it as a platform for a wide range of products to replace certain petroleum refining and petrochemical products. Important improvements are introduced to syngas production from biomass through both one-step process (biomass gasification to syngas) and two-step process (biomass fast pyrolysis to bio-oil followed by Catalytic Steam Reforming (CSR) of bio-oil to syngas). The two-step process seems to be better with regard to the % of H2 in the syngas. Certain difficulties associated with CSR of bio-oil are solvable

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through novel reformers configurations such as Circulating Fluidized Bed (CFB) reformers (Chen and Elnashaie, 2004a,b). An important challenge in the biomass to Fisher Tropsch (FT) BFs process is the integration of the endothermic catalytic CSR process with the exothermic catalytic FT process into one integrated membrane catalytic autotherm process. The choice of BFs is strongly location sensitive and is also affected by many other factors including, but not limited to, available capital investment, size of market, etc. For the same BF the technology to be used also depends upon the above factors and others. Although the interest in BFs is dominating now because of energy and fuel problems especially in the Middle East (ME), we do not live only on fuels; other products should be sustainable. IBRs should be able to contribute towards sustainability and not only renewable BFs; however, renewable BFs represent an essential subsystem of it. It is important for IBRs to include all of what is bio, whether with regard to feedstock, or processes or both, e.g.:

- Biomass utilizing sequential thermal catalytic processes to produce FT-BFs (the processes are not bio, but the feedstock is bio).
- Biological treatment of CO and water to produce CO_2 and hydrogen (bio-catalyzed Water Gas Shift-WGS-reaction). The feed is not bio, but the process is bio.
- Ligno-cellulose utilizing sequential bio-processes to produce cellulosic bio-ethanol. Both feedstock and processes are bio.
- Utilization of bio-processes to transfer one form of energy to another, e.g., Integrated Bio-Electrolysis coupled to Bio-Fuel-Cells (IBE-BFCs) to change intermittent solar energy into continuous electric energy, for many applications including auto-thermal housing.

IBRs can grow with time either as parts of existing plants (e.g., Pulp and Paper Industry), or start as IBR based on renewable fuels production and grow into a complete IBR. Other forms of RCE (when suitable, e.g., wind energy) can be integrated with the BFs to generate the total renewable energy profile of an IBR. The central intermediates (platforms) for the BFs part of the IBRs seem to be fermentable sugars suitable for fermentation to bio-ethanol and/or bio-butanol and syngas suitable for both hydrogen extraction and use in Fisher-Tropsch (FT) process for producing wide range of BFs. It is also to be noticed that it is possible to combine the gasification of biomass (or fast pyrolysis) to produce fuels from methanol

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up to diesel. It is also important to follow that by CSR of the product bio-oil followed by producing bio-syngas and with the fermentation of this bio-syngas produces bio-ethanol and or bio-butanol (Worden *et al.*, 1991). Direct utilization of solar energy through different direct techniques (e.g., photocells) without passing through the biosynthesis stage is a possibility, but it has its own bottlenecks and should be integrated with other technologies (e.g., bioelectrolysis-biofuel cell) to fully utilize it as a part of auto-thermal housing and IBRs. From the above it is clear that neither single BF, nor one technology will dominate for any single one of these BFs. Humanity will move from today's matrix of dirty non-renewable fuels to a future matrix of clean renewable fuels with the submatrix of different BFs from different technologies occupying a large portion of the clean fuels matrix; sustainability will not be achieved through BFs only but we should extend sustainability to IBRs combining BFs and other BPs together with efficient bio-energy in order to achieve SD. We can summarize the status of today's IBRs concept as shown in Figure 3.5 taken from the DOE site and the future view of a self-sustained clean town as shown in Figure 3.6, also taken from the DOE site (EPA, 2007).

3.3.2 Integrated System Approach

The current lack of success in improving industrial sustainability, coupled with the challenges of bio-complexity and resilience, indicates that sustainability is a system problem requiring collaborative solutions of an MD

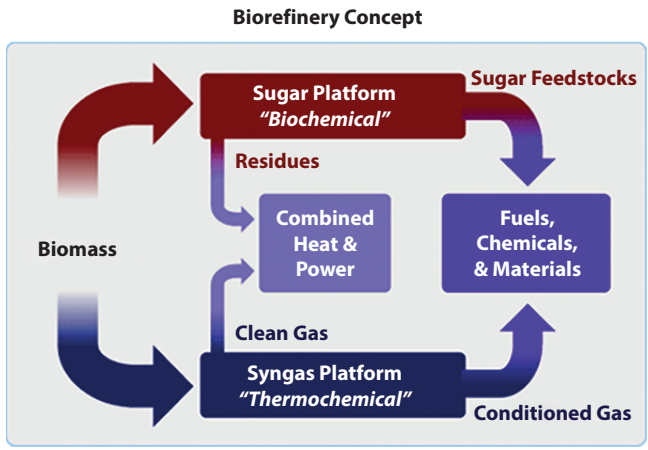

Figure 3.5 Preliminary bio-refinery structure with the main two sugar and syngas platforms.

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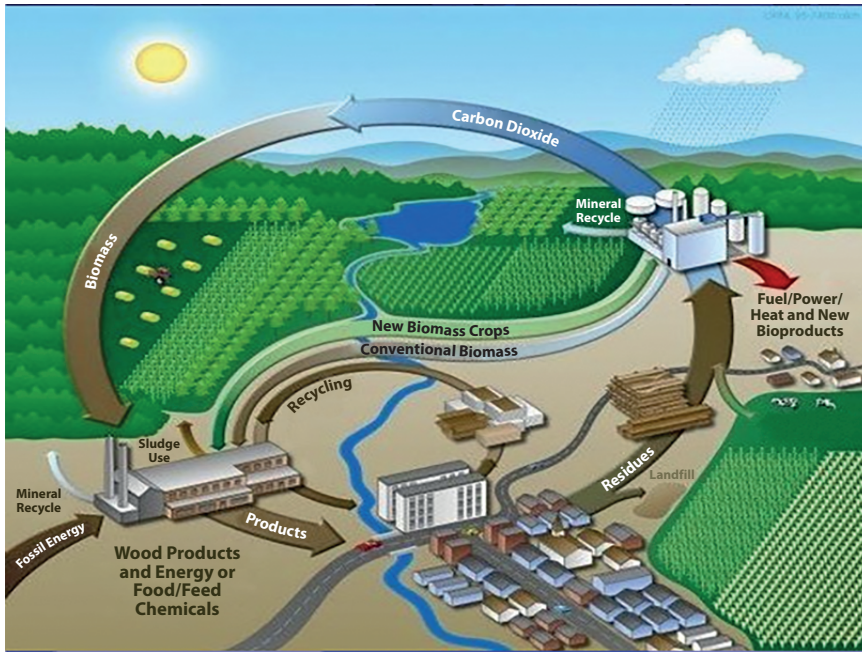

Figure 3.6 A sustainable and clean future town.

nature. Other issues presented in the introduction follow the same route. A number of technical advances will likely improve the usefulness of models, including rigorous methodologies for dealing with missing and uncertain information; improved methods for interpretation of multivariate data sets and for multi-objective decision making involving trade-offs among conflicting goals; and novel modeling methods as alternatives to traditional MM. More generally, there is a great need for operational definitions and metrics for sustainability and resilience in economic, ecological, and societal systems. SD in a changing global environment will require resilience at many levels, including human communities and economic enterprises. In the face of ever-increasing global COMP and volatility, it is essential to move beyond a simplistic "steady state" model of sustainability. Instead, we need to develop adaptive policies and strategies that enable societal and industrial institutions to cope with unexpected challenges, balancing their need to be able to achieve efficient sustainable BFs as one of the many challenges imposed by modern industry and societies and reflecting upon education, industry, research and the entire society in a global manner. ISA is the use of ST to tackle all these challenges in an integrated, efficient and well-organized manner; it utilizes MM and CS to the highest

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level coupled to experimental work and organized exploitation of industrial data not only to improve operation but to discover novel processes. It maximizes utilization of present technologies using on-line efficient computer optimization and control with objective functions being not only MPMP. It does not stop at that, it also considers conceptual optimization which may change the technology fundamentally, i.e., from fixed bed to fluidized bed by Grace and Lim and co-workers in UBC and Elnashaie and co-workers in Auburn and many others; using membranes to "break" thermodynamic equilibrium barriers for reversible reactions by Grace and Lim; Elnashaie and others and eliminate products inhibition in biological processes by Elnashaie and others; integrated membrane reactors having complementary reactions at both sides of a suitable membrane by Elnashaie and others, combining endothermic and exothermic reactions to achieve an auto-thermal process by Elnashaie and others; a continuous reactor-regenerator process such as FCC and its continuous development by petroleum companies, Pressure Swing Adsorption (PSA) to replace absorption-regeneration, Pinch Technology (PT) for maximum energy efficiency in Heat Exchangers (HEs) Net Works (NWs) and its extension to Mass Transfer (MT) NWs by El-Halwagi, M. and co-workers at UCLA, Auburn and Texas A&M (El-Halwagi, 2006), novel polymerization processes such as the fluidized bed UNIPOL process for polyethylene and polypropylene and their further development and also the bifurcation and chaotic characteristics of these and other polymerization reactors by Ray, Teymour and others at Wisconsin, Madison and Illinois Institute of Technology (IIT) (Teymour, 1989; Temour and Ray, 1992a,b; Ray and Villa, 2000; Georgia and Teymour, 2005). The list is endless and the efforts towards novel designs using conceptual debottlenecking are intensifying in academic research, research centers and industry (Chen and Elnashaie, 2004b).

3.4 Advanced Multi-Disciplinary Sustainable Engineering Education

Engineering education is considered in general not only with regard to CBE and its MD branching (NCSE, 2003; NGS-NANO, 2008). In the last two decades engineering has been quickly entering a new phase. The speed of transformation has been accelerating and the boundaries between different engineering disciplines are falling down very fast (Klein, 1990; Lattuca, 2001; Lattuca *et al*., 2004; Engineering Education Research, 2004; JEE, 2010; Borrego and Newswander, 2008). In addition, the boundaries

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between engineering, with its different specializations, and other scientific disciplines (chemistry, microbiology, mathematics, etc.) are becoming more permeable. Not only those, but also the engineering disciplines are becoming more integrated to socioeconomic, political and moral/ethical issues. Also the world economy is moving from national economies with continuously intensifying exchange to a global economy which is much more integrated and competition is more intensive. Moreover, awareness of the danger of depleting the non-renewable resources and exceeding the absorption capacity of our ecosystem is increasing.

This state of affairs calls for a radically new approach not only with regard to engineering research but also EE. Engineering is branching into more specializations, while at the same time is calling for closer integration between different engineering, scientific and humanitarian specializations.

In addition to the four main disciplines (CBE, ME and EE), among the newcomers SD gave birth to SDE and even before fitting the other newcomers (NT, NLD, B and C) into the framework the situation becomes quite complex. SDE shows very clearly that EE' and EE are necessary but not sufficient for sustainability. We can have very efficient designs and very clean technologies but they are not sustainable because they do not use RRMs.

Sustainability is becoming the modern focus of all research/development and the main challenge facing science and technology in the twenty-first century. Research on renewable energy is very important and is intensifying both in academia and industry. This is good, but modern societies do not live only on energy; there are other products and commodities that have to be produced from RRMs. Here comes strongly into the picture the concept of IBRs which will not only produce clean renewable BFs but also other products and commodities.

When the above four basics and three newcomers are added we have huge engineering designs and concepts attached to all other engineering and scientific disciplines. This huge MD engineering complex has its foundations based on fundamental knowledge; technological progress is limited by these foundations. Therefore fundamental research is extremely important in this challenging and interesting episode for the good of the entire world. The link between scientific discoveries and technological innovation through transformational engineered ISA is becoming very important.

These challenges call for MD research involving all types of the continuously evolving human knowledge. This MD research is evolving continuously, creating new ideas and innovative breakthroughs not expected before.

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This challenging and promising new trajectory needs a tool to help organize it and bring it to useful and dynamic conclusions. The ISA based on ST, both discussed above, are the best tools for the generation, organization and transfer of knowledge with positive synergetic effects maximizing the return on investment for research/development.

There is strong evidence that there are some contradictions between sustainability and profitability; some researchers are even claiming that there is a contradiction between sustainability and the second law of thermodynamics. The most suitable solutions to these contradictions are through innovation, which is, from an informatics point of view, a very good source of negative entropy.

From the above brief introduction we can clearly point to the following general needs of modern advanced economies and societies as briefly given below and condensed in Figure 3.1:

- Develop a culture of Discovery and Innovation (D&I) through the entire education/research system with special emphasis on engineering education and research.
- Find Innovative Solutions (ISs) for the contradiction between sustainability and profitability.
- Efficient approach linking fundamental scientific discoveries to engineering applications and Efficient Science to Technology (EST). The most promising is an integrated MD approach based on ST.
- Develop among different generations of engineers a strong spirit of entrepreneurship and of high-caliber engineers with strong MD capabilities suitable for leadership in a global economy.
- Expand the use/development of MM, CS and optimization techniques.
- Expand the domain of EE which aims at clean technologies to SDE aiming at SD.
- Develop an engineering awareness of the technological implications of the global economy in order to produce engineers and researchers able to define pathways to successfully explore and realize innovation opportunities and thus qualified to be in the forefront of competition in a global economy.
- Develop strong relations between academia, small innovative firms, and relevant large agricultural and industrial producers as well as federal, state and local authorities.

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These relations should be aimed at intensifying discoveries, innovation and their commercialization nationally and internationally. This will include not only MD research/development but also education and continuous training.
- In a global economy, teaching, research, design and production cross national borders, which calls for the development of partnerships with foreign universities, research centers and industries for teaching, training, research cooperation and innovation in a global economy.
- Develop different categories of MD engineering departments each involving an optimally chosen number of disciplines in order to achieve an integrated MD operation. These departments should be formed of diverse and talented domestic/international individuals preparing diverse talented individuals who can function in a global economy where design, production and innovation stretch across national borders.

Different engineering departments are needed with different engineering disciplines in order to achieve good step forward in the arena of strong competition in a growing global economy.

The framework of the above characteristics is essential for starting a successful CBE department including earlier well-established disciplines in the right way and also encompassing main newcomers. The department will have the components of the typical present CBE departments classified on the basis of ISA as follows in addition to necessary fundamental subjects such as chemistry, biochemistry, mathematics, physics, computer programming and humanities:

- Material and energy balances for chemical and biochemical reacting and non-reacting systems
- Transport phenomena
- Mass Transfer
- Heat transfer
- Sizing of reacting and non-reacting chemical and biochemical systems
- Process control for reacting and non-reacting chemical and biochemical systems
- Momentum balance; transfer and fluid dynamics
- Plant design and economics

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In addition to the classical components, condensed/organized using an ISA, such a department will have special emphasis regarding research/education on the points shown and condensed in Figures 3.1-3.5 as an umbrella:

3.4.1 Bio-Fuels

Including developing and optimization of novel efficient compact processes and comparing them as renewable energy sources. A good preliminary plan is to concentrate on:

3.4.1.1 Bio-Hydrogen

Including producing it through biological processes from non-bio raw materials (e.g., biological WGS of CO) and also thermo-catalytic from bio raw materials (e.g., hydrogen extraction from syngas produced from biomass through gasification or catalytic gasification or fast pyrolysis of biomass to bio-oil followed by steam reforming of bio-oil), or bio-processing of biomass (biological treatment of well-chosen biomass using suitable microorganisms). Both *in situ*/*ex situ* removal of hydrogen play important roles in the cutting-edge development of these processes to make them competitive with the classical CSR of natural gas and its recent improvements using bubbling and circulating fluidized bed membrane reformers.

3.4.1.2 Bio-Diesel

That includes the short-term small-scale bio-diesel from vegetable oils (or used oils) through esterification/trans-esterification using metals or enzyme catalysts and suitable alcohols. However, the main thrust will be regarding the long-term, large-scale production of FT-bio-diesel from syngas produced from biomass through one of the processes described above. The research should compare the two routes for syngas production with special emphasis on the percentage of the valuable component, hydrogen, in the syngas. The research should concentrate on developing a novel suitable and efficient membrane CFB process for CSR of bio-oil as well as a novel FT process that operates at relatively high temperatures and with a syngas having a very high yield of H_2 and CO_2/CO ratio which is a characteristic of the syngas produced from the efficient membrane reformer. Research will also extend to developing a novel compact autotherm membrane reactor combining both the endothermic steam reforming of bio-oil and the exothermic FT reaction of syngas to FT-bio-diesel. The research

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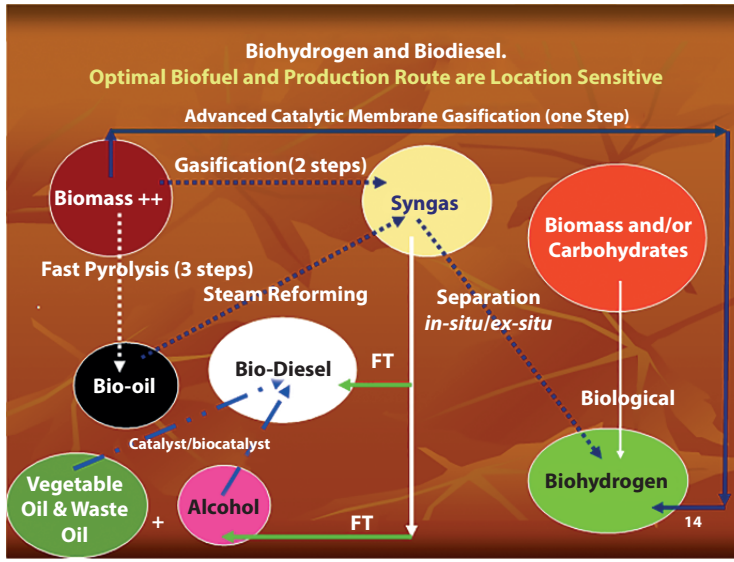

Figure 3.7 Some routes to bio-diesel and bio-hydrogen. FT= Fischer Tropsch.

will also include novel ideas to improve the fast pyrolysis and the catalytic gasification processes as well as the biomass collection, classification and pre-treatment before processing. In addition, the different FT-bio-diesels produced will go through the standard tests, including diesel engine testing and those characteristics related to parameters associated with the raw materials and novel technologies used. Figure 3.7 gives a flow chart for the production of Bio-hydrogen and Bio-diesel.

3.4.1.3 Bio-Ethanol

Cellulosic Bio-ethanol using different feed-stocks and different processes, e.g. lignocelluloses fractionation followed by hydrolysis of cellulose/hemicelluloses; followed by fermentation (Figure 3.8). The emphasis should also include bio-butanol because of its advantages over bio-ethanol. Novel processes, novel modes of operation as well as novel mutated microorganisms will be combined to exploit the positive synergies between these factors to achieve the highest possible efficiency. Continuous Stirred Tank Fermenters (CSTFs) as well as packed bed immobilized fermenters are to be considered. Different hydrolysis techniques should also be considered, both acidic and enzymatic, to reach the most efficient route for sugars production from cellulose/hemicelluloses. In the fermentation step, different

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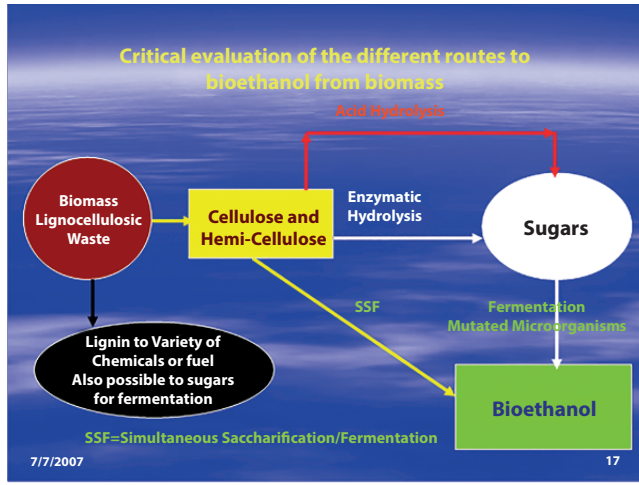

Figure 3.8 Routes for cellulosic bioethanol.

techniques for continuous ethanol removal are to be considered to maximize breaking the inhibitory effect of ethanol on the fermentation process (most successful is membrane separation of ethanol). Unusual modes of operation, e.g., Chaotic fermenter is also to be explored (Elnashaie and Garhyan, 2004; Chen and Elnashaie, 2008). Novel mutated microorganisms are developed in collaboration with microbiologists from other departments to ferment all the types of sugars (e.g., glucose, xylose and arabinose) resulting from the hydrolysis step, and to be tested in classical and novel membrane fermenters. Such a department will also address in an objective scientific manner the dispute regarding energy ratio (ER) and net energy ratio (NER) for BFs and fossil fuels which will address the energy from a quantitative as well qualitative points of view.

3.4.2 Bio-Products

They are a very important part of sustainability due to the simple fact that, although most of the attention is going to the important subject of sustainable energy, societies do not live only on energy; there are many other commodities (consumer goods) and capital products that need to be replaced by sustainable bio-products. Societies are alarmed about the fact that oil has passed its peak and will finish in a few decades, but what about other raw materials? In fact, copper is running short and its price is rocketing high. Thus research and preparation of engineers will not include only novel processes development, but also novel products development.

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The approach will depend upon the highlighting of the most critical raw materials that are dangerous to sustainability other than energy, as well as the commodities and capital products related to those raw materials coupled to the commodities and raw materials which are easiest to replace with renewable resources. This essential classification and focusing process will be followed first by identifying the state of the available technologies related to these factors. This process will then lead to the most important novel processes and products to develop and to establish the research program to develop them efficiently and cleanly.

3.4.3 Integrated Bio-Refineries

As described above, it is a concept which is still in its infantry. Relatively recently, NSF has offered a solicitation for the development of IBRs (Commercial Demonstration of an IBR has been carried out by the DOE). IBRs will be the tool, in the near future, to achieve the above points in an integrated manner that will produce BFs and other BPs in one IBR. In order to have a clear vision of IBRs it is essential to realize what a bio-product (or bio-fuel) is. It is any product produced from a biological process even if the raw material is not a bio (e.g., hydrogen from CO using biologically catalyzed WGS process). It is also any product produced from a bio-raw material using non-biological process (e.g., biomass to bio-diesel using any technique for the production of syngas followed by FT process). It can also be both, i.e., the raw material and the process are both bio (e.g., cellulosic waste to bio-ethanol through a number of steps, most of them bio-processes). Beside biomass and other forms of wastes there are also special crops which are being developed to be used for BFs and other bio-products (e.g., switch grass). In addition there are very important bio-raw materials which are treated now as waste or cheap fuels such as lignin which is separated from different types of lingo-cellulosic wastes (especially agricultural waste such as rice straw). Through intensive innovative MD research this lignin can be a base of a part of IBRs to compete, and eventually replace, the present petrochemical industry based on none-RRMs. Well-directed research can also produce sugars for fermentation to ethanol from this lignin waste which will increase the yield of the cellulosic bio-ethanol process more than 30%. It is also important to recognize the meaning of RRMs; this is very relative, for theoretically speaking, fossil fuel is also renewable, but its cycle is a million years or more. So what we mean by RRMs is a raw material which is renewable over a few months up to a maximum of a

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couple of years. We should also add that its LCA should show a net CO_2 (and any other harmful side product) of almost zero, i.e., CO_2 produced is consumed in photosynthesis to produce almost the same amount of RRMs. The socioeconomic implications of IBRs will include both production and consumption sustainability. Research should address, in an MD-integrated manner, all technological, socioeconomic, political and moral/ethical aspects.

3.4.4 Development of Novel Technologies

Through different intellectual innovation processes, e.g., sequential debottlenecking. The process of developing novel technologies is much more difficult than optimizing and improving the efficiency of an existing technology, and both are important. This is due to the fact that in the last few decades lots of very efficient, modeling and computer tools has been developed to efficiently achieve the optimization of existing technologies. However, the development of novel technologies takes lots of intelligent, intellectual efforts and development on the basis of a culture of discovery and innovation which is not strong enough in the present educational system. Innovation includes both novel configuration (e.g., efficient fluidized bed membrane steam reformer for hydrogen production instead of the inefficient present fixed bed reformer constrained by thermodynamic equilibrium limitations+ intra catalyst particles diffusional limitations + heat transfer limitations) and novel modes of operations (e.g., periodic or chaotic autonomous or non-autonomous processes leading to higher yields and productivity compared with optimal steady states). It may also involve a novel product or service. Researchers will work hard to become a focal point not only for developing specific novel technologies but also to develop the culture of discovery and innovation and to develop all possible intellectual tools for this process, e.g., sequential debottlenecking. In addition, novel configurations usually have more complex configurations than classical configuration (e.g., CFB membrane reformer compared with fixed bed reformers). This gives rise to mechanical and hydrodynamic challenges which will be tackled both experimentally and using advanced computer modeling and simulation.

3.4.5 Economics of Bio-Fuels and Bio-Products

Making these bio-processes and bio-products economically competitive, socially acceptable, sustainable and environmentally friendly requires also

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gaining political support for them. The main bottleneck for BFs and BPs is certainly economics. The main challenge is to break the contradiction between sustainability and profitability, in other words to present to consumers products which are reasonably priced, and for the producers (and the rest of the production-consumption chain) to achieve reasonable profit for the economic cycle. However, and despite the major importance of economics, other social, political and moral/ethical factors are not negligible at all. All the factors contribute to the success of achieving a sustainable economy which is also clean and leads to peaceful coexistence between peoples. The department will use an ISA to study the positive and negative synergy between these different factors associated with sustainable development and its relation to BFs and BPs.

3.4.6 Nano-Technology (NT)

Addressing this hot newcomer, this is NT in an MD manner and its applications in all fields of applications, especially chemical and biological engineering applications. This field opens new horizons in all applications and is multidisciplinary by its very nature. This new department will be the best focal point for the development of this strategic field in cooperation with other engineering and science departments.

3.4.7 Non-Linear Dynamics (NLDs), Bifurcation (B), Chaos (C) and Complexity (COMP)

This field (system) is usually considered to belong to the theoretical part of knowledge and investigation. However, in the last three decades these phenomena have been finding more practical applications and relevance both for autonomous and non-autonomous systems. They are important in understanding many phenomena which are not possible to understand without having the fundamental knowledge associated with this field. All systems are actually non-linear and therefore their dynamics lend themselves to this field; linear systems are actually approximations obtained by linearizing the system in the neighborhood of a specific state and therefore give local characteristics but not global ones. B has dismantled the boundaries between static and dynamic behavior and made them interdependent. This is a CD field by its very nature and is quite important to control when the behavior is harmful and exploit when it is useful. COMP belongs to this field and it is a very important subsystem of this system as briefly discussed above and also in Elnashaie and Grace (2007).

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3.4.8 Sustainable Development (SD), Sustainable Development Engineering (SDE), System Theory (ST) and Integrated System Approach (ISA)

Sustainability is still young and many of its aspects are not completely clear even among academicians. A simple example is the question, phrased in ST terminology, is EE a subsystem of SDE or the opposite? The preliminary belief accommodated at the present time by this research group is yes, EE is a subsystem of SDE and therefore EE is necessary but not sufficient for sustainability. This is due to the fact that you can have a very efficient, clean technology, but if it is based on non-RRMs then it is not sustainable. However, these concepts are still not deep enough, technologically, socioeconomically, politically and from a moral/ethical point of view. Even most definitions of sustainability and SD are not very accurate; they are more catchphrases than strong, meaningful and defensible definitions. The department will use ST and ISA to move forward in the direction of establishing stronger, clearer and more meaningful definitions to these important concepts. This effort will help all involved and others to achieve all other tasks.

3.4.9 Novel Education

This involves using CD teaching programs on the above subjects, preparing the graduates for leadership positions in a global economy as innovators. As it is required to shorten the period between scientific discoveries and their innovative technological application through transformational engineered systems approach, we want also to achieve the same with respect to education. This is best achieved using a new approach for engineering education based on ST, which is the best and most efficient means to organize and transfer knowledge and create a common language between different disciplines. This is due to its very nature and its definition of systems, subsystems, their boundaries and characteristics in general terms not restricted to specific systems or disciplines. It is also the best means to make the gap between scientific/technological discoveries and teaching/training as short as possible, which is very desirable in a very competitive global economy. The department will develop new educational programs based on ST, designed for:

- Strategically creating the capacity to initiate and exploit knowledge for technological innovation and minimize

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the gap between scientific/technological discoveries and education/training.
- Maximize engineers' ability to think positively and independently in contradistinction to memorizing or learning engineering as a craft.
- Develop graduates experienced in the creative process and cross-cultural collaboration.
- Develop graduates able to define pathways to explore and realize innovation opportunities for success in a global economy.
- Develop graduates who are leaders in a global economy.

These educational programs will be formed of diverse (domestic and international) and talented individuals as teachers/trainers who are part of the research program of the department. They will prepare diverse talented individuals (domestic and international) who can function in the global economy, where design and production efforts cross national borders. Diversity will also include a CD team of faculty members and students that is diverse with respect to gender, race, ethnicity, ability, and culture.

3.4.10 New Journal

The department may pioneer the publication of a modern international CD, SD journal. The aim of this journal is to be one of the tools to address the bio-energy, BFs, BPs, IBRs and sustainability challenges and make sure of publishing and spreading widely, nationally and internationally, the novel work of the department and similar departments worldwide, as well as relevant research nationally and internationally. The journal will emphasize novel ideas and enable them to reach the scientific community in an efficient manner. The journal will aim at the publication and dissemination of original research, reviews and discussions on the latest developments in the fields of BFs, BPs, IBRs, sustainability and their synergic relations to each other and to the global economy. It will also address challenging educational issues related to innovation and developing a new generation of innovative engineers suited for the global economy. It should also focus on research utilizing ST and ISA to develop novel technologies and methodologies which contribute to SD for the entire planet and its entire population in the framework of the global economy as well as advances in the foundations of fundamental knowledge. Papers may be theoretical (including computational), experimental or both. Also, intellectual conceptual ideas

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to advance the culture of discovery and innovative thinking should be given especial attention. At the present time there are hundreds of journals related to these subjects, to the extent that an internet site presents the top 100 journals on these disciplines. The expansion, interactions and continuous needs of the society justify the large number of journals and even more with time. Most of these journals, however, suffer from certain disadvantages:

1. Some recently issued journals are adopting the negative practice of asking the authors to pay certain fees for publishing their articles! This practice is usually and fairly rejected by the authors since it is good enough that the authors offer their papers to journals free of charge.
2. Most of these journals do not emphasize the important MD concept to the extent that some journals emphasis it only in its title for a wider variety of subjects.
3. Although peer-reviewing, in which the editor chooses a number of suitable reviewers to evaluate the paper (accept with: no revisions or minor revisions or major revisions with/without re-evaluation or reject + possible comments for any of the four cases with the editor having the final decision) is still the best way to evaluate presented papers to filter them for acceptance or rejection, this approach has some disadvantages:
   - The editor may not choose the correct and suitable reviewers.
   - Most journals do not offer the reviewers any compensation for their efforts.
   - Even when reviewers are well chosen by the editor, some excellent reviewers are not objective enough in the sense that they review the paper(s) on the basis of their own thinking, methodology, etc., and not that of the author(s) and may thus reject excellent papers. This causes strong disappointment to the author(s) leading him/her/them to either leave the research activity or adapt their research thinking to what they expect to be that of the reviewers, Neither situation helps in expanding the range of ideas, innovations, creativity, etc.

The solution to the above peer-reviewing problems is not easy; the best way is to emphasize avoiding them in the journals' directions to editors and reviewers.

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3.5 Novel Designs for Auto-Thermal Behavior Towards Sustainability

This section of the chapter will present earlier examples of integrated autotherm catalytic membrane reactors providing necessary but not sufficient conditions for sustainability and a series of suggestions to generalize this example and to make it not only necessary but also sufficient for sustainability. This section of the chapter will provide readers with a roadmap to achieve that through research using modeling coupled to experimental verification towards pilot plant and industrial development. The first suggestion is generalization of something carried out with colleagues at University of British Columbia (UBC), Canada; the PhD student was from King Fahad University of Petroleum and Minerals (KFUPM), Kingdom of Saudi Arabia (Abo-Ghander, 2011). The main parts of this PhD thesis were published in *Chemical Engineering Science* and *Chemical Engineering and Processing* (Abo-Ghander *et al*., 2008, 2010, 2014). It is important to generalize this configuration for almost all exo reactions (hydro reactions with H_2 selective membranes and other exo reactions with heat conductive walls) and endo reactions (dehydro reactions with H_2 selective membranes and other endo reactions with heat conductive walls) to make a petrochemical complex near zero energy consumption. In other words: make each exo reaction coupled to an endo reaction in an integrated reactor and find the design and operating conditions that make it possible and optimize it, including that when one of the reactions is dehydro (always endo) and the other is hydro (always exo) we use a hydrogen selective membranes so that the hydrogen of the dehydro side diffuses to the hydro side achieving *in-situ* hydrogen supply to the hydro reaction and also shifting the equilibrium conversion of the reversible dehydro to higher values at lower temperatures, and heat is supplied from the hydro reaction side to the dehydro side. A popular catalytic reaction which can be used in the dehydro side is the endo steam reforming of methane and higher paraffin. Many modeling and experimental investigations have been carried out with H2 selective membranes and in the other side sweep gas is used to carry out the diffused H_2 (Mahecha-Botero *et al*., 2007, 2009a-c; Vigneault *et al*., 2012; Abashar and Elnashaie, 2014). However, investigation of the possible use of exo reaction in the other side of hydrogen selective membrane has not been addressed and represents a wide scope for promising research. There are many other dehydro-endo- reactions such as the entire group of the dehydro of paraffins to olefins and gasification/pyrolysis of biomass to produce syngas. There are also many other hydro-exo- reactions other than hydro

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of NB to A, e.g., benzene to cyclohexane; all polymerization reactions, one of the most important is the UNIPOL process of fluidized bed catalytic polymerization of gas phase ethylene to polyethylene using Ziegler-Natta catalyst (Ghasem and Hussein, 2004); Fischer-Tropsch (FT) (Espinoza *et al*., 2000) for synthesis of liquid fuels using a mixture of H_2:CO with a ratio of about 2. Different integrated reactors with exo in one side and endo reactions in the other side without H_2 production-permeation-consumption but only heat transfer between the two sides are possible but have not been investigated; they open a wide door for innovative modeling and experimental research to achieve very high energy efficiency through autotherm designs. In general there are many cases where it will be possible to use tubes of dehydro (or any other endo) reaction(s) to cool exo reactors of any type instead of the ordinary cooling tubes and also tubes of hydro (or any other exo) reaction(s) to heat endo reactors instead of the ordinary heating tubes, etc. Other autotherm integrated reactors include react-regener with catalyst circulation as described below.

3.5.1 Integrated System Approach Classification

To summarize the above discussion and classify it on the basis of ISA, the types of this autotherm integrated units to increase efficiency and save energy are as follows:

1. Hydro- Dehydro- reactions with heat conductive hydrogen selective membranes between the two sides as described above; the best and most studied example is the dehydrogenation of EB to S in one side and NB to A in the other side described above and detailed in the references (Abo-Ghander, 2011; Abo-Ghander *et al*., 2008, 2010, 2014), in which the system is formulated as MPMP which is optimal with reference to heat and productivity of the couple of products (S and A) and also friendly to the environment. This makes the system necessary but not sufficient for sustainability because the raw materials are not RRMs. Further research should include the optimization of both sides in fixed bed and also having the shell side as bubbling fluidized bed using powder that will make the effectiveness factor equal to 1.0.
2. For the hydro-dehydro configurations there are two challenging routes. The first is solving for each process the problem of the heat driving force from the exo to the endo

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(and/or the hydrogen from dehydro side to the hydro side through hydrogen selective membrane) as both were achieved in the S and N production case. It will differ for each case (exo-endo-; Hydrogen production-consumption) from the other. Also it is important to consider using endo reactions tubes to cool exo reactors and exo reactions tubes to heat endo reactors.

3. There is still room for further research with regard to steam reforming of hydrocarbons using selective membranes to remove hydrogen from fluidized bed steam reformers and in the other side sweep gas by considering if in the other side we have hydro-exo reaction(s) instead of the sweep gas like the NB to A. The configuration/operation and efficiency will be revolutionized.
4. The effectiveness factor in fixed bed steam reformers is around 10^{-3} (0.001) in a fluidized bed configuration it will be almost 1.0; therefore the rate of reaction per unit mass of catalyst will increase 1,000 times (100,000.00%); that was explored earlier both modeling and experimentally. Also in the fluidized bed the bubbles act as natural membranes removing the hydrogen and shifting equilibrium conversion to higher values. This configuration and its great advantage needs more research to make it more attractive to industry; this is a good research work especially when the membranes exo reactions are used instead of sweep gas.
5. Researchers should also consider cases of highly exo reactions like polymerization reactions that need cooling tubes and instead of cooling tubes (of high thermal conductivity material) endo reactions are used instead and also producing extra product removing its excess exo to the endo heat in the tubes, e.g., EB to S. The challenge in this case is the temperature driving force from the exo side to the endo side with the temperature of each side suitable for its reaction(s).
6. Researchers should also consider cases of highly endo reactions other than the earlier EB to S reaction(s) that need heating and instead of heating tubes (of high thermal conductivity material) exo reactions are used that are more efficient heaters and also producing extra product, getting its necessary endo heat from the heat produced by the exo reaction(s). The challenge in this case is also the temperature

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driving force from the exo side to the endo side with the temperature in each side suitable for its reaction(s).

7. Another important autotherm is the react-regener system like the very successful different generations of FCC, of different types from type IV with bubbling fluidized beds for both react-regener up to the most modern riser and downer fluidized beds for react and regener (Iscol, L., 1970; Elnashaie, S. and El-Hennawi, I., 1979; Elnashaie, S. and Elshishini, S., 1990, 1996; Elshishini *et al*., 1992 and Elnashaie, S. *et al*., 2006). The challenge is to apply this configuration for different reactions accompanied by carbon formation in the react and catalyst regeneration in the regener and circulating the catalyst between the two vessels achieving authotherm.

The main idea of the other route to change the necessary condition but not sufficient for sustainability, e.g., MPMP to sufficient for sustainability is based on the fact that the MPMP is suffering from the fact that the feeds are not RRMs. If we change the feeds to RRMs then the configuration gives rise to sustainability. As an example we consider the case of EB to S in one side of the hydrogen selective membrane and NB to A in the other side and we change its feeds to RRMs. Therefore it is required to obtain EB and NB. Checking the literatures shows that there are many routes to achieve these:

1. Benzene and Ethylene are obtained from Biomass (Zhang *et al*., 2013)
2. Benzene and Ethylene can be catalytically reacted to give EB (Al-Kinany *et al*., 2012)
3. NB is obtained by the nitration of B (Thomas and Peter, 2018), and since B is obtained from biomass as shown above and Nitrogen is very abundant (75-80% of total earth air) and is naturally renewable (Eickhout, 2006), therefore NB is also a RRM.

From the above it is clear that feeds, EB and NB can be both obtained from RRMs and therefore they are themselves RRMs. The literature is crowded by research on the chemistry of the above three steps for making the feeds RRMs; however, there is little research regarding the design of reactors for these processes. A wide door for research is open for reactors research involving modeling, design, optimization start-up and control of the best reactors for the above three reactions. The main EB to S coupled to NB to A through a hydrogen selective heat conductive membrane + the

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above three reactors to make the feeds RRMs makes a novel IBR giving rise to SDE.

3.6 Conclusions

SDE, which is a subsystem of SD, and EE, which is a subsystem of SDE are analyzed using ST and ISA, which are the best tools for analysis and for CD research collaboration involving many disciplines. Through optimization of the processes within the framework of EE it is possible to achieve the very useful MPMP objectives which are necessary conditions for sustainability but not sufficient. To make them sufficient we have to introduce RRMs and their associated novel technologies. The analysis also introduces the very useful and rich concept of IBRs in order to optimally produce both BFs and BPs from RRMs. It seems that this chapter is addressing these important issues from an engineering and scientific points of view; however, the above aims are strongly dependent for their success upon the other non-engineering aspects, e.g., economics, politics, consumption habits, etc. Therefore the call of this chapter is for all disciplines to join forces in a CD effort to achieve the integrated aims of SD using CD tools.

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4

Biofuels

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Abstract
Biofuel is produced from biomass material, commonly used as an alternative, cleaner fuel source to burning fossil fuels. Though biofuel and fossil fuel may both be derived from organic matter the difference is how recently the organic matter has disintegrated. Its global production has increased over the last decade as a sustainable solution to harmful carbon emissions. Therefore, this chapter focuses on biofuels, a renewable energy source that can help a struggling economy and save the environment at the same time.

***Keywords*:** Biofuel, bioenergy, biomass, biodiesel, bio-alcohol, bioprocessing

4.1 Introduction

Biofuels (also known as non-conventional or alternative fuels) is a generic name for liquid or gaseous fuels that are derived from plant-based feedstocks and include products such as ethanol, methanol, and biodiesel. Biofuels are *bio-materials* produced from renewable biological sources such as: corn, soybeans, flaxseed, rapeseed, sugarcane, palm oil, sugar beet raw sewage, food scraps, animal parts, and rice. Unlike fossil fuels, which are necessarily derived from long deceased and metamorphosed biological organisms, biofuels (otherwise known as agrofuels) are obtained from only recently deceased or living biological organisms, or in other words, derived from biomass or bio-waste.

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Nour Shafik El-Gendy (ed.) Sustainable Solutions for Environmental Pollution Volume 1: Waste Management and Value-Added Products, (163–198) © 2021 Scrivener Publishing LLC

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The production of fuels (and chemicals) from renewable plant-based feedstocks utilizing state-of-the-art conversion technologies presents an opportunity to maintain competitive advantage and contribute to the attainment of national environmental targets (Figure 4.1).

Bioprocessing routes have a number of advantages over conventional petrochemicals production but it is only in the last two decades that rapid progress in biotechnology has facilitated the commercialization of a number of plant-based chemical processes.

Biofuels can be classified into (i) first-generation biofuels, (ii) second-generation biofuels, and (iii) third-generation biofuels – otherwise known as advanced biofuels. The composition of each type of biofuel varies according to the feedstock and conversion techniques used. First-generation biofuels are derived from simple materials, such as mono and disaccharides (simple sugars), amylose and amylopectin (starch), esters of glycerol and fatty acids, free fatty acids and mono and diglycerides (fats and vegetable oils for biodiesel) as shown in Table 4.1.

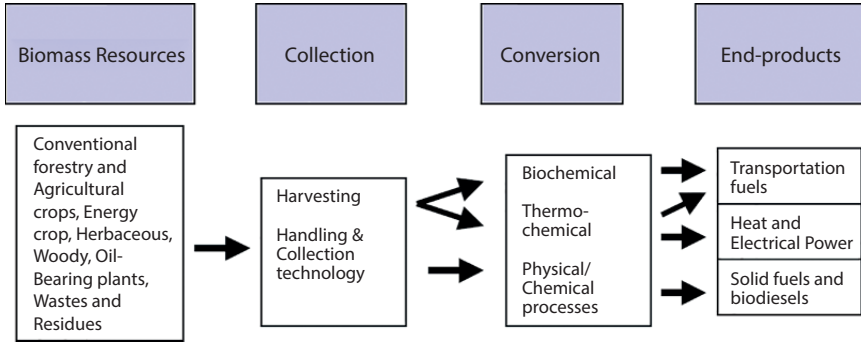

Figure 4.1 Typical sources and uses of biomass for energy purposes.

Table 4.1 Composition of various oils and fats used for biodiesel production (percentage of each type of fatty acid common to each type of feedstock).

Oil or fat	14:0	16:0	18:0	18:1	18:2	18:3	20:0	22:1
Soybean		6-10	2-5	20-30	50-60	5-11		
Corn	1-2	8-12	2-5	19-49	34-52	Trace		
Peanut		8-9	2-3	50-60	20-30			
Olive		9-10	2-3	73-84	10-12	Trace		
Cottonseed	0-2	20-25	1-2	23-35	40-50	Trace		

(*Continued*)

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Table 4.1 Composition of various oils and fats used for biodiesel production (percentage of each type of fatty acid common to each type of feedstock. (*Continued*)

Oil or Fat	14:0	16:0	18:0	18:1	18:2	18:3	20:0	22:1
Hi Linoleic Safflower		5.9	1.5	8.8	83.8			
Hi Oleic Safflower		4.8	1.4	74.1	19.7			
Hi Oleic Rapeseed		4.3	1.3	59.9	21.1	13.2		
Hi Erucic Rapeseed		3.0	0.8	13.1	14.1	9.7	7.4	50.7
Butter	7-10	24-26	10-13	28-31	1-2.5	0.2-0.5		
Lard	1-2	28-30	12-18	40-50	7-13	0-1		
Tallow	3-6	24-32	20-25	37-43	2-3			
Linseed oil		4-7	2-4	25-40	35-40	25-60		
Yellow grease	2.43	23.24	12.96	44.32	6.97	0.67		
		16:1 = 3.97						

Second-generation biofuels use biomass to liquid technology (Carere *et al*., 2008) to produce fuels such as ethanol from lignocellulose, biohydrogen and wood diesel. Third-generation biofuel is a biofuel from algae otherwise known as oilgae. *Botryococcus braunii* and *Chlorella vulgaris,* as well as macroalgae (seaweed) are typically used. The main feedstock for biofuels are food sources and plant crops; therefore the adverse effects of biofuel production on the natural resources of any particular region must be taken into consideration.

4.2 Composition

Biomass is a term used to describe any material of recent biological origin, including plant materials such as trees, grasses, agricultural crops, and even animal manure. Other biomass components, which are generally present in minor amounts, include triglycerides, sterols, alkaloids, resins, terpenes, terpenoids and waxes. This includes everything from *primary sources* of crops and residues harvested/collected directly from the land, to *secondary sources* such as sawmill residuals, to *tertiary sources* of post-consumer

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residuals that often end up in landfills. A *fourth source*, although not usually categorized as such, includes the gases that result from anaerobic digestion of animal manures or organic materials in landfills.

Biomass can be used for fuels, power production, and products that would otherwise be made from fossil fuels. The character and properties of the biofuels produced are very dependent upon the initial biomass. Biomass can be burned directly for heat or converted to renewable liquid and gaseous fuels through various processes.

4.3 Classification of Biofuels

Generally, the classification of biofuels is related to the method of preparation which, in turn is related to the starting material of the agent by which the biomass is converted to biofuels. For practicality, biofuels are generally classified as being (i) first generation, (ii) second generation, and (iii) third generation.

4.3.1 First-Generation Biofuels

The first-generation biofuels are those fuels directly prepared from biomass which is often a direct part of the food chain. Such fuels, with purification, can be used as fuel for various types of equipment. Such fuels are, for example, the alcohol fuels that are prepared from sugar, starches, and cellulose. However, before dealing with the character and properties of such fuels, an introduction to the structure and chemistry of the sugars is warranted.

4.3.1.1 Sugars and Starch

Biomass is typically composed of 75 to 90% by weight sugar species, the other 10 to 25 wt.% being mainly lignin.

Plants capture solar energy as fixed carbon during which carbon dioxide is converted to water and sugars $(CH_2O)_x$:

$$CO_2 + H_2O \rightarrow (CH_2O)_x + O_2.$$

The sugars produced are stored in three types of polymeric macromolecules: (i) starch, (ii) cellulose, and (iii) hemicellulose.

Monosaccharides (the simple sugars) (Figure 4.2) are colorless, water soluble crystalline solids. Because of the presence of numerous chiral centers, various isomeric forms of the different monosaccharides exist.

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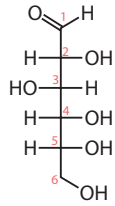
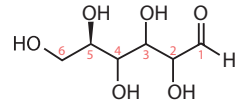
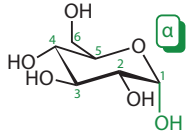


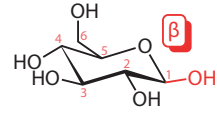
(**a**) The Fischer projection of the chain form of D-glucose



(**b**) The chain form of D-glucose



(**c**) α-D-glucopyranose



(**d**) β-D-glucopyranose

Figure 4.2 The various representations of the naturally occurring form of the simple monosaccharide, glucose.

However, since biofuels are necessarily obtained from natural sources, the forms which are abundant in nature predominate.

In general, sugar polymers such as cellulose and starch (Figure 4.3) can be readily broken down to their constituent monomers by hydrolysis, preparatory to conversion to ethanol or other chemicals. In contrast, lignin is a complex structure containing aromatic groups and is less readily degraded.

Although lignocellulose is one of the cheapest and most abundant forms of biomass, it is difficult to convert this relatively unreactive material into sugars. Among other factors, the walls of lignocellulose are composed of lignin, which must be broken down in order to render the cellulose and

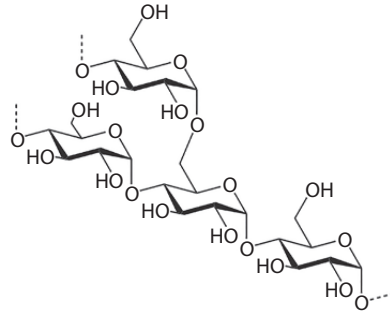


Figure 4.3 Portion of the polysaccharide, starch, which is used as a feedstock to produce biofuel.

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hemicellulose accessible to acid hydrolysis. For this reason, many programs focused on ethanol production from biomass are based almost entirely on the fermentation of sugars derived from the starch in corn grain, which has increased in production over the past century.

Glucose (dextrose), fructose (laevulose), galactose, xylose and ribose are common. Glucose is a simple sugar that can be readily fermented into biofuel if it can be accessed; the equation for its combustion is given here:

$$C_6H_6O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(g)\ \Delta H = 2810\ \text{kJ mol}^{-1}$$

Glucose and other simple sugars are normally fermented into alcohols for direct use as a fuel. Starch, otherwise known as amylum, is the polysaccharide present in all green plants and is the form by which food is stored. Glucose monomers are joined by β1-4 glycosidic bonds in the linear helical portions of the polymer (amylose) and by β1-5 glycosidic bonds in the branched portions (amylopectin). Plant sugars or starches of biofuel crops such as sugar cane and maize are fermented to produce ethanol (Constable *et al*., 2009).

4.3.1.2 Cellulose

Cellulose is the main material, which is used as solid biofuel, the biomass being obtained from corn, switchgrass and sawdust. Cellulosic ethanol is obtained through fermentation of the monomers of the polysaccharide, as with starch, but a greater amount of processing is required to liberate the simpler sugars.

Cellulose is a linear chain polymer made up of thousands of glucose residues lined through β1-4 glycosidic linkages. Cellulose is the most abundant, naturally occurring polymer on earth, and its availability from switchgrass and miscanthus has encouraged biofuel production.

4.3.1.3 Lignin

Lignin is a complex chemical compound that is most commonly derived from wood and is an integral part of the cell wall of plants. The chemical structure of lignin is unknown and, at best, can only be represented by hypothetical formulas.

Lignin makes up about one-quarter to one-third of the dry mass of wood and is generally considered to be large, cross-linked hydrophobic moieties, aromatic macromolecule with a molecular mass that is estimated to be in excess of 10,000. Degradation studies indicate that the molecule consists of various types of substructures which appear to repeat in random manner. Also, lignin fills the spaces in the cell wall between cellulose, hemicellulose,

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and pectin components and is covalently linked to hemicellulose. Lignin also forms covalent bonds to polysaccharides and thereby crosslinks different plant polysaccharides.

4.3.2 Second-Generation Biofuels

Second-generation biofuels are produced from plants which are necessarily not part of the food chain. Hence, their production relies heavily on biomass materials such as waste from urban, forestry and agricultural sources, as well as the non-reusable portion of municipal solid waste, which is generally landfilled. Since the main component of these biomass materials is cellulose, second-generation biofuels are also known as *cellulosic fuels*. Residual forest biomass, such as bark, needles, limbs etc., as well as the non-sugar portions of plants which are left in the fields after harvesting and processing, such as bagasse, rice hulls and wheat straw are utilized.

Other than cellulosic ethanol, which is the principal second-generation biofuel, biomethanol, dimethyl ether, biohydrogen, synthetic diesel and synthetic gasoline are also emerging from the aforementioned biomass materials. These are the biomass-to-liquid projects which seek to further diversify the product range which can be derived from lignocellulose using advanced technologies, such as the Fischer-Tropsch process.

The drive towards second-generation biofuels has been due to studies carried out which suggest that first-generation biofuel production may actually produce more carbon-dioxide emissions than they save, as in many instances, natural habitats are converted into cropland, thus releasing the carbon contained in trees and grasses and in the soil they grow on. Next-generation fuel producers have adopted two main approaches: an enzymatic platform for homogeneous biomass or a thermochemical platform for a variety of feedstock, including non-homogeneous residues.

The reduction of landfills, which ultimately are converted to methane (important greenhouse gas) and reduction on petroleum dependence are amongst the benefits of second-generation biofuels. Ongoing research involves increasing supply from available acreages and alteration of the composition of feedstock for reduction of processing cost and increasing the value of co-products.

4.3.3 Third-Generation Biofuels

Third-generation biofuels (sometimes called "oilgae") are derived from algae, which are either unicellular or multicellular autrophic organisms. They are able to photosynthesize, but do not contain typical plant organs. During

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photosynthesis, the algae are able to convert carbon dioxide and the energy from sunlight into biomass and oxygen. The veg-oil algae product can be harvested and converted into biodiesel, whilst the algae's carbohydrate content can be fermented to produce bioalcohols. Some studies have shown that algae can produce up to 60% of their biomass in the form of oil, which can be converted into biodiesel for use in automobiles, hence the energy utilized for transesterification in the production of oil from alcohol and catalyst is eliminated. Algae can be grown on saline, arid or drought-stricken land, and have a harvesting cycle of one to ten days. This minimizes use of land for the production of food crops (Christi *et al.*, 2007). Algae are also completely biodegradable and can be produced on ocean or fresh water – if there is a spill, this can be easily dealt with. A third-generation biofuel via direct cellulose fermentation has also been reported (Carere *et al.*, 2008). This involves a process called consolidated bioprocessing (CPB), in which cellulase production, substrate hydrolysis and fermentation are accomplished in a single step process by microorganisms. Metabolic and bioengineering techniques allow for the anchoring of the enzymatic subunits via scaffolding proteins, which accelerate cellulose degradation, simplifying its processing for ethanol production. This simpler feedstock processing leads to lower energy inputs, lower costs and higher conversion efficiencies.

4.4 Examples of Biofuels

4.4.1 Biodiesel

Biodiesel is produced from long chain alkyl esters of fatty acids (Figure 4.4) and is commonly called fatty acid methyl (or ethyl, depending on the alkyl group used) ester or FAME. The lipid portion of the ester may be derived from animal or fat, and normally a simple alcohol, such as ethanol or methanol is involved in the transesterification.

Waste oil or lower quality vegetable oil can be used for the purpose of biodiesel as shown in Table 4.2, and this can normally be used on its own as a direct fuel, without the addition of any additives. In its production, the biomass (rapeseed, soybean oil, sunflower, Jatropha, mahua, flax, hemp, palm oil, coconut, etc.) is mixed with a base (sodium hydroxide) and methanol. Since biodiesel

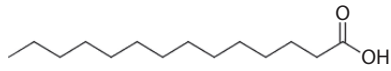

Figure 4.4 A typical saturated fatty acid.

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Table 4.2 Properties of vegetable oil biodiesel and diesel fuel (Bajpai and Tyagi, 2006).

Vegetable oil	Kinematic viscosity at 38°C (mm^2/s)	Cetane number (°C)	Flash point	Lower heating value (MJ/kg)	Cloud point (°C)	Density (kg/l)	Pour point (°C)
Peanut	4.9	564	176	33.6	5	0.883	-
Soybean	4.5	45	178	33.5	1	0.885	-7
Sunflower	3.6	63	127	31.8	4	0.875	-
Palm	5.7	62	164	33.5	13	0.880	-
Babassu	4.6	49	183	33.5	1	0.860	-
Tallow	-	-	96	-	12		9
Diesel	3.06	50	76	43.8	-	0.855	-16
20% biodiesel blend	3.2	51	128	43.2	-	0.859	-16

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shares many similar properties with diesel, the two can easily be mixed to create a homogeneous, cheaper fuel, as these cut the costs of processing.

Biodiesel contains a lower carbon to oxygen ratio than fossil diesel, and therefore its combustion is easier. Since it is also an effective solvent, less deposits accumulate on engines over time.

Chemically, transesterified biodiesel comprises a mix of mono-alkyl esters of long chain fatty acids. The most common form uses methanol to produce methyl esters as it is the cheapest alcohol available, though ethanol can be used to produce an ethyl ester biodiesel and higher alcohols such as iso-propanol and butanol have also been used. Using alcohols of higher molecular weights improves the cold flow properties of the resulting ester, at the cost of a less efficient transesterification reaction.

A lipid transesterification production process is used to convert the base oil to the desired esters. Any free fatty acids in the base oil are either (i) converted to soap which is removed from the process or (ii) they are esterified – yielding more biodiesel – using an acidic catalyst. After this processing, unlike the vegetable oil, biodiesel has combustion properties similar to those of petroleum diesel and can replace it in most current uses.

A byproduct of the transesterification process is the production of glycerol (glycerin). For every unit of biodiesel that is manufactured, 0.1 unit of glycerol is produced. Originally, there was a valuable market for the glycerol, which assisted the economics of the process. However, with the increase in global biodiesel production, the market price for this crude glycerol (containing 20% water and catalyst residues) is lower and affords an operational challenge. Usually the crude glycerol has to be purified, typically by performing vacuum distillation after which the refined glycerol (98%+ purity) can then be utilized directly or converted into other products.

Biodiesel has a viscosity similar to diesel produced from crude oil (petrodiesel) (Table 4.3). It can be used as an additive in formulations of diesel to

Table 4.3 Kinematic viscosity in diesel fuel standards.

Standard	Location	Fuel	Method	Kinematic viscosity (mm^2/s)
ASTM D975	U.S.	Petrodiesel	ASTM D445	1.9 – 4.1
ASTM D6751	U.S.	Biodiesel	ASTM D445	1.9 – 6.0
EN 590	Europe	Petrodiesel	ISO 3104	2.0 – 4.5
EN 14214	Europe	Biodiesel	ISO 3104	3.5 – 5.0

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increase the lubricity of pure ultra-low sulfur diesel (ULSD) fuel, which is advantageous because it has virtually no sulfur content. Much of the world uses a system known as the "B" factor to state the amount of biodiesel in any fuel mix, in contrast to the "BA" or "E" system used for ethanol mixes.

For example, fuel containing 20% biodiesel is labeled B20. Pure biodiesel is referred to as B100. Blends of 20% biodiesel with 80% petroleum diesel (B20) can generally be used in unmodified diesel engines. Biodiesel can also be used in its pure form (B100) but may require certain engine modifications to avoid maintenance and performance problems. Biodiesel has about 5 to 8% less energy density, but better lubricity and more complete combustion can make the energy output of a diesel engine only 2% less per volume when compared to petrodiesel — or about 35 MJ/L.

Biodiesel can be used in pure form (B100) or may be blended with petroleum diesel at any concentration in most modern diesel engines. Biodiesel will degrade natural rubber gaskets and hoses in vehicles (mostly found in vehicles manufactured before 1992), although these tend to wear out naturally and most likely will have already been replaced to gaskets that are non-reactive to biodiesel.

The higher lubricity index of biodiesel compared to petrodiesel is an advantage and can contribute to longer fuel injector life. However, biodiesel is a better solvent than petrodiesel, and has been known to break down deposits of residue in the fuel lines of vehicles that have previously been run on petrodiesel. As a result, fuel filters and injectors may become clogged with particulates if a quick transition to pure biodiesel is made, as biodiesel cleans the engine in the process.

The temperature at which pure (B100) biodiesel starts to gel varies significantly and depends upon the mix of esters and therefore the feedstock oil used to produce the biodiesel. For example, biodiesel produced from low erucic acid varieties of canola seed (RME) starts to gel at approximately -10°C. Biodiesel produced from tallow tends to gel at around +16°C. As of 2006, there are a limited number of products that will significantly lower the gel point of straight biodiesel. Winter operation is possible with biodiesel blended with other fuel oils including #2 low sulfur diesel fuel and #1 diesel/kerosene, but the exact blend depends on the operating environment.

Biodiesel may contain small but problematic quantities of water. Although it is hydrophobic (non-miscible with water molecules), there are indications that biodiesel is said to be, at the same time, hygroscopic to the point of attracting water molecules from atmospheric moisture. In addition, there may be water that is residual to processing or resulting from storage tank condensation. The presence of water is a problem because:

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(i) water reduces the heat of combustion of the bulk fuel which means more smoke, harder starting, less power, (ii) water causes corrosion of vital fuel system components: fuel pumps, injector pumps, and fuel lines, (iii) water freezes to form ice crystals at 0°C (32 °F) and the crystals provide sites for nucleation and accelerate the gelling of the residual fuel, and (iv) water accelerates the growth of microbe colonies, which can plug up a fuel system so biodiesel users who have heated fuel tanks therefore face a year-round microbe problem.

The common international standard for biodiesel is EN 14214 while ASTM D6751 is the most common standard referenced in the United States and Canada. In Germany, the requirements for biodiesel are fixed in the DIN EN 14214 standard and in the U.K. the requirements for biodiesel is fixed in the BS EN 14214 standard, although these last two standards are essentially the same as EN 14214 and are just prefixed with the respective national standards institution codes.

There are standards for three different varieties of biodiesel, which are made of different oils: (i) RME, rapeseed methyl ester, DIN E51606, (ii) PME, vegetable methyl ester, purely vegetable products, DIN E51606), and (iii) FME, fat methyl ester, vegetable and animal products, according to DIN V51606. The standards ensure that the following important factors in the fuel production process are satisfied: (i) complete reaction, (ii) removal of glycerin, (iii) removal of catalyst, (iv) removal of alcohol, (v) absence of free fatty acids, and (vi) low sulfur content.

Basic industrial tests to determine whether the products conform to the standards typically include gas chromatography, a test that verifies only the more important of the variables above. Fuel meeting the quality standards is very non-toxic, with a toxicity rating (LD50) of greater than 50 mL/kg.

4.4.2 Bio-Alcohols

Bio-alcohols are one of the most commonly utilized biofuels, which are produced from the fermentation of sugars by various enzymes and micro-organisms. Methanol, ethanol and to a lesser extent, propanol and butanol are the organic alcohols used either "straight" or mixed as additives with gasoline. These are of interest since they can be synthesized biologically. Feedstock sources for the production of alcohol fuel are potato, corn, wheat, sugar cane, beets, and any other saccharide source from which alcohol can be obtained by fermentation. Corn is the single largest source of crop residue in the United States and accounts for a disproportionate amount of crop residue produced annually. The advantage corn stover holds over alternative crops, such as switchgrass (*Panicum virgatum* L.)

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and miscanthus (*Miscanthus giganteus*), is that it is already produced with grain as the target and does not require dedicated land.

The main issue is how much stover can be collected on a sustainable basis without adversely affecting soil health (Wright *et al*., 2006). Ethanol is the most widely produced since it is biodegradable and reduces harmful noxious emissions. It burns cleanly with a high-octane value and can often be grown locally from renewable sources, which make it a cheaper fuel than petrol. Another popular biofuel, bio-butanol (Figure 4.5) which is produced from the fermentation of acetone, butanol and ethanol (ABE), has been claimed to be a direct replacement for gasoline. Biobutanol offers better fuel economy than gasoline-ethanol blends, improving vehicle fuel efficiency and mileage. It can be mixed alongside ethanol, decreasing the effective vapor pressure of ethanol in formulations and also has

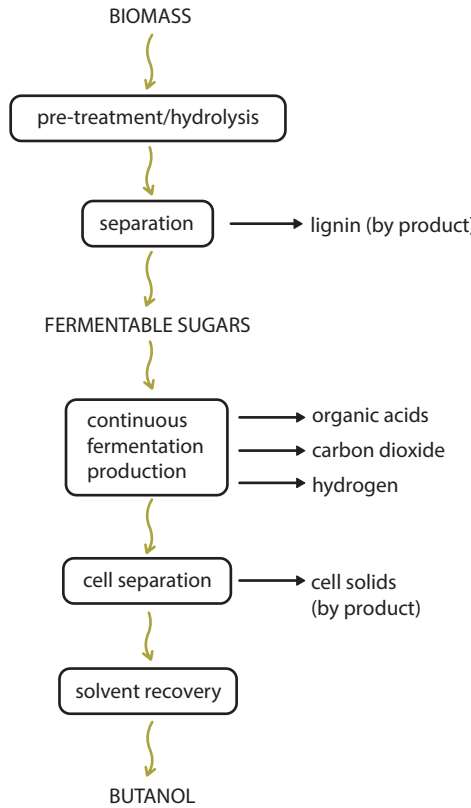

Figure 4.5 Bio-butanol is produced through the fermentation of starch and sugars by Clostridium bacteria.

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a high tolerance to water contamination. It has been shown that ethanol has a lower energy density (meaning a larger number of moles of fuel are required to do the same amount of work) than biobutanol; however, the production of ethanol is much simpler and easily achieved.

As one of the bioalcohols (if not the major bioalcohol), bioethanol (C_2H_5OH or EtOH) is a clear, colorless liquid with a characteristic, agreeable odor and is typically derived from plants such as wheat, sugar beet, corn, straw, and wood. Bioethanol and bioethanol/gasoline blends have a long history as being an alternative transportation fuel. Bioethanol has a higher octane number (108), broader flammability limits, higher flame speeds, and higher heats of vaporization than gasoline (Demirbas, 2007). These properties allow for a higher compression ratio and shorter burn time, which lead to theoretical efficiency advantages over gasoline in an internal combustion engine.

The cellulose, or carbohydrates, contained in biomass, can be turned into bioethanol through pretreatment, hydrolysis, fermentation, and product separation/distillation. In order to produce bioethanol from cellulosic biomass, a pretreatment process is used to reduce the sample size, break down the hemicelluloses to sugars, and open up the structure of the cellulose component. The cellulose portion is hydrolyzed by acids or enzymes into glucose sugar that is fermented to bioethanol.

Carbohydrates (hemicelluloses and cellulose) in lignocellulosic materials can be converted to bioethanol. The lignocellulose is subjected to delignification, steam explosion and dilute acid pre-hydrolysis, which is followed by enzymatic hydrolysis and fermentation into bioethanol. A major processing step in a bioethanol plant is enzymatic conversion of cellulose to sugars through treatment by enzymes; this step requires lengthy processing and normally follows a short-term pretreatment step.

In addition, to bioethanol, biomethanol (CH_3OH) is an alcohol-based fuel. Many tests have shown promising results using 85-100% by volume methanol as a transportation fuel in automobiles, trucks and buses. Methanol can be used as one possible replacement for conventional motor fuels. Methanol has been seen as a possible large volume motor fuel substitute at various times during gasoline shortages.

4.4.3 Bioethers

Bioethers are produced by dehydration of bio-based alcohols and are claimed to have superior combustion and emission characteristics when compared with other biofuels and are otherwise called fuel oxygenates or fuel ethers. The most common bioethers are dimethyl ether (DME),

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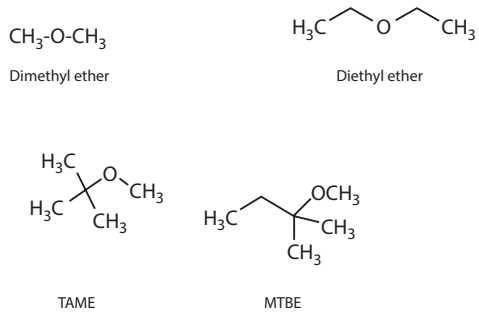

Figure 4.6 Examples of typical bioethers.

diethyl ether (DEE), methyl tertiary-butyl ether (MTBE), and tertiary-amyl methyl ether (TAME) (Figure 4.6). Bioethers are compatible with engine systems and act as octane enhancers and were introduced in the 1970s to replace lead in fuels. They, like the bioalcohols previously mentioned, are able to enhance engine performance, whilst reducing engine wear and toxic exhaust emissions.

An interesting point about fuel ethers is that they are greatly able to reduce the amount of ground-level ozone, thereby improving the quality of the air we breathe. Carbon monoxide, which results from incomplete burning of fuel, makes a significant contribution to ground-level ozone. Adding oxygen to gasoline (in the form of fuel ethers) makes for more efficient and completer fuel combustion. For 1 or 2% addition of fuel ether, there is a 1% reduction in total hydrocarbon emissions.

4.4.4 Biogas

Biogas, sometimes incorrectly known as swamp gas, typically refers to a biofuel gas produced by anaerobic digestion or fermentation of organic matter including manure, sewage sludge, municipal solid waste, biodegradable waste or any other biodegradable feedstock, under anaerobic conditions. Depending on where it is produced biogas is also called swamp gas, marsh gas, landfill gas, and digester gas.

The composition of biogas varies depending upon the composition of the waste material in the landfill and the anaerobic digestion process. Landfill gas typically has methane concentrations around 50%. Advanced waste treatment technologies can produce biogas with 55 to 75% methane; often air is introduced (5% by volume) for microbiological desulfurization. For example, the constituents (by volume) of biogas generally are methane

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(50 to 75%), carbon dioxide (25 to 50%), nitrogen (0 to 10%), hydrogen (0 to 1%), hydrogen sulfide (0 to 3%), and oxygen (0 to 2%).

If biogas is cleaned up sufficiently, biogas has the same characteristics as natural gas. In this instance the producer of the biogas can utilize the local gas distribution networks. The gas must be clean to reach pipeline quality. Water (H_2O), hydrogen sulfide (H_2S) and particulates are removed if present at high levels or if the gas is to be completely cleaned. Carbon dioxide is less frequently removed, but it must also be separated to achieve pipeline-quality gas. If the gas is to be used without extensively cleaning, it is sometimes co-fired with natural gas to improve combustion. Biogas cleaned up to pipeline quality is called *renewable natural gas*. In this form the gas can be used in any application in which natural gas is used.

Biogas is almost identical to natural gas (methane or CH_4) (Table 4.4). The equation for the complete combustion of methane is given:

$$CH_4\,(g) + 2\,O_2\,(g) \rightarrow CO_2\,(g) + 2\,H_2O\,(l)\ \Delta H = 891\ kJ\ mol^{-1}$$

Natural gas, which is generally found associated with fossil fuels, coal, and gas hydrates (clathrates of methane in ice crystals), may also contain small amounts of ethane, propane, butane, and pentane, which are heavier hydrocarbons removed prior to use as a consumer fuel, as well

Table 4.4 Composition of biogas from different sources (Spiegel and Preston, 2003).

Component	Agricultural biogas	Sewage gas	Landfill gas
Methane	55-75%	55-65%	40-45%
Carbon dioxide	25-45%	30-40%	35-50%
Nitrogen	0-10%	0-10%	0-20%
Hydrogen sulfide	0-1.5%	Up to 200 ppm	Approx. 200 ppm
Water	Saturated	Saturated	Saturated
Halogens	Trace amount	Up to 4 ppm	Amount dependent on the landfill
Higher hydrocarbons	Trace amount	Trace amount	Up to 200 ppm

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as carbon dioxide, nitrogen, helium and hydrogen sulfide. Biogas is produced by methanogenic organisms in landfills, swamps and marshes, by the decomposition of organic (both animal and plant) matter. The anaerobic (low or no oxygen present in the system) decomposition produces methane, carbon dioxide, a small amount of hydrogen and a small amount of heat. Acidity, the carbon to nitrogen ratio of the feedstock, temperature and percentage of solids all influence the quality and quantity of biogas produced. Normally, cow manure, enriched by vegetable matter is the ideal feedstock. The other principal type of biogas is wood gas which is created by gasification of wood or other biomass. This type of biogas is comprised primarily of nitrogen, hydrogen, and carbon monoxide, with trace amounts of methane. Industrial anaerobic digesters and mechanical biological treatment systems are becoming increasingly popular. Methane is a potent greenhouse gas but is also a clean, easy burning fuel, and hence harnessing it from natural sources such as landfills is beneficial to the natural environment.

4.4.5 Bio-Oil

Bio-oil (sometimes called *bio-crude*) is the liquid condensate produced from biomass (forestry residues, crop residues, wastepaper and organic waste) by means of processes such as pyrolysis and thermochemical conversion. Depending on the feedstock, the bio-oil could be compatible with existing refinery technology and can be converted into fuels, such as *green* diesel.

In the hydrothermal upgrading process (HTU process), biomass is treated with water at high temperature (300 to 350°C, 570 to 660°F) and pressure 1,770 to 2650 psi) to produce bio-crude. This can be separated by flashing or extraction to heavy crude (suitable for co-combustion in coal power stations) and light crude, which can be upgraded by hydrodeoxygenation (HDO) to biofuels.

The *rapid thermal processing* process (RTP™ process) occurs at a temperature of about 500°C (930°F), when a turbulent stream of hot sand flashes the biomass into a vapor. The vapor is then rapidly condensed into a liquid. This process occurs in less than two seconds, yielding high quantities of bio-oil (typically 65 to 75% w/w yield of pyrolysis oil from dried lignocellulosic biomass).

Bio-oil is a dark brownish viscous liquid that bears some resemblance to fossil crude oil. However, bio-oil is a complex oxygenated compound comprised of water, water soluble compounds, such as acids, esters, etc., and water-insoluble compounds, usually called pyrolytic lignin because it

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comes from the lignin fraction of the biomass. The elemental composition of bio-oil is similar to that of the parent biomass. Because of its high oxygen content, the heating value (Btu per gallon) of bio-oil is lower than fossil fuel, typically only about half the heating value of fossil crude such as heavy fuel oil. However, it contains less nitrogen and only traces of metals or sulfur.

Bio-oil is acidic with a pH in the 2-4 range, making it highly unstable and corrosive – the acidity can be lessened by the addition of readily available base compounds. It, therefore, presents transportation/piping and storage challenges including the tendency to corrode most metals. Hence it is usually transported and stored in stainless steel containers.

Like other biofuels, the properties of bio-oil are variable and dependent on the feedstock. The specific gravity of the liquid is about 1.10-1.25, which means it is slightly heavier than water, heavier than fuel oil and significantly heavier than the bulk density of the original biomass. The viscosity of the oil varies from as low as 25 cP up to 1,000 cP, depending on the water content and the original feedstock.

4.4.6 Synthesis Gas

Synthesis gas (frequently referred to as *syngas*) is produced by a process known as gasification, of organic matter (can be wood, plastic, biomass, organic waste or fossil fuels like petroleum), into the two principal gases, hydrogen and carbon monoxide – the concentrations of these and the presence of other minor molecules can be tailored by using different thermochemical reaction conditions. Thus:

$$C_nH_m + n\,H_2O \rightarrow n\,CO + (m/2 + n)\,H_2$$

Typically, the biomaterial is allowed to react with a proportioned amount of oxygen and/or steam, at elevated temperatures (>700°C). Raw syngas contains water, alkalis, halides, metals (such as Hg, As and Se), condensable products, and acid gases as well as fatal levels of hydrogen sulfide, the combination of which is explosive. The extraction of clean syngas followed by controlled expansion, dilution, thermal conditioning, and rapid sample transport in an inert environment to avoid condensation is an ongoing challenge for technicians and engineers. The main purpose of gasification of the original fuel, in the case of fossil fuels, is that burning of syngas can be carried out at greater temperatures and can be used directly in engines. Syngas is also used to produce hydrocarbons or methanol via the Fischer-Tropsch process or it can be converted into a range of other products synthetic fuel.

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4.5 Property Variations with Source

The quality and composition of a biofuel depends on the source of the bio mass/feedstock as well as the types of processing and conversion techniques utilized in its manufacture. Biomass feedstock composition ultimately decides the yield from the chemical or biochemical conversion processes, which in turn, affects the economics involved. There are many plant varieties which are used as biofuel sources – the geography, weather conditions, soil composition and legislation of a location normally dictates what types are grown specifically for biofuel production. Ethanol, biodiesel and butanol are the main types of commercially produced biofuels (Ezeji *et al*., 2007). In a study performed (Dhugga, 2007) the maize biomass yield and composition for biofuels was studied. It was found that the ethanol production from maize is almost doubled when the stover fraction increased from one-third to one-half of the percentage of the total biomass.

The soil organic matter content contributes greatly to the grain and stover, and hence carbohydrate content of maize plants. Lignin and cell-wall cross-linking also affect the ethanol production. Selection for reduced lignin and increased cellulose in stover can potentially be expected to increase mechanical strength as well as ethanol yield (Appenzeller *et al*., 2004). Although pretreatment and enzyme hydrolysis constitute two of the more costly steps in cellulosic ethanol production, stover with reduced lignin may still need to be treated before being subjected to enzyme hydrolysis. It seems unlikely that the cost savings in pretreatment from reduced lignin can be fully realized because of an accompanying reduction in biomass. However, for ethanol production to be commercially viable, improvements must not only be made to the efficiency of ethanol production per unit dry mass, but also per unit land area. It was postulated (Thomas *et al*., 2001) that corn stover (a popular biomass material) composition can vary over such a wide range such that the Minimum Ethanol Selling Price (MESP) of the bioethanol produced from it can vary from $1.04 to $1.36 per gallon, assuming all other process variables remain the same amongst the various batches.

The production of biofuels from lingo-cellulosic feedstocks can be achieved through two different processing routes. These are 1) biochemical, whereby enzymes and other micro-organisms are used to convert cellulose and hemicelluloses components of the feedstocks to sugars prior to their fermentation to produce ethanol, and 2) the thermochemical route, where pyrolysis and gasification technologies produce a synthesis gas (CO and H_2) from which a wide range of long chain biofuels, such as synthetic diesel

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or aviation fuel, can be reformed. For the biochemical route, much remains to be done in terms of improving feedstock characteristics, reducing the costs by perfecting pretreatment, improving the efficiency of enzymes and lowering their production costs and improving overall process integration.

One key difference between the biochemical and thermochemical routes is that lignin component is a residue of the enzymatic hydrolysis process and can be used for heat and power generation.

The production of biogas is essentially done by wastewater treatment facilities which use anaerobic digestion to reduce the organic content of sewage sludge and animal wastes. The variation in percentages of gases present will depend on the organic content of the biomass as well as the pretreatment and processing (Table 4.4). In addition to the main components (methane and carbon dioxide), biogas can also contain a variety of contaminants and impurities, such as sulfur compounds (hydrogen sulfide, mercaptans etc.), halogens, ammonia and dust particles.

Transesterification optimization is desired, which would depend on the chemical composition of alkyl esters of vegetable oils, animal fats and cooking oil. Most common feedstocks possess fatty acid profiles consisting mainly of five C16 and C18 fatty acids, namely, palmitic (hexadecanoic), stearic (octadecanoic), oleic 9(*Z*)-octadecenoic, linoleic (9(*Z*),12(*Z*)-octadecadienoic) and linolenic (9(*Z*),12(*Z*),15(*Z*)-octadecatrienoic) acids, with the exception of a few oils such as coconut oil, which contains high amounts of saturated acids in the C12–C16 range or others as shown in Tables 4.2 and 4.3 (Knothe, 2009). Changing the fatty acid profile can be achieved by physical means, genetic modification of the feedstock or use of alternative feedstocks with different fatty acid profiles, such as wood-derived fatty-acids and related compounds.

Tall oil is a dark, viscous, and odorous liquid that phase-separates from the used pulping liquor (alkaline black liquor) that remains after the pulping of wood chips, and contains sodium soaps of rosin and fatty acids (Lee *et al*., 2006) (see Table 4.5).

Table 4.5 Composition of tall oil extractives from Kraft Black Liquor (Holmlund and Parviainen, 2000).

Component(%)	N. American Softwood	Scandinavian Pine	Scandinavian Spruce	N. American Hardwood	N. American Birch
Rosin acids	42	30-35	20-30	-	-
Fatty acids	47	50-55	35-55	76	55-90
Neutrals	11	5-10	18-25	24	5-35

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Fish oil is also a potentially good source of fatty acids for the production of bio-oil. In a particular study, waste fish oil was converted into bio-oil by a fast pyrolysis process at 525°C in a continuous pilot plant reactor with 72-72% yield (Wiggers *et al*., 2009a). Many different chemical groups can be produced during the pyrolysis reaction and the liquid product (bio-oil) obtained from triglyceride pyrolysis has a complex composition. This bio-oil can be used directly as fuel or can be fractionated to obtain purified hydrocarbons in the range of gasoline and diesel. The GC-MS analysis of waste fish oil showed the main composition of fatty acids to be the following: $C_{16:0}$ (15.87%), $C_{18:2}$ (20.96%), $C_{18:1}$ (17.29%), $C_{20:5}$ (5.11%), $C_{20:1}$ (7.59%), $C_{22:6}$ (4.53%), $C_{22:1}$ (10.42%) and the GC-FID analysis of the light bio-oil showed 482 compounds that were classified as paraffins (4.48%), iso-paraffins (8.31%), olefins (26.56%), naphthenes (6.07%) and aromatics (16.86%) (Wiggers *et al*., 2009b). Table 4.6 gives a comparison of the composition of light bio-oil with two random petroleum-based fuels, A and B (Wiggers *et al*., 2009b).

Green algae (aquatic and unicellular) biomass is also used in biodiesel production, and is an attractive source of triglycerides, as under good conditions, green algae can double its biomass in less than twenty-four hours (Table 4.7). Factors such as carbon dioxide availability, sunlight, water, and space affect algal density, and the annual productivity and oil content of algae is far greater than seed crops. Soybean can only produce about 450

Table 4.6 Classification of light bio-oil.

Classes	% (v/v) Light bio-oil	% (v/v) Gasoline A	% (v/v) Gasoline B
Aromatics	16.86	14.81	18.85
Iso-paraffins	8.31	19.35	23.67
Naphthenes	6.07	16.26	19.89
Olefins	26.56	11.72	13.53
Oxygenates	0.06	17.76	0.16
Paraffin	4.48	13.65	16.55
C_{14+}	5.30	0.00	0.00
Unclassified	32.38	6.44	7.36
Total	100.00	1000.00	100.00

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Table 4.7 A comparison of the oil content found in green algae.

Species	Oil content (% based on dry weight)
Chorella sp.	28-32
Nitzschia sp.	45-47
Nannochloropsis sp.	31-68
Schizochytrium sp.	50-77

liters of oil per hectare. Canola can produce 1,200 liters per hectare, and Palm can produce 6,000 liters. Algae on the other hand can yield 90,000 liters per hectare (Campbell, 2008).

In conclusion, biofuels are classed according to source and type. They are derived from forest, agricultural or fishery products or municipal wastes, as well as from agro-industry, food industry and food service byproducts and wastes. They may be solid, such as fuelwood, charcoal and wood-pellets; liquid, such as ethanol, biodiesel and pyrolysis oils; or gaseous, such as biogas. Table 4.8 gives the biofuel yields for different feedstocks and countries.

Table 4.8 Biofuel yields for different feedstocks and countries (Rajagoopal *et al.*, 2007).

Crop	Location	Biofuel	Crop yield (tones/ha)	Conversion efficiency (liters/ton)	Biofuel yield (litres/ha)
Sugar beet	Global	Ethanol	46.0	110	5060
Sugar cane	Global	Ethanol	65.0	70	4550
Cassava	Global	Ethanol	12.0	180	2070
Maize	Global	Ethanol	4.9	400	1960
Rice	Global	Ethanol	4.2	430	1806
Wheat	Global	Ethanol	2.8	340	952
Sorghum	Global	Ethanol	1.3	380	494
Sugar cane	Brazil	Ethanol	73.5	74.5	5476
Sugar cane	India	Ethanol	60.7	74.5	4522

(*Continued*)

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Table 4.8 Biofuel yields for different feedstocks and countries (Rajagoopal *et al*., 2007). (*Continued*)

Crop	Location	Biofuel	Crop yield (tones/ha)	Conversion efficiency (liters/ton)	Biofuel yield (litres/ha)
Oil Palm	Malaysia	Biodiesel	20.6	230	4736
Oil Palm	Indonesia	Biodiesel	17.8	230	4092
Maize	U.S.	Ethanol	9.4	399	3751
Maize	China	Ethanol	5.0	399	1995
Cassava	Brazil	Ethanol	13.6	137	1863
Cassava	Nigeria	Ethanol	10.8	137	1480
Soybean	U.S.	Biodiesel	2.7	205	552
Soybean	Brazil	Biodiesel	2.4	205	491

4.6 Properties Compared to Fuels from Crude Oil Tar Sand Bitumen, Coal and Oil Shale

According to a report in 2005 by the US Department of Agriculture, by the time a large-scale biorefinery industry can be developed, roughly around the mid-21st century, an annual biomass supply of more than 1.3 billion dry tons, or if converted to alcohol, it could replace approximately 39% of oil-derived fuels, can be produced with relatively modest changes in land use and agricultural and forestry practices. In order to elucidate the attractiveness of replacing fossil fuels with renewable biofuel options, it is necessary to look at how the properties of these two sets of fuels compare. One would want to necessarily look at noxious emissions, cost, availability and infrastructure required to create as well as use alternative fuels as opposed to traditional conventional fuels. It must be noted, however, that the overall environmental impact can vary under geographical and climatic conditions. In a report produced in 2006 (Fontaras and Samaras, 2008), the biofuel consumption in Europe was found to be 71.6% biodiesel, 16.3% ethanol and others, 12.1%, and there is an increasing use under the EU policy framework. Skepticism about biofuels in terms of utilization of food crops and expense in production are justified but emerging second- and third-generation biofuels seem to be overcoming these obstacles.

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One of the largest issues seems to be overall greenhouse gas emissions from the various biofuels when compared with petroleum fuels. To estimate the impacts of increases in renewable and alternative fuels on greenhouse gas emissions, the entire fuel life cycle including fossil fuel extraction or feedstock growth, fuel production, distribution, and combustion should be accounted for.

The fuels are compared on an energy equivalent or BTU basis. Thus, for instance, for every BTU of gasoline which is replaced by corn ethanol, the total life cycle greenhouse gas emissions that would have been produced from that BTU of gasoline would be reduced by 21.8%. These emissions account not only for CO_2, but also methane and nitrous oxide (EPA, 2007).

It is generally accepted that biofuels have the potential to drastically lower carbon-dioxide emissions than oil-derived fuels, but in many instances, this is not the case. For example, ethanol made from corn requires a substantial amount of energy in fertilization, irrigation, harvesting and fermentation processes and most of this energy comes from fossil fuels. As a result, some ethanol production scenarios emit more life cycle carbon-dioxide emissions than gasoline. Cellulose-based ethanol however, allows for more efficient and cost-effective fuel production, and the carbon footprint is decreased (Weber, 2007).

In another report (Manuel, 2007) it was stated that biodiesel reduces carbon dioxide emissions by 41% compared with conventional diesel, whereas ethanol yields only a 12% reduction compared with gasoline. Hence, ethanol fares worse than biodiesel when it comes to the emission of air-pollutants and greenhouse gases compared with their petroleum counterparts. The use of ethanol as an oxygenate has long been thought as being helpful in reducing air pollution. This same report stated that 10% ethanol used as an additive instead of methyl *tert*-butyl ether (MTBE) can reduce emissions of carbon monoxide, volatile organic compounds, and particulate matter with a diameter of less than 10μm. However, because of the emissions involved in the production, transportation, and conversion of corn into ethanol, the popular E85 ethanol–gasoline blend (which is 85% ethanol and 15% gasoline) results in higher total life-cycle emissions of these three pollutants as well as of oxides of sulfur and nitrogen.

Conversely, biodiesel blended into diesel at low levels reduces emissions of volatile organic compounds, carbon monoxide, particulate matter, and sulfur oxides during combustion. Further, over the full life cycle, biodiesel blends reduce carbon monoxide, particulate matter, and sulfur oxides compared with diesel.

Table 4.9 gives the chemical characteristics of some common bioenergy feedstocks, and liquid biofuels compared with coal and oil. Clearly seen is larger sulfur content for fossil fuels compared with agrofuels and

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Table 4.9 Selected properties of certain common bioenergy feedstocks and biofuels, compared with coal and oil (Wright *et al.*, 2009).

		Chemical characteristics				
		Heating value (GJ/t)	**Ash (%)**	**Sulfur (%)**	**Potassium (%)**	**Ash melting temperature (°C)**
Bioenergy Feedstocks	Corn stover	17.6	5.6			
	Sweet sorghum	15.4	5.5			
	Sugarcane bagasse	18.1	0.2-5.5	0.10-0.15	0.73-0.97	
	Sugarcane leaves	17.4	7.7			
	Hardwood	20.5	0.45	0.009	0.04	900
	Softwood	19.6	0.3	0.01		
	Hybrid poplar	19.0	0.5-1.5	0.03	0.3	1350
	Bamboo	18.5-19.4	0.8-2.5	0.03-0.05	0.15-0.50	
	Switchgrass	18.3	4.5-5.8	0.12		1016
	Miscanthus	17.1-19.4	1.5-4.5	0.1	0.37-1.12	1090
	Arundo donax	17.1	5-6	0.07		

(*Continued*)

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Table 4.9 Selected properties of certain common bioenergy feedstocks and biofuels, compared with coal and oil (Wright *et al.*, 2009). (*Continued*)

		Chemical characteristics				
		Heating value (GJ/t)	**Ash (%)**	**Sulfur (%)**	**Potassium (%)**	**Ash melting temperature (°C)**
Liquid biofuels	Bioethanol	28		< 0.01		N/A
	Biodiesel	40	< 0.02	< 0.05	< 0.0001	N/A
Fossil Fuels	Coal - low rank; lignite/ sub-bituminous	5-19	5-20	1.0-3.0	0.02-0.3	~1300
	Coal - high rank; bituminous/ anthracite	27-30	1-10	0.5-1.5	0.06-0.15	~1300
	Oil (typical distillate)	42-45	0.5-1.5	0.2-1.2		N/A

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intermediate heating values (related to moisture content) and ash content between solid and liquid biofuels. Generally, biomass feedstocks are fairly uniform in many of their fuel properties, compared with fossil fuels.

Many types of coal possess gross heating value ranges from 20 to 30 GJ/tonne, whereas most biomass feedstocks fall within the range 15 to 19 GJ/tonne. The bulk density (related to energy density) of most solid biomass feedstocks is generally low, even after compression, and is approximately between 10 and 40% of the bulk density of most fossil fuels; however, liquid biofuels have comparable values. Since biomass materials are more reactive, with higher ignition stability, they are generally easier to gasify and thermochemically process into methanol and hydrogen (higher-value fuels). Coal ash may contain toxic metals and small amounts of other trace contaminants, while biomass ash may be used as a soil amendment to assist in replacing nutrients removed by harvest. Bioethanol possess approximately 70% of the heating value of petroleum distillates, but its sulfur and ash contents are appreciably lower.

The use of biodiesel in a conventional diesel engine results in substantial reduction of unburned hydrocarbons, carbon monoxide, and particulate matter compared to emissions from diesel fuel. In addition, the exhaust emissions of sulfur oxides and sulfates (major components of acid rain) from biodiesel are essentially eliminated compared to diesel. Of the major exhaust pollutants, both unburned hydrocarbons and nitrogen oxides are ozone or smog forming precursors. The use of biodiesel results in a substantial reduction of unburned hydrocarbons. Emissions of nitrogen oxides are either slightly reduced or slightly increased depending on the duty cycle of the engine and testing methods used. Based on engine testing, using the most stringent emissions testing protocols required by EPA for certification of fuels or fuel additives in the U.S., the overall ozone forming potential of the speciated hydrocarbon emissions from biodiesel was nearly 50% less than that measured for diesel fuel. In a review published in 2009 (Gomes and Araujo, 2009), the environmental indicators related to biofuel production were examined.

The postulated superior properties of agrofuels when compared with fossil fuels, as we have seen, must be weighed very carefully amongst the various factors of cost, environmental impact, energy density, chemical composition and availability and life cycle of food crops. No doubt, increasing advances in technology will tip the scales in favor of biofuels.

4.7 Fuel Specifications and Performance

ASTM International (ASTM), formally known as the American Society for Testing Materials, is an international organization which develops and

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publishes information on the technical standards of various products, materials, systems and services. It is one of the largest and most highly regarded standards development organizations in the world. The available literature on the performance of biofuels when compared with traditional fossil fuels normally uses ASTM and ISO (International Standards Organization) specifications and parameters. The specifications provide details on requirements for fuel characteristics as well as the relevant standard test methods to use for each.

With regard to biodiesel, most of the world uses a system known as the "B" factor to state the amount of biodiesel in any fuel mix, in contrast to the "BA" or "E" system used for bioalcohol. Pure biodiesel is referred to as B100, while fuel containing 20% biodiesel is labeled "B20". The common international standard for biodiesel is EN 14214, whilst ASTM 6751 is most referenced in the U.S. In Germany, the requirements for biodiesel are fixed in the DIN EN 14214 standard.

There are standards for three different varieties of biodiesel, which are made of different oils: (i) RME (rapeseed methyl ester, according to DIN E 51606), (ii) PME (vegetable methyl ester, purely vegetable products, according to DIN E 51606), and (iii) FME (fat methyl ester, vegetable and animal products, according to DIN V 51606).

The standards ensure that the following important factors in the fuel production process are satisfied:

- Complete reaction
- Removal of Glycerin
- Removal of catalyst
- Removal of Alcohol
- Absence of free fatty acids

Basic industrial tests to determine whether the products conform to the standards typically include gas chromatography, a test that verifies only the more important of the variables above. Fuel meeting the quality standards is very non-toxic, with a toxicity rating (LD50) of greater than 50 mL/kg.

In 2008, ASTM published the new Biodiesel Blend Specifications, which included:

- ASTM D975-08a, Specification for Diesel Fuel Oils is used for on- and off-road diesel applications; revised to include requirements for up to 5% biodiesel.
- ASTM D396-08b, Specification for Fuel Oils is used for home heating and boiler applications; revised to include requirements for up to 5% biodiesel.

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- ASTM D7467-08, Specification for Diesel Fuel Oil, Biodiesel Blend (B6 to 20) is a completely new specification that covers finished fuel blends of between 6 (B6) and 20 (B20) percent biodiesel for on- and off-road diesel engine use.

The first national biodiesel specification in the U.S. was the ASTM standard D6751, "*Standard Specification for Biodiesel Fuel (B100) Blend Stock for Distillate Fuels*", adopted in 2002. The D6751 standard covers biodiesel (B100) used as a blending component with petroleum diesel fuels. No standards currently exist in the United States that would cover neat biofuel (B100) for use as automotive fuels. Labeling of the finished blend is not required, so it may not be possible for the purchaser to know whether or not the fuel contains biodiesel unless an analysis is carried out.

One of the most important fuel properties of biodiesel and conventional diesel fuel derived from petroleum is viscosity, which is also an important property of lubricants. Ranges of acceptable kinematic viscosity are specified in various biodiesel and petroleum standards. Reducing viscosity is one of the main reasons why vegetable oils or fats are transesterified to biodiesel because the high viscosity of neat vegetable oils or fats ultimately leads to operational problems such as engine deposits (Knothe and Steidley, 2005). Table 4.3 gives the kinematic viscosity (at 40°C) specifications contained in standards for biodiesel and conventional, petroleum-derived diesel fuel in the United States and Europe.

The viscosity of biodiesel is slightly greater than that of petrodiesel but approximately an order of magnitude less than that of the parent vegetable oil or fat. Biodiesel and its blends with petrodiesel display temperature dependent viscosity similar to that of neat petrodiesel. Influencing factors are chain length, position, number and nature of double bonds as well as the nature of the oxygenated moieties.

Classic biodiesel has a higher cloud point (temperature at which a fuel becomes hazy or cloudy and starts to gel) than petrodiesel. This makes its use impractical in cooler climates and limits its potential market. Other important chemical and physical properties described in ASTM standards for biodiesel are acid number (TAN – total acid number, indicates the presence of free fatty acids and carboxylic acids present), corrosion (describes the potential for copper corrosion, measured using ASTM method D-130), low temperature performance (describes pour points, PP, and cloud points, CP, using ASTM D-5949 and ASTM D-5773 methods), and oxidation stability (normally evaluated using Differential Scanning Calorimetry and Oxidation Stability Index) (Sharma *et al*., 2009).

According to the EMA (Engine Manufacturers Association), a blend of petroleum diesel fuel meeting ASTM D975 and 100% (neat) biodiesel fuel

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Table 4.10 Final blend fuel requirements (at point of delivery).

Item	Performance characteristic	Requirements		Test procedure
		D1 blends	*D2 blends*	
1	Flash Point, °C, min	38	52	ASTM D93
2	Water and Sediment, vol %, max	0.05	0.05	ASTM D2709 or D1796
3	Physical distillation, T90, °C, max	343	343	ASTM D86
4	Kinematic Viscosity, cSt@40°C	1.3 - 4.1	1.9 - 4.1	ASTM D445
5	Ash, mass %, max	0.01	0.01	ASTM D482
6	Sulfur, wt%, max	Per regulation	Per regulation	
7	Copper Strip corrosion rating, max	No. 3	No. 3	ASTM D130
8	Cetane Number, min	43	43	ASTM D613
9	Cloud point	≤ 10^{th} percentile min. ambient temp in geographical area and seasonal timeframe		ASTM D2500
10	Ramsbottom carbon residue on 10% distillation residue, wt%, max	0.15	0.35	ASTM D524
11	Lubricity, HFRR@60°C, micron, max	460	460	ASTM D6079
12	Acid number, mg KOH/g, max	0.3	0.3	ASTM D664
13	Phosphorous, wt%, max	0.001	0.001	ASTM D4951
14	Total Glycerin	…….	……..	N/A

(*Continued*)

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Table 4.10 Final blend fuel requirements (at point of delivery). (*Continued*)

Item	Performance characteristic	Requirements		Test procedure
		D1 blends	*D2 blends*	
15	Alkali metals (Na+K), ppm, max	Nd	Nd	EN14108
16	Alkaline metals (Mg+Ca), ppm, max	Nd	Nd	EN14108
17	Blend Fraction, vol.%	+/-2%	+/-2%	EN14108
18	Thermo-oxidative Stability, insolubles, mg/110mL, max	10	10	Modified ASTM D2274
19	Oxidation Stability, Induction time, hours, minimum	6	6	EN14112

meeting either ASTM 6751 or EN 14214, where the biodiesel content of the blended fuel is no more than 20% biodiesel by volume (B20), shall meet the requirements identified in Table 4.10 at the point of delivery of the fuel to the end user.

In terms of the effects of biodiesel on fuel filters, use of biodiesel blends which do not meet up to the designated specifications have been shown to drastically reduce filter life. Blends greater than B20 may have enough of a solvent to break down the varnish deposits on the walls of existing fuel storage tanks or fuel systems. The break-down of these varnish deposits will contaminate the fuel with particulate, which can cause fuel filters to plug rapidly.

Another disadvantage of biodiesel is that it tends to reduce fuel economy. Energy efficiency is the percentage of the fuel's thermal energy that is delivered as engine output, and biodiesel has shown no significant effect on the energy efficiency of any test engine. Volumetric efficiency, a measure that is more familiar to most vehicle users, usually is expressed as miles traveled per gallon of fuel (or kilometers per liter of fuel). The energy content per gallon of biodiesel is approximately 11% lower than that of petroleum diesel. Vehicles running on B20 are therefore expected to achieve 2.2% (20% x 11%) fewer miles per gallon of fuel.

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Approximately 11% of the weight of B100 is oxygen. The presence of oxygen in biodiesel improves combustion and therefore reduces hydrocarbon, carbon monoxide, and particulate emissions; but oxygenated fuels also tend to increase nitrogen oxide emissions. Engine tests have confirmed the expected increases and decreases of each exhaust component from engines without emissions controls.

Biodiesel users also note that the exhaust smells better than the exhaust from engines burning conventional diesel.

The European Union has set challenging targets for European refiners by increasing the minimum biofuel content in fuels to 5.75% (compared with the previous 5.0% minimum requirement) by the year 2010. Refiners recognize the advantages of using bioethers as a stable biofuel component, so other technologies are required to maximize the production of bioethers. Current European gasoline specifications call for a maximum ethanol content of 5% v/v, a maximum ether content of 15% v/v, a maximum oxygen content of 2.7% w/w and a maximum olefin content of 18% v/v (with pressure for reduction to 10% v/v by the Worldwide Fuels Charter) (Rock and Korpelshoek, 2008).

Areas of concern and interest are for the biofuels industry to have in place a good quality control protocol for the measurement of bioalcohols, to avoid metal corrosion from water and acid corrosion (due to weak and strong acids and inorganic chlorides in solution). Also, of importance are the limits set on phosphorous content (less than 5.0 mg/L in ethanol) to prevent engine catalyst deterioration, and copper content (less than 0.1 mg/kg), along with a sulfur content less than 10 mg/kg.

Up to a 10% blend level, the performance of bioethanol-blended petrol is similar to ordinary petrol. At higher levels however, some engines may begin to exhibit problems; for example, stumbling under slight acceleration. The fuel also has more aggressive properties at higher concentrations of bioethanol which increases the possibility of deterioration of some components. Petrol must be volatile enough to move from the carburetor or injectors into the cylinders and to vaporize prior to combustion. However, it can't be so volatile that it vaporizes and boils in the injectors, carburetor, fuel lines or fuel pump, which could prevent it from being metered correctly. Also, if petrol is too volatile, moiré evaporates into the air adding to environmental problems. There are a number of volatility specifications to ensure suppliers get this balancing act right. Adding bioethanol to petrol as low-level blends increases volatility of the blended fuel. The Engine Fuel Specifications Regulations specify volatility measures for bioethanol-blended petrol and petrol. The limits for blends are similar to those for petrol so to ensure no changes in vehicles are required. Bioethanol

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Table 4.11 Climate-related requirements and test methods.

Property	Units	Class A	Class B	Test method
Ethanol + higher alcohols	% (V/V), min	75	75	EN 1601 EN 13132
Premium grade unleaded petrol as specified in EN 228	% (V/V)	14-22	14-30	100 minus the sum of the % content of water and alcohols
Vapor pressure	kPa, min kPa, max	35.0 60.0	50.0 100.0	EN 13016-1
Final Boiling Point	*°C, max*	210	210	EN ISO 3405
Distillation residue	% (V/V), max	2	2	EN ISO 3405

introduces more oxygen into the fuel. In vehicles with simple fuel metering systems such as carburetors, this causes the mixture to become a little leaner. Leaning is good for fuel economy and is generally good for lowering some types of exhaust emissions. However, it may cause some engines to stumble if they are already tuned reasonably lean. If a vehicle stumbles on bioethanol-blended petrol, re-tuning should solve the problem. A vehicle tuned correctly for use on ordinary petrol would normally not exhibit problems when using bioethanol blend.

To meet hot and cold vehicle driving requirements under the European seasonal and geographical conditions, two volatility classes are defined as shown in Table 4.11.

Regardless of the blend level, the quality of the ethanol added to gasoline is important. The industry standard for ethanol is ASTM D 4806 Standard Specification for Denatured Fuel Ethanol for Blending with Gasoline for Use as Automotive Spark Ignition Engine Fuel. The primary quality specifications contained in ASTM D 4806 are given in Table 4.12.

4.8 Conclusion

In summary, the Alternative Energy Industry has a fair way to go in convincing governments, as well as the general public, that biofuel production

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Table 4.12 ASTM D 4806 Standard Specification for denatured fuel ethanol for blending with gasoline for use as automotive spark ignition engine fuel.

ASTM D 4806		
Property	**Specification**	**ASTM test method**
Ethanol volume %, min	92.1	D5501
Methanol, volume %. max	0.5	
Solvent-washed gum, mg/100 mL max.	5.0	D381
Water content, volume %, max	1.0	E203
Denaturant content, volume %, min	1.96	
Denaturant content, volume %, max	4.76	
Inorganic Chloride content, mass ppm (mg/L) MAX	40	D512
Copper content, mg/kg, max	0.1	D1688
Acidity (as acetic acid CH_3COOH), mass percent (mg/L), max	0.007	D1613
pH	6.5 – 9.0	D6423
Appearance - clear and bright	visibly free of suspended or precipitated contaminants	

and use is sustainable, environmentally friendly and progressive. The factors of availability, price, and independence of manufacturer, health benefits, engine improvements and political implications must all be carefully weighed and assessed, before educated decisions can be made by the powers that be. It is hoped, however, that despite some of the obvious setbacks of biofuel production, that it is still viewed as a step in the right direction, and emerging technologies and innovative ideas will encourage improvements in what is, undoubtedly, the future of fuel.

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5

Sustainable Valorization of Waste Cooking Oil into Biofuels and Green Chemicals: Recent Trends, Opportunities and Challenges

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Abstract

Food waste reduction and utilisation are paramount to achieve the United Nations (UN) goals for sustainable development. The exploitation of food waste valorization into green chemicals, materials and biofuel is crucial to curtail the economic and environmental impact of food waste disposal. Specifically, WCO is considered as a major stream of the food waste that has high concentration of lipids that are easily reachable.

The approachable lipids in WCOs have boosted the research on valorization technologies to produce biofuels and green chemicals. Biodiesel has been reported as the major product of WCO utilisation using various catalytic and non-catalytic techniques. On the other hand, the valorization of WCO into sustainable oleo-chemical products has captured high interest from different researchers.

This chapter highlights the main progress and developments in WCO valorization technologies into biofuels and oleo-chemical products including biodiesel, biojet fuels, bio-lubricants, surfactants, asphalt rejuvenator, plasticizers, etc. This work has a main focus on both catalytic and non-catalytic production processes of biodiesel from WCO. Challenges in up-scaling and commercialising the developed

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Nour Shafik El-Gendy (ed.) Sustainable Solutions for Environmental Pollution Volume 1: Waste Management and Value-Added Products, (199–228) © 2021 Scrivener Publishing LLC

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technologies have been addressed. Finally, recommended bio-refinery approaches to integrate WCO processes with other technologies have been discussed.

***Keywords*:** Food waste, waste cooking oil, biofuels, biodiesel, oleo-chemical products

5.1 Introduction

Food wastes are considered as national resources that should be utilised into beneficial products. The United Nations (UN) Sustainable Development Goals have included No poverty, Zero hunger, clean water and sustainable cities, and the reduction and recycling of food waste is a crucial step for the fulfilment of these developmental goals. The European Union (EU) publication office has reported that 60% of food wastes are unavoidable including waste cooking oils (WCO), animal bones and leftovers. Accordingly, the valorization of food waste into valuable products is crucial (Caldeira *et al.*, 2017).

Food wastes are categorised according to the composition of the materials and the potential applications. Generally, food wastes are composed of carbohydrates, oils and fats (Melikoglu, 2020). Carbohydrates composed of cellulosic and hemi-cellulosic materials are very commonly used for bioethanol production via fermentation (Alayoubi *et al.*, 2020; Mehmood *et al.*, 2018). Fats and oils are traditionally converted into biodiesel, biojet fuels and have the potential for green chemicals production. Particularly, WCO is considered as a major food waste that is heavily produced from households and food industries. The disposal of WCO into drainage significantly affects the water, which contradicts one of the UN goals of clean water and is considered as a loss of a valuable resource of energy (Melikoglu, 2020; Orjuela and Clark, 2020; Sahar *et al.*, 2018).

Generally, there are some difficulties in converting waste materials into valuable products due to their complex compositions, high acidity contents, etc. Several pre-treatment processes have been recently developed including ionic liquids, neutralisation and other physical pre-treatments (Huet *et al.*, 2020; Omran *et al.*, 2020). Specifically, WCO physical pre-treatment through filtration is an essential step prior to any processing to remove the residual food from the cooking process (Knothe and Razon, 2017).

This chapter's overarching aim is to review the recent work on WCO valorization into biofuels and value-added chemicals. The chapter provides a comprehensive review on the conversion methodologies of WCO

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into biodiesel and biojet fuels and highlights the most recent pathways for WCO valorization into asphalt rejuvenator, plasticizers, polyurethane foam, bio-lubricants and surfactants.

5.2 Waste Cooking Oil (WCO)

WCO is the edible oil that has already been used for cooking and frying food. Generally, edible oils are heated at elevated temperature to be used for cooking purposes of different kind of foods and mainly used in frying vegetables, fruits, chicken, meat, fish, etc. Cooking oils are derived from various resources including plants, animals and synthetic fats. They are in generally liquid phase at room temperature and have high bubble points. However, some oils are in solid phase at room temperature due to the presence of high saturation in their chains. The most commonly used oils for cooking processes are palm, corn, sunflower, rapeseed and olive oils (U.S. Department of Health and Human Services and Agriculture, 2015).

Generally, vegetable oils are composed of fatty acids bonded in a solid backbone of tricarbons (triglycerides). The composition of triglycerides includes three different long chains fatty acids between C14-C19 that are responsible for defining the name of triglycerides. For instance, having three chains of identical chains of oleic acids make the triglyceride named as "triolein". The composition of oils is dependent on its origin and saturation level. However, oleic acid represents a high proportion of most of the cooking oils where some researchers consider it as triolein as a model compound for cooking oils (Nasir *et al*., 2013; Orsavova *et al*., 2015).

WCO has the same structure of the fresh edible oil used in the cooking process. Generally, WCO includes high percentage of free fatty acids (FFA) resulting from the cracking of triglycerides due to the elevated temperature cooking process. In addition, several reactions occur for the oil during the cooking process including hydrolysis, thermal degradation, oxidation and polymerisation (Orjuela and Clark, 2020; Warner and Moser, 2009). Table 5.1 illustrates a summary of the reactions, causes and consequences on the oil structure. It has been reported that the composition of the WCO is also a function of the cooking duration and repeatability where in developing countries the cooking oil is used several times due to the high price of fresh oils. In addition, the collected WCO from households and industries could not be from a single source and hence is

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Table 5.1 Summary of the reactions, causes and consequences on the cooking oil structure.

Reaction	Conditions	Products
Thermal degradation	Cooking oil operated for cooking process at elevated temperature (>300 °C)	Short chains fatty acids and hydrocarbons, oxopropyl esters, dimeric compounds, syngas and ketones
Polymerisation	Unsaturated acyl groups reaction with triglycerides and FFAs	Dimers, oligomers and polymerised triglycerides
Hydrolysis	Reaction between water in the atmosphere (humidity) with triglycerides at elevated temperatures	Polar compounds, FFAs and glycerol
Oxidation	Reaction between triglycerides and FFAs with oxygen in the atmosphere at elevated temperatures	Hydroperoxides groups

considered a mixture of different triglycerides, FFAs and undesired products (Hajjari *et al.*, 2017).

Unfortunately, a high percentage of households WCO is disposed in the drainage and causes significant difficulties in wastewater treatment plants. Accordingly, collection and valorization of WCO into valuable products including biofuels and green chemicals has recently received great attention from researchers and industries. WCO has been recently valorised into several products including biodiesel, biojet fuels, bio-lubricants, asphalt rejuvenator, syngas, sorbents, surfactants, volatile organic compounds (VOCs) and bio-plasticizers. From the mentioned products, biodiesel production from WCO through transesterification reaction is the most common pathway that has been implemented at commercial scale (Ahmed and Hossain, 2020; Li *et al.*, 2015; Orjuela and Clark, 2020).

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5.3 Biofuels from WCO

5.3.1 Biodiesel

Biodiesel is defined as monoalkyl esters of long chain fatty acids derived from animal fats, vegetable oils and microalgae. Conventionally, biodiesel is produced through the transesterification reaction of triglycerides with alcohol into fatty acid alky esters. Methanol is considered the most commonly used alcohol for biodiesel production due to the high similarity of the fatty acids methyl esters (FAME) with petroleum diesel. Alkaline catalytic processes using sodium and potassium methoxides are commercially used for the production of biodiesel (Aboelazayem *et al*., 2018a; Kumar and Singh, 2019; Singh *et al*., 2020).

Specifically, the valorization of WCO into biodiesel is slightly different due to the fact that it has high concentration of FFAs and water that would lead to saponification reactions with alkaline catalysts that scientifically decrease the biodiesel yield. In addition, the application of heterogeneous catalysts is very sensitive to the high-water content of WCO. Accordingly, different approaches have been developed for WCO valorization into high yield biodiesel (Aboelazayem *et al*., 2019; Eze *et al*., 2018; Fonseca *et al*., 2019; Sahar *et al*., 2018).

Pre-treatment of WCO has been proposed as an initial step prior to alkaline transesterification to reduce the FFA content of the feedstock through esterification and neutralisation. Further, a two-step reaction mechanism has been introduced for esterification of FFAs into FAMEs followed by alkaline transesterification reaction of triglycerides (Thoai *et al*., 2019). Acidic catalysts have been also implemented in conversion of WCO into biodiesel due to their capability to convert both FFAs and triglycerides into FAMEs. However, the long reaction time, lower yield of biodiesel and the requirement of corrosion resistant material for the reactor have limited the applications of acidic catalysts (Kim *et al*., 2011). Heterogeneous catalysts have been also used for simultaneous esterification and transesterification reaction of WCO. The heterogeneous catalysts have many advantages including high yield of biodiesel, simplified separation of products and high tolerance with acidic feedstock. The high cost of the catalyst preparation has been considered as the main disadvantage of heterogeneous catalytic pathway (Semwal *et al*., 2011; Talebian-Kiakalaieh *et al*., 2013). Rcently, bio-based heterogeneous catalysts have shown low-cost and high conversion pathway for the acidic WCO (Naeem *et al*., 2021).

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On the other hand, several methodologies have been recently developed for biodiesel production from WCO including supercritical methanolysis, high-shear mixing, ultrasonic-assisted, microwave-assisted and microreactors. High-shear mixing has provided forced miscibility of methanol in WCO which resulted in high-yield biodiesel at very low temperature (similar to room temperatures) (Sánchez-Cantú *et al.*, 2019). Microreactors have provided high mass transfer and enhanced the rapid biodiesel production (Andreo-Martínez *et al.*, 2020). Table 5.2 summarises the detailed recently developed methodologies including the reaction conditions and the yield of biodiesel produced.

Table 5.2 Recently developed methodologies for biodiesel production from WCO.

Method	Biodiesel yield (%)	Operating conditions	Catalyst	Ref
Microreactor	91.8	Temp. 65 °C M:O ratio 9:1 Time: 6 s	KOH, H_2SO_4	(Tanawannapong *et al.*, 2013)
T-shaped Microreactor	89	Temp. 60 °C M:O ratio 9:1 Time: 3 min	KOH	(Rahimi *et al.*, 2014)
High-shear mixer	99.8	Temp. 22 °C M:O ratio 5:1 Time: 1 min	NaOH	(Sánchez-Cantú *et al.*, 2017)
High-shear mixer	94.5	Temp. 25 °C M:O ratio 5:1 Time: 10 s	NaOH	(Sánchez-Cantú *et al.*, 2019)
Microwave-assisted	97	Temp. 78 °C Ethanol to oil ratio 12:1 Time: 30 min	NaOH	(Lertsathapornsuk *et al.*, 2008)
Microwave-assisted	99.4	Temp. 70 °C M:O ratio 12:1 Time: 105 s	NaOH	(Choedkiatsakul *et al.*, 2015)

(*Continued*)

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Table 5.2 Recently developed methodologies for biodiesel production from WCO. (*Continued*)

Method	Biodiesel yield (%)	Operating conditions	Catalyst	Ref
Ultrasonic-assisted	96.6	Temp. 59 °C M:O ratio 6:1 Time: 10 min	KOH	(Aghbashlo *et al.*, 2017)
Ultrasonic-assisted	98	Temp. 50 °C M:O ratio 8.5:1 Time: 30 min	H_2SO4	(Trinh *et al.*, 2018)
Supercritical methanolysis	95.7	Temp. 271 °C M:O ratio 34:1 Time: 20 min	N/A	(Ghoreishi and Moein, 2013)
Supercritical methanolysis	98	Temp. 265 °C M:O ratio 25:1 Time: 20 min	N/A	(Aboelazayem *et al.*, 2018c)

On the process level, several techno-economic studies have been developed to assess the profitability of biodiesel production plant using different methodologies (Budiman Abdurakhman *et al.*, 2018). Non-catalytic supercritical methanolysis processes have been superior to other processes due to the simplified process without the requirement of any pre-treatment steps or catalysts separation units (Andreo-Martínez *et al.*, 2020). However, the harsh reaction conditions, high methanol to oil (M:O) molar ratio and process safety concerns are the main disadvantages of the process (Aboelazayem *et al.*, 2017). Several process integration techniques have been applied to lessen the intense energy consumption of biodiesel production through supercritical methanolysis (Aboelazayem *et al.*, 2018b; Akkarawatkhoosith *et al.*, 2019; Gutiérrez Ortiz and de Santa-Ana, 2017). Recently, the integration of organic Rankin cycle (ORC) to recover the residual waste heat streams of biodiesel process have resulted in electric power that has not only provided self-sufficiency to the process but also exceeded the process requirements and considered as process revenue (Aboelazayem *et al.*, 2021).

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On the other hand, other researchers have developed a novel technique for valorization of glycerol side product in biodiesel process into hydrogen through glycerol steam reforming process. The produced hydrogen was used as a clean energy resource for the processes and hence increased the process profitability (Ziyai *et al.*, 2019).

In summary, various techniques have been developed for the production of high-quality biodiesel from WCO. Recently, microwave and ultrasonic assisted methods have received immense attention due to their efficient conversion in shorter reaction time. Similarly, supercritical methanolysis was proven as a sustainable economic viable approach for direct conversion of WCO without any pre-treatment or catalysts. Most of the recent developed methods are still at the laboratory scale and require more upscaling studies to be implemented into the commercial scale.

5.3.2 Biojet Fuel

In addition to the aforementioned research on biodiesel production, several researchers have introduced the production of biojet fuels from WCO. Jet fuels are comprised of a mixture of hydrocarbon chains between C_8 and C_{16} that are produced from petroleum crude oil using distillation process. The air travel industry is continuously increasing with an expected growth of 5% annually until 2026, which has dramatically increased the demand of jet fuels. It has been reported that the global consumption of jet fuels reached 13.6 EJ in 2012 and expected to reach 24.1 EJ by 2040, which represents nearly 15% of global energy consumption. As a fossil fuel, jet fuels are also contributing to global warming and the increasing production of greenhouse gases. Therefore, the introduction of a sustainable alternative clean resource including biojet fuels to the air industry is crucial for a greener environment. It has been reported that the development of a sustainable biojet fuel production for the air industry can hypothetically reduce the emissions of CO_2 in 2050 by 68% (Goh *et al.*, 2020; Wei *et al.*, 2019; Why *et al.*, 2019).

The similarity of the physicochemical properties of biojet fuels to commercial jet fuel is essential to be directly used for the existing planes' infrastructure. Blending biojet fuels with conventional jet fuels should be limited to a value of which the blend should have a minimum heating value of 42.8 MJ/kg according to ASTM D7566 standard. Hence, having high hydrogen/carbon ratio is vital to achieve an improved combustion of the fuel. The performance evaluations of biojet fuels and alternative jet fuels are reported in the standard procedures of ASTM 4054 where the analyses

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include engine tests, fuel properties, component tests and fit for purpose (FFP) properties (Chiaramonti *et al*., 2016; Eller *et al*., 2016).

Several pathways have been reported for biojet fuels production including catalytic hydrogenation, decarboxylation, hydro-deoxygenation cracking/isomeration and catalytic hydro-thermolysis. Among the potential pathways, catalytic hydro-treatment has been recognised as a promising method for production of biojet fuel from WCO. Hydro-treatment process consists of converting triglycerides and FFAs of WCO into hydrocarbons within the jet fuel range. Due to the fact that the triglycerides have a long carbon chain with a length between C_{14} to C_{22}, they are not suitable for direct application as jet fuels. Accordingly, cracking and isomeration processes are required for the long carbon chains to be reduced. Generally, the process is separated into two steps in which triglycerides and FFAs are saturated with hydrogen at high temperature and pressure with the aid of a catalyst (catalytic hydrogenation), followed by reduction of carbon chains via thermal and catalytic cracking processes. The presence of catalysts enhances the selectivity of the reactions to obtain the expected products (Y. Li *et al*., 2018; Wei *et al*., 2019).

The ASTM D7566-19b aviation fuel standard has approved the standard methodology of producing biojet fuels from fatty acids via catalytic hydrothermal jet (CHJ) and hydrogenated esters and fatty acids (HEFA) pathways. The standard has approved blending up to 50% of biojet fuels with petroleum-based jet fuel. The long carbon chain of triglycerides and FFAs resulted in a diesel range fuel with higher freezing point than jet fuels. Accordingly, the fatty acids methyl esters (FAME), also known as "biodiesel", content is considered as a contaminant in jet fuels as it significantly reduces the cold flow properties of the fuel. FAME content in jet fuels is limited to 5 ppm according to ASTM D1655-19a (Bergthorson and Thomson, 2015). Similarly, the freezing point of jet fuel is relatively lower than FAME as it has been implemented at lower temperature (higher altitudes). Accordingly, highly efficient cracking of long chain hydrocarbons in triglycerides and FFAs is crucial to obtain high-quality jet fuels (Gutiérrez-Antonio *et al*., 2017; Yang *et al*., 2019).

The application of WCO as a feedstock for biojet fuels production requires a significant physical pre-treatment, i.e., filtration, to remove any cooking food residuals following water removal via heating. The pre-treatment processes are then followed by two-step hydro-treatment and cracking processes for the production of biojet fuels (Buffi *et al*., 2017; Li *et al*., 2015; Wako *et al*., 2018; Yıldız *et al*., 2020). Recently, a novel method of combining hydro-treatment and cracking processes in a single-pot reactor has been reported (Chen and Wang, 2019).

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5.3.2.1 Hydro-Treatment Process

Hydro-treatment is the conversion process of unsaturated hydrocarbon chains of triglycerides and fatty acids into saturated carbon chains (alkanes) that is performed with three main reactions, namely hydro-deoxygenation, decarboxylation and decarbonylation. The hydro-deoxygenation includes the removal of oxygen from the oxygenated compounds using reaction with hydrogen to produce deoxygenated compounds and water. On the other hand, decarboxylation includes the removal of carboxylic acid from the compound by breaking the C-C bond for the production of carbon dioxide without the aid of hydrogen. Finally, decarbonylation includes the scission of C-O bond with hydrogen for the production of carbon monoxide gas.

Table 5.3 Recent reports for catalytic hydro-treatment of WCO into saturated hydrocarbons.

Feedstock	Catalyst used	Yield	Reaction conditions	Reference
WCO	Ni-Cu	92%	350 °C 40 bar 3 h	(Santillan-Jimenez *et al.*, 2018)
WCO	Ni_2P with activated carbon support	89 %	320 °C 1 bar	(Pham *et al.*, 2019)
Palmitic acid	Ni with ZSM-5 support	96 %	300 °C 20 bar	(Li *et al.*, 2015)
WCO	Ni with HMS support	92.5 %	300 °C Vacuum pressure 3 h	(Zulkepli *et al.*, 2018)
WCO	NiMo/γ-Al_2O_3-β-zeolite	98 %	350 °C 50 bar 3 h	(Z. Li *et al.*, 2018)
WCO	CaO-La_2O_3	72 %	330 °C 4 h	(Alsultan *et al.*, 2017)
WCO	CaO and treated hydrotalcite (MG70)	83%	400 °C 15-20 bar 3 h	(Romero *et al.*, 2016)

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Both decarboxylation and decarbonylation produce shorter alkane with a removed carbon atom in either CO or CO_2 (Cao *et al.*, 2018; Chu *et al.*, 2017; Khan *et al.*, 2019; Zadeh *et al.*, 2020).

The process efficiency is highly affected by selection of the used catalysts, reaction conditions and catalysts support. Generally, the metal catalysts are implemented in the hydro-treatment processes including pure, metal mixtures and metallic compounds. Specifically, platinum group metals have been implemented due to their high corrosion and oxidation resistance. Doping platinum catalysts with zeolites, activated carbon and oxides have delivered higher conversion rates and selectivity of the desired products. Although the application of Platinum group as catalysts provides an excellent yield of paraffinic straight hydrocarbons, the high cost and deactivation due to poisoning by intermediate products are considered the main challenges for commercialisation (Galadima and Muraza, 2015). It has been reported that Bimetallic catalysts are superior to monometallic ones due to their high catalytic activity (Jin and Choi, 2019; Lee *et al.*, 2020). Cheah *et al.* (2020) have reported that the presence of Nickel or Copper with Palladium, specifically Nickel, has enhanced the accessibility of hydrogen to saturate the fatty acids. Pham *et al.* (2019) have conducted hydrodeoxygenation of WCO with Ni_2P catalysts at 320 °C and at atmospheric pressure resulting in oxygen removal with 89%. Similarly, Z. Li *et al.* (2018) have reported 98% yield of diesel range hydrocarbons at 350 °C, 50 bar within 3 h using NiMo/γ-Al_2O_3-β-zeolite as a catalyst. Table 5.3 summarises the recent reports for catalytic hydro-treatment of WCO into saturated hydrocarbons.

5.3.2.2 Cracking and Isomerisation Processes

Cracking and isomerisation processes are responsible for breaking the long complex chains of hydrocarbons into shorter ones and converting the straight hydrocarbon chains into branched chains, respectively. Cracking and isomerisation are essential for converting the low-quality lipids into high-quality jet fuels and also to improve the low cold flow properties of the saturated cooking oils. The two processes are usually coupled together in a single catalytic process. Recently, thermal cracking at harsh temperatures (>600 °C) has not been preferred due to the production of high yield of undesirable lower economic value and shorter hydrocarbons between C_1 to C_4. Accordingly, catalytic cracking coupled with isomerisation is the preferred pathway for upgradation of saturated lipids into biojet fuels (Galadima and Muraza, 2015; Ju *et al.*, 2016; Khan *et al.*, 2019; Wang and Tao, 2016).

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The acidity of catalyst is considered as a significant variable affecting the process efficiency and selectivity of jet-range fuels. Saturated chains are initially dehydrogenated on the metal site of the catalysts followed by production of branched olefins using carbocation reactions on the acid site of the catalyst for the production of alkylcarbenium ion. An arrangement scheme will then occur on the branched chain (mono, di, tri) and finally hydrogenated again to produce the branched shorter high-quality paraffins. Commonly, bimetallic catalysts are applied for this process including Ni-Mo, Co-Mo and Ni-W supported with silica and alumina. Wako *et al*. (2018) have investigated the application of ZrO_2 catalyst for the production of biofuel hydrocarbons from WCO. They have reported 83% yield of organic hydrocarbon at 475 °C and 4% catalyst loading within 2 h. Further, HZSM-5 catalyst has been used due to its high acidity, activity and excellent selectivity for the required products (Gutiérrez-Antonio *et al*., 2017; Shahinuzzaman *et al*., 2017; Wako *et al*., 2018; Wang and Tao, 2016).

There is still large room for improvements and studies to be conducted in the field of biojet fuels production from waste oils. The catalytic pathways are not yet mature enough to be scaled up for commercial scale. Wang (2019) has analysed the potential feedstocks for the production of biojet fuels and highlighted that the feedstock price is the most significant parameter that affects the price of the final product. Hence, the application of WCO (as a cost-effective feedstock) would enhance the process profitability. On the other hand, the strict aviation fuel restrictions and the lack of interest from the industry have discouraged a research group in China from extending their laboratory scale work into pilot scale (Gosens *et al*., 2018).

5.4 Green Chemicals from WCO

The exploitation of WCO as a sustainable feedstock for the oleochemicals industry would significantly contribute to the circular economy portfolio and reduce the social impact of using edible oils for chemicals production. Oleochemicals represent the chemicals that are derived from oleic acid compound including cooking oils, grease and lipids. The oleochemicals industry includes lubricants, drying oils, plasticizers, surfactants, etc. This section provides a review of the application of WCO in the production of sustainable green chemicals.

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5.4.1 Asphalt Rejuvenator

Roads are essential for transportation and serve as a backbone for the economic growth of countries. Thousands of roads are built annually all over the world to replace old roads and to provide an access for modern civilisation. The high rate of extension and maintenance of roads (pavement) has significant impact on energy consumption and environmental pollution. In an attempt to reduce the impact of the asphalt pavement industry, the recycling of reclaimed asphalt pavement (RAP) has been introduced. RAP represents the removed and old pavements that are replaced during the reconstruction and/or maintenance of roads. The recycling of RAP into the pavement industry again is called "Rejuvenation", where RAP is upgraded and treated to restore its properties as fresh pavement (Ahmed and Hossain, 2020; Aurangzeb and Al-Qadi, 2014; Behnood, 2019; Zahoor *et al*., 2021).

Rejuvenation is defined as the reviving process of the properties of aged pavement by reviving the asphaltene and maleness with the aid of a rejuvenator. It also aims to advance the insufficiencies of having high ratio of RAP in the pavement mixture. The rejuvenation of RAP would decrease the reliance on petroleum-based products and enhance the sustainability of the pavement industry (Ahmed and Hossain, 2020; Zahoor *et al*., 2021).

Conventionally, rejuvenators are petroleum-based compounds and engineered products. The main two properties that define the quality of the pavement are rutting and cracking efficiency where the asphalt mixture should have the capability to resist rutting and minimise fatigue. Mixing the virgin binder with RAP and rejuvenators is determined using the degree of blending (DOB) (Shirodkar *et al*., 2013; Zaumanis and Mallick, 2015).

Recently, WCO has been introduced as a sustainable feedstock for the upgradation of aged pavement (Xinxin *et al*., 2018). Asli and Rehan (2011) have reported the high potential of WCO as a rejuvenating agent for aged bitumen in bituminous pavements. Wen *et al*. (2013) have defined the rejuvenated asphalt using bio-based material as "bioasphalt". They have evaluated the effect of blending bioasphalt with fresh petroleum-based asphalt instead of traditional binders during the hot mix asphalt (HMA). They have tested the constant shear loading and multiple stress creep on both mixtures with bioasphalt and conventional binders. They have reported that the mixture with bioasphalt blend has resulted in increasing the resistance on thermal cracking. However, it reduced the resistance on rutting and fatigue cracking (Zargar *et al*., 2012).

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Similarly, Azahar *et al*. (2017) have explored the impact of adding treated and untreated WCO into HMA on the resulted asphalt mixture. They have described the advantages of adding both treated and untreated WCO including the increased modulus stiffness, stability and tensile strength of the mixture. The authors have also highlighted that pre-treating WCO with a catalytic alkaline transesterification reaction has significantly improved the properties of the produced asphalt mixture. Treated WCO has led to a high creep stiffness for rutting deformation resistance and enhanced intermolecular adhesion bonding of the produced mixture (Azahar *et al*., 2016).

In conclusion, the application of WCO as an asphalt rejuvenator has been proven as an efficient pathway to improve the sustainability of the pavement industry and to reduce its carbon footprint. WCO has been applied as a rejuvenator for aged asphalt to improve its properties for reviving it as a blend with fresh asphalt and as a bio-based binder to improve the properties of petroleum-based asphalt during the HMA process. In both applications, WCO has been proven as an effectual additive that has a significant impact on improving the properties of the produced asphalt mixture. It has also provided a sustainable pathway to restore the original properties of aged asphalt, so it could be reused in pavement industry (Ahmed and Hossain, 2020).

5.4.2 Plasticizers

Plasticizers are a central class of chemicals that are used as additives in plastic industries. They are significantly used in the processing of polyvinyl chloride (PVC) production that provides the product with high flexibility and durability. There is a huge market for the plasticizers globally, where 5 million tonnes per annum are considered as the average production of plasticizers in the last decade. Among the produced plasticizers, petroleum-based phthalates represent more than 80%. Dioctyl phthalate (DOC) is a common type of the plasticizers that is heavily used in the PVC industry. However, the high toxicity risk to humans of DOC has been recently reported where toxic phthalate materials represent about 40% of the plasticized PVC products. Further, some countries have banned their applications in food packaging and toys due to their high risk for children and pregnant women (Bueno-Ferrer *et al*., 2010; Chen *et al*., 2015; Greco *et al*., 2010; Nihul *et al*., 2014; Zheng *et al*., 2018).

The aforementioned challenges have boosted the research for alternative non-toxic and environmentally benign plasticizers. Benaniba *et al*. (2001) have reported that epoxy compounds have the capability to act as acceptor for the hydrogen chloride compound in PVC and hence serve

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as a plasticizer and improve the elasticity, flexibility, stability and toughness of the material. Bueno-Ferrer *et al*. (2010) have reported a similar effect of using bio-based plasticizer and stabilizer derived from epoxidized soybean oil in comparison with conventional plasticizers. However, the reliance on edible oils as a feedstock for the production of bio-based plasticizer will promote undesirable social impact as it will create a competition with the food industry and would lead to a steep increase in food prices. In addition, edible oils as feedstock for plasticizer will increase the cost of the process and hence will reduce the competition with the conventional plasticizer.

In this regard, attention has shifted toward low-cost and renewable materials, of which biomass wastes, i.e., WCO, would be the ideal solution for the production of economic viable and environmentally benign plasticizers. Verma *et al*. (2014) have studied the epoxidation of oleic acid 2-ethylhexyl ester using tert-butyl hydroperoxide (TBHP) using Immobilized oxo-vanadium Schiff base on graphene oxide as a heterogeneous catalyst. Zheng *et al*. (2018) have studied the transesterification of WCO with 2-ethylhexanol for the production of Epoxidized 2-ethylhexyl fatty ester (WCOEtHE) as a bio-based plasticizer. They have reported that WCOEtHE has significantly improved the overall mechanical property and thermal stability of PVC. They have also performed a comparison with conventional plasticizer where they have observed that WCOEtHE is superior in providing a higher oxidation stability, lower temperature properties and lower glass transition temperature of the produced PVC. Similarly, Suzuki *et al*. (2018) have stated that epoxidized WCO was implemented as a primary plasticizer for the production of PVC films. They have obtained similar thermal and mechanical properties for the produced films in comparison with the commercial PVC films that are synthesised using petroleum-based plasticizers. Further, Feng *et al*. (2018) have produced bio-based plasticizers from WCO and citric acids. Interestingly, they have declared that the WCO-based plasticizers have better properties than the epoxidized soybean oil (ESO) and have similar properties with the dioctyl phthalate (DOP) petroleum-based plasticizer.

In summary, the research on the replacement of petroleum-based toxic plasticizers with bio-based ones has recently received very high attention due to the promising results obtained. Epoxidized edible oils have been firstly implemented where they have reported similar impact on the properties of PVC products as the conventional plasticizers. Very recently, WCO has been introduced as a sustainable low-cost feedstock for the production of bio-based plasticizers. The plasticizers produced from WCO have reported superior properties than those produced from edible oils

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and very similar to the conventional plasticizers. Hence, WCO-based plasticizers pathway is considered as a cleaner route for plastic industries.

5.4.3 Polyurethane Foam

Polyurethane foam is generally synthesised from petroleum-derived polyester polyols and polyisocyanates. In order to reduce the reliance on petroleum-based products, many researchers are working on discovering renewable materials as sustainable feedstock for polymers industry. In regard to polyurethanes, vegetable oils have the potential to be used as a renewable feedstock for polyols synthesis (main component of polyurethanes). Significant chemical modifications are required for vegetable oils to be used as polyols feedstock. The implementation of WCO is considered as an ideal route to avoid competition with the food industry on edible vegetable oils (Kurańska *et al*., 2020; Orjuela and Clark, 2020; Schmidt, 2020).

Bio-based polyols production from WCO has been reported using a two-step process including epoxidation with peracetic acid followed by ring opening with diethylene glycol. Kurańska *et al*. (2019b) have defined different sustainable pathways for solvent-free epoxidation of WCO for the production of epoxidized oils. They have used both homogeneous and heterogeneous catalysts and achieved a maximum conversion of 81% of WCO. The same research group have extended their findings and proposed an efficient pathway for the conversion of epoxidized oils into bio-polyols using ring opening reactions (Kurańska *et al*., 2019a). They have then utilised the produced bio-polyols for the production of open-cell rigid polyurethane bio-foams (Kurańska *et al*., 2020). Accordingly, the valorization of WCO into polyurethane bio-foams requires three-step processes including conversion of WCO into epoxidized oil, then ring opening reactions are used to produced bio-polyols from the epoxidized oil. Finally, polyurethane bio-foams are synthesised via foaming process of bio-polyols.

Similarly, Dang *et al*. (2016) have proposed a sustainable pathway for the conversion of WCO and Polyethylene terephthalate (PET) bottles into biodiesel and polyurethane bio-foams. As mentioned earlier, polyols are the main reactants for the production of polyurethane bio-foams. In this method, WCO was converted into biodiesel and glycerol using the conventional transesterification reaction. The glycerol was then valorised with the residual PET bottles via glycolysis process for the production of polyols. Finally, the produced polyols were converted into polyurethane bio-foams via foaming process. Srikumlaithong *et al*. (2001) have also produced polyurethane sheets from WCO.

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5.4.4 Bio-Lubricants

The Lubricants market for industrial and automotive applications is growing continuously due to population growth, increasing demand of energy and metropolitan industrialisation. Lubricants are generally derived from petroleum via fractionation of crude oil. In Europe, the annual average consumption of lubricants has exceeded 1.1 million tonnes of petroleum lubricants (Paul *et al*., 2018). The introduction of bio-based lubricants is crucial to decrease the reliance on petroleum products and provide a sustainable greener approach for the lubrication industry.

Bio-based lubricants (bio-lubricants) have recently received great attention from the researchers. Vegetable oils, in general, have very good preferred lubricity properties including high flash point, low volatility and high viscosity. They also show excellent anti-wear and fatigue resistance. However, they have poor low temperature properties, low thermo-oxidation and hydrolytic stabilities. The main reason behind the poor properties of vegetable oils is the existence of unsaturated fatty acids that favour the oxidation reaction for the production of non-favoured peroxides and polar products. Many pathways have been applied to enhance the thermo-oxidative stability via epoxidation of unsaturated chains into oxirane, deoxygenation, transesterification, esterification and selective hydrogenation. Specifically, the epoxidized oils have received high interest due to their improved stability and potential to be used as biolubricants (Lopes *et al*., 2020; Singh *et al*., 2019).

Paul *et al*. (2018) have investigated the application of WCO as bio-lubricant via chemical modification of the fatty acids through epoxidation. Further, Borugadda and Goud (2019) have proposed a novel process for the production of bio-lubricants from WCO. Their novel process includes the epoxidation of WCO, hydroxylation of epoxidized WCO (ring opening) with the aid of alcohol and finally functionalization of anhydride groups into resultant hydroxyl group. They have reported 99.5% conversion of epoxidized WCO into bio-lubricant oil with high lubricity properties.

5.4.5 Surfactants

Surfactants are chemical compounds that reduce the surface tension between phases, either two liquids or liquid/gas and liquid/solids. Surfactants are generally petroleum-based products and usually have sulphonate group, i.e., 4-(5-dodecyl)benzenesulfonatem and perfluorooctanesulfonate (PFOS) (Khalaf *et al*., 2020).

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Recently, renewable surfactants have received great attention as a way to decrease dependency on petroleum products. WCO has been proposed as a sustainable resource for production of surfactants, i.e., methyl ester sulfonate (MES) (Orjuela and Clark, 2020). Permadani *et al*. (2018) have discussed the potential of utilisation of WCO into MES. They mentioned that the process consists of pre-treatment of WCO followed by transesterification to produce methyl esters. Finally, methyl esters are sulphonated with sodium bisulphite ($NaHSO_3$) to produce MES. The authors have reported 77.2% yield of MES that have shown excellent surface activity and potential application as liquid detergent.

Khalaf *et al*. (2020) have synthesised novel gemini-surfactants from WCO for the applications of inhibiting the corrosion of N80-steel. They followed a specified pathway for their process including WCO pretreatment, extraction of fatty acids and esterification of fatty acids. Then, they added $LiAlH_4$ to the esterified fatty acids to produce fatty long chain alcohols including 1-hexadecanol and 1-octadecanol. The produced alcohols reacted with chloroacteic acid to produce 2-chloroacetate. The surfactants were synthesised via the reaction of 2-chloroacetate with N,N,N′,N′-tetramethylethylenediamine (TMEDA) at reaction temperate of 25 °C for 2 days. The produced precipitates were then separated and washed with diethyl ether which is considered as the final targeted surfactants. The produced surfactants have shown an excellent corrosion inhibition performance in comparison with conventional inhibitors of N-80 steel. The developed novel process for valorization of WCO into surfactants has provided a sustainable and economic-viable pathway for the production of bio-based surfactants.

The published research articles on WCO valorization into bio-based surfactants are very limited in the literature, and there is huge room for improvements and innovation in this field in order to limit and decrease the reliance on conventional surfactants and propose a greener approach for the production of bio-based surfactants that have wide applications in the industry.

5.5 Challenges and Future Work

WCO has been proven as a potential feedstock for a variety of biofuels and value-added chemicals. The chosen applications of WCO should be tailored based on the available composition and properties of the feedstock and national need of specific chemicals or biofuels. Additionally, the supply chain has a key role in successful valorization of WCO with

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the sustainability collection processes from households and industries. Further, awareness campaigns are crucial to encourage people not to dispose of the WCO in the drainage. Accordingly, the deployment of specified policies and systems of WCO collection with specified agreement between the collectors and consumers should be considered.

The miscellaneous nature of WCO with a high variability in the composition and properties is another major challenge. Continuous analysis of the WCO prior processing is essential where the physical filtration pre-treatment is most likely required for all valorization processing. Some impurities that can be found in the WCO might have a poisoning effect on the process catalysts, reactant or materials and hence efficient analysis prior to processing is very important.

The market demand is another major issue for WCO valorization. The demand of the targeted products should be studied prior to scaling-up any process into commercial scale. For instance, the production of biodiesel from WCO might not be favoured in countries that are subsidising the price of petroleum diesel as people will definitely choose the lower-price fuels. Finally, global trading has significantly been affected by the recent COVID-19 pandemic and hence influenced the potential profitability of the bio-based product industries. Future work should focus on advancing the potential applications of WCO into green chemicals in addition to the biofuels research. The recent work on production of surfactants, biolubricants and other chemicals from WCO should receive more attention as they are considered as the main profitable products in the near future.

5.6 Conclusion

The large variety of products that could be produced from WCO has made it a very valuable and economic food waste. The integration of the production of biofuels and green chemicals, i.e., surfactants, bio-lubricates, plasticizers and asphalt rejuvenator, from WCO would enhance the sustainability of the processes and will significantly reduce the reliance on petroleum-based products. Further, the application of WCO as a feedstock for biofuels and green chemicals has considerably reduced the competition with food industries on edible vegetable oils. Although the valorization of WCO seems very attractive from the circular economy and environmental point of view, the implementation of commercial-scale processes has faced several challenges. To overcome these challenges, extensive improvements should address the supply chain management for the collection of WCO from households and industries, development of rapid analysis of WCO

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impurities, advancing the conversion/upgradation processes of WCO that will have the ability to operate WCO with different compositions and impurities.

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6

Waste Valorization: Physical, Chemical, and Biological Routes

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Abstract

Rapid urbanization, industrial revolution, booming economies, and improvements in standards of living around the globe have tremendously altered the features of various solid, liquid, and gaseous nature wastes. The intermixing of these types of wastes incorporated with harmful and noxious chemicals with water, air, and soil media accelerate the contamination of these mediums, which is responsible for the ecological imbalance and environmental disturbance. In the 20th century, it was understood that both the chemical and allied industries must adopt greener and more sustainable routes to minimize the generation of unwanted wastes for risk management. To obtain this objective, there is a need to reshape the old-style schemes of the process with a variety of newly invented technical routes including physical, chemical, and biological methods. Valorization is a technical route adopted for the recycling of waste into desirable products having economic worth and which are also non-toxic. Recently, waste valorization has attracted scientists and researchers to find out possible alternatives to avoid the dumping of remainders having zero value by transformation of an extensive range of such remainders

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Nour Shafik El-Gendy (ed.) Sustainable Solutions for Environmental Pollution Volume 1: Waste Management and Value-Added Products, (229–256) © 2021 Scrivener Publishing LLC

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into desired products as well as to prevent secondary pollution spreading. This chapter will emphasize the valorization of different sectors' generated wastes.

***Keywords*:** Valorization, green approach, treatment technologies, wastes, sustainability

6.1 Background

Due to rapid population expansion, various advanced technical routes and scientific innovation pathways are adopted to cope with society's future needs. The advancement in technology becomes a cause to make our world modernize day by day. For example, an intense increase in agriculture, as well as industrialization activities, causes massive solid waste generation and wastewater production. It is stated that ten years ago an overall 0.68 billion tonnes of waste was generated per year and it has been further increasing at a relatively high rate. It is estimated that its value will increase to 2.2 billion tonnes of waste by 2025 (Hoornweg and Bhada-Tata, 2012). The improper disposal of this enormous volume of generated waste results in several environmental- and health-based concerns such as contaminated soil and water resources. Different factors including the prevailing energy crisis, climate change concern, lack of resources and pollution spreading are considered as the fundamental dilemma that will be faced by humankind in the near future. Sustainable development has become an essential need for the survival of humanity around the globe, as suggested by the world's policy makers. Sustainable development is a way of development adopted through which existing resources are utilized in such a manner that current needs of humanity are fulfilled without depletion of these resources for future generations (Brundtland *et al*., 1987). Figure 6.1 depicts the possible adoptable measures for sustainable growth.

It is agreed that both the chemical and allied industries must adapt greener and more sustainable routes to minimize the generation of unwanted wastes for the sake of risk management. Due to stringent policies launched by governments, citizens are required to follow the proper waste disposal routes. For sustainable growth, it is suggested that the adapted waste management routes should be financially affordable, technically viable, socially and legally adaptable as well as environmental friendly in nature, as presented in Figure 6.2.

The term waste protection or waste conservation mainly expresses the precautionary measures to be adopted for the sake of less waste

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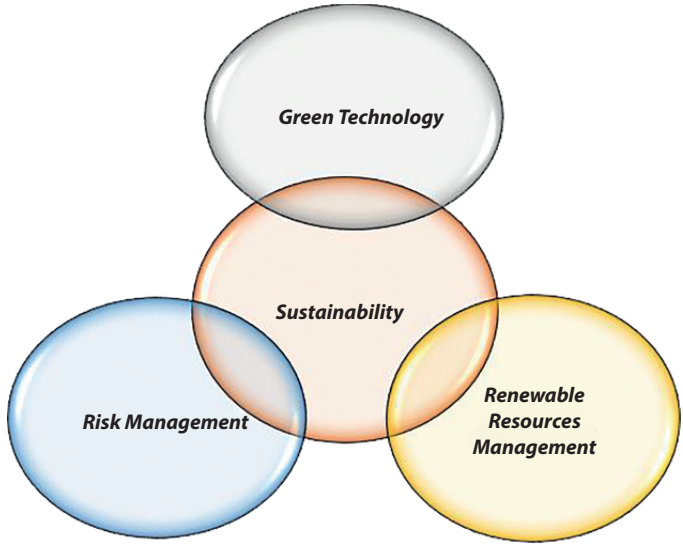

Figure 6.1 Interplay between possible adoptable measures for sustainable growth.

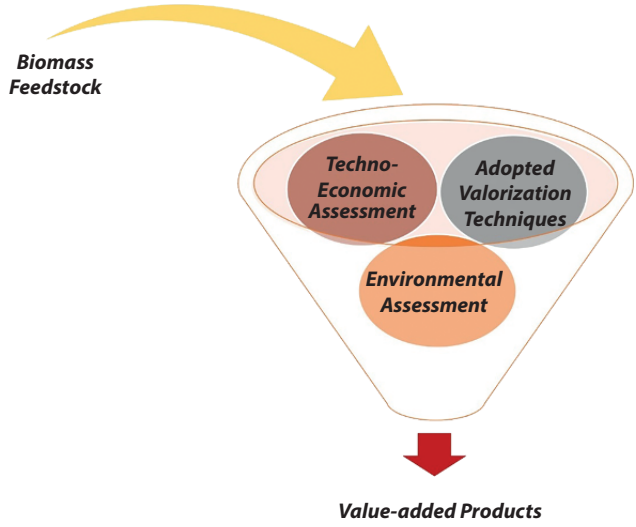

Figure 6.2 Raw biomass to value-added products: A perspective to achieve sustainable development goals.

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generation during process or operation. One can also define it as the potential usage of different available resources in an efficient manner in order to get maximum economic benefits along with an environmental protection guarantee.

Efficacious waste usage is a crucial way for sustainable development in society. Typically, biomass wastes obtained from the agriculture sector have been used as a lower energy resource and sometimes discarded or burned in the agriculture field, which is an improper way to reuse or dispose of biomass, and it also deteriorates the atmospheric environment. However, the recycling of biomass into the forest could provide soil full of nutrition as a result of the decomposition of fallen parts of trees and plants, mainly including leaves and branches parts that provide organic waste, which enhances soil fertility that promotes plants' growth rate and yield. Moreover, Agro-industries generate an abundance of various types of wastes, which are obtained after processing activities as well as waste management routes.

So, it is better to use these low-value biomasses for obtaining the desired products (activated carbon, biochar, hydrochar, electrode, bio-fertilizer, and energy storage materials) after they are subjected to various treatment routes, which can be further used for various environmental applications. This way also follows the 4R's rule of integrated solid waste management, i.e., reduce, reuse, recycle, and recovery of the waste generated, as shown in Figure 6.3. It is endorsed that the products collected using the 4R's rule could be utilized as primary raw material for the manufacturing of other desirable products. This gives us an environmentally friendly way to reduce the generated waste on the one hand but also reduce the burden on solid waste management facility.

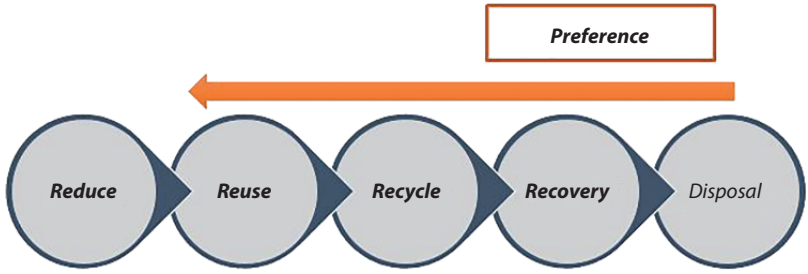

Figure 6.3 Intergrated Solid waste management for waste minimization and proper disposal.

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6.2 Land Biomass vs. Oceanic Biomass

Waste obtained from various sources including wood and forest resources (Puy *et al.*, 2011), crops and food associated industries (Federici *et al.*, 2009; Lin *et al.*, 2013; Pfaltzgraff *et al.*, 2013), sludge and municipality originated (Kang *et al.*, 2010; Sadhukhan *et al.*, 2016), bakery and from other agro-industries routes (Galanakis, 2012) as presented in Figure 6.4 have been employed as raw materials to get the wide range of fuel and chemicals as valuable end products. Besides, oceanic biomass is also another source, which is an abundantly available and easily accessible renewable resource that has been mostly unnoticed and therefore not considered for various potential environmental applications especially valorization of oceanic originated waste biomass for its catalytic performance potential (Lucas *et al.*, 2019).

6.3 Waste Management

What is waste? Anything out of its place is termed as waste. Figure 6.5 represents the global average waste generation (kg/capita/day) from different sectors. Waste management covers the activities and actions needed to manage generated waste from its origination to its final disposal. This process overall covers different phases including collection, transportation, and ultimate disposal of waste. However, waste valorization is a technique

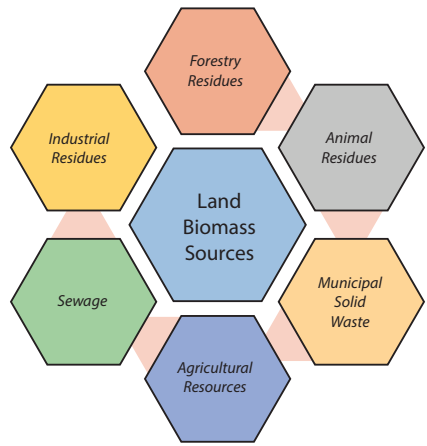

Figure 6.4 Pictorial representation of land-based biomass sources.

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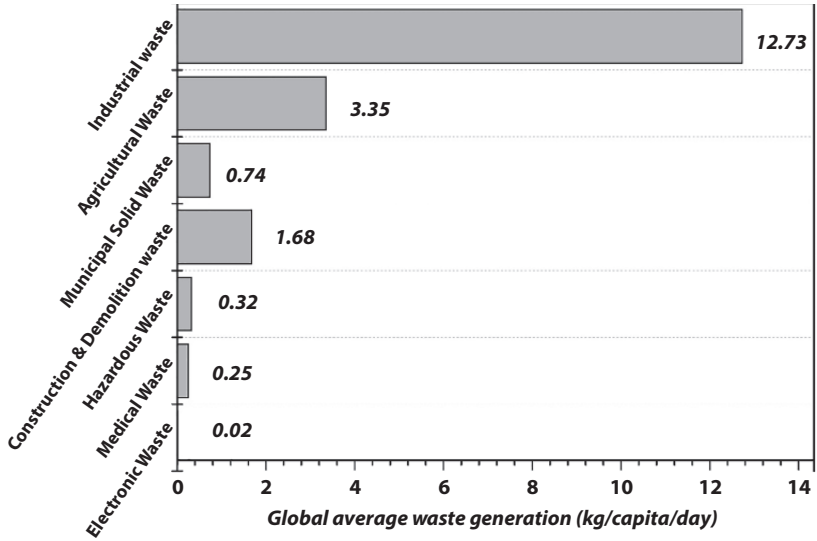

Figure 6.5 Global average waste generation (kg/capita/day), Source: (Kaza *et al*., 2018).

customarily adopted for the modification of waste materials to get the desired properties and functions in targeted or desired products. As shown in Figure 6.6, during waste valorization, waste material is subjected to one or a sequence or combination of various modification routes, including physical, chemical, and biological routes.

6.4 Waste Valorization for Adsorbents Development

Waste generated from various sectors has focused attention on converting it into useful adsorbents having potential for the uptake of a variety of typical environmental pollutants from a different medium (Table 6.1). Adsorption is considered a low-cost wastewater treatment technology, which saves natural resources due to potential use of wastes/raw materials when subjected to various treatment routes including physical, chemical as well as biological treatment to get adsorbent with unique features (Adegoke and Bello, 2015). For example, physical treatment enhances the surface area, which provides additional active sites for the adsorptive uptake of targeted pollutants. AlOthman *et al*. have successfully valorized waste streams into activated carbon with the assistance of the co-pyrolysis technique by using different oil waste to palm stem ratio under different carbonization temperature. The as-obtained optimize adsorbent reflects a

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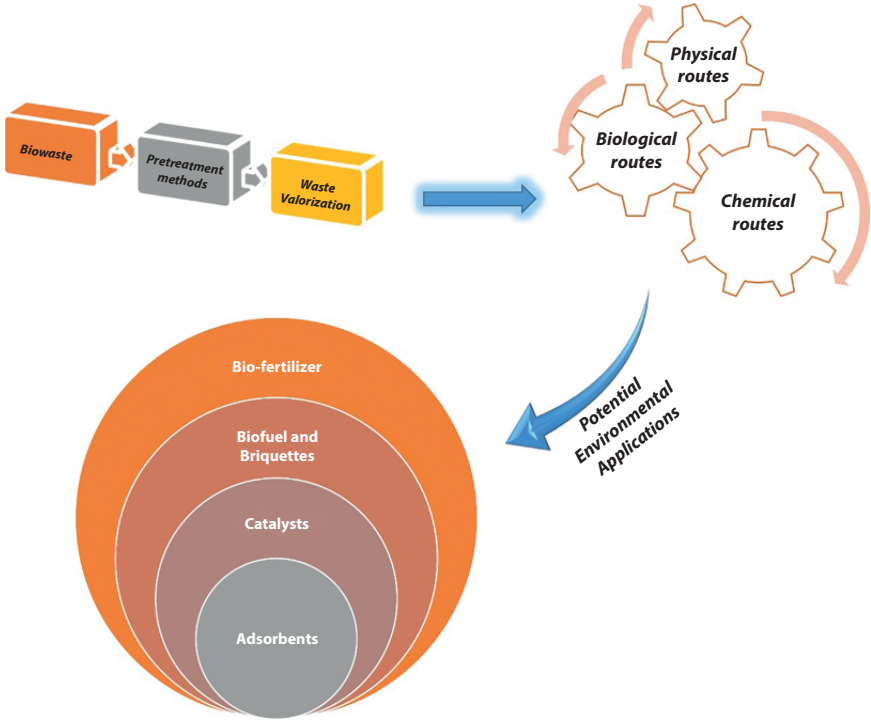

Figure 6.6 Various treatment routes applied for the sake of waste valorization and the potential environmental applications of valorized materials (Value-added Products).

maximum adsorption capacity of 128.89 mg g^{-1} for methylene blue dyes molecules (AlOthman *et al.*, 2014). Moreover, chemical modification results in a change in surface charge which directly correlates with surface chemistry of adsorbents, which is based upon the availability of existing functional groups on their surface that attracts plenty of pollutants covering heavy metals, dyes, organic pollutants, and oxyanions (Faheem *et al.*, 2020a). The phosphorous/magnesium-engineered biochar (P/Mg- engineered biochar) was derived from poultry litter waste through chemical modification route. The as-prepared P/Mg- engineered biochar was tested for the uptake of Cadmium ions (Cd^{2+}). The batch adsorption test revealed that Cd^{2+} was removed as a result of various removal mechanisms including complexation, cation exchange, and precipitation reactions, which endorsed the involvement of various FGs for Cd^{2+}-polluted wastewater streams (Penido *et al.*, 2019).

Besides, biological and bio-accumulative route is another proposed modification route applied to improve the uptake properties of an adsorbent

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Table 6.1 Different treatment routes for adsorbents preparation from waste materials and their potential application.

Biomass type	Biochar production temperature	Chemical reagent	Targeted pollutants	Functional sites	Uptake capacity	References
Corncob	400/N_2/1 h	H_2O_2 DETA[a]	Hg^{2+}	-COOH, NH_2	14.1 mg/g	Faheem *et al.* (2018a)
Corncob	400/N_2/1 h	H_2O_2 DETA	Congo Red dye	-COOH, NH_2	89.3 mg/g	Faheem *et al.* (2019)
Pine tree	550	H_3PO_4	Fluoride	Surface area	885 mg/kg	Guan *et al.* (2015)
Rice husk	450-500	H_2SO_4	Tetracycline	-CO, -COOH, -OH	23.28 mg/g	Liu *et al.* (2012)
Rice straw	550	KOH	Phenol	O-Functional Groups	93.5 mg/g	Yakout (2015)
Rice husk	450-500	CH3OH	Tetracycline	-OH, Ketone moiety	Not available	Jing *et al.* (2014)
Rice straw	550	H_2O_2	Methylene Blue	-COOH, Phenolic	39.3 mg/g	Yakout (2015)
Medicinal residue	80	HCl	Hg^o	Cl^- moieties	279.3 µg/g	Shen *et al.* (2015)
Switch grass	450/20 min	Surfactant (TTAB[b])	Reactive red 195A	Not available	1288.44 mg/g	Greluk and Hubicki (2010)

[a] DETA, Diethylenetriamine.
[b] TTAB, Tetradecyltrimethyl.

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for a variety of targeted contaminants. Biological engineering focuses on biomass degradation through microbes under the oxic and anoxic regime that provides the substrate with a more porous carbon structure due to the involvement of hemicellulose and cellulose limited part only. The as-obtained resultant digested residuals exhibited the higher concentration of anionic nature species including CO_3^{2-} PO_4^{3-} MgO along with cationic consist of Ca, Mg, N, P, K, and S as well as inorganic species depending on the feedstock treated. Bio-accumulation is a way to enhance the desired chemical elements in biomass; the derived enriched biomass can be further transformed into engineered biochar that can be applied for targeted specific contaminants uptake. For example, the growth of tomato plants by irrigating with Hoagland solution enriched with the Mg element provides tomato tissues with plenty of elemental Mg. The resultant Mg-biochar composites exhibited remarkable uptake of phosphate ions from aqueous solution (Yao *et al*., 2013a; Yao *et al*., 2013b). It was deduced that both $Mg(OH)_2$ and MgO nano-size particles served as an active site for adsorption assisted removal of prevailing phosphate ions. Despite these positive results, so far little research work has been carried out in this specific direction that provides biochar having interesting physicochemical properties.

6.5 Waste Valorization for Catalysts Preparations

Utilization of abundantly generated waste streams up to the value of millions to hundreds of millions of tonnes per annum scale has been reported, which is more interesting if the catalysts prepared from them have potential applications in major industrial processes. Waste materials obtained from different sectors have been generating interest as a renewable feedstock for the preparation of catalysts (Faheem *et al*., 2020b; Faheem *et al*., 2018b), fuels (Bridgwater, 2012; Tabatabaei *et al*., 2015), and value-added chemicals (Sheldon, 2014). During the past two decades, the use of agriculture biomass and sewage sludge associated waste materials has become a more popular route for the synthesis of heterogeneous catalysts. The derived catalysts features are mainly based on the properties of waste source applied for this purpose, and therefore catalysts obtained for the specific targeted application comes from a similar group of waste materials. The utilization of waste materials is highly recommended, and it has more advantages when the existing financial and environmental costs are associated with their disposal costs, because these factors overall alleviate or negate the waste material diversion to a targeted valuable catalyst.

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Traditionally, biochars derived from different biomass sources have been commonly applied for carbon sequestration, for improving soil physical properties as well as for enhancement of crop yield purposes (Ferreira *et al*., 2019; Montanarella and Lugato, 2013). Biomass source can also be converted into biochar having catalytic properties after being subjected to various treatment methods. Currently, there is a growing trend concerning the redox properties of biochar for different environmental application perspectives (Yuan *et al*., 2017b). It is suggested that redox properties of biochar are mainly based on the presence of specific functional groups, radicals as well as the availability of redox-active nature of metals including manganese and iron oxide on its surface (Chacón *et al*., 2017; Joseph *et al*., 2015). Zheng *et al*. stated that the biochar obtained through pyrolysis route has exhibited plenty of quinones, hydroquinone moieties as well as conjugated π-electrons clouds domain found in the condensed aromatic structure of biochar (Zhang *et al*., 2019). These active moieties served as redox-active sites due to their unique nature of donating and accepting electrons at the same time. For example, phenolic moieties (C-OH) found on biochar structure have been considered as the main functional group liable for its electron donating properties. In contrast, quinoid moieties (C=O) are identified as the main contributor behind its electron accepting features (Klüpfel *et al*., 2014). It is acknowledged that the reactive oxygen species (ROSs) including $^{\cdot}OH$, $SO_4^{\cdot -}$, $^1O_2$, and $O_2^{\cdot -}$ can be obtained, when the applied biochar is served as an electron donor to the reagent H_2O_2, $S_2O_8^{2-}$ as well as dissolved oxygen, respectively (Fang *et al*., 2015a).

Moreover, for the sake of enhancement of the biochar redox properties, there is a need to manipulate the quantity of these contributing functional groups. Functionalization of biomass-derived carbonaceous materials can be achieved through an oxidation route (Liu *et al*., 2015). After successful oxidation of carbonaceous materials, the evolution of oxygen functional groups tends to follow these steps as depicted in Eq. (6.1) to (6.5):

$$C - C \rightarrow C - OH \tag{6.1}$$

$$C - H \rightarrow C - OH \tag{6.2}$$

$$C - OH \rightarrow C = O \tag{6.3}$$

$$C = O \rightarrow COOH \tag{6.4}$$

$$COOH \rightarrow CO_2 \tag{6.5}$$

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Consequently, it is recommended that the applied oxidation route should be strong enough for the incorporation of new functionalities, but not excessive in nature that becomes a cause to produce redox-inactive –COOH functional groups or even ejected as CO_2.

Besides, persistent free radicals (PFRs) in biochar has its importance due to its long life as compared to other short-lived radicals (Qin *et al*., 2018; Yang *et al*., 2016). The long-life time of biochar-associated PFRs is attributed to the biochar aromatic structure feature, which maintains by resonance phenomenon of the unpaired electrons that become a cause of an increase in their half-life period from few hours to months and some cases, even years (Fang *et al*., 2015a; Liao *et al*., 2014). Radicals' nature including both aryl radicals as well as semiquinoid radicals, ultimately affects the redox properties of biochar. Higher reactivity of PFRs permits them to interact with molecular oxygen, which results in the generation of ROSs, which have been proved to accelerate different reactions rates, such as the mineralization of contaminant in aqueous solution (Fang *et al*., 2014; Fang *et al*., 2015b).

For example, coking residues show potential application to activate persulfate for the sake of catalytic degradation of adsorbed anthracene (ANT). The results demonstrated that PFRs shared electrons to persulfate or/and O_2, which results in the formation of $SO_4^{\cdot -}$, H_2O_2, and $^{\cdot}OH$. The as-obtained ROSs then react with adsorbed ANT that results in its detoxification through complete mineralization and/or oxidation route (Jia *et al*., 2018). Similarly, photochemistry of hydrochar (carbonaceous materials generated from biomass through hydrothermal route) was evaluated, and its potential for the oxidation of sulfadimidine was tested with the assistance of generated ROSs. It was revealed that sulfadimidine degradation rate enhanced by 6 times higher under daylight irradiation than it is monitored in the dark. This was attributed to the presence of abundantly available photoactive oxygen FGs (O-FGs) on hydrochar surface that is the leading cause of the formation of H_2O_2 and $^{\cdot}OH$ due to electron transfer from O-FGs to molecular oxygen (Chen *et al*., 2017).

Moreover, different from the radical-based oxidation route, singlet oxygen and non-radical pathways have been discovered too, which are involved for the oxidation of organic pollutants (Zhou *et al*., 2020). For example, Zhu *et al.* have successfully synthesized low-cost N-doped graphitic biochar (N-BCs) with efficient catalytic properties for peroxydisulfate activation and mineralization of a variety of organic pollutants (Zhu *et al*., 2018). It was monitored that higher annealing temperature biochar sample (at 900 °C) demonstrated a higher degradation rate than the lower annealing temperature sample (at 400 °C). Highly graphitic nanosheet

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moieties and rich structural defects formed on biochar surface especially at higher annealing temperature provide active site for the pre-adsorption of reactants as well as facilitate faster π-electron transfer, which boost up nonradical oxidation of various nature organic pollutants. The doping of quaternary N leads to an asymmetric spin density as well as it becomes a cause of the prevailing low electron density to the adjoining carbons, which promote the chemical bonding with negative-potential oxygen atom found in peroxide O-O bond of PDS.

Besides, the commonly found inherent inorganic fraction of biochar such as Fe and Mn redox active metals might also contribute to catalytic reaction both as electron donors and acceptors depending upon the oxidation states/speciation of prevailing redox active metals (Dieguez-Alonso *et al*., 2019; Risch *et al*., 2017; Sander *et al*., 2015). Despite redox-active metals found in biochar as a minute fraction, there are plenty of examples found in literature, which affirm the improvement in some of its properties through preloading the biomass before and after pyrolysis technique applied (Chen *et al*., 2011; Faheem *et al*., 2016; Wang *et al*., 2015).

6.6 Bio-Based Waste Valorization for Bio-Fuel and Bio-Fertilizer Production

There are plenty of treatment technologies available to handle biowaste. These technologies have the potential to convert biowaste into value-added chemicals, bio-fertilizer, and energy fuels (Matsakas *et al*., 2017). For example, recently, the concept of biowaste-based bio-refineries has gained attention because of a promising route for the processing of agriculture and food sectors' generated waste streams. Besides, biological treatment routes have exciting features, such as, there is no need for energy acquired from an external source, and the treatment process mainly depends on the energy produced during the process. However, the incorporation of co-processing materials, as well as the adjustment in processing parameters, could enhance the potency of these treatment techniques (Majbar *et al*., 2018).

6.6.1 Biomass Briquetting: (Bio-Fuel)

Plenty of biomass is generated from the agriculture sector and it is available in various forms, including straw, husk, and stalks of different varieties of numerous crops. Typically, these biomasses have been used as a lower energy resource and sometimes discarded or burned in the agriculture

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Figure 6.7 Different stages from biomass to briquette production.

field, which is an improper way to reuse or dispose of biomass, and it also deteriorates the atmospheric environment. Biomass is ranked as the third-largest energy resource around the globe out of all energy sources. There is a way to convert this biowaste into high-density briquettes for energy purposes. The overall process of briquetting has different stages as presented in Figure 6.7. Through the densification route, the biomass can convert it to briquette, which is a better alternative renewable energy source than fossil fuels (Kpalo *et al.*, 2020). Biomass briquettes are considered as the best value-added product, which generates energy from biomass for household heating. However, the heterogeneous nature of biomass limits its utility for energy purposes and restricts the energy conversion process to specific biomass. Moreover, the term composite-briquettes is commonly used, when different materials having different properties are blended to tackle the strengths and weakness issues of the developed briquettes (Heschel *et al.*, 1999; Huko *et al.*, 2015; Muazu and Stegemann, 2015).

6.6.2 Composting: (Bio-Fertilizer)

The controllable disruption of solid organic matters under aerobic environment with the assistance of microorganisms including bacteria, yeasts,

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and fungi, which results in reduction of the volume as well as moisture content of solid organic matters, while producing fertile humus, CO_2, water, and heat is termed as composting (Wang *et al*., 2016a; Wang *et al*., 2016b).

The humus is enriched by plant nutrients (N, P, and K) and minerals (Ca and Mg) fraction. The application of humus derived from composting route to agriculture fields remarkably enhance soil fertility, improve crop production yield, soil pH, as well as organic carbon fraction (Qian *et al*., 2014). The degree of stabilization, sanitization, and humification is dependent on the biological activities, physiochemical features of raw feedstock applied as well as the operating procedure for composting purposes (Li *et al*., 2013; Mustafa *et al*., 2017).

The overall composting process consists of different phases, including mesophilic, thermophilic, and curing phase (Partanen *et al*., 2010). Microbial activity got started during the mesophilic stage that results in the consumption of easily degradable compounds, usually starch, fats, sugars, and proteins. The temperature rose to 45°C during mesophilic phase. After that, the thermophilic stage prevails; during this phase, the pathogen destruction occurred due to rise in temperature up to 55°C. Besides, organic matter degradation and particle size reduction happened too. Also, seed destruction, as well as Fly-larvae killing, was achieved because of a rise in temperature up to 65°C. Finally, compost enriched with minerals and nutrients fraction was obtained, which is applied as an organic fertilizer to soil (Luo *et al*., 2013).

Recently, various attempts have been made to improve compost performance by adjusting composting parameters. Recent findings have further endorsed this technique to make it commercially feasible and even more attractive for various sector generated biomass valorization purposes. Some of the adopted key approaches are a) enhancing rate of aeration (Chowdhury *et al*., 2014b; Jiang *et al*., 2015b), b) incorporation of mineral additives and chemical agents (Jiang *et al*., 2015a), c) use of various types of bulk agents (Chowdhury *et al*., 2014a), d) through various co-composting routes with various add-ons (Awasthi *et al*., 2016; Zhang and Sun, 2017), and e) bacterial inoculation (Xie *et al*., 2017).

For example, higher temperature during composting accelerates the degradation of seaweeds and pathogens as well as hastens the efficacy of organic matter decomposition (Wang *et al*., 2016b). However, to maintain high temperature is a difficult task; it can be achieved through the addition of various chemicals, bulking (Yuan *et al*., 2017a), and microbial (Xie *et al*., 2017) amendments such as polyethylene glycol, jaggery, sawdust, wood peat, medical stone, biochar, Ca-bentonite, *Bacillus altitudinis*,

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and *Streptomyces albus* amendments. These amendments not only raise the temperature but also enhance organic matter degradation efficiency.

For the sake of optimal performance, it is suggested that compost porosity should be between 35-50%. In case, porosity > 50% becomes a cause of heat loss due to increase in air flow rate that results in decrease in temperature of the pile. On the other hand, lower porosity promotes the release of greenhouse gases due to prevailing anaerobic condition. Furthermore, composting process efficiency is also closely dependent on moisture content level (MCL) of initial feedstock. Generally, for solid organic matters, MCL range from 50-60% during the composting process (Guo *et al*., 2012). However, organic wastes, including animal dung, antibiotic residues, and olive waste require relatively higher MCL of about 80-90%. It is monitored that higher MCL become a cause of obstruction in oxygen diffusion in pile which accelerate anaerobic fermentation activity, while lower MCL during composting process suppresses the growth of microorganisms involved (Qian *et al*., 2016). Commonly, various kinds of bulk agent are applied to regulate the suitable MCL before the start of the composting process. In addition, the MCL can also be controlled with the assistance of aeration rate and frequency of turning piles (Petric *et al*., 2012).

Furthermore, there is a need for optimization of another factor, i.e., C/N ratio. Generally, for composting process C/N ratio of 25-30 is considered as acceptable. In cases when C/N ratio becomes higher than 35, prevailing microbes community passed through multiple life cycle processes with the main aim of oxidation of excess carbon to attain an acceptable value of C/N ratio (Petric *et al*., 2015). Hence, it becomes a cause to extend the composting process, which is the main reason behind the lowering of maximum composting temperature. For the scenario, when C/V ratio is meager, it provides the message about the release of nitrogen from compost in the form of NH_3 that is the main cause behind the deterioration of the quality of targeted compost (Li *et al*., 2015). It has been stated that suitable C/N ratio assists in decline of NH_3 and greenhouse gases into the atmosphere, as well as suppresses bioavailability of heavy metals in metal polluted soil (Liang *et al*., 2017; Wu *et al*., 2017; Yang *et al*., 2015).

6.6.3 Anaerobic Digestion: (Bio-Fuel)

Anaerobic digestion is a route consisting of sequences of biological processes through which microorganisms break down organic matter and biodegradable material such as animal or food waste in the absence of O_2. This process is commonly applied for industrial as well as domestic purposes to control the generated waste or to obtain biogas or fuel as a product. Overall,

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anaerobic digestion is considered as green and as a potential alternate solution for the eradication of toxic waste and to get bio-energy (Ashraf and Faheem, 2020; Bedoić *et al*., 2019). There are several steps, including acidogenesis, hydrolysis, methanogenesis, and acetogenesis involved during anaerobic digestion system in reactors to produce biogas from biomass (Mao *et al*., 2015). In addition, based on the partition of the digestion process into various steps, the anaerobic digestion system is categorized into single-, two-, and three-stage digestion systems. The parameters like temperature, pH, and nutrients are termed as growth parameters because they affect the living condition of anaerobes, which is a driving force for the digestion of biomass. However, operating parameters including loading rate and detention time are selected on behalf of the type of reactor as well as growth parameters.

6.7 Biochemical Mechanism Involved in Anaerobic Digestion System

The anaerobic digestion process mainly consists of several bio-metabolism steps; the details of each one are given below.

6.7.1 Hydrolysis

Hydrolysis is the first step of anaerobic digestion process in which water is utilized to break down the bond of high molecular weight components into small organic component parts (i.e., polymers into monomers) including glucose, fatty acid, and amino acid by the assistance of special enzyme. Although hydrolytic microbes have a unique feature of resistance even at higher pH values, pH 6-8 is considered as the optimum pH value for hydrolysis (Trzcinski and David, 2017). As hydrolysis is a rate-limiting step, so different pre-treatment routes including physical, chemical, and biological routes, are adopted to overcome this aspect (Ariunbaatar *et al*., 2014).

6.7.2 Acidogenesis

Acidogenesis is the second step of anaerobic digestion process, which is carried out through the help of acidogenic bacteria that can grow faster with a typically minimum replicating rate of about 30 min (Ramos-Suárez *et al*., 2015). It is a biological reaction in which monomers are further transformed into volatile fatty acids. It is recommended that the optimum pH range of 5.5-6.5 is proper for acidogenic reaction (Mao *et al*., 2015).

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6.7.3 Acetogenesis

Acetogenesis is the third stage in the four stages of anaerobic digestion process. It is the conversion of volatile fatty acids into H_2, CO_2, and acetic acid through biological reaction. Acetogenesis is relatively slower than acidogenesis reaction, and it requires almost double the time, ranging from 1.5 to 5 days with maximum performance under weakly acidic environment (Ramos-Suárez *et al*., 2015).

6.7.4 Methanogenesis

It is the last step of four stages of anaerobic digestion process in which acetotrophic bacteria assist in the fermentation of acetic acid to get the final targeted product methane gas along with CO_2 as a byproduct of the reaction. It is suggested that for methanogens, the optimum performance achieved at pH 7.0-7.2 (Mao *et al*., 2015).

6.8 Challenges and Recent Advances in Anaerobic Digestion

Besides the potential opportunity of using organic biowaste through anaerobic digestion route, this route also has few limitations like low efficiency in term of biogas production, inferior fermentation stability, and suppression of process as a result of intermediary accumulation (Tufaner and Avşar, 2016). Anaerobic digestion process efficacy is dependent on the quality and nature of biowaste substrate applied. For example, heterogeneous nature waste such as organic portion of municipal solid waste has features like high solid content, bigger particle size, and fractious woody parts take more time for their degradation, which is particularly challenging. Moreover, polluted biowaste fraction suppresses the anaerobic digestion process and the as-obtained digestate quality is unacceptable for its application as compost or landfill purpose (Wilson *et al*., 2015). This is attributed to the drop in microbial activity by toxic metabolic intermediates. As a result, these intermediates got accumulated that hinders methane gas produced during anaerobic digestion process. This becomes a cause of increase in NH_3 and volatile fatty acids concentration, which results in a drop of pH levels (Wu *et al*., 2016). These unwanted things disturb the stability as well as the progress of anaerobic digestion setup working. The application of as-obtained contaminated digestate to farmlands accelerate nutrients loss both via volatilization route to atmosphere and leaching to

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adjacent water bodies—these unwanted activities overall result in ecosystem deterioration (Jiang *et al*., 2020).

There are many potential routes available for the remediation of the inhibitory effect of substrate-induced stability on the anaerobic digestion performance. For instance, substrate inhibitory effect can be reduced by adopting co-digestion approach or through microbial adaptation mode. The co-digestion approach has the dual benefit of reduction in inhibition as well as an increase in microbial biodiversity that promote anaerobic digestion activity (Wang *et al*., 2018). However, the selection of co-digestate must be made by taking these parameters into account: a) to avoid changing into hydraulic retention time, organic matter composition should be matched with that of biomass feedstock, b) readily biodegradable with ability to produce biogas, c) have sufficient nutrients, d) with no harmful compounds, e) easy, inexpensive, and local supply and f) easy to control in a reactor.

Two-stage anaerobic systems have been considered as the best approach that boosts the growth of both acidogenic and methanogenic microbes and also controls the optimum pH value, which facilitates all the targeted reactions both oxidation and reduction reactions happened in the anaerobic digestion system (Wu *et al*., 2016). However, single-stage anaerobic digestion system has its own worth due to its robust and stable features along with less production of wastewater. Moreover, small size reactors single-stage systems provide multiple benefits of easy, smooth economical feasible operation (Angelonidi and Smith, 2015).

6.9 Bio-Based Waste and Bioeconomy Perspective

Recently, sustainable development has gained attention at national and international levels. The concept of sustainable development refers to sustainable production and its consumption without compromising the potential for future generations to fulfil their own needs. The bioeconomy is a new model for industry and economy, which is referred to as knowledge-based production and utilization of biological resources to supply products (food, energy), processes as well as services in different economic sectors under the main objective of sustainable economic growth. Bioeconomy aims to shift the usage of fossil resources/non-renewable resources by renewable resources. Basically, the bioeconomy involves the conversion of biogenic waste materials into value-added products when subjected to many coordinated process steps by adopting

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various potential routes such as biorefineries and thermochemical treatments (Usmani *et al.*, 2020).

Besides bioeconomy, there are several other related terms, including green economy, circular economy, and bio-based economy. The green economy is generally taken as an umbrella concept, which covers bioeconomy, bio-based economy, and circular economy. The objective of a green economy is to improve human well-being as well as social equity without environmental deterioration and ecosystem disturbance. However, the bioeconomy is obliged as a component of green economy. Moreover, bio-based economy is taken as a component of bioeconomy, which deals with the transformation of biological resources into value-added products. The interplay of green economy, circular economy, and bioeconomy has been presented in Figure 6.8. In contrast to the linear-based economic model, which follows a "take-make-utilize-dispose of" pattern, the circular economy has a different perspective where materials and final products exhibit a higher level of recycling and reduction ability (Buongiorno, 2018). Besides, the shift of non-renewable resources with renewable bio-based resources is also a key part of the circular economy. Therefore, it is the necessity of the current age to adopt various potential treatment routes including physical, chemical, biological, and the combination of these treatment ways for the valorization of biowaste originated from multiple sources to get the targeted value-added products, which contributed to bioeconomy through different aspects. It will also reduce the load on solid waste management facility as well as it will reduce collection, transportation and segregation cost.

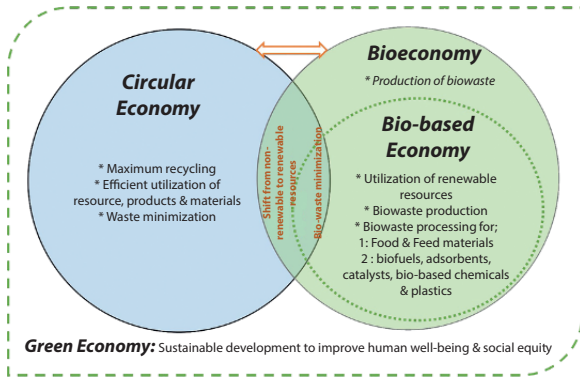

Figure 6.8 The Interplay of green economy, circular economy, and bioeconomy.

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6.10 Conclusion

The use of biogenic waste material has gained attention due to its low cost and locally available features for the sake of sustainable growth and economic development. It has been concluded that biowaste valorization can be done to get the targeted products when subjected to various treatment processes. From the last few decades, it has been observed that technological improvement for biowaste valorization has been able to obtain a variety of value-added products including adsorbents, catalysts, compost digestate, biofuels, energy materials, etc., that have tremendously contributed to the circular economy. Waste valorization techniques provide opportunities to extend bio-based industrial set up to obtain bio-based value-added products/chemicals and to utilize available renewable resources in a more effective and eco-friendly manner. Recently carried out studies have affirmed the effectiveness of the biorefinery process to improve the yield of value-added products.

Moreover, there is still a need to scale-up the techniques to process biogenic waste materials from bench scale to full-scale systems.

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7

Electrocoagulation Process in the Treatment of Landfill Leachate

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Abstract

The rapid fiscal growth of any nation has caused an increase in population, urbanization, and industrialization, thus leading to high generation of Municipal Solid Waste (MSW). Due to its complex properties and composition, MSW often produces a by-product known as leachate, high-strength wastewater which may become a major contribution to water pollution if not properly tended. Optimizing the treatment of landfill leachate to minimize its adverse impacts on the natural ecosystem is an urgent concern. Over the last decades, sophisticated technological innovations in landfill leachate treatment have gained increasing attention. Recently, advanced oxidation processes in leachate treatment such as the electrocoagulation (EC) method have been receiving much focus due to their outstanding ability in eliminating pollutants, economic viability, and green approaches. Therefore, this chapter presents an overview of the basic characteristics of landfill leachate and the promising electrocoagulation process in decontaminating leachate pollution. Reviews on the fundamentals and mechanism of an electrocoagulation process, including its history and theory as well as its benefits and drawbacks, are updated with a focus on landfill leachate treatment. The influences of the treatment process variables toward its performance efficiency, including the need for electrolyte, are discussed and critically analysed. A case study on the application of the EC method in treating local landfill leachate is reviewed.

***Keywords*:** Electrocoagulation, municipal solid waste, landfill, leachate, electrolyte

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Nour Shafik El-Gendy (ed.) Sustainable Solutions for Environmental Pollution Volume 1: Waste Management and Value-Added Products, (257–304) © 2021 Scrivener Publishing LLC

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7.1 Introduction

The elevated generation of municipal solid waste (MSW) throughout the globe in view of the advancing inhabitancy in urban areas has developed an extensive measure to its management (Hannan *et al*., 2015; Bong *et al*., 2017). As of now, several reliable approaches are available in the management of MSW. These include landfilling, framing, open disposal, shredding, incineration, compaction, recycling, waste reduction, and anaerobic digestion (Aziz *et al*., 2010). Most countries are practicing the landfilling method in managing bulk MSW owing to its relatively inexpensive and unsophisticated process. In addition, this method allows a complete decomposition of MSW into unreactive and stable substances in the long run (Aziz *et al*., 2018). Despite its great benefits, the landfilling technique is, however, being replaced with other secure methods at present. This is attributable to the critical environmental issue arising from the immense release of concentrated wastewater or landfill leachate, wherein its treatment is complex (Aziz and Sobri, 2015). According to Peng (2017), landfill leachate is a toxic fluid generated from the percolation of water and natural humidity through waste piles, thus stimulating the biological decomposition of organic matter. Landfill leachate exhibits variable contents of chemical and microbiological compounds due to several parameters such as the type of waste, waste disposal method, landfill age, disposal location, and the change in the degradation process (Moravia *et al*., 2013; Mata-Alvarez, 2015; Zainal and Aziz, 2017).

Landfill leachate is often recognized by its dark colouration and distinctive odour. The composition of this liquid is rather intricate with a diverse mix of toxic compounds originated from four major groups of organic matter, inorganic substances, heavy metals, and xenobiotic organics (Liu *et al*., 2015; Ghosh *et al*., 2017). In addition to its colour and odour characteristics, the identification of landfill leachate is also carried out based on its pH, suspended solids (SS), turbidity, dissolved oxygen (DO), total dissolved solids (TDS), chemical oxygen demands (COD), biological oxygen demands (BOD), biodegradability ratio (BOD_5/COD), and contents of sulfate (SO_4^{-2}), phosphorus (P), ammoniacal nitrogen (NH_3-N), and Total Kjeldahl Nitrogen (TKN) (Saleem *et al*., 2017). Improper treatment of landfill leachate and its discharge into open water sources may negatively impact the aquatic organisms due to their toxic substance content. Therefore, effective approaches have to be considered in treating this harmful liquid to fulfil the recommended discharge specifications prior to its release. However, the available treatment processes are found to be

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incompetent and less effective in treating landfill leachate as a result of its complex and erratic compositions. To date, several treatment methods are available in addressing the management of water and wastewater through biological and chemical processes, oxidation, nanofiltration, and adsorption.

Nevertheless, researchers all around the world have recently become intrigued by leachate treatments using the electrochemical approach in place of the processes mentioned earlier. These electrical-based techniques such as electrooxidation (EO), electrodeposition (ED), electroflotation (EF), and electrocoagulation (EC) have been gaining recognition particularly in the treatment of wastewater of different types owing to their simple operation and moderate dependency on chemical usage (Barrera-Díaz *et al*., 2012). In comparison to all the electrochemical methods, the EC treatment demonstrates the most promising technique of contaminants elimination in different types of water and wastewater such as groundwater, urban sewage and wastewater, as well as effluents from fabric manufacturing, slaughterhouses, and tanneries. Moreover, according to several prior studies conducted by Dia *et al*. (2017), Kasmuri *et al*. (2018), Bharath *et al*. (2019), and Hamid *et al*. (2020), the EC method is equally excellent for landfill leachate treatment. In view of this, the fundamentals and mechanism of the electrocoagulation method in the treatment of landfill leachate are extensively reviewed and emphasized throughout this chapter.

7.2 Decomposition of Solid Waste

The disposed of solid materials in sanitary landfills generally undergo decomposition under three major means of physical, chemical, and biological accordingly (Kamaruddin *et al*., 2017). The varying traits of solid waste are the key parameter to the progression in waste decomposition. In physical decomposition, solid waste undertakes two primary processes of separation and mechanical size reduction. Meanwhile, a set of processes, including gasification, pyrolysis, and combustion is involved in the chemical decomposition of solid waste. Among all decomposition types, the biological mean represents the most crucial stage in the waste decomposition process in general. Harmful and immensely lethal liquid (leachate) and gas (methane) substances are commonly produced via gasification and solubilization phases, respectively, where solid wastes are biologically decomposed through aerobic and anaerobic digestions (Pawłowska, 2014). These digestions are carried out by microorganisms which often

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originated from decomposed solid waste, vegetation or soil cover, treated slurry, as well as recycled landfill liquid. Various harmful pollutants, for instance, NH_3-N and carbon dioxide (CO_2) are promoted by these microorganisms during solubilization phase. Consequently, leachate of a higher degree of BOD and lower pH is produced. Similarly during gasification phase, organic acid gases are released thus reducing the degree of BOD as well as pH (Matsufuji, 2007). In the following Figure 7.1, the components of water balance that are commonly encompassed in a landfill site are

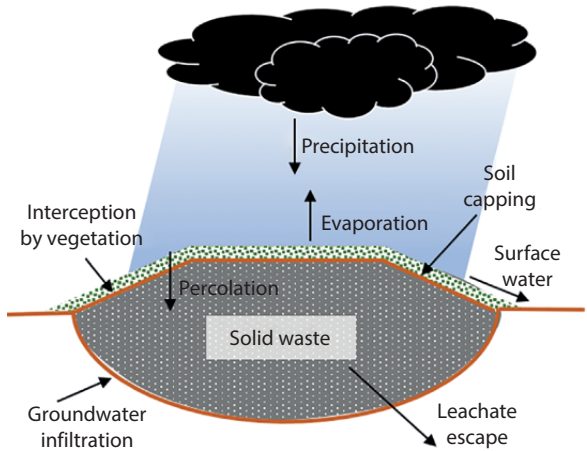

Figure 7.1 Schematic diagram of water balance components within a landfill site.

Table 7.1 The constituents of landfill leachate in different waste biodegradation phases. Adopted from Worrell and Vesilind (2012).

No.	Constituent	Biodegradation phase			
		Transition	Acid formation	Methane fermentation	Maturation
1	BOD_5 (mg/L)	–	4000 - 40000	20 - 550	–
2	COD (mg/L)	480 - 18000	1500 – 71000	580 - 9760	31-900
3	Ammonia (mg/L)	120 - 125	2 - 1030	6 - 430	6 – 430
4	Conductivity (µS/cm)	2450 - 3310	1600 - 17100	2900 - 7700	1400 – 4500

(*Continued*)

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Table 7.1 The constituents of landfill leachate in different waste biodegradation phases. Adopted from Worrell and Vesilind (2012). (*Continued*)

No.	Constituent	Biodegradation phase			
		Transition	Acid formation	Methane fermentation	Maturation
5	pH	6.7	4.7 – 7.7	6.3 – 9.0	7.1 – 9.0
6	Acetic acid (mg/L)	100 - 3000	3000 - 18800	250 - 4000	0
7	BOD_5/COD ratio	> 0.5	0.58	0.06	< 0.1
8	Chloride		2120		
9	Zinc	–	0.1 - 120	0.03 - 4	–
10	Sodium	–	1340	–	–
11	Chromium		0.28	–	–
12	Lead	–	0.09	–	–
13	Copper	–	0.065	–	–
14	Cobalt	–	0.05	–	–
15	Nickel		0.17	–	–
16	Sulphate	–	70 - 1750	10 - 420	–
17	Calcium	–	10 - 2500	20 - 600	–
18	Magnesium	–	50 -1150	40 – 350	–
19	Manganese	–	0.3 - 65	0.03 - 45	–
20	Potassium	–	1085	–	–
21	Phosphorus	–	6	–	–
22	Iron	–	20 - 2100	3 - 280	–
23	Cadmium	–	0.005	–	

comprehensively illustrated. Nonetheless, leachate production in landfills is ultimately complex, as it relies on the inconsistent characteristics of solid waste as well as the surrounding condition of the disposal site.

In another report by Worrell and Vesilind (2012), the biodegradation of solid waste involves four consecutive and discrete phases of transition,

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acid formation, fermentation of methane, and finally maturation. Table 7.1 classifies the constituents present in landfill leachate with reference to the biodegradation phases. This identification is beneficial in investigating the degree of waste stabilization, improving the treatment process of landfill leachate, as well as environmental monitoring (Matsufuji, 2007; Worrell and Vesilind, 2012).

7.3 Landfill Leachate Properties

As previously mentioned, several types of compound are present in landfill leachate as a result of different solid waste disposal in landfills. These compounds include organic matter, inorganic substances, heavy metals, and xenobiotic organics (Zolfaghari *et al*., 2016; Ghosh *et al*., 2017). In view of this, the strength of leachate is extremely dependent on the association among these substances (Garaj-Vrhovac *et al*., 2013). Extensive information on the major substance classes making up landfill leachate is discussed in the upcoming sub-sections.

7.3.1 Organic Matter

Organic matter acts a key substance for the biochemical activities in waste disposal sites and is often associated readily with other organic and inorganic pollutants present in landfill leachate (Bilgili *et al*., 2008; Liu *et al*., 2015). Waterborne microorganisms tend to secure their survival and reproductivity through organic matter decomposition by means of oxidation or digestion. This condition consequently depletes the dissolved oxygen in water and threatens the lives of other aquatic organisms. Several parameters, such as BOD, COD, and total organic carbon (TOC) are considered in the evaluation of organic matter content in landfill leachate. Besides, the characteristics of landfill leachate are determined based on the parameters of BOD and COD, wherein the oxygen demands by microorganisms and chemical agents, respectively, in liquid are assessed. Aziz and Ramli (2017), in their study, mentioned that the classification of landfill leachate is made according to its biodegradability ratio (BOD_5/COD). The ratio ranges of greater than 0.5, 0.1 to 0.5, and less than 0.1 represent young, intermediate, and matured or stabilized landfill leachate, respectively. Information of leachate class is extremely critical, particularly in determining the most appropriate and effective system for treating leachate (Mojiri *et al*., 2014). On top of that, organic matter is also associated with complex humic substance (HS) macromolecules. In landfill sites, the excessive presence of

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living organisms such as flora and fauna, microorganisms, and pesticides promotes the generation of HS (Bhatnagar and Sillanpää, 2017). Humic acid (HA) and fulvic acid (FA) are the two major classes of HS. In terms of solubility, HA is only soluble in alkaline medium, whereas FA is capable of solubilizing in any conditions of pH (Schellekens *et al*., 2017). In another study by Wu *et al*. (2010) and Oulego *et al*. (2016), the physical appearance of leachate (colour) is related to the concentration of HS, where darker coloured leachate is associated with higher HS content. Moreover, the organic matter content and the degree of contamination could be determined from the colour appearance of landfill leachate (Aziz and Ramli, 2018).

7.3.2 Inorganic Substances

Cationic (calcium (Ca^{2+}), magnesium (Mg^{2+}), ammonium (NH^{4+}), potassium (K^{+}), sodium (Na^{+})) and anionic (hydrogen carbonate (HCO^{3-}), sulphate (SO_4^{2-}), nitrite (NO^{2-}), nitrate (NO^{3-}) and chloride (Cl^{-})) compositions are the common major contributors of inorganic compounds within landfill leachate (Puvvadi and Thallak, 2014; Adhikari, 2015). In the methanogenic process of solid waste, the elevation in pH gives rise to various complexes formation. Moreover, the biological reactions taking place cause depletion in the concentrations of anions and cations in the leachate over time. Inorganic nitrogen by-products, including nitrogen dioxide (NO^{2-}), ammoniacal-nitrogen (NH_3-N), and nitrate (NO^{3}) are generated as a result of nitrogen-based compounds and protein decomposition in leachate. These by-products are extremely toxic and harmful to the environment and are often found in abundance in mature landfill leachate as primary contaminants (Aziz *et al*., 2016; Ghosh *et al*., 2017). It was reported that excessive amounts of NH_3-N in water or wastewater could necessitate eutrophication and thus depleting the content of dissolved oxygen (Huang *et al*., 2014).

7.3.3 Heavy Metals

The disposal of wastes originated from various sources such as mines, incinerators, and industrial sites, as well as toxic materials (e.g., power cells, dyes, etc.) in landfills has caused the generation of heavy metals in leachate (Kanmani and Gandhimathi, 2013). In reference to several studies conducted by Shehzad *et al*. (2015), Naveen *et al*. (2017), and Moody and Townsend (2017), the major possible metallic elements to exist in water and wastewater in order to be classified contaminated and toxic are

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nickel (Ni), manganese (Mn), cadmium (Cd), iron (Fe), zinc (Zn), chromium (Cr), and lead (Pb). In an acidic environment, particularly in the course of the acetogenic stage, heavy metals (e.g., Mg, Mn, Cd, and Fe) are presented in abundance in leachate due to the advanced solubility of these elements in this condition. In contrast, the solubility of heavy metals in landfill leachate is unfavourable during the methanogenic decomposition stage thus yielding minimal content of heavy metals. Therefore, pH condition plays a critical role in determining the formation and dissemination of heavy metals in landfill leachate (Xie *et al*., 2015). Heavy metal pollution on earth is commonly caused by unethical human activities with the discharge of untreated leachate into the environment being one of the primary contributors. This consequently contaminates the environment, particularly open water sources and endangers the aquatic lives. However, Kamaruddin *et al*. (2017) in their study revealed the inverse relationship between heavy metals content in leachate and the age of landfill, wherein the content of heavy metals is relatively high in young leachate. This is in opposition to the contents of organic and inorganic substances in landfill leachate.

7.3.4 Xenobiotic Organics

According to Adhikari (2015), the presence of xenobiotic organics (XO) in landfill leachate is rather low (< 1 mg/L) and they are commonly derived from chemical wastes of suburban areas and industrial sites. Polngam *et al*. (2015), in their analysis of leachate from Lamchabang landfill in Thailand, disclosed at least 20 different types of XO that were present in the landfill liquid. There are a few aspects influencing the diversity in the compositions of XO, including the type of solid waste, the technique of landfilling, and landfill age (Adhikari, 2015). Among all XO substances, the halogenated hydrocarbons (trichloroethylene and tetrachloroethylene) and monoaromatic hydrocarbons (benzene, ethylbenzene, toluene, and xylenes) are the most typical types found in landfill leachate (Kale *et al*., 2010). Since these dual XO compounds inflict the most detrimental effects on the environment, extensive measures have been taken in their assessment. On top of that, despite the diverse and complicated compositions of landfill leachate, a very straightforward analysis is required for the XO evaluation (Adhikari, 2015).

7.4 Characteristics of Landfill Leachate

The characteristics of landfill leachate are determined based on various criteria in accordance with the variable landfilling phases with respect to

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time. Table 7.2 provides a summary of the parameters involved in leachate properties characterization. Leachate can be categorized as young (acidic phase), intermediate (medium phase), or stabilized (methanogenic phase) depending on the age of the landfill (Zhang *et al.*, 2016). For young leachate, it is commonly distinguished by its immense COD content (> 10000 mg/L) and a high ratio of biodegradability (BOD_5/COD) of exceeding 0.5. As a result, biological treatment is mostly preferred in remediating young landfill leachate.

Table 7.2 Characteristics of landfill leachate in different phases. Adopted from (Tchobanoglous and Kreith, 2002; Foo and Hameed, 2009; Deng, 2009; Li *et al.*, 2010).

No.	Parameter	Unit	Landfill leachate		
			Young	**Intermediate**	**Stabilized**
1	Landfilling phase	-	Acidic	Medium	Methanogenic
2	Age	years	< 2	2 - 10	> 10
3	pH	-	< 6.5	6.5 - 7.5	> 7.5
4	NH_3-N	mg/L	< 400	-	> 400
5	BOD_5	mg/L	2000 - 30000	-	100 - 200
6	COD	mg/L	> 10000	4000 - 10000	< 4000
7	TOC	mg/L	1500 - 20000	-	80 - 160
8	BOD_5/COD	-	> 0.5	0.5 – 0.1	< 0.1
9	TOC/COD	-	< 0.3	0.3 - 0.5	> 0.5
10	Biodegradability	-	High	Medium	Low
11	Organic compounds	-	80% VFA	5 – 30% VFA+HA+FA	HA and FA
12	Kjeldahl nitrogen	g/L	0.1 – 0.2	-	-
13	Heavy metal	mg/L	> 2.0	< 2.0	< 2.0
14	Nitrate	mg/L	5 - 40	-	5 - 10

(*Continued*)

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Table 7.2 Characteristics of landfill leachate in different phases. Adopted from (Tchobanoglous and Kreith, 2002; Foo and Hameed, 2009; Deng, 2009; Li *et al*., 2010). (*Continued*)

No.	Parameter	Unit	Landfill leachate		
			Young	Intermediate	Stabilized
15	Alkalinity	mg/L	1000 - 10000	-	200 - 1000
16	Total hardness	mg/L	300 - 10000	-	200 - 500
17	Total suspended solid (SS)	mg/L	200 - 2000	-	100 - 400
18	Total phosphorus	mg/L	5 - 100	-	5 - 10
19	Orthophosphate	mg/L	4 - 80	-	4 - 8
20	Calcium	mg/L	200 - 3000	-	100 - 400
21	Magnesium	mg/L	50 - 1500	-	50 - 200
22	Potassium	mg/L	200 - 1000	-	50 - 400
23	Sodium	mg/L	200 - 2500	-	100 - 200
24	Chloride	mg/L	200 - 3000	-	100 - 400
25	Sulphate	mg/L	50 - 1000	-	20 - 50
26	Total iron	mg/L	50 - 1200	-	20 - 200

*VFA: volatile fatty acid, HA: humic acid and FA: fatty acid.

Even so, the treatment of stabilized or mature landfill leachate is not feasible through biological means (Foo and Hameed, 2009; Foo *et al*., 2013; Zamri *et al*., 2015). This is due to the pH elevation to more than 7 as a result of microbiological reduction of volatile fatty acid (VFA) and the depleting leachate strength during the methanogenic phase (Puvvadi and Thallak, 2014; Zakaria and Aziz, 2018). In addition, at the end of its decomposition stage, landfill leachate is frequently left with high-molecular-weight humic compounds in its composition. Stabilized landfill leachate is generated from extended anaerobic degradation process of over 20 to 50 years duration. It is identified by its high content of NH_3-N (> 400 mg/L), moderate level of COD (< 4000 mg/L), and a very low ratio of BOD_5/COD (< 0.1).

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7.5 Electrocoagulation Process

The electrochemical treatment of water commenced in 1889 in the United Kingdom, through the development of a remediation method using electrical approach on saline wastewater which was prepared by mixing water discharge of residential areas with seawater (Kabdaşlı *et al*., 2012).

While the idea of electrocoagulation (EC) remediation of water was initially patented by A.E. Dietrich in 1906, where this technique was implemented in treating the bilge water of ships, in 1909, J.T. Harries introduced the application of sacrificial Fe-based and Al-based electrodes in the electrochemical treatment of wastewater in the United States (Naje and Abbas, 2013). Following this, the EC treatment has been gaining popularity for diverse types of water and wastewater. As a result of its high dependency on electricity and financial support, the EC treatment was not globally approved for extensive applications despite its vast implementation in the United States until 1946 (Chen, 2004). Nevertheless, the fundamentals and mechanism of this treatment process started to be widely exposed and comprehended in the 20th century owing to the dedicated research work conducted in the United States and the Soviet Union. In fulfilling the rigid standards and requirements for water quality and its discharge, the technology of electrochemistry in water remediation is deemed necessary, particularly in the current time. Thus, various methods of electrochemical water treatment were introduced, with the EC process being one of the most reputable techniques (Sahu *et al*., 2014). On account of its convenient, versatile, low-cost, and safe operation as well as its suitability for large-scale treatment, the EC process is often preferred in the management of various pollutants in water and wastewater (Sahu *et al*., 2014; Moussa *et al*., 2017). Numerous successful researches have been conducted globally in the application of the EC process for water and wastewater treatment. This also applies to the remediation of landfill leachate, where various studies using the EC method either as the sole or integrated treatment, were conducted.

7.5.1 Fundamentals of Electrocoagulation Process

The process of electrocoagulation operates by means of molecules disintegration via electrolysis under the influence of electricity (Sahu *et al*., 2014). The exchange of active ions between electrodes is the key mechanism involved within an EC process. Electrical energy is required to simultaneously drive negative ions toward the anode (reduction) and positive ions

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toward the cathode (oxidation). This mechanism occurs in the presence of the water sample, saline or salt solution, and electrolyte. In general, both physical and chemical reactions are taking place during an EC process. Figure 7.2(a) illustrates the processes involved in an EC process which includes flocculation, precipitation, and coagulation. The generation of metal hydroxide is influenced by the ions of coagulant under three major mechanisms; oxidation of sacrificial anode by electrolyte, destabilization of contaminants by molecules breakdown, and flocculation by particles accumulation (Naje and Abbas, 2013). Generally, an electrolytic cell is established as the reactor for an EC treatment. The common experimental set-up for this process is as illustrated in Figure 7.2(b). Two metal electrodes are arrayed as the anode and cathode accordingly and submerged in an electrolyte. Based on recommendations, aluminium (Al) and iron (Fe) are the two main materials used for electrodes fabrication particularly for their easy accessibility, the excellent capability to eliminate contaminants, and steady production of active ions (Cheballah *et al.*, 2015; Zailani and Zin, 2018; Mothi *et al.*, 2019). Electrical energy is provided from a direct power supply throughout the cell in order to stimulate the processes of oxidation and coagulation. The consistency of an EC process is sustained by agitating the electrolyte using a magnetic stirrer. Ultimately, once the subjected water or wastewater is properly treated via this technique and meets the required regulations, it is safe to be consumed or released into the open water sources.

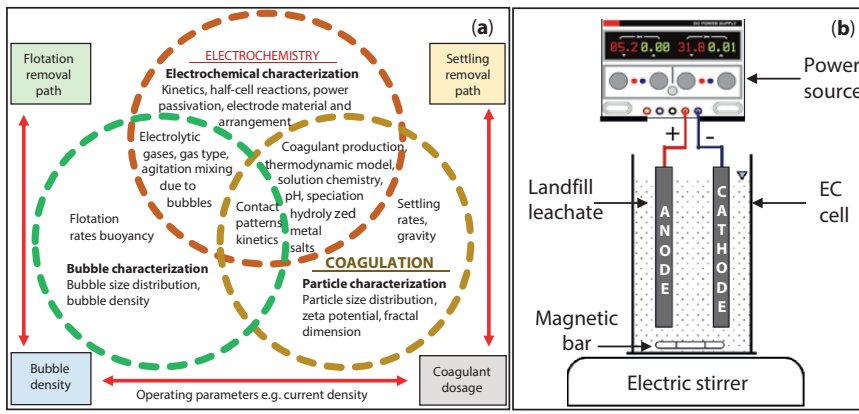

Figure 7.2 Electrocoagulation treatment process: (a) conceptual framework and (b) schematic diagram of an EC reactor. Adopted from Holt *et al.* (2005).

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7.5.2 Mechanism of Electrocoagulation Process

The concept of electrocoagulation entails the destabilization of residual substances or dissolved contaminants in an aqueous environment by the aid of electrical power. The mechanisms of EC process in the aqueous system are rather complicated, which can be further divided into electrolysis, electroflotation, and electrooxidation (Sahu *et al.*, 2014). Electroflotation refers to the flotation of contaminants and particles together with flowing bubbles of H_2 and O_2 towards the surface of the electrolyte. In electrooxidation, organic compounds undergo an oxidation stage and are decomposed into water molecules, carbon dioxide, and oxide compounds (Kuokkanen *et al.*, 2013). As previously studied by Rosie *et al.* (2012) and Chen *et al.* (2018), the solubility of the sacrificial electrode (anode) into hydroxides is the key mechanism towards the treatment of water or wastewater, in addition to some processes including coagulation and adsorption. The materials for anodes and cathodes are chosen either of the same type of variable, with the most common ones being Al and Fe. Reactions take place simultaneously at the anodes and cathodes in the event of electrolysis, where the elimination of contaminants proceeds as a result of ions neutralization.

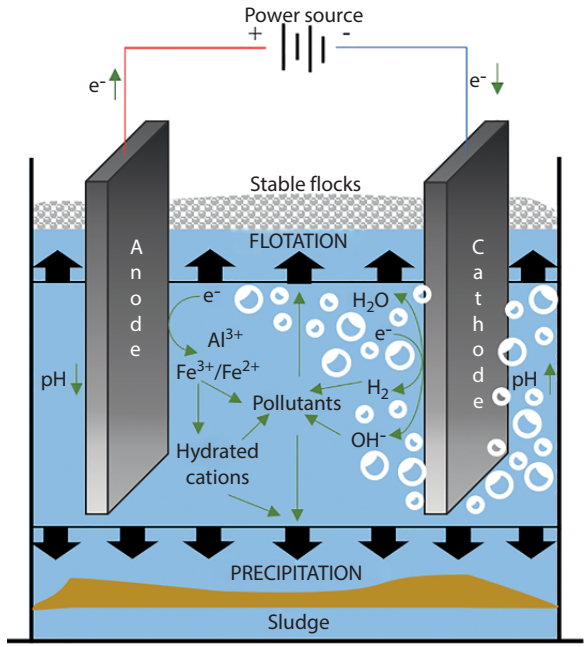

Figure 7.3 Basic reaction in the electrocoagulation process.

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This is caused by the flocculation and precipitation of particles, as well as the flotation of agglomerated compounds. Song *et al.* (2014), in their study, claimed that the EC technique utilizes both physical and chemical means as supported by Figure 7.3. Table 7.3, on the other hand, lists the potential chemical reactions to take place at metal electrodes during an EC process. Despite its complicated mechanisms, the EC method is deemed versatile in treating various types of pollutants by the integration of multiple processes and customization of operating parameters (Chopra *et al.*, 2011).

Through the EC method, dispersed particles in electrolyte could be stabilized by the abundant presence of cations into complex polyvalent polyhydroxide composites. Moreover, the cationic activities in this

Table 7.3 Chemical reactions involved in metal electrodes in the electrocoagulation process. Adopted from Song *et al.* (2017).

Anode		**Cathode**	
Basic oxidation reactions			
$4OH^- - 4e^- = 2H_2O + O_2$ (g)	(7.1)	$2H_2O + 2e^- = 2OH^- + H_2$ (g) (alkali electrolyte)	(7.2)
$2H_2O - 4e^- = 4H^+ + O_2$ (g)	(7.3)	$2H_2O + O_2 + 4e^- = 4OH^-$	(7.4)
		$2H_3O^+ + 2e^- = 2H_2O + H_2$ (g) (acid electrolyte)	(7.5)
Iron (Fe) electrode			
$Fe(aq)^{2+} + 2H_2O = Fe(OH)_2 + 2H^+$	(7.6)	$[Fe(OH)_4]^- + 2OH^- = [Fe(OH)_6]^{3-}$ (alkali electrolyte)	(7.7)
$Fe(s) - 2e^- = Fe(aq)^{2+}$	(7.8)	$Fe(OH)_3 + OH^- = [Fe(OH)_4]^-$	(7.9)
$Fe^{3+} + 3H_2O = Fe(OH)_3 + 3H^+$	(7.10)		
$Fe^{2+} + 3OH^- - e^- = FeOOH + H_2O$	(7.11)		
$Fe^{2+} - e^- = Fe^{3+}$	(7.12)		
Aluminum (Al) electrode			
$Al(aq)^{3+} + 3H_2O = Al(OH)_3 + 3H^+$	(7.13)	$Al(s) + 4OH^- = [Al(OH)_4]^- + 3e^-$ (alkali electrolyte)	(7.14)
$Al(s) - 3e^- = Al(aq)^{3+}$	(7.15)		

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method could as well promote the generation of O_2 and H_2 gases in excess. Hydroxides and polyhydroxides of variable surface areas are formed from the voluntary reactions of $Fe(aq)^{2+}$, $Fe(aq)^{3+}$, and $Al(aq)^{3+}$ ions released in the electrolyte. This kinetic mechanism is based on the concept of the intricate process of precipitation (Kobya *et al*., 2003). The excellent interaction between the dispersed molecules and these ionic substances promotes the coagulation process. Upon the oxidation of electrolyte, iron hydroxides ($Fe(OH)_2$ or $Fe(OH)_3$) are generated from iron metal, and this reaction is influenced by the pH condition of the electrolyte. Moreover, simultaneous electrolysis of water molecules takes place in electrolyte thus yielding

Table 7.4 Advantages and disadvantages of electrocoagulation process.

No.	Advantages	Disadvantages
1	Simple equipment design and easy operation	Requires high electrolyte conductivity
2	Requires less or no additional chemical	The anode electrode (sacrificial) must be periodically replaced
3	Capable of eliminating various pollutants more than other conventional methods	Low removal of ammoniacal nitrogen in cases of inorganic pollutant
4	Almost no sludge formation and easy dewatering	High electrical consumption which leads to increased operating costs
5	Relatively low operating cost	Possibility of low EC process efficiency due to cathode passivation
6	No generation of secondary pollutants	
7	Less retention treatment time	
8	Generation of more stable flocks	
9	Formation of hydrogen and hypochlorite which is beneficial in water treatment	
10	*In situ* production of coagulant agents	

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bubbles of H_2 and O_2 at the cathode and anode, respectively. Owing to their light weight and extremely fine properties in addition to continuous production, the yielded bubbles may flow upward onto the surface of electrolyte while transporting dispersed substances along. This contributes to higher removal of contaminants. Filtration may be applied to effectively eliminate contaminants in flocs due to their excellent stability, large particles size, and lowly hydrophobic nature (Emamjomeh and Sivakumar, 2009; Kobya *et al*., 2011; Bazrafshan *et al*., 2015).

7.5.3 Advantages and Disadvantages

Since the EC process is capable of remediating diverse types of water and wastewater, it is extremely effective in treating highly contaminated wastewater, particularly landfill leachate (Shah *et al*., 2017). On account of this, the EC treatment is deemed superior to other conventional chemical methods in water and wastewater remediation (Khandegar and Saroha, 2013; Apshankar and Goel, 2018). Even so, the EC process as any other remediation methods possesses advantages and disadvantages. Hence, in minimizing the downsides of the EC process while improving its functionality, optimization of working conditions is necessary (Apshankar and Goel, 2018). Some of the reported major benefits and drawbacks of the EC treatment by Khandegar *et al*. (2013), Can *et al*. (2014), Fernandes *et al*. (2015), Elabbas *et al*. (2016), Moussa *et al*. (2017), Ahangarnokolaei *et al*. (2018), Al-Qodah *et al*. (2019), and Rodriguez *et al*. (2020) are listed in Table 7.4.

7.6 Key Parameters of Electrocoagulation Process

There are several key operating parameters affecting the overall performance of an electrocoagulation process in the removal of various contaminants in landfill leachate. According to Khandegar and Saroha (2013), Sharma *et al*. (2020), and Kobya *et al*. (2020), the efficiency of pollutants removal by the EC technique is highly dependent on the type, arrangement, and spacing of electrodes, current density, electrolysis time, initial pH, agitation speed, electrolyte conductivity, and mode of operation.

7.6.1 Electrodes Material

In general, the type of material used for the electrodes in the EC process has a major impact on treatment performance efficiency and overall operating

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costs (Tahreen *et al*., 2020). In fact, the type of electrode material applied is vital in determining the electrochemical reactions and active metallic coagulant ions formation in electrolytes. Previously, Garcia-Segura *et al*. (2017) elucidated that a larger capacity coagulant is more preferred because of the electrode capability to enhance the coagulation of contaminants by the aid of a greater electrical compression. In literature, several types of electrode material such as graphite, carbon, boron-doped diamond, stainless steel, copper, etc., are proposed and utilized in the EC process. Nevertheless, among all materials, Al and Fe are the most widely used in electrodes due to their ability to remove different types of pollutants, efficient coagulation, easy availability, stability, and non-toxic properties (Hakizimana *et al*., 2017; Tirado *et al*., 2018; Mothi *et al*., 2019). Despite Al and Fe electrodes involving relatively similar electrochemical reactions, the differences in their ions' dissolution rates lead to variable outcomes in an EC process. In all cases, aluminium metal is soluble as Al^{3+}, whereas iron oxidizes into either Fe^{2+} or Fe^{3+} in the presence of oxidants such as oxygen (Un and Ocal, 2015; Kuokkanen, 2016; Alimohammadi and Dalvand, 2017). However, Fe^{2+} is less effective as a coagulant relative to Fe^{3+} due to the increased solubility of hydroxides and the lower positive charge it carries (Un and Ocal, 2015; Moussa *et al*., 2017).

Hence, a smaller positive charge suggests the lower capability of ions to compact the electrical double layer or destabilize pollutant molecules (Moussa *et al*., 2017). In most researches, Al electrodes typically demonstrated better efficacy for removing pollutants in various types of wastewater in comparison to Fe electrodes (Lekhlif *et al*., 2014; Vepsäläinen and Sillanpää, 2020). In a case study of leachate treatment, for instance, unsatisfactory results were revealed in the removal of organic pollutants of COD and colour using Fe electrodes (15% and 16% removals) in comparison to Al electrodes (70% and 60% removals) as reported by Bouhezila *et al*. (2011). However, Fe electrodes are found to be highly effective in treating various heavy metal substances (Orescanin *et al*., 2012; Bhagawan *et al*., 2014). Despite the superior removals of organic and inorganic pollutants by Al electrodes, Fe electrodes are undoubtedly more efficient in EC treatment than aluminium in terms of electrical energy consumption (Fernandes *et al*., 2015). Thus, numerous prior literature has been reporting on the combination of Al and Fe electrodes in the remediation of landfill leachate. Kasmuri *et al*. (2018) in their study achieved a better removal of heavy metals by Fe electrodes, whereas Al electrodes were found efficient in eliminating inorganic pollutants. A combination of Fe and Al electrodes was highly capable of removing the pollutants of zinc (89%), iron (75%) and NH_3-N (93%). Nevertheless, the efficiency of an EC process is not

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solely dependent on the types of electrode material but also other parameters such as the characteristics of leachate and other operating parameters (Anjali *et al.*, 2018).

7.6.2 Electrodes Arrangement

The electrode configuration in an EC cell affects the processability to remove contaminants and its operational costs (Kobya *et al.*, 2011). According to Sahu *et al.* (2014), anode and cathode electrodes can be connected using several connection modes (Figure 7.4 (a)); monopolar parallel (MP), bipolar series (BS), and monopolar series (MS). In general, an electrodes configuration simply consists of a pair of or multiple anode and cathode electrodes arranged in an EC cell. Previously, Hakizimana *et al.* (2017) explained that in the MP electrode connection mode, the sacrificial anode is directly connected to other anode electrodes, and the same arrangement is applied for cathodes. Meanwhile, in MS configuration, a single pair arrangement of anode and cathode electrodes is internally connected without connecting to the external electrodes. The BS mode, on the other hand, involves the arrangement of specific electrodes to modify

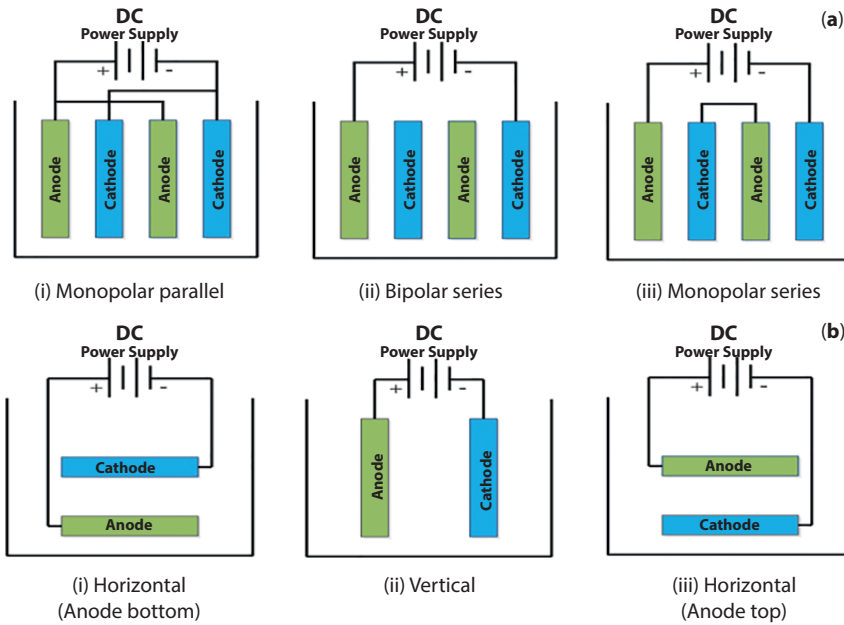

Figure 7.4 Electrodes arrangement in the electrocoagulation process: (a) connection modes and (b) electrodes orientations. Adopted from Zaied *et al.* (2020).

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their polarity at a certain electrode edge with reference to the electrode charges. This configuration is always set in a series connection. In the literature, some studies have revealed the effects of electrodes orientation on an EC process (Figure 7.4(b)). Nasrullah *et al.* (2017) reported that the variation of electrode orientations of either vertical or horizontal affects the performance of an EC process depending on the selected pollutants to be removed. However, recent researchers including Rabahi *et al.* (2018), Preethi (2019), Muhammad Niza *et al.* (2020) have evaluated the effectiveness of the orientation of the vertical electrodes for landfill leachate treatment via EC process. Ding *et al.* (2018) have conducted a study on the effect of electrode arrangement (monopolar and bipolar) on the removal of COD, ammonia, and phosphorus in leachate by utilizing iron electrodes in 60-min electrolysis using 10V applied voltage. The study revealed higher removals of COD, ammonia, and phosphorus using bipolar electrode configuration (65%, 100%, and 91%) in comparison to the monopolar configuration (45%, 61%, and 40%).

Another study by Shukla and Makwana (2017) concerning the cost-effectiveness of the EC process using three different connection modes (MS, MP and BS) for the removal of COD in leachate was investigated. The authors claimed that the energy consumption efficiencies for COD removal (91% to 95%) using MS and MP modes, respectively, were of 3.3 kWh/kg and 3.9 kWh/kg, which were much lower than in BS mode (6.5 kWh/kg). It is conclusive from the above-mentioned studies that in comparison to bipolar electrodes arrangement, monopolar arrangement yields lower pollutants removal efficiency as well as less efficient energy consumption. This is attributable to the higher surface area of the bipolar electrodes which leads to more oxidation reaction at the anode electrode thus increasing the generation of the sacrificial anode as compared to monopolar connection mode (Naje *et al.*, 2016). Besides, the arrangement of the bipolar electrodes also offers an easy physical setup that allows easier substitution of sacrificial anode electrode (Ding *et al.*, 2018).

7.6.3 Electrode Spacing

The internal electrode spacing (IES) plays an essential role in the electrocoagulation process since the field of electrostatic current is dependent on the anode and cathode spacing (Bazrafshan *et al.*, 2015; Naje *et al.*, 2016). Furthermore, IES and effective electrode surface area is the significant parameters to consider during the optimization of an EC cell and its overall operating costs (Bazrafshan *et al.*, 2015). IES also greatly affects the flow and movement of ions in electrolytes, cell size, mass transfer,

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and energy consumption in wastewater treatment (Song *et al*., 2017). Preethi (2019) in their investigation on the effect of varying IES (1 cm to 2.5 cm) in the treatment of leachate for removing COD, TSS, and TDS revealed high removal efficiencies of more than 71% using an optimum IES of 1.5 cm in comparison to the initial distance of 1 cm (less 50%). This is because, at lower IES, the yielded metal hydroxides act as flocs which remove degraded pollutants upon their interaction (solid and fluid transfer congestion) due to high electrostatic attraction, thus resulting in higher electrical resistance (Verma *et al*., 2013; Khandegar and Saroha, 2013). In particular, the removal efficiency of pollutants increases with increasing spacing between anode and cathode to optimum IES. This fact was proven in an earlier study by De *et al*., (2019) who examined the influences of variable IES in the range between 1.5 cm to 3.5 cm on the removal of mercury (Hg) in a similar electrolyte. It was revealed that the removal efficiency of Hg increased from 60% to 80% at the respective IES of 1.5 cm to 2.5 cm (optimum IES). This condition can be explained by the effect of increasing IES, which reduces the electrostatic influences in electrolyte hence resulting in slower movements of produced metal ions (De *et al*., 2019). It also provides sufficient amalgamation duration for the generated metal hydroxides which in turn promotes flocs formation and ultimately improves the pollutants removal capacity in the electrolyte (Verma *et al*., 2013; Khaled *et al*., 2015). On the other hand, an increment of IES to more than the optimum will reduce the removal percentages of pollutants due to decreasing electrostatic attraction which further reduces the formation of the floc (Verma *et al*., 2013; Singh and Ramesh, 2014). The duration of ions' movement is directly proportional to electrodes spacing. However, to reduce the consumption of electrical energy in EC process, IES can be reduced in cases of low conductivity electrolyte, and vice versa for high conductivity electrolyte (Bazrafshan *et al*., 2015).

7.6.4 Current Density

Current density (CD) is considered as a major operating parameter influencing the overall EC process since it affects the generation rate of coagulant, gases production, bubbles size, as well as flocs formation (Naje *et al*., 2016; Ensano *et al*., 2017). In the EC treatment, the rate of anode dissolution is directly proportional to CD when electrical energy is supplied. Abbas *et al*. (2018) and Islam (2019) reported that when higher electrical energy is used, the anodic dissolution rate will increase, which in turn increases the formation of cationic hydroxyl complexes, responsible for improving the removal of pollutants. However, excessive CD in EC cell

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beyond the optimal value may not be efficient in removing pollutants (Khaled *et al.*, 2015; Islam, 2019). In cases of Al and Fe anode electrodes, the dissolution responses are more necessary than other responses at specific CD. Moreover, electrodes are highly potential at natural pH condition or acidic environment (Verma *et al.*, 2012). However, the rate of dissolution of sacrificial Fe anode may be lower in an alkaline environment based on Faraday's law (Equation 7.16), attributable to other potential responses taking place at the anode electrode (Un and Ocal, 2015).

$$\text{Faraday's Law}\,(\text{kg/m}^3) = \frac{\text{ItM}}{\text{zFv}} \tag{7.16}$$

Where I is electrical current (I), t is electrolysis time (s), M is the molecular mass of anode (Al: 0.02698 kg/mol or Fe: 0.05585 kg/mol), z is the number of metal electrons (2: F^{2+} or 3: F^{3+} and Al^{3+}), F is the Faraday's constant (96,485 C/mol), and v is the electrolyte volume (m^3).

Based on Faraday's law, it is noted that the concentration of produced metal coagulants is generally proportionate to electrical current. However, the rate of coagulant dissolution is also affected by chemical dissolution at low pH, and CD effect on the cathode electrode thus contributes to the generation of hydroxyl ions (Naje *et al.*, 2016). An investigation by De Pauli *et al.* (2017) in the treatment of landfill leachate showed that at higher CD (128.57 A/m^2), higher colour, turbidity, and iron pollutants removal efficiencies of above 90% were achieved. In another report, Asaithambi *et al.* (2018) evaluated the removal of organic matter from stabilized leachate at different CD between 105 A/m^2 to 625 A/m^2. The study exhibited that at the optimum CD (525 A/m^2), the removal of organic pollutants of colour and TOC of up to 75% and 54%, respectively, were yielded. This indicates that the applied CD (525 A/m^2) is sufficient in removing both pollutants, where a further increase in CD did not improve the removal efficiency. In addition, a recent study by Preethi (2019) on the application of EC method to remove organic and inorganic pollutants from leachate yielded the highest removals of TDS (67%), TSS (58%), chlorides (61%), sulphates (77%), and COD (46.75%) at an optimum CD condition of 600 A/m^2.

7.6.5 Electrolysis Time

Zaied *et al.* (2020) described the rises in hydrogen gas and ions' generation are due to the dissolution of the anode and the reduction of the cathode as attributable by the introduction of steady electrical energy with extended

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electrolysis time. In general, the removal efficiency of pollutants via the EC process is directly proportional to treatment time and current density to the extent of optimum conditions. In the EC process, large molecular weight pollutant compounds are degraded by low molecular weight and hydrophilic compounds (Mohora *et al*., 2014). Likewise, pollutants are drawn to the electrode ions, which in turn enhances their removal efficiency. According to De Pauli *et al*. (2017), by extending electrolysis time, more metal hydroxide ions are generated by electrodes, thus improving the adsorption of pollutants as well as the production rate of flocs and bubbles. Nevertheless, excessive electrolysis time may not effectively improve removal of pollutants as it tends to consume high electrical energy and more metal electrodes (Zaied *et al*., 2020). De *et al*. (2019) revealed from their study that the removal of mercury (Hg) pollutant in landfill leachate was less significant in the first 15 min of electrolysis with the removal of only 32%. Nevertheless, by increasing the electrolysis time to 60 min, the EC treatment demonstrated an acceptable pollutant removal of up to 58%. The authors also reported that within the electrolysis time range of 15 to 120 min, the higher removal efficiency of Hg with electrolysis time progression could be described as a result of high Fe hydroxide ions formation by the sacrificial anode electrode to remove Hg pollutant from leachate. Another research by Bharath *et al*. (2019) was conducted to analyze colour and COD pollutants removal in mature landfill leachate using various electrolysis time from 20 to 200 min. It was reported that high removals of colour and COD of 78% and 77%, respectively, were obtained at optimum electrolysis time of 120 min. However, beyond the optimum electrolysis time, a substantially lower pollutants removal rate was recorded which is due to the abundant production of metal ions from the electrodes prior to their transfer into electrolytes (Kabdaşlı *et al*., 2012).

7.6.6 Initial pH

In the treatment of wastewater, its initial pH inflicts numerous effects on most physical and chemical processes, particularly the electrocoagulation process (Omwene and Kobya, 2018). The initial pH value of an electrolyte is also considered as a critical variable due to its effects on the electrical conductivity of electrolytes (Naje *et al*., 2016). In addition, the pH parameter highly affects the speciation of electrode materials such as Al and Fe, where it significantly influences the removal of various pollutants in landfill leachate treatment. The formation of Al and Fe hydroxides cations may destabilize colloidal particles generated in all pH region (acidic, neutral and alkaline). However, the ions of $Al(OH)^{4-}$ and $Fe(OH)^{4-}$ are

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generated in the highly alkaline region which has inefficient coagulation capacity. In contrast, Fe^{3+} ions are produced at a higher pH range (slightly alkaline) than Al^{3+}. For iron electrodes, Fe^{2+} ions generation from Fe^{3+} is greatly influenced by acidic pH, and the surface changes for coagulation may also differ based on the value of pH (Farhadi *et al*., 2012). In reference to Zaied *et al*. (2020), the generated Fe^{2+} ions at the anode electrode at low pH value fasten the elements of the anionic colloidal present in electrolytes, thus deactivating their charges and reducing their solubility in the precipitation process. In the EC process, adsorption mechanism takes place at high pH values of more than pH 7, which involves the adsorption of different pollutant compounds in unstructured metal hydroxide precipitation. Meanwhile, at low pH values of less than pH 7, the key mechanism is diffusion, which is operated by monomeric cations (Mbacké *et al*., 2018; Omwene and Kobya, 2018). Hence, the efficiency of pollutants removal may decrease when the pH of electrolyte adapts to alkaline or acidic environment. An earlier investigation on the EC process in treating leachate was conducted to evaluate the initial pH effect using variable pH values ranging from 3 to 9 with an interval of 2 and a pair of iron electrodes. The performance of the EC process was found to be influenced by the initial pH value. A maximum COD pollutant removal was achieved up to 69% at initial pH 5 (Tezcan Un *et al*., 2018). Another experiment conducted by Bharath and Krishna (2019) evaluating the effect of initial pH in a smaller pH range from 8.6 to 9.8 indicated that high COD and colour pollutants removals were obtained respectively at 74% and 65% at initial pH of 9.8. They also concluded that in neutral and alkaline environments, effluent decolourization is very high compared to the acidic environment.

7.6.7 Agitation Speed

Agitation serves to maintain the homogeneous condition of electrolytes through the forced movement of ionic molecules to pollutants and to prevent the establishment of a concentration gradient in the EC reactor (Gönder *et al*., 2019). Furthermore, it also provides homogeneity in the reactor contents, which further increases the rate of ions transfer and enhances the distribution of metal hydroxide flocs from the electrode surrounding throughout the whole EC reactor (Yang *et al*., 2016; Hakizimana *et al*., 2016). If metal coagulant substances are not efficiently distributed, the content of the EC reactor could not be homogeneous, and thus the intensity of the regional variation can be clearly identified (Bayar *et al*., 2011). Besides, the speed of agitation could also result in different homogenization conditions in the EC process variables such as pH and temperature

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of electrolytes. A previous study has claimed that when the agitation speed achieves its optimum condition, the highest removal efficiency pollutants will be obtained. However, at a lower or higher agitation speed than the optimal, lower pollutants removal capacity is yielded. Preethi (2019) in their study on the removal of organic and inorganic pollutants in leachate under the influence of agitation concluded that within the agitation speed range of 100 to 500 rpm, the highest removal rates of COD (76%), TSS (81%), sulphate (79%), and chlorides (83%) were achieved at the optimum agitation speed of 300 rpm. Moreover, a reverse effect was observed when the agitation speed was reduced or increased from the optimum speed, which is attributed to the decreasing of ions' mobility at low speed and the degradation of flocs at high speed due to collisions (Al-Qodah and Al-Shannag, 2017). Another similar experimental work was carried out by Naje *et al.* (2019) to optimize the COD, TSS, and TDS removal efficiency from similar wastewater using a relatively lower agitation speed range of between 75 to 200 rpm and Al electrodes. High removal percentages of COD, TSS, and TDS (85%, 90%, and 83%, respectively) were achieved at an optimum agitation speed of 150 rpm attributable by the sufficient increment in agitation speed which leads to the incorporation of the produced flocs with $Al(OH)_3$, hence improving the rate of coagulant precipitation (Naje *et al.*, 2019).

7.6.8 Electrolyte Conductivity

The conductivity of electrolytes in the EC process is an important parameter as it directly impacts the energy required and operating cost for achieving a performance efficiency (Sharma *et al.*, 2020). Thus, for less energy consumption, a high conductivity electrolyte is needed. In certain water matrix, if the conductivity is too low, then it is necessary to add salts or mix with seawater (Sharma *et al.*, 2020) to enhance the electrolyte conductivity thereby improving the removal efficiency (Bazrafshan *et al.*, 2012; Thakur and Mondal, 2016). Salt additives such as potassium sulphate (K_2SO_4) and sodium chloride (NaCl) as well as sodium sulphate (Na_2SO_4) are usually introduced at the earlier stage before treatment for pH adjustment procedure (Anantha and Ramesh, 2013; Naje *et al.*, 2016). According to Dalvand *et al.* (2011) and El-Ashtoukhy *et al.* (2013), electrolyte conductivity is very important in the EC process as it could result in reduced operating electrical consumption, which in turn increases current density. However, it was found that increasing electrolyte conductivity from 100 - 10,000 μmhos.cm^{-1} could help minimise the reaction time for similar experimental conditions but only slightly (Apshankar

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and Goel, 2018). In the contribution of ions as electrical charge carrier, it has been noticed that the chloride ions (Cl^-) of NaCl can greatly decrease the negative impacts from several anions like HCO_3^- and SO_4^{2-} (G. Chen, 2004). Furthermore, by the presence of Cl^- ions, the adverse effects by CO_3^- or/and SO_4^{2-} may also be decreased through the prevention of both Ca^{2+} and Mg^{2+} precipitation, as well as the establishment of an oxide layer on the electrode surface that can rapidly reduce the efficiency of electrical current (Liu *et al*., 2010; Anantha and Ramesh, 2013). Therefore, it is suggested that 20% of Cl^- ions be present in an electrolyte among the existing anions in order to assure a normal EC operation system (G. Chen, 2004). Rosie *et al*. (2012) reported that high removal efficiency rate of COD (74%) was achieved at optimum electrical conductivity of 28 ms/cm (28 to 31 ms/cm) by the addition of NaCl in the treatment of mature landfill leachate. During an EC treatment, Cl^- ions will be removed to produce Cl_2 at the anode electrode, followed by Cl_2 evolution into hypochlorite (ClO^-) ions which could effectively oxidize pollutants (Mussa *et al*., 2013). However, findings revealed that the pollutant removal efficiency of COD decreases with increasing conductivity over the optimal level due to changes in the ionic strength and increasing electrolyte conductivity. According to Wang *et al*. (2009), in cases of Al electrodes, if excess NaCl is added into the electrolyte, Cl- ions will multiply to form transient compounds such as $AlCl_3$, $Al(OH)_2Cl$, and $Al(OH)Cl_2$ which pose a detrimental effect on the formation of $Al(OH)_3$ coagulants and thus decrease the pollutant removal efficiency. Other research conducted by Ubale and Salkar (2017) revealed that by adding 4 mg/L NaCl into the electrolyte, efficient pollutants, removals with respect to turbidity (97.63%), colour (87.87%), COD (93.3%), TSS (94.02%), and TDS (52.13%) were obtained. This, in turn, reduced the electrical and specific electrical current consumptions respectively in the ranges of 13.33 to 2.67 kWh/m^3 and 23.84 to 4.77 kWh/kg Al. Nevertheless, an additional increase in conductivity by supporting electrolyte addition does not significantly reduce the pollutant removal efficiency and electrical energy consumption.

7.7 Operating Mode

A wide range of landfill leachate concentrations has been treated using different EC operating modes either in batch or continuous process. In batch EC operation, the process behaviour seems to be inherently dynamic, resulting in the need for complex mathematical modelling (Song *et al*., 2017). Whereas in continuous EC operation, steady system

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conditions with consistent pollutants concentration and inflow/outflow rate are required. Thus, a batch reactor basically serves to evaluate the optimization of an EC process based on several main operating parameters (electrode material, current density, electrolysis time, etc.) and it is a more effective operating mode compared to continuous EC process (Kobya *et al*., 2013; Sahu *et al*., 2014; Song *et al*., 2015). However, the operating parametric optimization of a batch system is important to serve as guidelines and support in operating a continuous EC reactor (Kobya *et al*., 2014). The continuous EC system is therefore ideally suited for industrial treatment of a large amount of effluent, whereas the batch EC system is appropriate for laboratory experiments and pilot-scale studies (Prince Periyasamy *et al*., 2018; Ding *et al*., 2018). Nevertheless, in certain cases, a laboratory-scale continuous EC process was conducted to validate the electrical energy and materials consumption for large-scale EC process (Fekete *et al*., 2015). Besides, due to its excellent control, easier pollutant monitoring, consistent performance, and undynamic characteristics, the continuous operation is preferred compared with the batch EC process (Khandegar and Saroha, 2013; Kobya *et al*., 2020). Furthermore, the metal dissolution and flocs formation by electrodes are some extra advantages of the continuous EC process. In contrast, the batch mode EC process is a dependent time process since metal coagulants are consistently formed in the EC reactor when the anode electrode is dissolved continuously (Naje *et al*., 2016). Hence, the concentrations of pollutants and generated metal coagulants, as well as pH values, are continuously varying over time. Besides, the batch mode EC process does not produce any effluent inflow/outflow during the electrolysis process as the continuous mode operation. A comparative study between batch and continuous operation modes EC reactors using a 120-min electrolysis for removing NH_3-N (110 mg/L) and COD (180 mg/L) from leachate has been reported by Ding *et al*. (2018). In this study, high reduction in NH_3-N and COD concentrations to 33 mg/L and 40 mg/L was obtained in continuous mode, while in batch operation; the final concentrations were 80 mg/L and 59 mg/L, respectively. In another study by Silveira *et al*. (2015), they were able to successfully remove COD and NH_3-N up to 55% and 71%, respectively, in the continuous EC treatment of leachate using 42 min of electrolysis time. Therefore, the high performances demonstrated by continuous operation mode EC process could be attributed to the high amount of metal ions released by scarification of anode while the flocs formation is probably due to the proportional relationship between current density and electrolysis duration (Phalakornkule *et al*., 2009).

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7.8 Economic Analysis

To date, many water and wastewater treatment systems are available for removing various pollutants; however, the electrocoagulation method is deemed as one of the most promising and economical processes to be applied in landfill leachate treatment. Two significant criteria shall be considered in determining the EC process performance, i.e., total operating cost and pollutants removal capacity. These criteria are very crucial in determining the viability of a treatment process prior to its commercial-scale implementation (Al-Shannag *et al.*, 2015; Martínez-Huitle *et al.*, 2015). The economic assessment of a commercial-scale EC process includes the electrical energy consumption, type of metal electrode, sludge management, and operation maintenance as well as the depreciation value of the plant (Moussa *et al.*, 2017; Kobya *et al.*, 2016). However, several main parameters such as the consumptions of metal electrodes, electrical energy, and chemical reagents have to be considered in the evaluation of the operational cost of the electrocoagulation treatment process (Kobya *et al.*, 2011; Bazrafshan *et al.*, 2015). The following Equations 7.17 to 7.20 describe the operating costs calculations involved in an EC process. Therefore, the potential treatment methods either in single EC process or combined treatments should be low cost, simple to utilize, and highly efficient in removing pollutants (Nguyen *et al.*, 2014). Very limited researches have been conducted evaluating the total economic efficiency of the EC process in landfill leachate treatment. The total operating cost under optimum EC treatment conditions for different COD pollutant removal was examined by Tanyol *et al.* (2018) on stabilized landfill leachate. The removal efficiency of COD was 72.13% achieved at the optimum operating conditions with the highest electrical energy, electrode consumption, and operating consumption cost of 0.055 kWh/kg COD, 3.43 kg/kg COD, and 1.41 US$/kg COD, respectively. Meanwhile, Hamid *et al.* (2020) investigated the performance of augmented zeolite EC process for removing high-strength inorganic pollutant of ammonia in mature landfill leachate. They concluded that at optimum conditions, high removal efficiency of ammonia up to 71% was achieved with an overall estimated operating cost of 36.46 US$/m^3 covering the costs for the consumptions of electrical energy, Al electrode, chemical reagents, and zeolite.

$$\text{EU) Electrode use (kg/m}^3\text{):}\ \frac{\text{ITM}}{\text{nFV}} \tag{7.17}$$

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$$\text{CU) Chemical use (kg/m}^3\text{): } \frac{W}{V} \tag{7.18}$$

$$\text{EEU) Electrical energy use (kWh/m}^3\text{): } \frac{UIT}{V} \tag{7.19}$$

$$\text{Overall operating cost (US\$/m}^3\text{): } aEU + bCU + cEEU \tag{7.20}$$

Where I is the electrical current (A), U is the voltage (V), T is time (min), M is the molecular mass (Al: 26.98 g/mol or Fe: 55.84 g/mol), n is the number of mole of the electron (Al: 3 or Fe:2), W is the chemical weight (kg), F is the Faraday's constant (96500 c/Mol), V is the volume of treated effluent (m^3), a is the price of Al or Fe electrodes used (US$/kg), b is the cost of the chemical reagents used (US$/kg), and c is the cost of electricity consumption (US$/kWh).

7.9 Case Study: Removal of the Organic Pollutant of Colour in Natural Saline Leachate from Pulau Burung Landfill Site

Numerous extensive studies and reviews are available regarding the electrocoagulation process in treating water and wastewater for removing various. But to date, there are no studies utilizing high natural conductivity leachate, which is saline in nature to further enhance the efficiency of the electrocoagulation process. The requirement of high electrolyte conductivity in water and wastewater treatment is the main limitation of the electrocoagulation treatment (Labanowski *et al*., 2010; Norma *et al*., 2012; Kuokkanen, 2016; Ding, Wang, *et al*., 2018). The stabilized leachate samples acquired from Pulau Burung Landfill Site (PBLS) were characterized with complex compounds of biodegradable and non-biodegradable pollutants such as organic and inorganic compounds as well as heavy metals, in addition to their physical properties of dark black-green colour with an unpleasant smell. PBLS leachate is considered mature and underwent the methanogenic phase since its pH exceeded 7.5, and the biodegradability ratio was extremely low (< 0.1). These observations were proven by several studies conducted by Mohd Azme and Murshed (2018), Mohajeri *et al*. (2019), and Azme *et al*. (2020). This leachate was found to contain high-strength pollutants of organics (BOD: 220 mg/L, COD: 5096 mg/L, colour: 8427 Pt-Co) and inorganic compounds (NH_3-N: 2542 mg/L, SS:

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1011 mg/L) as well as salinity (15.13 ppt). An earlier study by Aziz *et al.* (2015) reported that the high intensity in pollutants concentrations in PBLS leachate is closely related to its high natural salinity and ammonia content which restrict the development of bacterial survival. The fact of high salinity value in PBLS leachate is due to the site location of adjacent to the shoreline (Mohajeri *et al.*, 2010; Hamid *et al.*, 2020) which is contributed by the easy percolation of seawater (Aziz *et al.*, 2015). There are a few studies applying the electrocoagulation treatment as reported by Mohajeri *et al.* (2018), Mahmad *et al.* (2016), and Muhammad Niza *et al.* (2020) using leachate from aeration pond (1-2 ppt) in this landfill site. However, this specific case study is profoundly different since raw leachate collected directly from the leachate outlet point before undergoing any biological pre-treatment and containing high salinity value (15.13 ppt) was utilized. This could, in turn, overcome the drawbacks of the EC process in removing high-strength colour pollutant without the need for any external supporting auxiliary.

7.9.1 Pulau Burung Landfill Site

PBLS is a semi-aerobic site which is situated in the Nibong Tebal district of Penang at Byram Forest Reserves. The total area of this site is 62.4 ha, and at present, only 33 ha are utilized for the daily operation which approximately receives about 2000 tons of MSW (Mohd Azme and Murshed, 2018). On average per day, only 650 tons of MSW is disposed of Penang Island while the remaining 1350 tons are contributed from the mainland area. This

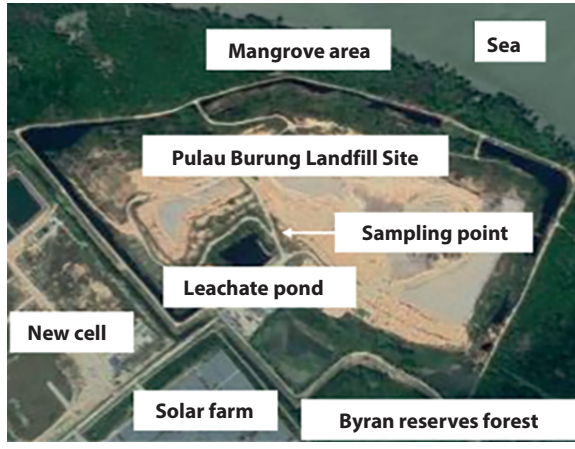

Figure 7.5 Satellite image of PBLS and sampling location.

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landfill has natural oceanic clay lining since it is located nearby the western coast of Malaysia (Figure 7.5). In its first ten years of operation starting from early 1980, MSW was disposed of without any appropriate treatment. Then in 1991, this site operated as a semi-aerobic sanitary landfill system (level 2) with tipping-controlled management before being further upgraded as a sanitary landfill (level 3) by establishing a leachate-controlled system after ten years of excellent operation (Kamaruddin *et al.*, 2016). In order to ensure effective routine of waste disposal management operation and high environmental preservation, PBLS was privatized to the concessionaire in 2012. Today, PBLS is well known as one of the sophisticated sanitary landfill sites in the northern region of Peninsular Malaysia.

7.9.2 Experimental Design

The experiment commenced by first rinsing the electrocoagulation cell with pure water and later desiccated at the room atmosphere (25°C). 750 mL of PBLS leachate electrolyte was poured into the EC reactor with a total capacity volume of 1000 mL (Figure 7.6). This intensity will allow the formation of flocs secondary to the oxidation process. DC power supply was used by connecting the positive (anode) and negative (cathode) terminals to a pair of Al electrodes (Grade 6065). The Al electrodes were submerged

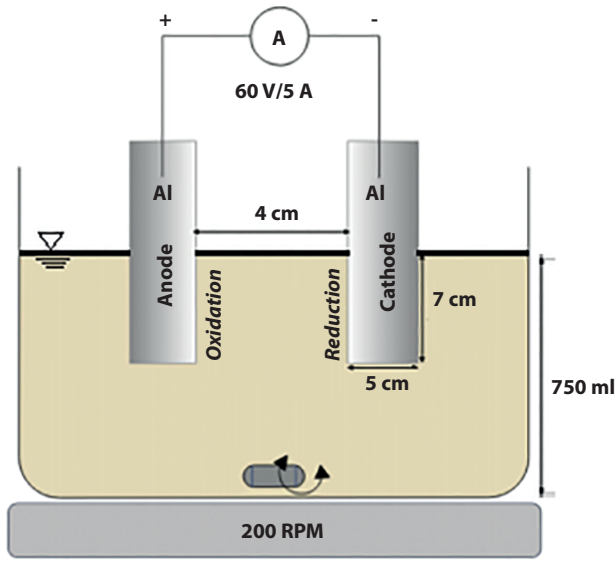

Figure 7.6 Schematic diagram of the EC experimental set-up. Adopted from Hamid *et al.* (2020).

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in the electrolyte, and the DC power supply was promptly switched on. The colour parameter and electrolyte salinity were examined before and after the EC process, respectively, using the standard method for water and wastewater examination, APHA 2017 (2120 C) and Multi-parameter probe YSI Professional Plus. The total effective area of the electrode was 35 cm^2 when immersed 70 mm in the electrolyte while the electrode dimensions were 16 cm x 5 cm x 1 cm. A magnetic stirrer was set to agitate the electrolyte at a constant speed of 200 rpm while the spacing distance between both electrodes was set at 3 cm.

7.9.3 Results and Discussion

Figure 7.7(a) shows the effects of current density and salinity on the colour removal rate studied using a variable current density of 60 A/m^2 to 780 A/m^2 with an increment of 60 A/m^2 for each interval. It can be clearly seen that the removal rate of colour increased with the rise in current density from 60 A/m^2 to 540 A/m^2. This phenomenon can be explained from the higher amount of iron ions produced by the electrode, which will destabilize the pollutant molecules. Therefore, when the current density is set beyond the optimum, the destabilization of particles happens and thus retards the removal (Ulu *et al*., 2014). Meanwhile, in the same range of current density, the salinity curve was observed constant from the beginning of the experiment up till the 10th reading. It then faces a sudden deflation after the current density of 540 A/m^2, which indicates that the removal of colour and the influence of salinity are no longer significant. The different salinity value beyond the optimum condition is due to the rapid motion of ions in electrolytes driven by high conductivity assistance.

Meanwhile, in Figure 7.7(b), the relationship between reaction time and the removal effectiveness of colour with respect to 5 min contact time interval until 70 min is reported. At the average salinity value of 15 ppt, the maximum percentage removal was obtained during the 60 min streak treatment time with 67% removal rate of colour pollutant. This condition is due to the high and constant solution salinity (NaCl) which does not only raise the conductivity but also commits strong oxidizing factor on the electrocoagulation method (Wei *et al*., 2012). Another study by Joseph and Chigozie (2014) revealed that the concentrations of iron ions and hydroxide would rise when the electrolysis duration is proportionally increased to improve reduction of pollutants before hitting a stagnant removal efficiency.

Finally, the investigation of colour removal in nature saline landfill leachate extensively confirms that the influence of pH gives a significant effect on the performance of EC operation as depicted in Figure 7.7(c).

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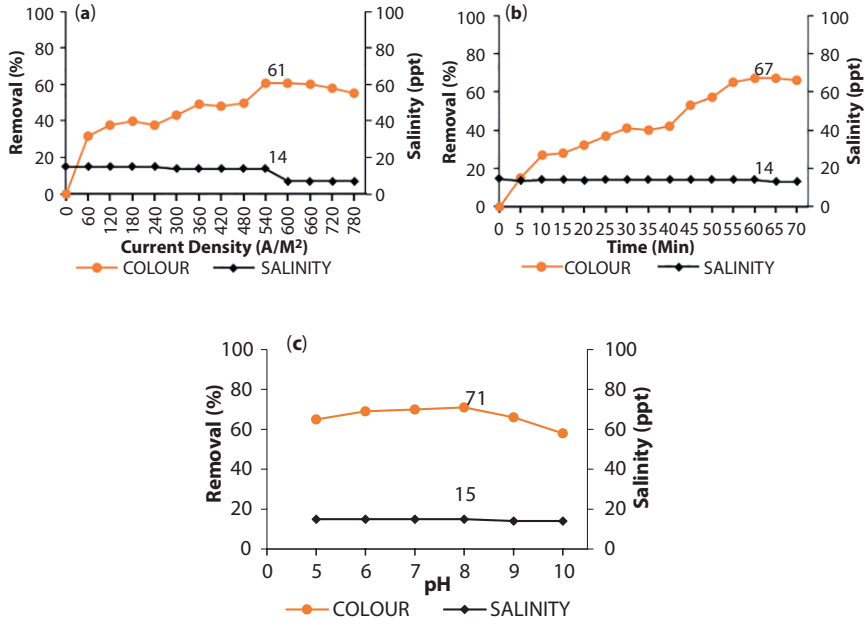

Figure 7.7 The effects of varying (a) current density, (b) contact time, and (c) pH in EC process. Adopted from Hamid *et al.* (2020).

Saraswat *et al.* (2015) stated that electrolyte salinity induces pH changes in an EC system; however, the response on pollutants removal is not in a linear condition. It can be clearly seen that by utilizing natural salinity landfill leachate, the percentage removal of colour increased to more than 67% from pH 5 to pH 8 with the highest percentage removal of the colour of 71% achieved at pH 8. On the other hand, the effect of salinity on pH has resulted in a stable condition from pH 5 to 8 at 15 ppt. The removal of colour started to drop after pH 8 from 71% to 66%, but the reduction in salinity at this point was insignificant as it only dropped from 15 ppt to 14 ppt. Therefore, these findings confirm the effectiveness of the EC process for removing high-strength colour by utilizing natural salinity landfill leachate. The natural salinity of this leachate has also successfully enhanced the efficiency of the EC process without the need for any additional supporting electrolyte.

7.10 Gaps in Current Knowledge

Given that landfill leachate is characterized as high-strength wastewater, the electrochemical technology of electrocoagulation process is potentially an

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effective option for landfill leachate treatment. Nevertheless, there are still several aspects that require considerable attention for further study. Most of the previous researches were conducted using low- to moderate-strength leachate rather than high-strength landfill leachate. The passivation of electrodes is also a vital factor influencing the efficiency of the electrochemical responses, especially in continuous EC operation (Deng *et al.*, 2020). Besides, during an EC treatment, an amount of metal electrodes becomes soluble in the treated effluent, which consequently results in the formation of sludge containing dissolved metal ions originated from the sacrificial anode electrode. This condition makes its recovery a challenging task to tend to. Furthermore, in some cases of EC treatment, additional supporting electrolytes such as NaCl are purposely utilized in landfill leachate treatment to increase the amount of Cl^- ions and hence raise the electrolyte conductivity. Nevertheless, the use of a large amount of NaCl would further increase the overall operating costs of the EC process and initiate the formation of secondary hazardous compounds within treated water (Kumar and Sharma, 2019). Therefore, investigations toward the implementation of naturally high conductivity landfill leachate should be critically tackled.

7.11 Conclusion and Future Prospect

The electrocoagulation process is a promising technology in waste and wastewater purification, which has shown potential either as a pre/post-treatment method, particularly in the landfill leachate treatment application. Based on the literature, it was proven that a single electrocoagulation process with optimized conditions could be applied to effectively and simultaneously remove pollutants from leachate compounds. Nevertheless, in order to further enhance the pollutants removal efficiency and achieve the allowable landfill leachate discharge limit, the electrocoagulation method is suggested to be incorporated with other potential treatment techniques to establish a hybrid electrocoagulation process. Hence, a further study into the best options of matching application and optimizing this integrated process is required to establish a high-end electrocoagulation process in the treatment of landfill leachate. In addition, precise and thorough knowledge of the possible risks from this treatment will facilitate the treatment design change to further improve the pollutants removal capacity. Therefore, it is also a wise move to improve the total cost-effectiveness of this electrocoagulation process by utilizing the existing natural resource in leachate which in turn offers research significance for future landfill leachate treatment system.

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8

Sustainable Solutions for Environmental Pollutants from Solid Waste Landfills

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Abstract

Over the last few decades and due to the rapid population growth, solid waste generation is increasing rabidly. The landfilling process is considered as the main disposal method for municipal solid waste (MSW) due to the simple and applicable technique, and economic features. However, different environmental problems resulting from solid waste landfills have been reported. Landfills contain high levels of organic materials, ammonia, and heavy metals are producing leachate, which causes a possible future pollution of soil, ground and surface water. Moreover, the mismanagement of non-sanitary landfills and dumping sites may contribute to more complicated problems in the environment. In this chapter, the main environmental problems related to landfills including soil, water and air contamination are discussed and evaluated. The sustainable solutions and management for the environmental problems related to solid waste landfills including landfill design and location, leachate management and treatment, and gas emission control are highlighted and discussed. Moreover, the effect of unsuitable locations of landfills on the environment is discussed and evaluated.

***Keywords*:** Landfills, environmental pollution, leachate, management, sustainable

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Nour Shafik El-Gendy (ed.) Sustainable Solutions for Environmental Pollution Volume 1: Waste Management and Value-Added Products, (305–342) © 2021 Scrivener Publishing LLC

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8.1 Introduction

Increasing population and industrial development has led to increased solid waste generation especially in urban areas. Solid waste management and its environmental risks are still considered one of the main challenges to the local authorities and public sectors in most countries worldwide. In many countries, landfilling is still considered the most common and suitable method for municipal solid waste (MSW) elimination and final disposal (Renou *et al*., 2008). There are many advantages of open dumping and sanitary landfills, such as their ability to deal with large quantity of generated solid waste from different sources with different composition (Tengrui *et al*., 2007). Nevertheless, despite the advantages of landfills for solid waste disposal and management, landfills have an adverse effect on groundwater and air quality. A landfill contains a high level of organics as it can be the source of volatile organic compounds (VOCs) which results in a series of environmental repercussions. These volatile organic matters as the landfill gas which is a result of natural decomposition of the landfill waste over a period of time (Allen *et al*., 1997). It has been found that some of these VOCs are responsible for the formation of photochemical smog and ozone (Ying *et al*., 2012). Moreover, the generation of a large quantity of leachate, which forms when rainwater infiltrates and reacts with waste (Ghafari *et al*., 2005), presents a high risk to soil and groundwater (Kjeldsen *et al*., 2002). Christensen *et al*. (2001) reviewed Surface water pollution caused by leachate. Therefore sustainable solutions for municipal solid waste landfill issues are required. In this chapter, the critical environmental issues for solid waste landfilling are reviewed and discussed. The gas emission from landfills and its effect on the air quality is discussed. Leachate characterization and its effect on surface and groundwater are assessed. The effect of unsuitable locations for solid waste landfill on the environment is highlighted. Sustainable solutions and techniques for gas emission and leachate are presented and discussed.

8.2 Domestic Solid Waste and Its Critical Environmental Issues

Waste generation can be associated with indicators of affluence, energy consumption and the lifestyle of people (OECD, 2004). In recent years, solid waste management in the world has involved complex and multifaceted

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trade-offs amid an excess of economic instruments, technological alternatives and regulatory frameworks resulting in a variety of environmental, economic, and regulatory impacts in waste management which not only complicate policy analysis but also reshape the model of global sustainable development (Bogner *et al*., 2003). According to many international studies, most of the waste in the world is generated from rich people. But ultimately the burden and impact is felt by all the people across the world. The per capita generation of MSW has also increased tremendously with improved lifestyles and social status of the populations in urban centres (Sharholy *et al*., 2007). As more land is needed for the ultimate disposal of these solid wastes, issues related to disposal have become highly challenging (Idris *et al*., 2004). Landfilling is a suitable and applicable option for solid waste disposal. More than 70% of solid wastes in the world are disposed of in landfills (Slack *et al*., 2005). However, many environmental issues and challenges related to solid waste and landfilling are recorded such as land availability, landfill lifetime, the suitable location and design of landfills. Moreover, the final disposal options in low-income developing countries are open dumping and open burning, which have a direct effect on health and the environment (Ferronato and Torretta, 2019). A landfill contains highly toxic and hazardous waste materials, and most landfills in developing countries have no sanitary design; also, the selection of landfill locations is random and does not meet any suitable selection criteria (Abdul Aziz *et al*., 2016; Abujayyab *et al*., 2017).

8.3 Landfill Leachate Characterization and Its Impact on the Environment

Leachate is the liquid that is generated from solid waste landfills. The quantity and compositions of leachate are the main two factors used to evaluate the leachate characterizations (Renou *et al*., 2008). A schematic diagram of leachate generation from landfill is presented in Figure 8.1. Leachate composition varies significantly among landfills depending on waste composition, waste age, and landfilling technology. Leachate sampling methods and sample handling routines may also influence the measured leachate quality. For example, colloids have a high affinity for heavy metals (Gajski *et al*., 2012; Lou *et al*., 2009). Table 8.1 presents ranges of general leachate parameters from various reports. In general, landfill leachates may contain very high concentrations of dissolved organic matter and inorganic macrocomponents. The concentrations of these components may typically

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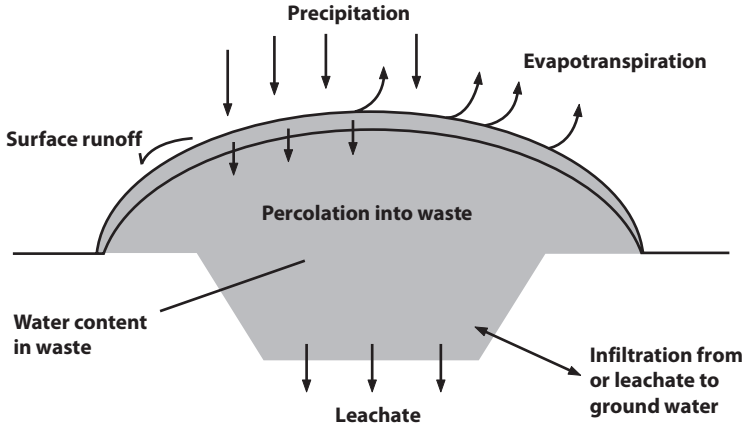

Figure 8.1 Scheme of leachate generation in a landfill (Eggen *et al*., 2010).

be up to a factor 1,000 to 5,000 times higher than concentrations found in groundwater. Several parameters change dramatically as the landfill stabilizes.

Leachate can be categorised into three types based on landfill age: young (less than 5 years), intermediate (5–10 years) and stabilized (old) leachate (more than 10 years) (Schiopu *et al*., 2010). The young leachates contain high concentration of total and biodegradable organics (BOD 4,000–13,000 mg/L; COD 10,000–60,000 mg/L), low concentration of ammonia (NH_4^+-N < 400 mg/L) and a high biodegradable ratio (BOD/COD 0.4–0.7). As the landfill age increases, the biodegradable organics break down, leading to a reduction in the organic content, an increase of non-biodegradable fractions, ammonia (NH_3^+-N 2,500–5,000 mg/L) and increases of pH (> 7.0) (Kurniawan *et al*., 2011). The classification of landfill leachate by landfill age with some general parameters is presented in Table 8.2.

Leachate plumes can be formed from unlined landfills and dumping sites. The large plumes percolate into subsurface aquifers (Slack *et al*., 2005). The processes that lead to the formation of leachate plume and leachate migration plume through landfill liners was discussed by several researchers (Kjeldsen *et al*., 2002; Varank *et al*., 2011). Scott *et al*., (2005) discussed leaching tests technique to evaluate the toxic materials

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Table 8.1 General composition of landfill leachate (Values in mg/l unless otherwise stated) (Kjeldsen *et al.*, 2002).

Parameter		**Range mg/l**
pH		4.5-9
Elec. Cond. ($\mu S\ cm^{-1}$)		2500-35000
Hardness		400-2,000[b]
Total Dissolved Solids (TDS)		2000-60000
Organic Matter	Total Organic Carbon (TOC)	30-29000
	Biological Oxygen Demand (BOD_5)	20-57000
	Chemical Oxygen Demand (COD)	140-152000
	BODS/COD (ratio)	0.02-0.30
	Organic nitrogen	14-2500
Inorganic Macrocomponents	Total phosphorous	0.1-23
	Chloride	150-4500
	Sulphate	8-7750
	Hydrogen bicarbonate	610-7320
	Sodium	70-7700
	Potassium	50-3700
	Ammonium-N	50-2200
	Calcium	10-7200
	Magnesium	30-15000
	Iron	3-5500
	Manganese	0.03-1400
	Silica	4-70[a]

(*Continued*)

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Table 8.1 General composition of landfill leachate (Values in mg/l unless otherwise stated) (Kjeldsen *et al.*, 2002). (*Continued*)

Parameter		**Range mg/l**
Heavy metals	Arsenic	0.01-1
	Aluminum	<0.01-2[b]
	Barium	0.1-2[b]
	Beryllium	<0.0005[b]
	Boron	0.5-10[b]
	Bromide	<1-15[b]
	Cadmium	0.0001-0.4
	Chromium	0.02-1.5
	Cobalt	0.005-1.5
	Copper	0.005-10
	Lead	0.001-5
	Mercury	0.00005-0.16
	Nickel	0.015-1.3
	Zinc	0.03-1000
	Iron	0.2-5,500[b]

[a]Values based on Owen and Manning (Owen *et al.*, 1997).
[b]Values based on Crutcher and Yardley (Crutcher *et al.*, 1992).

transported from landfills into the surface and groundwater. The subsurface migration of leachate depends on the complex leachate matrix and groundwater system. Alslaibi *et al.* (2017) evaluated the risk of nitrate transport from the unlined landfill to subsurface layers and groundwater in the Gaza Strip, Palestine, using experimental results and the SESOIL model. Banch *et al.* (2019) evaluated the impact of landfill leachate on groundwater and surface water in Malaysia using statistical multivariate test analysis.

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Table 8.2 Landfill leachate classification (Alvarez-Vazquez *et al.*, 2004).

Type of leachate	Young	Intermediate	Stabilized
Age of landfill (years)	<5	5-10	>10
pH	<6.5	6.5-7.5	>7.5
BOD_5/COD	>0.5	0.1-0.5	<0.1
COD (g/L)	10-60	4-10	5-20
Organic compounds	80% volatile fatty acids (VFA)	5–30% VFA+ humic and fulvic acids	Humic and fulvic acids
NH_4^+-N (mg/L)	<400	NA	2,500–5,000
TOC/COD	<0.3	0.3-0.5	>0.5
Kjeldahl nitrogen (g/L)	0.1-2	NA	NA
Heavy metals (mg/L)	>2	<2	<2
Biodegradability	Important	Medium	Low

8.4 Effect of Landfills on Air Quality

Landfills have an adverse effect on the air quality as it can be the source of volatile organic compounds (VOCs) which results in a series of environmental repercussions. These volatile organic matters as the landfill gas which is a result of natural decomposition of the landfill waste over a period of time (Allen *et al.*, 1997). Methane is the major constituent of the landfill gas comprising of 50-60% followed by CO_2 (~30-40%) and other trace gases (Jafari *et al.*, 2017). These trace gases include hydrogen sulfide, benzene, vinyl chloride, trichloroethylene and other hazardous pollutants (Rezaee *et al.*, 2014). Methane and carbon dioxide are well-known greenhouse gases; however, the hazardous nature of other VOCs is equally significant as they have a major role in the tropospheric chemistry. These VOCs are produced as a result of aerobic and anaerobic degradation of landfill waste by microorganisms in the presence of water and gases (Scaglia *et al.*, 2011).

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In the presence of water, these microorganisms target the organic matter in the landfills and convert them into soluble acids over a period of time. These acids then turn into acetate and hydrogen resulting in the release of methane, carbon dioxide and trace amount of different VOCs. The emission rate of these VOCs is greatly influenced by environment and condition of landfill such as ambient temperature, pH, humidity, bacterial composition, and age of the landfill (Majdinasab and Yuan, 2017). Therefore, variations in the contents of VOCs are very common among the landfills. However, it has been found that higher ambient temperature and moisture content results in faster degradation of organic matter, thus resulting in increased VOCs (Carriero *et al*., 2018).

It has been found that some of these VOCs are responsible for the formation of photochemical smog and ozone (Ying *et al*., 2012). Alkenes and alkynes are also part of the trace gases and they have been found to cause secondary organic aerosols resulting in particulate matter in air (Chu *et al*., 2013). Apart from that, sulfur containing organic compounds can cause severe odor problems. Volatile compounds like benzene and formaldehyde have been found to be carcinogenic to the surrounding population near landfills (Majumdar and Srivastava, 2012). These emissions continue until the organic matter has been completely decomposed by the bacterial action in different phases. There is ongoing research on the effect of these VOCs on the health of landfill workers and nearby residents. Table 8.3 concludes the details of VOCs emitted from a typical landfill site.

As methane is the major component of the landfill gases, so there exists a major safety hazard if the landfill is not properly managed. Methane is explosive by nature in the concentration range of 5-15% (Nair *et al*., 2019). In the U.S alone, 839 fire incidents have occurred related to landfills between 2004 and 2010 (Nair *et al*., 2019). The fire incidents are more common in developing countries where the landfills are not maintained properly. Apart from methane, other combustible materials in the waste are also responsible for fires in unsegregated landfills (Peter *et al*., 2018). Deliberate burning of landfills is also common in the developing world to reduce the waste volume and recover valuable materials. The amount of VOCs increased manyfold during the direct burning of waste in an uncontrolled manner. Table 8.4 contains a summary of major VOCs in $\mu g/m^3$ in summer and winter season in China (Duan *et al*., 2014). It can be seen that the concentration is greater in summers for all VOCs, mainly due to increase in temperature. The halogenated compounds are mainly due to the presence of plastics, textile and cleaning chemicals waste in landfills while aromatic compounds and terpenes are produced because of food and lignin-based waste (Nair *et al*., 2019).

These VOCs contain many greenhouse gases (GHGs) like CH_4, CO_2 and N_2O formed mainly because of the anaerobic digestion of the organic waste.

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Table 8.3 Details of the possible volatile organic compounds from a landfill site depending upon the conditions (Temperature, humidity, pH, etc.).

S/No	Type of waste	Resulting volatile organic compounds	Reference
1	Organic food waste	Hydrogen Sulfide, di-methyl sulphide, disulphide, methyl mercaptan, isovaleric acid, acetaldehyde, butyraldehyde, propionaldehyde, toluene, isovaleraldehyde, styrene, methyl ethyl ketone, para-xylene, methyl isobutyl ketone, isobutyl alcohol, butyric acid, propionic acid, valeric acid	Kabir and Kim (2011)
2	Textiles waste from various sources	m,p-xylene, formaldehyde, ethylbenzene, acrylonitrile, trimethyl-benzene, acetaldehyde, o-xylene, tetradecane, toluene	Igielska *et al.* (2003)
3	Cleaning chemical waste from homes/ factories	Chlorobenzene, limonene, o-xylene, isopentane, 1-propanol, isopropanol, phenol, decane, toluene, ethanol, dichlorobenzene, butoxyethanol	Rahman and Kim (2014)
4	Home care/ Personal Care product waste	alcohol, ethyl alcohol, propa terpene, ne, aldehyde, methyl formate, hexane, toluene, benzene, methyl formate, propionaldehyde, butyraldehyde, acetaldehyde, methyl ethyl ketone	Rahman and Kim (2014) Weschler and Carslaw (2018)

(*Continued*)

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Table 8.3 Details of the possible volatile organic compounds from a landfill site depending upon the conditions (Temperature, humidity, pH, etc.). (*Continued*)

S/No	Type of waste	Resulting volatile organic compounds	Reference
5	Paint, broken furniture, etc,	propylene glycol, benzene, ethyl benzene, p-diethly benzene, m-diethly benzene, trimethly benzene, methyl propanol, toluene, methlyhexane, cyclohexane, methyl cyclopentane, hexane, methyl hexane, methyl pentane, heptane, methyl heptane	Can *et al.* (2015)

Table 8.4 General summary of volatile organic compounds from landfill during summers and winters in China (Duan *et al.*, 2014).

Name of the compound	Concentration (μg/m^3)	
	Summer	Winter
Aldehyde and ketones	207.4 ± 255.2	5.1 ± 11.4
Esters and ethers	151.8 ± 160	31.1 ± 41.8
Alcohols	2350 ± 1791	1537 ± 710.8
Reduced sulfur compounds	160.8 ± 84.3	235.7 ± 66
Halogenated Compounds	330.6 ± 175.4	95.4 ± 109.2
Aromatics	319.8± 163	144.4 ± 130.3
Alkanes	863.8 ± 424.1	355.7 ± 329.9
Alkenes	292 ± 40.1	45.6 ± 31.2
Terpenes	99.2 ± 44.4	450.9 ± 475.5
Total	4513 ± 2250	2901 ± 1653

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As per an estimate, each ton of MSW can generate combine GHG ranging from 40 m^3 up to 250 m^3 (Lou and Nair, 2009). Globally, landfills sites have been responsible for the emission of total 794 Mt of CO_2 equivalent from 1990 until 2005 and it is expected to grow up to 959 Mt of CO_2 equivalent by 2030 (Nair *et al*., 2019). It has been found that many of the released VOCs are hazardous and carcinogenic in nature. Exposure to these VOCs through direct inhalation can cause a series of health problems like asthma, allergy, and other respiratory problems (Su *et al*., 2012). Apart from that, the VOCs which are produced by various biochemical processes are highly pungent and cause odor nuisance (Chemel *et al*., 2012). Because of their bad odor, they cause severe problems in the nearby communities. The compounds that cause severe odor problems are mostly sulfur containing compounds like hydrogen sulfide, dimethyl sulfide/disulfide, carbon disulfide and other compounds like alkyl benzene, esters, limonene (Xia *et al*., 2015). In summary, VOCs pollute the air, causing a series of health problems and odor nuisance for the landfill workers and nearby communities.

8.5 Effect of Unsuitable Location of Landfill on Environment and Community

Selecting the suitable location of the landfill is a complex decision for decision-makers in the rapidly growing areas around the world (Islam *et al*., 2020). Complexity arises from the several challenges faced by decision-makers such as minimizing the adverse consequences of landfills for the environment and reducing the cost of the establishment and running of the landfill sites (Baiocchi *et al*., 2014). Selecting of the landfill site is a complex issue because of the need to fulfil several requirements required by environmental communities, governments, residences, landowners' and engineering requirements, and limited financial capacities for the establishment and running of the sites (Abdullah *et al*., 2011; Ahmad *et al*., 2011; Majedi *et al*., 2015; Sakib *et al*., 2020; Younes *et al*., 2015). In addition, the selection of suitable sites needs to comply with legislative guidelines and local regulations as well as meet social necessities.

The selection of landfill sites usually encounters local residents' opposition, the so-called "not in my back yard" (NIMBY) phenomenon. This opposition arises due to the truth that landfills produce bad smells, the spread of raptors, rodents, insects, and scavengers. The main direct danger from these elements is its high possibility of infection and disease transmission and

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also the danger of birds for the flight of aircraft. An example of birds and scavengers spreads over the landfill is presented in Figure 8.2.

Moreover, garbage like plastic and paper fly over or spread around the dumps. There is the potential of explosions caused by pressure and blocked methane gas under heavy garbage layers. Another problem is the smoke from the landfill made by accidents or by scavengers, which leads to very polluted black clouds. Polluted clouds are highly risky for public health. An example from the landfill locations polluted by smoke is illustrated in Figure 8.3. Moreover, the problem of landfill leachate and the difficulty in drainage and treatment of leachate are other examples, where leachate causes pollution to soil and groundwater. Leachate exposes river streams to pollution. The general shape of the landfill site distorts the urban form. In addition, the danger resulting from the passage of heavy trucks, trucks' noise pollution, fall of garbage, and smell from trucks during their passage. Besides the direct effects of landfill sites, there are some indirect effects in the long term from allocating landfill sites close to urban areas, such as decreasing real estate prices and decreasing land value. In addition, there is the effect of landfills destroying the tourism sector in the place, as well as population shrinking.

An example of the unsuitable location of a landfill is illustrated in Figure 8.4. This landfill is located in Penang city in northwest Malaysia. The landfill was allocated directly beside the urban area. The bad smell raised from this landfill can be noticed around the location. The other dangers from the

Figure 8.2 An example of birds and scavengers spreading over the landfill.

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Figure 8.3 Smoke from landfill due to fire.

Figure 8.4 This landfill is located in Penang city in northwest Malaysia.

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Figure 8.5 Deir Al Balah landfill location from Gaza in Palestine.

landfill negatively affect the urban area. Another example of an unsuitable location of landfill is presented from Gaza in Palestine.

Figure 8.5 illustrates the Deir Al Balah landfill location. Although the location is far away from the urban area, it is directly above the main groundwater aquiver and is very close to the municipality drinking wells of the city (Alslaibi, 2009). Alslaibi determined that boreholes were contaminated, and the concentration of chemical and physical factors was over the reasonable standard degrees required by international and local criteria for irrigation and potable water (Alslaibi, 2009).

8.6 Recent Sustainable Technologies for Leachate Treatment

There are different biological and physico-chemical technologies for leachate treatment. Aerated lagoons, simple aerobic and anaerobic digesters, filtration, advanced oxidation Activated carbon adsorption (Wang *et al*., 2009; Perrich 2018), coagulation/flactulation process), and ion exchange are well-known wastewater and leachate treatments (Aziz *et al*., 2010; Mohajeri *et al*., 2010)

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and were considered as an efficient application for leachate treatment (Amr *et al*., 2013; Aziz *et al*., 2013; Liu *et al*., 2018; Bashir *et al*., 2017; Li *et al*., 2001; Orupold *et al*., 2000; Aziz *et al*., 2015; Li *et al*., 1999; Mojiri, 2011; Esteva and Prakash, 2014; Oraeki *et al*., 2018). However, it was reported that these treatment applications were still insufficient to meet the final leachate effluents discharge limits due to the high concentration of leachate parameters such as organics, inorganics, ammonia, heavy metals and toxic materials. Recently, some efficient technologies were introduced for removing of high levels of organic and ammonia from leachate such as advanced oxidation processes (AOPs). Advanced oxidation involves the release of highly reactive oxidizing radicals such as hydroxyl ($OH^{\bullet}$) and sulphate ($SO_4^{\bullet -}$) (Deng *et al*., 2011; Huling *et al*., 2006) which have high oxidation potential to degrade a variety of organic pollutants compared with other oxidation processes (Table 8.5).

Both radicals ($OH^{\bullet}$ and $SO_4^{\bullet -}$) can be released by activation of hydrogen peroxide (H_2O_2) and persulfate ($S_2O_8^{-2}$) (Eq. 8.1–8.3). Abu Amr *et al*. (2013a) utilized ozonation combined with Fenton reagent to generate $OH^{\bullet}$ for stabilized leachate treatment. Ozonation, UV, Fenton and H_2O_2 were employed to activate persulfate and release $SO_4^{\bullet -}$ for concentrated landfill leachate treatment (Hilles *et al*., 2016, Abu Amr *et al*., 2013b).

$$Fe + H_2O_2 \rightarrow OH^{\bullet} + OH^- \tag{8.1}$$

$$S_2O_8^{2-} + \text{Initiator} \rightarrow SO_4^{\bullet -} + SO_4^{\bullet -} \tag{8.2}$$

$$S_2O_8^{2-} + Fe^{+2} \rightarrow Fe^{+3} + SO_4^{\bullet -} + SO_4^{2-} \tag{8.3}$$

Table 8.5 Oxidation potential for some common oxidants (Huling *et al*., 2006).

No.	Oxidant radical	Oxidation potential (E_h)
1	Hydroxyl radical $OH^{\bullet}$	2.8V
2	Sulfate radical $SO_4^{\bullet -}$	2.6V
3	Ozone O_3	2.1V
4	Persulfate anion $S_2O_8^{-2}$	2.1V
5	Hydrogen peroxide H_2O_2	1.8V
6	Permanganate ion MnO_4^-	1.7V
7	Peroxymonosulfate anion HSO_5^-	1.4V

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Table 8.6 Summary of advanced oxidation applications for the treatment of stabilized leachate.

	COD		Color		References
	Initial (mg/L)	**Removal (%)**	**Initial (Pt. Co)**	**Removal (%)**	
$S_2O_8^{2-}$	2480	39	3450	55	Abu Amr *et al.* (2013a)
$S_2O_8^{2-}/H_2O_2$	22000	86	54000	93	Hilles *et al.* (2016)
Fenton	2180	55	4100	71	Abu Amr *et al.* (2013a)
Fenton+ Ozone	3125	80	12474	99	Abu Amr *et al.* (2016)
O_3/UV	7800	78	-	-	Lee *et al.* (2011)
$S_2O_8^{2-}/O_3$	2480	72	3450	93	Abu Amr *et al.* (2013b)
O_3/H_2O_2	5678	90	-	-	Naumczyk *et al.* (2012)
Fenton/O_3	2180	65	4100	98	Abu Amr *et al.* (2013a)

Table 8.6 summarized recent advanced oxidation processes used for leachate treatment.

8.6.1 Effects of AOPs on Leachate Biodegradability

Stabilized leachate, indicated by a low biochemical oxygen demand (BOD_5)/COD ratio (i.e., low biodegradability) is seen in many old landfills and is particularly difficult to treat biologically (Mohajeri *et al.*, 2010a; Abu Amr *et al.*, 2014). Therefore, additional physico-chemical processes are

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necessary for the pre-treatment and post-treatment of leachate (Tauchert *et al.*, 2006).

In this regard, dedicated treatment facilities are required before leachate can be discharged to the environment. Various site-specific treatment techniques can be used to treat hazardous wastewater depending on leachate characteristics, operation and capital costs, and regulations. Leachate treatment schemes likely include biological, physical, and chemical processes; their combination and specific modification are greatly influenced by the

Table 8.7 Biodegradability improvement after different AOPs.

Process	Initial COD (mg/L)	Initial BOD_5/ COD ratio	Final BOD_5/ COD ratio	References
O_3	5230	0.1	0.2	Tizaoui *et al.* (2007)
O_3/H_2O_2	5230	0.1	0.7	Tizaoui *et al.* (2007)
O_3/H_2O_2	743	0.01	0.17	Cortez *et al.* (2010)
O_3/H_2O_2	4960	0.22	0.43	Naumczyk *et al.* (2012)
O_3	743	0.01	0.15	Cortez *et al.* (2011)
Coagulation + O_3	6500	0.06	0.6	Wu *et al.* (2004)
Coagulation + O_3	2422	0.05	0.3	Bila *et al.* (2004)
Fenton + O_3	743	0.01	0.24	Cortez *et al.* (2011)
Fenton + O_3	14000	0.2	0.5	Goi *et al.* (2009)
O_3/Persulfate				Abu Amr *et al.* (2014)
O3/Fenton				Abu Amr *et al.* (2014)
Persulfate/ H_2O_2				Hilles *et al.* (2015)

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characteristics of leachate produced (Goi *et al*., 2009; Baig and Liechti, 2001). Advanced oxidation processes (AOPs) have received considerable attention as alternative methods for improving leachate biodegradability by transforming non-biodegradable pollutants into nontoxic substances (Catalkaya and Kargi, 2007).

A combination of biological and chemical oxidation processes is usually applied to enhance the effluent biodegradability standards. The chemical oxidation processes can lead either to a total degradation of chemical compounds or to the transformation of resistant highly hydrophobic organics into more polar molecules. These processes can be preferably used to transform recalcitrant organic wastewater constituents to biodegradable organics (Derco *et al*., 2001). Advanced oxidation can increase the biodegradability of high-molecular-weight organic compounds through the decomposition of large organic molecules, thereby increasing the effectiveness and turning them into compounds that are easily assimilated biologically (Bila *et al*., 2005). Table 8.7 presents an improvement of leachate biodegradability after different AOPs applications. AOPs (Fenton, photo-Fenton, H_2O_2/UV, and O_3/UV) are considered promising technologies for mature leachate treatment because they cause a powerful increase of leachate biodegradability (De Morais and Zamora, 2005; Kurniawan *et al*., 2006). Wu *et al*. (2004) found that the O_3/UV process is more efficient in enhancing biodegradability.

8.6.2 Case Study and Proposed Data for Leachate Treatment Plant Using AOPs

Table 8.8 presents data on the proposed leachate treatment plant for treating 100 m^3 of stabilized leachate by using the ozone/persulfate process (Abu Amr, 2013). Based on the proposed quality and quantity of the leachate, organic loading was 253 kg COD. According to the optimal conditions and maximum treatment efficiency for the ozone/persulfate process, a persulfate reagent dosage of 253 kg and ozone dosage of 151.8 (kg O_3 gas) were required to remove 72% of organic loading. Persulfate reagent was added to the leachate, and pH was adjusted to a high range (10) immediately after adding Fenton's reagent and prior to 210 min of ozonation as optimal contact time. A schematic diagram of the leachate treatment plant using the ozone/persulfate process is shown in Figure 8.6.

Aeration would facilitate further organic degradation and ammonia removal. Based on the batch aeration reactor results, around 72% of COD was removed from the effluent of the ozone/process at 9 d of aeration using air pump output 2 L/min/1 L leachate.

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Table 8.8 Data for treat 100 m^3 of stabilized leachate using ozone/persulfate process.

Materials and quantities								
Leachate Volume (m3)	COD Concentration		O_3Consumption (kg O_3/kg COD)	Persulfate (kg)				
	mg/L	Kg/100 m^3						
100	2530	253	15.18	253				
Operational conditions (Ozonation)								
Contact time (min)			pH					
210			10					
Expected effluent quality after ozonation								
COD			Colour			NH_3-N		
mg/L		Removal (%)	Pt-Co.		Removal (%)	mg/L		Removal (%)
Initial	Final		Initial	Final		Initial	Final	
2530	708	72	4530	181	96	1170	281	76
Aeration process								
Aeration time (Day)			Air flow rate (M^3/min)					
9			200					
Expected effluent quality after aeration process								
COD			NH_3-N (after 2 days of aeration)					
mg/L	Removal (%)		mg/L	Removal (%)				
431	83		0	100				

During processing in the batch aeration reactor, ammonia was completely removed after 4 d of aeration at pH 8 to 9 as pH was readjusted between 8 and 9 after ozonation. Accordingly, air pump output of 200 m^3/min was required for aeration of 100 m^3 treated effluent, and the final expected effluent concentrations met the acceptable levels of ammonia and were very close for COD and colour set by the Malaysia Environmental Quality Act of 1974 (MDC Sdn. Bhd., 1997).

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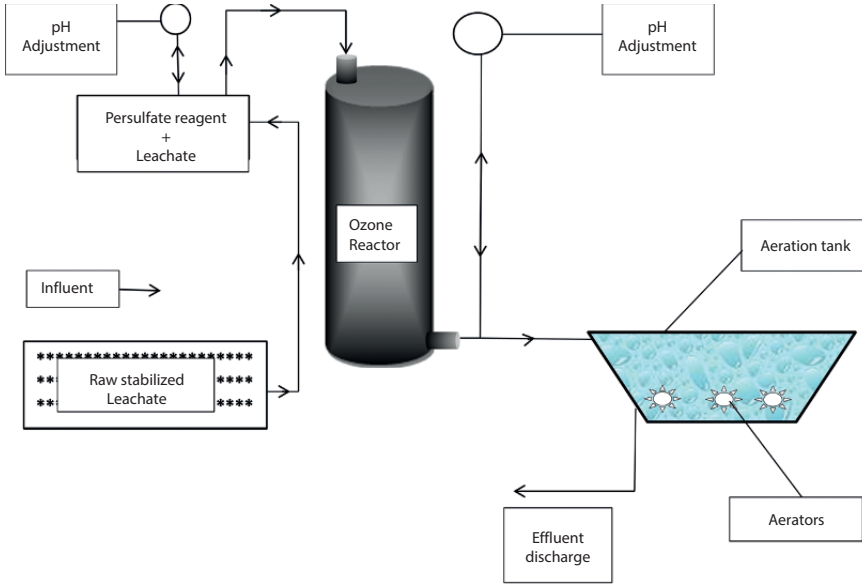

Figure 8.6 Schematic diagram for stabilized leachate treatment plant by ozone/persulfatein AOPs.

8.7 Sustainable Solutions for Gas Emission

The development of an optimized and efficiency technology to process the waste in landfill into energy and other useful products is a challenge the world needs to solve. Organic and food waste mainly accounts for the release of GHGs from the landfills. One sustainable and effective method is to treat the waste through composting prior to landfilling (Rastogi *et al*., 2020). Composting degrades the organic matter present in the waste through natural microbial action and converts the organic matter into stabilized form. The composted waste can be utilized as a fuel, fertilizer and soil amendment rich in humus (Hande and Deshpande, 2014).

Furthermore, the various thermochemical conversion pathways can be applied to make the landfill completely sustainable in a controlled system. Figure 8.7 summarizes the techniques to convert a landfill into a sustainable biorefinery (Madadian *et al*., 2020). Landfills are designed to safely store the waste; however, this approach of biorefinery aims at targeting each component of the waste to produce high-value-added products at each stage (Madadian *et al*., 2020).

It is recommended to collect gas-generated energy, for example, the design of Bukit Tagar landfill site with well-engineered calculation and

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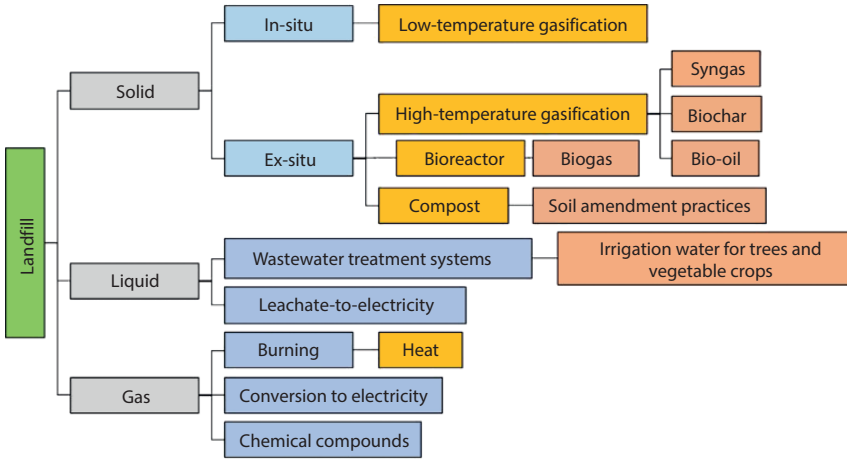

Figure 8.7 Various techniques to convert landfill into sustainable biorefinery. Taken from (Madadian *et al.*, 2020).

planning. There are total six layers of liner and protection before the wastes are discharged on the landfill site. Figure 8.8 depicts the base liner system together with the cross-section of the overall landfill design. The BTSL is designed for incoming waste of 5,000 tonnes per day for 40 years' capacity. The average for current incoming waste is 3,250 tonnes per day. If the waste generated is more or less as the average amount, the landfill could contain waste for KL and Selangor central for more than 40 years. In other words, less land is needed to be re-exploited for designing sanitary landfill. Based on the cross-sectional diagram as depicted in the Figure, the landfill is designed with the groundwater monitoring probes. The purpose of these probes is to measure and monitor the groundwater quality to ensure that no leachate or contaminants infiltrate to the ground and pollute the groundwater. Besides, the design of surface drainage on the landfill could reduce the amount of infiltration of water to mix and react with the wastes. Furthermore, the landfill gas (CH_4) generated from the degradation of solid waste anaerobically also been collected and treated.

The landfill is designed with installation of LFG collection system. The LFG composed mainly methane (CH4) gas, which is combustible and capable of generating enormous heat energy. In this renewable energy (RE) centre, BTSL implemented the WTE project by converting the LFG into electricity via the gas engine. The collected LFG first undergoes a series treatment process before being sent to the 3.2 MW gas engine for electricity. The detailed process for each step is depicted in Figure 8.9. By 2019, biogas to energy centre successfully generated 10.4 MW electricity.

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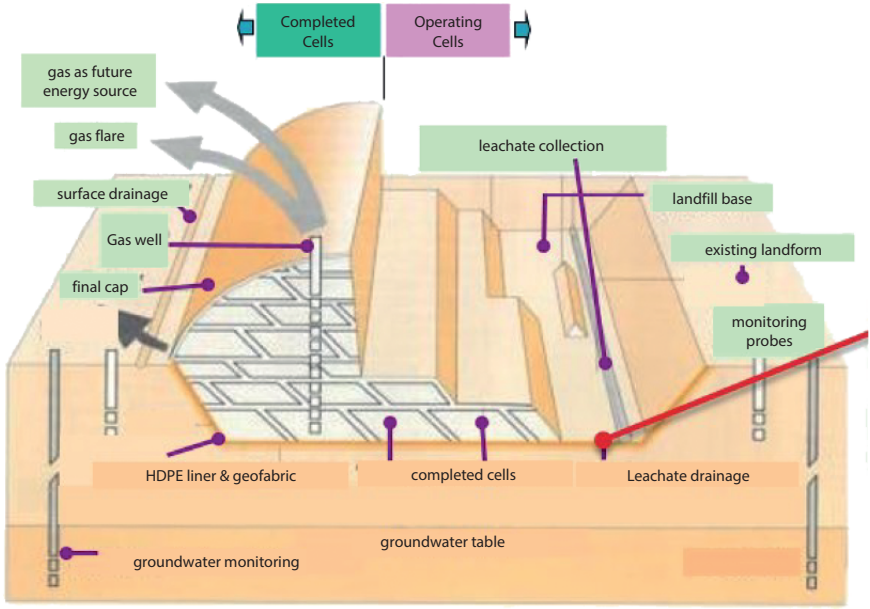
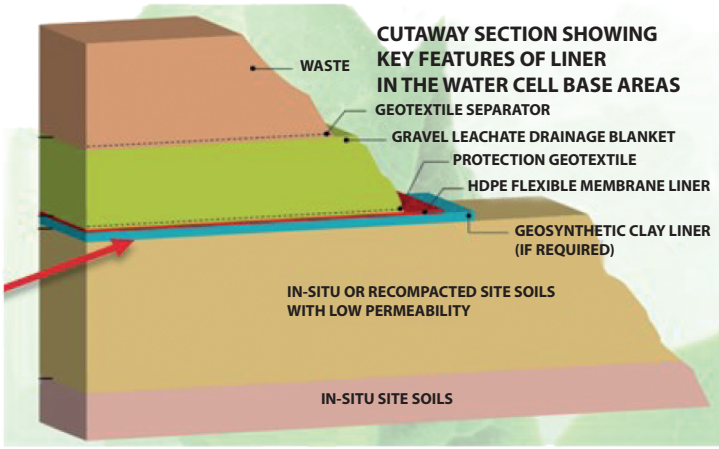


Illustration on Sanitary Landfill design



Base liner system

Figure 8.8 Cross-sectional diagram for the design of landfill site and the base liner system (Kub-Berjaya Enviro, 2017).

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Bukit Tagar Renewable Energy Centre

Gas Engine 1.2MW and 2 Units of 2500Nm3/hr Flares

3.2MW Gas Engine

Figure 8.9 The 3.2 MW gas engine for the generation of electricity.

Besides the WTE facility, BTSL is also equipped with pilot solar project. The capacity of this pilot-scale solar project in BTSL is about 125 kW. There are different solar panel technologies such as flexible solar membrane and crystalline solar panel. This is to test the most effective technology to be adopted for future development. The energy generated from this pilot solar project will also be supplied back to TNB under the Feed-in Tariff scheme. Figure 8.10 below illustrates the pilot solar project conducted in BTSL.

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Figure 8.10 Pilot solar power project on top of the closed landfill cells.

8.8 Consideration for Selection of Sustainable Locations for Landfills

The selection process of sustainable locations for landfills has been studied since the 1990s. In 1997, Basaiaoclu conducted the first work for landfill site selection (Basaiaoclu *et al*., 1997). Since 1997 massive works have been developed to improve the methods to find the best landfill locations according to different considerations. These considerations differed from location to location as well as differing due to the objectives of decision-makers.

From the literature, tens of criteria have been utilized for sustainable landfill location. An example is the meteorological considerations such as evaporation, precipitation, and temperature (Yesilnacar and Cetin, 2005; Khamehchiyan *et al*., 2011; Al-Ansari *et al*., 2013; Paul *et al*., 2014). The general target of considering the meteorological criteria is the direct influence of the factors in increasing or decreasing the leachate amount due to precipitation and evaporation as well as methane gas emission increment in the air from the waste due to high temperature. In addition, the geological factor has been employed during the site selection process such as landslides, lithology, earthquake zones and distance from geological faults (Delgado *et al*., 2008; Dadras *et al*., 2010; Milevski *et al*., 2012; Mănoiu *et al*., 2013). The aim of using geological factors is to avoid allocating landfill sites in risky locations due to unstable land formation and avoid the possibility of harming the groundwater resources and Aquifers (Demesouka *et al*., 2013). In the same context, placing the landfills near to surface water such as lakes, rivers, springs, flood plains, marshes as well as wetlands is to

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be avoided (Basaiaoclu *et al*., 1997; Banar *et al*., 2007; Moeinaddini *et al*., 2010; Abdalqader, 2011; Effat and Hegazy, 2012; Uyan, 2014).

The elevation, land slope, and land aspect factors are utilized to select sustainable locations for landfills (Nazari *et al*., 2012; Gbanie *et al*., 2013; Paul *et al*., 2014). Additionally, the soil type and depth employed are to avoid high permeability sole types due to the high possibility of contaminating the underground water (Moghaddas & Namaghi, 2011).

Sensitive zones such as Sensitive ecosystems, protected forests, cultivation land, and natural cover make them unsuitable locations for landfills (Delgado *et al*., 2008; Azman *et al*., 2012; Kontos *et al*., 2003; Shahabi *et al*., 2014).

To fulfill the socioeconomic target, several considerations have been employed such as land use, land ownership, distance from coastlines, industrial areas, land cost, future use of the land, compliance with current landfills, availability of cover materials, and salinization zones (Lin and Jehng-Jung, 1999; Biotto *et al*., 2009; Wan Hussin, 2010; Abdalqader, 2011; Moghaddas and Namaghi, 2011; Ahmad *et al*., 2013b; Demesouka *et al*., 2013; Houshyar, 2014).

Regarding the infrastructures, several factors are taken into consideration such as public utilities, ground infrastructures, communication infrastructures, railways, road accessibility to the site, water facilities, municipal and local wells, and waste production centers (transfer station) (Şener *et al*., 2006; Delgado *et al*., 2008; Jaafar, 2008; OzeairAbessi, 2009; Nas *et al*., 2010; Demesouka *et al*., 2013; Romali *et al*., 2013). Public acceptability aspects include visible travel distance from roads, visibility from residential areas, wind direction, wind speed, distance from residential areas, archaeological, tourism, and cultural sites, sports, natural parks, theaters, hospital, schools, universities, and airport (Shaikh, 2006; Despotakis and Economopoulos, 2007; El Alfy *et al*., 2010; Moeinaddini *et al*., 2010; Nazari *et al*., 2012; Milevski *et al*., 2012; Babalola and Busu, 2011; Ahmad *et al*., 2013a; Demesouka *et al*., 2013; Eskandari *et al*., 2013; Houshyar, 2014; Paul *et al*., 2014). Proximity to the dense population, villages/rural areas, population of urban centers are other factors (Şener *et al*., 2006; Gorsevski *et al*., 2012).

The difference in the number of considered factors was the availability of the data in different geographical areas. A case study to select the best sustainable site applied in Karabuk-Turkey to show how the location can be selected based on multiple considerations. In the case study, eight criteria were employed based on data availability and the characteristic of this geographical area of Karabuk. The model is presented in Figure 8.11.

The data (roads, water streams, natural plants, geology, geological faults, and land use) were collected from "Harita Genel Komutanlığı".

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Figure 8.11 The model developed in ArcGIS to select the sustainable location of a landfill in Karabuk.

The elevation data was collected from ASTER data (NASA/METI/AIST/Japan Spacesystems, 2019). The slope layer was computed from the elevation map. The database was prepared in ArcGIS 10.5, while the model was established in the Model builder in ArcGIS. Weighted Linear Combination (WLC) algorithm was one of the Multicriteria decision analysis (MCDA) methods that was utilized to find the best location. The outcomes of this model are presented in Figure 8.12. The output suitability map presented in Figure 8.6 shows that the best suitability degree using 8 parameters is 9 out of 10 levels. The area of the best location is quiet enough for several years for Karabuk state.

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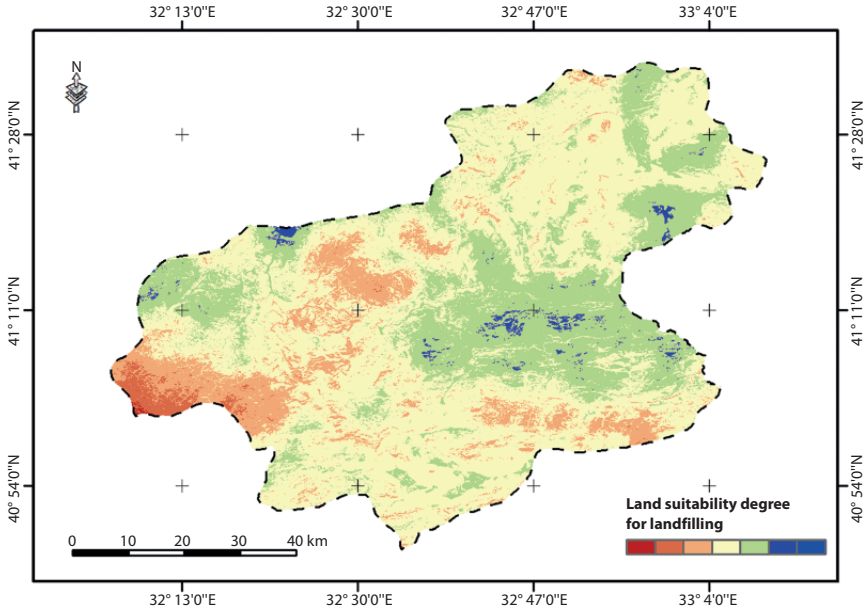

Figure 8.12 Land suitability evaluation. A case study in Karabuk, Turkey.

8.9 Conclusion

In this chapter, the global issues for solid waste landfills and their effects on the environment are summarized. Landfill location criteria and the effect of unsuitable locations for landfills are discussed. The gas emission and leachate generation from landfills and their effect on air and water quality are evaluated. Sustainable solutions for selecting suitable locations for landfills are highlighted. Several factors should be taken into consideration for selection of suitable locations for landfills, such as public utilities, ground infrastructures, communication infrastructures, railways, road accessibility to the site, water facilities, municipal and local wells, waste production centers (transfer station), leachate generation rate, topographic slope and soil type. Recent technologies for leachate treatment are summarized and discussed. Advanced oxidation processes can be recommended as sustainable treatment methods due to their effectiveness for removing of highly concentrated parameters as well as their performance for enhancing the biodegradability of treated leachate.

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9

Progress on Ionic Liquid Pre-Treatment for Lignocellulosic Biomass Valorization into Biofuels and Bio-Products

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Abstract

Energy security and environmental features are nowadays two major issues that have boosted the exploitation of an eco-friendly and renewable alternative to petrochemical resources. Lignocellulosic biomass (LCB) is an abundant and sustainable feedstock of great interest for the production of valuable chemicals and biofuels. It consists of three major components: cellulose, hemicellulose, and lignin. However, access to these biopolymers is impeded by the recalcitrance and the complex structure of the plant cell walls. Thus, a pre-treatment step is necessary to disorganize and/or fractionate the lignocellulosic matrix.

The use of Ionic Liquids (ILs) in the LCB pre-treatment has gained considerable attention in recent years. ILs are emergent solvents with high thermal and chemical stability, low vapor pressure and tuneable properties, which allow an energy-efficient LCB pre-treatment in eco-friendlier conditions than conventional ones. However, the large-scale uptake of IL to pilot and industrial level is still hindered by their production cost and the need to understand more deeply the mechanism of their interaction with LCB, hydrolytic enzymes and microbial cells.

This chapter outlines the potential application and the confronted challenges of IL use in LCB pre-treatment, their mechanism of interaction and dissolution of LCB and their biocompatibility.

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Nour Shafik El-Gendy (ed.) Sustainable Solutions for Environmental Pollution Volume 1: Waste Management and Value-Added Products, (343–374) © 2021 Scrivener Publishing LLC

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***Keywords*:** Lignocellulosic biomass, valuable chemicals, biofuels, pre-treatment, ionic liquids

9.1 Introduction

Nowadays, the growing energy demand is almost entirely dependent on petroleum-based fuels that account for more than 80% of the total energy (Zabed *et al.*, 2016). This intensive use of fossil fuels has contributed to increased emissions of greenhouse gases into the atmosphere, global warming and global climate change. Over the past decades, the production of fuels and chemicals from renewable resources has gained increasing interest in order to limit our reliance on fossil fuels (Zabed *et al.*, 2017).

Hence, many efforts have been directed towards boosting the renewable energy share to reduce the reliance on fossil fuels and to target new renewable and abundant raw materials for a sustainable production of energy, fuels and chemicals. Lignocellulosic biomass (LCB) as forest residues, agricultural waste and energy crops, represents a promising renewable and non-food feedstock for the production of carbon neutral fuels and value-added chemicals which fulfils the conception of the circular economy. The conversion of LCB into bioethanol and biodiesel for substitution of fossil fuels mainly petrol and diesel is grasping global interest particularly from an environmental viewpoint. Indeed, bioethanol and biodiesel, unlike fossil fuels, are produced from a renewable and abundant feedstock and their use as alternative fuels, mainly in the sector of transport, will widely decrease the emission of greenhouse gases (Halder *et al.*, 2019). Therefore, switching to biofuels could enhance air quality, reduce global warming and contribute to waste management since it is based on waste biomass conversion (Halder *et al.*, 2019). LCB comes mainly from forestry and/or agricultural waste (wood, sugar cane straw and bagasse, etc.) and dedicated herbaceous crops (Miscanthus, Switchgrass, etc.) (Zabed *et al.*, 2016). In addition to the various biomasses of forest, agricultural and herbaceous origin mentioned above, municipal organic waste could also represent an additional resource for application in the biorefinery. In this regard, waste cooking oil generated from household and restaurants represents a promising waste feedstock to be valorised into second-generation biodiesel (Aboelazayem *et al.*, 2017, 2019).

LCB, consisting of three major biopolymers, cellulose, hemicellulose and lignin, represents the main component of plant cell walls. The former ones are both polysaccharides that could be enzymatically hydrolysed into simple sugars that can be converted to biofuels, namely bioethanol and/or

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other chemicals products, i.e., alcohols, organic acids and amino acids via microbial fermentation. However, the polysaccharides are linked to each other by covalent and hydrogen bonds and both are further connected to the lignin which is a highly branched aromatic polymer, delivering to the LCB a robust and recalcitrant matrix (Mosier *et al.*, 2005). Hence, a pre-treatment step is required in order to disrupt the LCB tridimensional architecture and make the polysaccharides more accessible to hydrolytic enzymes. Different pre-treatment techniques have been reported in the literature and can be classified into several categories (Hendriks and Zeeman, 2009; Zhao *et al.*, 2012; Haghighi Mood *et al.*, 2013; Saini *et al.*, 2015): i) biological pre-treatments, involving microorganisms and/or lignocellulolytic fungi, capable of degrading polysaccharides and/or lignin; ii) physical pre-treatments, involving mechanical grinding, extrusion and acting by reducing the particle size and crystallinity of lignocellulose; iii) chemical pre-treatments, which are carried out, in most cases, under aggressive conditions, allow the structural disorganisation of the lignocellulose, either in dilute/concentrated acidic or alkaline medium, either by applying organic solvents or ionic liquids; iv) physicochemical pre-treatments, including organosolv processes, steam explosion, expansion of fibers by ammonia (AFEX), supercritical CO_2; and v) pre-treatments based on the combination of several approaches, such as pre-treatment with dilute acid combined with ionic liquids (Auxenfans *et al.*, 2014), pre-treatment with ionic liquids combined with ultrasound (Yu *et al.*, 2018), sequential pre-treatment with dilute acid and sodium hydroxide (Lee *et al.*, 2015), pre-treatment combining extrusion and CO_2 (Wu *et al.*, 2018).

Herein, the state of the art of ILs application in lignocellulose pretreatment, dissolution and modification is reviewed. Later in this chapter, the impact of ILs on enzymes and microorganisms as well as the current challenges in the field are discussed.

9.2 Lignocellulosic Biomass for Biofuels and Bio-Products

Lignocellulosic biomass (LCB) including forestry and agricultural wastes such as woody sawdusts, corn stover, rice and wheat straw and herbaceous crops, is a renewable raw material that is available in large quantities. LCB, being mainly composed of polysaccharides, is considered a promising source of fermentable sugars for the production of biofuels, bio-products and biomaterials without necessitating extra land or affecting food and crop production (Halder *et al.*, 2019). Lignocellulose materials are mainly

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composed of three biopolymers: cellulose at 38–50% (w/w), hemicelluloses 23–32% (w/w), and lignin 12–25% (w/w) (Elgharbawy *et al.*, 2016). The ratios of the three components vary depending on the source of the LCB, which will affect the pre-treatment and deconstruction process and determine the methods for the valorization of the feedstock into specific products (Brandt *et al.*, 2013).

9.2.1 Cellulose

The cellulose molecule is a linear homopolysaccharide made up of D-glucose units linked together by β-(1,4) glycosidic bonds. The cellulose chains are linked together via hydrogen bonds and form so called cellulose fibrils. Intra- and inter-chain hydrogen bonds, induced by hydroxyl functions present on glucose units, provide cellulose a highly organised crystalline structure. However, cellulose fibrils enclose amorphous regions with a less organised structure; these regions are more susceptible to biodegradation than the crystalline regions (Nagarajan *et al.*, 2017).

The polysaccharides, namely cellulose and hemicellulose need to be hydrolysed in order to release the glucose and the other fermentable sugars. Moreover, the complex structure of lignocellulose makes it more resistant to depolymerisation (Phitsuwan *et al.*, 2013), thus impeding the hydrolysis of polysaccharides and rendering the LCB pre-treatment a crucial and unavoidable step in the process. After an effective pre-treatment of cellulose using ILs, its crystalline structure is broken down which leads to the isolation of hemicellulose and lignin from the cellulose rich fraction (CRF) (Elgharbawy *et al.*, 2016; Halder *et al.*, 2019).

Unlike crystalline cellulose, CRF regenerated from IL-pre-treatment is of amorphous structure that can be more easily subjected to enzymatic hydrolysis and then converted into bioethanol through microbial fermentation (Elgharbawy *et al.*, 2016). Although the conversion of the cellulosic glucose into bioethanol via microbial fermentation represents the main and very frequently studied pathway, multiple other bioproducts could also be produced. Based on the employed microorganism and under specific process variables, the valorization process could be tailored to produce other biofuels such as biogas, biobutanol and hydrogen. The CRF could also be favourable for the production of acetone, and various acids, i.e., lactic acid, succinic acid, propionic acid, fumaric and α-ketoglutaric acids (Ntaikou *et al.*, 2008; Qureshi *et al.*, 2010; Litsanov *et al.*, 2012; Ryu *et al.*, 2015). Polymerisation of lactic acid molecules enables the synthesis of polylactic acid, a biodegradable thermoplastic material that has experienced remarkable industrial development (Jamshidian *et al.*, 2010). Furthermore, the

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aforementioned acids represent high value-added molecules with various interesting applications. For instance, α-ketoglutaric acid is used for the synthesis of food supplements, pharmaceutical and cosmetic products and heterocyclic compounds (Chin *et al.*, 2014; Ryu *et al.*, 2015).

On the other hand, several platform molecules could be produced after acidic hydrolysis of CRF, including furfural, 5-hydroxymethylfurfural (5-HMF), levulinic acid (LA), ethyl levulinate, ethyl formate and lactones (Kang *et al.*, 2018). Nevertheless, the use of acidic ILs represents a promising alternative pathway enabling the direct hydrolysis of CFR for the production of platform chemicals instead of employing harmful acidic catalysts (Ramli *et al.*, 2015).

Besides, CRF appears to be a promising material in its polymeric form that could be used for the production of nano-fibres and could enter the pyrolysis pathway (Halder *et al.*, 2019). For instance, various platform chemicals including as levoglucosan and furfurals can be selectively produced via pyrolysis of CRF. Moreover, upgrading bio-oils could also be generated from CRF pyrolysis and subsequent reduction of aldehydes and ketones in oil (Muhammad *et al.*, 2012; Zheng *et al.*, 2017).

9.2.2 Hemicellulose

Unlike cellulose, hemicellulose is heterogeneous in chemical composition as well as in structure. It is a branched polysaccharide consisting of hexoses (β-D-glucose, β-D-mannose, β-Dgalactose) and pentoses (β-D-xylose, α-L-arabinose and/or uronic acid) (Menon and Rao, 2012). Hemicelluloses are characterised by shorter molecular chains and lower molecular weight than cellulose but their structure and composition vary from a biomass to another. For instance, glucuronoxylan constitutes the main hemicellulose of hardwoods while galactoglucomannan represents up to 20-25% of the dry matter of softwoods (Gírio *et al.*, 2010). Hemicelluloses are cross-linked to the cellulose and lignin which enhances the LCB matrix rigidity and recalcitrance.

Similar to cellulose, hemicelluloses, particularly xylans, constitute a potential source of sugars that can be massively converted into second-generation bioethanol. Moreover, hemicellulose can be dedicated in a wide variety of applications and are receiving increasing attention. The monomers released from the hydrolysis of hemicelluloses consisting of C6 and C5 sugars can be converted to many other value-added chemicals utilised in several fields including nutrition, cosmetology, medicine, chemical industry or polymer materials (Canilha *et al.*, 2003). Xylans, due to their original physicochemical properties similar to hydrocolloids, are used as

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thickeners, emulsifiers or gelling agents in the food and pharmaceutical industries.

Xylose, obtained from the hydrolysis of xylans, can be converted to xylitol by catalytic hydrogenation, is known to exhibit sucrose-like sweetening properties with lower caloric intake and to prevent the development of dental caries. In addition, hemicellulose can also be converted, by employing acidic catalysts, into C5 sugars that can be subsequently dehydrated to generate furfural, an organic compound used as a synthetic intermediate for the production of solvents; in the manufacture of resins or certain food flavourings (Peleteiro *et al.*, 2015).

9.2.3 Lignin

Lignin is defined as a heterogeneous, hydrophobic, high molecular weight three-dimensional biopolymer containing 61-65% carbon and representing the most abundant source of aromatic carbon on earth. The aromatic and phenolic backbone of lignin results from the conjugation of three phenylpropanoid moieties or mono lignols (coumaryl (H unit), coniferyl (G unit) and sinapyl (S unit) alcohols) via ether linkages (Gillet *et al.*, 2017; Ponnusamy *et al.*, 2019). The lignin content and the ratio between the different monomers vary depending on the plant species but also within the same species depending on the cell type, the age of the cell and its location. In fact, the lignin content of the different LCBs decreases as follows: softwood wood (27 - 33%) > hardwood wood (18 - 25%) > herbaceous biomass (17 - 24%) (Azadi *et al.*, 2013). Softwood lignin consists mainly of coniferyl alcohol while hardwood lignin is composed from both coniferyl and sinapyl alcohols with traces of coumaryl alcohol (Li *et al.*, 2015). Finally, the lignin constituting the herbaceous biomasses contains the three monomers in various ratios. Lignin is linked to polysaccharides by covalent and hydrogen bonds, and more particularly by ester bonds that are established with hemicelluloses which gives more rigidity and recalcitrance to the lignocellulose matrix (Lupoi *et al.*, 2015; Gillet *et al.*, 2017).

Lignin remains currently underutilised since it is mainly burnt as low-grade fuels or used as additives. Emerging exploitations have been envisaged as new avenues for lignin valorization in its polymeric form or after depolymerisation. Lignin is considered as potential replacements for synthetic polymers such as polyacrylonitrile in the production of carbon fibres (Norberg *et al.*, 2013; Halder *et al.*, 2019).

Lignin can be depolymerized, for example, into vanillin and syringaldehyde (Araújo *et al.*, 2010; Pandey and Kim, 2011) and other aromatic

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compounds that can be functionalised for the production of high value-added platform molecules including benzene, phenol, catechol, cresol, eugenol, syringol, coniferol and guaiacol (Gillet *et al.*, 2017; Ponnusamy *et al.*, 2019). In addition, under different conditions, the oxidation of lignin generates vanillic acid, aliphatic and aromatic acids, aromatic aldehydes, quinones and cyclohexanols (Ponnusamy *et al.*, 2019).

The gasification of lignin generates what are called syngas such as carbon monoxide and hydrogen that can be converted or upgraded into methanol, dimethyl ether, ethanol, blended or mixed alcohols, Fischer–Tropsch–fluids and C1–C7 gases (Ponnusamy *et al.*, 2019). Lignin valorization via pyrolysis is an alternative pathway for the production of high yield bio-oil that could be upgraded to renewable biofuels (Zadeh *et al.*, 2020). Additionally, ILs have been involved in the depolymerisation process of lignin for the production of guaiacol (Jia *et al.*, 2010). More recently, Lei *et al.* (2015) have demonstrated the efficient application of ILs in the pre-treatment of lignin in the improvement of pyrolysis oil by increasing the production of phenolic compounds.

In this regard, lignin valorization is increasingly grasping researchers' attention and efforts to explore and develop potential routes and valorization processes.

9.3 Pre-Treatment Technologies for Lignocellulosic Biomass

Within the LCB, the different biopolymers of the plant cell wall form a complex matrix which aims to ensure the rigidity of the wall and to protect cellulose from pathogens. The entanglement of the polymers as well as the lignin layer surrounding the microfibrils of cellulose severely limits the effectiveness of hydrolysis.

In the attempt to valorise the major biopolymers constituting the LCB, the process is started by a pre-treatment step in order to disrupt/fractionate the complex of cellulose, hemicellulose and lignin and to subsequently enhance the digestibility of polysaccharides and the extraction of lignin. The main objectives of the pre-treatment are to deconstruct the recalcitrant structure of the three biopolymers within the LCB, to remove or redistribute the hemicelluloses and lignin in the plant wall, and to reduce the crystallinity or the degree of polymerisation of cellulose (Zabed *et al.*, 2016).

So far, several pre-treatment techniques have been extensively described in the literature based on biological, physical, chemical and physicochemical

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methods or on their combination as classified in Table 9.1 (Menon and Rao, 2012; Elgharbawy *et al.*, 2016; Zabed *et al.*, 2016; Halder *et al.*, 2019).

Although the role of the pre-treatment is to alter or deconstruct the LCB recalcitrant matrix and to increase the accessible surface area, the mode of action, the reaction conditions and the pre-treatment outcomes vary from one method to another. Each pre-treatment technique has several advantages and drawbacks regarding the techno-economic conditions, the energy input and the environmental concerns. The choice of a

Table 9.1 A comparative summary of the most studied pre-treatment techniques.

Pre-treatment method	Category	Advantages	Drawbacks
Milling	Physical	Reduction in cellulose crystallinity Reduction in degree of polymerisation Increase of surface area	High energy consumption No lignin removal
Fungal pre-treatment (white, brown and soft-rot fungi)	Biological	Degradation of lignin Low capital cost Low energy consumption Eco-friendly process: no chemicals required Mild operating conditions: low inhibitor production	Long treatment time (10-14 days) Degradation of the residual polysaccharides and their consumption by microbes
Dilute-acid pre-treatment (hydrolysis)	Chemical	Increase of accessible surface area High reaction rate Removal of hemicellulose (degradation of 80-100%) Alteration and redistribution of lignin without solubilisation	High temperature required pH neutralisation required Disposal of neutralisation salts required Little removal of lignin Inhibitor formation

(*Continued*)

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Table 9.1 A comparative summary of the most studied pre-treatment techniques. (*Continued*)

Pre-treatment method	Category	Advantages	Drawbacks
Concentrated-acid pre-treatment (hydrolysis)	Chemical	Shorter residence time compared to dilute-acid Hydrolysis Hydrolysis of hemicellulose and cellulose Applicability to different feedstock More applied process at pilot and large scale	High temperature required pH neutralisation required Acid recovery required Formation of inhibitors and generation of by-products Corrosion of equipment High equipment cost
Alkaline pre-treatment	Chemical	Lower equipment cost compared to acidic pre-treatment Removal of hemicellulose and lignin Alteration in lignin structure Lower inhibitor formation Generation of by-products	Long residence time, Formation of irrecoverable salts pH neutralisation required
Liquid hot water	Physico-chemical	Structural and chemical alteration of lignin No catalysts or chemicals required Increase of accessible surface area No or low inhibitor formation Removal of hemicellulose	High temperature and pressure High water demand Degradation of hemicellulose

(*Continued*)

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Table 9.1 A comparative summary of the most studied pre-treatment techniques. (*Continued*)

Pre-treatment method	Category	Advantages	Drawbacks
Ammonia Fiber Explosion (AFEX)	Physico-chemical	Removal of lignin and hemicellulose Reduction in cellulose crystallinity	Not efficient for biomass with high lignin content i.e. softwood based biomass High pressure needed Environmental concerns
Organosolv	Chemical	Almost total hydrolysis of hemicellulose Almost total solubilisation of lignin Low cellulose degradation	Requirement of solvent recovery Formation of inhibitors
Wet oxidation	Physico-chemical	Dissolution of major part of hemicellulose Removal of lignin Reduction in cellulose crystallinity	Inhibitor formation Lignin degradation High cost for oxygen and catalysts High temperature and pressure required
CO_2 explosion	Physico-chemical	Increase of cellulose digestibility Increase in surface area Removal of lignin Low temperature Low sugar degradation	High cost equipment required

(*Continued*)

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Table 9.1 A comparative summary of the most studied pre-treatment techniques. (*Continued*)

Pre-treatment method	Category	Advantages	Drawbacks
Ozonolysis	Chemical	Lignin degradation with minimum impact on cellulose and hemicellulose Low inhibitor formation: no generation of Furfural and hydroxyl-methylfurfural Ambient temperature and atmospheric pressure	Long residence time Dangerous process due to ozone properties: Highly reactive, toxic, flammable and corrosive High cost process Cooling systems required due to process exothermic characteristics
Ionic liquids	Chemical	Salts exist in liquid form often at room temperature No production of toxic or explosive gases Possible dissolution of lignin and polysaccharides Minimum degradation of biopolymers Relatively low temperature Atmospheric pressure High lignin solubility Improve enzymatic delignification	Most of effective ILs are expensive Extensive washing needed prior enzymatic hydrolysis Solid – liquid separation Lack of commercial recovery methods of ILs Enzymatic hydrolysis rate depends on the pre-treatment temperature and biomass loadings

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pre-treatment method depends mainly on the desired final product, the conversion pathway to achieve it and the LCB to be processed.

However, the integrity and non-damage of the biopolymers constituting the LCB, the absence or minimisation of inhibitory co-products resulting from the degradation of sugars and/or lignin, which are considered inhibitors of subsequent steps and the reduction in heat and power requirements are all factors that determine the effectiveness of the pre-treatment (Zheng *et al.*, 2009; Tadesse and Luque, 2011; Zabed *et al.*, 2016).

9.4 Ionic Liquids for Lignocellulosic Biomass Pre-Treatment: Characteristics and Properties

ILs are organic salts stable at temperatures up to 300°C, liquid at temperatures below 100°C and some of which have the property of being liquid at room temperature, designated by the term Room Temperature Ionic Liquids (RTILs) (Huddleston *et al.*, 2001). ILs consist only of ions, an organic cation and an inorganic or organic anion (Huddleston *et al.*, 2001; Gomes *et al.*, 2019).

The anion moiety of IL seems to control its miscibility with water, whereas the cation can also influence the hydrophobicity and the capacity to establish hydrogen bonds (Visser *et al.*, 2000). The fact that ILs are liquid at temperatures below 100°C is attributed to the difference in size between cation and anion, the bulk and asymmetry of the cation as well as the delocalization of charges on some atoms. This generates weaker electrostatic (or Coulomb) forces and minimal lattice (crystal) energy, thus preventing crystallisation (Huddleston *et al.*, 2001; Hunt *et al.*, 2006; Gorke *et al.*, 2010).

Some ILs have interesting characteristics due to their thermal stability, their non-flammability and their negligible vapour pressure. For these reasons, they are considered more environmentally friendly and less hazardous than conventional organic solvents (Zhu *et al.*, 2006; Hanabusa *et al.*, 2018; Gomes *et al.*, 2019). Thanks to their particular properties and their great diversity, ILs have been involved in many fields of chemistry and have very varied applications including chemical synthesis, (bio) catalysis, battery electrolyte, lubricants, gas absorption agent, or additives for materials. More recently, ILs have been shown to be effective solvents for dissolving lignocellulose and improving its enzymatic digestibility (Swatloski *et al.*, 2002; Bose *et al.*, 2010; Hanabusa *et al.*, 2018).

ILs can be synthesised from a large number of combinations of cations or anions which could be estimated at 10^9 possible combinations (Mora-Pale

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et al., 2011). Thus, the physicochemical properties of ILs (polarity, viscosity, melting point, ability to establish hydrogen bonds) can be modulated according to the cation/anion combinations but also according to the substituents of the cation, in particular by varying the length of the alkyl chain. The most common combinations of current ILs are based on organic cations such as quaternary ammonium ions, quaternary phosphoniums and heterocyclic aromatic cations including imidazolium, and pyridinium. In regard to the constitutive anion of IL, it can be organic or inorganic, aliphatic or cyclic, polyatomic or even mono-atomic (case of halogenated anions).

Many researchers pointed out that ILs are promising solvents for dissolving cellulose and enhancing its digestibility when subjected to enzymatic hydrolysis. Imidazolium-based ILs such as 1-Ethyl-3-methylimidazolium acetate ([Emim][OAc]) and 1-Butyl-3-methylimidazolium Chloride ([Bmim][Cl]) have been recognised as most studied ILs for cellulose dissolution and pre-treatment (Swatloski *et al.*, 2002; Yamamuro *et al.*, 2006; Cuissinat *et al.*, 2008; Xing *et al.*, 2014; Alayoubi *et al.*, 2020). Some physicochemical properties of the aforementioned imidazolium-based ILs are represented in Table 9.2.

Subsequently, several studies have focused on the dissolution of lignocellulosic materials instead of cotton cellulose and microcrystalline cellulose, such as wheat straw, rice straw, wood pulp, woody sawdusts, *Miscanthus* and so on, paving the way for promising valorization of LCB using ILs as pre-treatment solvents (Li *et al.*, 2009; Hou *et al.*, 2013; Alayoubi *et al.*, 2020; Huet *et al.*, 2020).

Besides the use of ILs in the pre-treatment of cellulose and lignocellulosic materials, a number of studies have centred the attention on the application of ILs for the modification of cellulose.

The homogeneous acetylation and carbonylation of cellulose in [Bmim][Cl] were reported by Schlufter *et al.* (2006). Furthermore, Hinner *et al.* (2016) demonstrated the ability of [Emim][OAc] to proceed the homogenous vinyl esterification of cellulose. In addition, Hanabusa *et al.* (2018) revealed the acetylation of cellulose in some protic ILs composed of amidine and acetic acid under mild conditions without any catalyst. This leads to the formation of cellulose acetate, a resin derived from biomass that shows superior properties over existing resin derived from fossil fuels, particularly from the viewpoint of green chemistry.

On the other hand, due to the multi-step synthetic pathways applied to prepare them, the cost of conventional ILs is very expensive, which hinders their effective application at industrial scale processes.

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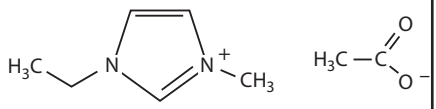
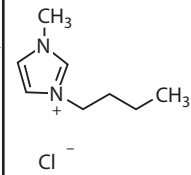
Table 9.2 Physico-chemical properties of the most studied imidazolium-based ILs (according to Solvionic SA, France; Skarmoutsos *et al.*, 2012; Dharaskar *et al.*, 2013).

Ionic liquid	**1-Ethyl-3-methylimidazolium acetate [Emim][OAc]** 	**1-Butyl-3-methylimidazolium Chloride [Bmim][Cl]** 
Molecular weight (g/mol)	170.22	174.67
Melting point	< -20°C	67-73°C
Density (g/cm^3)	1.03	1.08
Viscosity (25°C)	93 cP	56 cP
Properties	Hydrophilic	Hydrophilic
Water Solubility	Soluble in water, acetonitrile, acetone, dichloromethane Insoluble in diethyl ether	Soluble in water, dichloromethane, acetonitrile, isopropyl alcohol, methylene chloride, ethanol and methanol Insoluble in ethyl acetate, hexane, diethyl ether and toluene
Stability	Hygroscopic	Hygroscopic

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9.5 Insights into Pre-Treatment Performance of Ionic Liquids

9.5.1 Interactions of Ionic Liquids with Lignocellulose

Due to its crystalline nature, cellulose is not soluble in water or common organic solvents (Wahlström and Suurnäkki, 2015). However, solvents such as trifluoroacetic acid, molten salts or ILs can solubilise it (Nagarajan *et al.*, 2017). The ILs are considered, by their properties discussed above, as more "green" amphiphilic solvents allowing the solubilisation of cellulose.

After pre-treatment, the irreversible form of cellulose, cellulose II, can be regenerated through precipitation by adding an antisolvent such as water, ethanol, methanol, acetone, acetone-water mixture or dilute acid (Li *et al.*, 2009; Halder *et al.*, 2019). The thermal stability of the regenerated CRF has been the subject for several contradictory studies. Some researchers found that the thermal stability of the recovered CFR is reduced in comparison to the untreated cellulose (Hou *et al.*, 2017). According to this study, the pre-treatment of LCB causes a deconstruction of its structure that leads to lower the molecular weight of the materials in the pretreated CRF, exhibiting reduced thermal stability (Hou *et al.*, 2017). Similar to cellulose, lignin recovered after pre-treatment exhibits a reduced thermal stability compared to commercially available lignin because of the cleavage of β-O-4 bonds that occurs during pre-treatment (Wen *et al.*, 2014). In contrast, a few other studies have shown that the CRF crystallinity and thermal stability have increased compared to untreated cellulose due to the removal of hemicellulose and lignin (Hou *et al.*, 2012; Moniruzzaman and Ono, 2012). Nevertheless, dissolving cellulose in ILs is not a new concept. It was reported in 2002, that cellulose was dissolved in 1-methyl-3-butyl imidazolium chloride (Swatloski *et al.*, 2002).

Generally speaking, a cellulose-solubilising solvent requires the ability to interact with the hydroxyl groups of glucose residues and therefore to eliminate, at least partially, the strong intermolecular hydrogen bonds between the polymer chains (Medronho and Lindman, 2014). Cellulose dissolving ILs are generally hydrophilic while hydrophobic ILs do not solubilise cellulose or other polysaccharides (Zhao *et al.*, 2008).

The dissolution of cellulose is based on the breaking of intra- and interchain hydrogen bonds of cellulose and the formation of new hydrogen bonds between the protons of the hydroxyl groups of cellulose and the anion of ILs (Shill *et al.*, 2011; Tadesse and Luque, 2011). Therefore, the anion seems to determine the capacity of ILs to solubilise cellulose since it would fulfill the role of an electron donor in the donor - acceptor electron

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complex taking place between the anions of the IL and the equatorial hydroxyls of cellulose (Swatloski *et al.*, 2002).

The role of the cation in the solubilisation of cellulose in IL has been the subject of many contradictory studies. NMR analyses attributed the dissolution of cellulose in 1-butyl-3-methylimidazolium chloride ([Bmim][Cl]) mainly to interactions between the chloride ion and cellulose (Remsing *et al.*, 2006). However, other studies suggest that both anion and cation are important for the solubilisation of cellulose. Cho *et al.* (2011) found that during the dissolution of cellulose in [Bmim][Cl], the cation would also be involved to interact with cellulose. Thus, the anion and the cation would both be involved in interactions with glucose residues and solubilisation of cellulose is attributed to their coupled action (Cho *et al.*, 2011). In addition, NMR analyses performed on the model cellobiose and [Emim][OAc] indicated that hydrogen bonds are established between the hydroxyls of cellulose and both the anion and the cation of the IL (Zhang *et al.*, 2010). Likewise, studies of the solubilisation of cellulose in 1-allyl-3-methylimidazolium chloride ([Amim][Cl]) as well as in 1-butyl-3 methylimidazolium formate ([Bmim][OFm]) have shown that the anion and the cation both form hydrogen bonds with the hydroxyls of cellulose (Zhang *et al.*, 2005; Medronho and Lindman, 2014).

Solubilisation is induced by the formation of electron acceptor/electron donor complexes between the oxygenates of cellulose hydroxyls and the aromatic protons of the constituent cations of the IL, on the one hand, and between the hydrogens of cellulose and the constitutive anions of IL, on the other hand (Zhu *et al.*, 2006; Medronho and Lindman, 2014). In addition, molecular dynamics simulations carried out on cellulose oligomers in the presence of [Emim][OAc] have revealed hydrophobic interactions between the cation and cellulose (Liu *et al.*, 2010).

Finally, it is important to indicate that the origin of cellulose as well as its degree of polymerisation (DP) could impact the solubilisation mechanism of the cellulose in the IL, the higher the DP, the more the rate of cellulose solubilisation decreases (Wahlström and Suurnäkki, 2015). In addition, the presence of impurities in the IL, particularly water, could significantly affect the solubility of cellulose (Swatloski *et al.*, 2002; Shill *et al.*, 2011). In this context, it has been shown that the addition of 20% (m/m) of water would prevent the dissolution of cellulose in 1-ethyl-3-methylimidazolium acetate (Gericke *et al.*, 2011) while the presence of 1% (m/m) of water would render the cellulose insoluble in 1-butyl-3-methylimidazolium chloride (Swatloski *et al.*, 2002). An explanatory hypothesis would be that water would establish, in a competitive manner, hydrogen bonds with the anion of the IL, thus reducing the interactions between the anion and the

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cellulose (Shill *et al.*, 2011; Hauru *et al.*, 2012). The presence of water is a delicate parameter to control since moisture can come from the air (ILs are hygroscopic) and the cellulose itself generally contains water (Wahlström and Suurnäkki, 2015).

The principle of solubilisation of the LCB in ILs is similar to that detailed for cellulose given that the LCB consists mainly of polysaccharides. In addition to cellulose, hemicelluloses, lignin and extractives interact with the IL. During the pre-treatment of LCB with ILs, the deconstruction of LCB matrix leads to typical dissolution of lignin in ILs by cleaving the bonds between the lignin rings, particularly the β-O-4 linkage that accounts for almost 50 to 60% of the lignin inter-unit bonds. This resulted in the formation of strong ion-dipole linkages that promotes the dissolution of lignin in ILs, decreased crystallinity and improves porosity of LCB (Shi *et al.*, 2014).

ILs can establish different types of bonds with LCB including dispersion interactions, hydrogen bonds, ionic interactions as well as hydrophobic and Van der Waals interactions (Anderson *et al.*, 2002; Zavrel *et al.*, 2009). These varied interactions could be the source of the ability of certain ILs to solubilise LCB. In addition to the hydrogen bonds between the IL (anion and cation) and lignocellulose that would destroy the three-dimensional architecture of LCB, the hydrophobic/ dispersion interactions between the cation and the aromatic rings of the lignin would play a role in their solubilisation (Zavrel *et al.*, 2009; Shill *et al.*, 2011; Wahlström and Suurnäkki, 2015).

Moreover, it is considered that the dissolution of LCB in an IL would be intimately dependent on several factors including the nature of the IL (with however an important role of the constitutive anion), the type of LCB (the herbaceous plants being more easily solubilised than forestry feedstock) and reaction conditions (substrate load, substrate/IL ratio, time and temperature) (Sun *et al.*, 2009).

9.5.2 Effect of the Ionic Liquid Pre-Treatment on the Recovered Biomass

The dissolution of the cellulose or the LCB in the IL is followed by a regeneration step consisting in adding to the IL - substrate mixture, a polar anti-solvent. This will allow the precipitation of a solid fraction enriched in cellulose (CRF) and separate it from the liquid fraction corresponding to the IL and anti-solvent mixture. The regenerated biomass can be recovered by filtration or centrifugation and washed extensively with water in order to remove residual IL as much as possible (Dadi *et al.*, 2006; Shill *et al.*, 2011).

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Precipitation of solubilised cellulose can be achieved efficiently by the addition of polar protic solvents, such as water, methanol, ethanol, acetone or a combination of these solvents (Zhao *et al.*, 2009). The effect of cellulose regeneration could be explained by the selective extraction of ions from the IL in the aqueous phase through hydrogen bonds, dipole interactions and Coulomb forces (Crosthwaite *et al.*, 2005; Zavrel *et al.*, 2009). In order to explain the mechanism of cellulose precipitation, Zavrel *et al.* (2009) suggested that the molecules of the anti-solvent surround the ions of the IL causing the disruption of their interactions with (ligno)cellulose. As a result, intra- and intermolecular hydrogen bonds are again established within the cellulose, which leads to its precipitation.

The first studies on the use of ILs for the pre-treatment of cellulose were reported by Dadi *et al.* (2006) and Dadi *et al.* (2007) who solubilised then regenerated microcrystalline cellulose in 1-n-butyl-3-methylimidazolium chloride ([Bmim][Cl]) and then in 1-allyl-3-methylimidazolium chloride ([Amim][Cl]). These studies showed that the initial rate of enzymatic hydrolysis of IL-pretreated cellulose was 90 times higher than that of non-pretreated cellulose, which is attributed to the transition from crystalline cellulose I to amorphous cellulose II (Dadi *et al.*, 2007). After pre-treatment with IL, cellulose exhibits a weakening in its crystallinity and/or a disruption of its fibres organisation (Kilpeläinen *et al.*, 2007; Zhao *et al.*, 2009; Husson *et al.*, 2011). On the other hand, it was revealed that the cellulose-enriched fraction recovered after pre-treatment with IL had a DP and a polydispersity similar to the initial cellulose, but significant differences in macro- and micro-structures were noticed (Zhu, 2008). Access to cellulose is thus facilitated by increasing the specific surface area, which improves the efficiency of hydrolysis (Zavrel *et al.*, 2009).

Concerning the LCB, the components other than cellulose (hemicelluloses and lignin) could also be dissolved in varying percentages depending on the nature of the IL, the type of LCB and also the reaction conditions, particularly the temperature and the duration of the pre-treatment. High temperatures and/or long pre-treatment times lead to greater solubilisation of lignin and hemicelluloses in the IL. However, the cellulose fraction is mainly recovered after pre-treatment with IL and regeneration of the LCB (Miyafuji *et al.*, 2009; Arora *et al.*, 2010; Li *et al.*, 2010; Li *et al.*, 2011).

Some authors suggest that performing IL-pre-treatment at high temperature could lead to degradation and elimination of lignin and hemicellulose while low temperature would allow recovery of the three biopolymers of lignocellulose with better integrity by reducing their degradation (Parthasarathi *et al.*, 2016; Moyer *et al.*, 2018). The pre-treatment by the IL at mild temperature would reduce the entanglement between the

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polysaccharides (cellulose and hemicelluloses) and the lignin leading to an improvement in the yields of enzymatic hydrolysis (Singh *et al.*, 2009; Labbé *et al.*, 2012). Lignin can thus be recovered in the solid fraction of the regenerated substrate (Moyer *et al.*, 2018). ILs can thus be considered as solvents allowing the solubilisation of the LCB but also its deconstruction and the fractionation of its components.

9.5.3 Impact of Ionic Liquids on the Biological Tools

The pre-treatment of LCB using ILs represents the first step in the process of valorization of lignocellulosic materials through the biochemical pathway. After IL-pre-treatment and biomass regeneration, it is envisaged to convert the recovered polysaccharides, namely cellulose and hemicellulose into fermentable sugars via enzymatic hydrolysis and most frequently, later into biofuels or value-added chemicals via microbial fermentation. Accordingly, it is important to study the impact of ILs on the biological tools used in the subsequent step of the process, namely enzymes and microbial cells. Traditionally, the IL-pre-treatment step is separated from the downstream processes and is followed by extensive water washings of the regenerated biomass due to the reported negative cytotoxicity effect of ILs. However, extensive washing of regenerated biomass remains most frequently insufficient and residual IL could lead to toxic effect on enzymes and fermentative cells (Sitepu *et al.*, 2014; Mehmood *et al.*, 2015; Wahlström and Suurnäkki, 2015; Sivapragasam *et al.*, 2016; Mehmood *et al.*, 2018). Therefore, it is worthy to assess the impact of ILs on the process biological tools and to focus on understanding the possible mechanisms of interactions between them.

During the last decade, the study of the activity of enzymes in unconventional media (in the presence of IL) has been the subject of several fundamental and applied researches (Gorke *et al.*, 2010; Naushad *et al.*, 2012; Wahlström and Suurnäkki, 2015; Sivapragasam *et al.*, 2016). The behaviour of enzymes, in unconventional medium (in the presence of IL) depends on the enzyme, its origin, the type of the catalysed reaction and the type of IL, which is why it seems difficult to generalise the effect of IL on the activity of enzymes. Some enzymes show catalytic activity in IL while others become inactive.

Polarity, nature of cation, alkyl chain length, anion, hydrophobicity and viscosity of the IL are among the factors that can affect the performance of enzymes in the presence of IL (Geng *et al.*, 2010; Sivapragasam *et al.*, 2016). More particularly, the constitutive anion of the IL impacts the stability and the activity of enzymes due to its nucleophilic properties (Naushad *et al.*,

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2012). In fact, anions with a strong hydrogen bond acceptor capacity could interact strongly with enzymes leading to a change in their conformation (Sivapragasam *et al.*, 2016). For instance, the work of Noritomi *et al.* (2011) demonstrated the role of the anion of the IL on lysozyme activity; the enzyme showed significantly lower activity in the presence of 1-ethyl-3-methylimidazolium chloride [Emim][Cl] than in the presence of 1-ethyl-3-methylimidazolium tetrafluoroborate [Emim][BF_4] and 1-ethyl-3-methylimidazolium trifluoromethanesulfonate [Emim][NTf_2]. It is considered that anions whose negative charge is distributed over several atoms (trifluomethanesulfonate, hexafluorophosphate, tetrafluoroborate, methylphosphonate) are more stabilising than those carrying the negative charge on a single atom (halide, acetate) (Gorke *et al.*, 2010; Sivapragasam *et al.*, 2016).

The presence of residual IL would appear to negatively impact the enzymatic hydrolysis of cellulose by deactivating cellulases. For example, the presence of low concentrations (10% v/v) of 1-ethyl-3-methylimidazolium acetate [Emim][OAc] or 1-butyl-3-methylimidazolium chloride [Bmim][Cl], known to effectively dissolve cellulose, causes a severe decrease in cellulase activity (85% loss of activity) (Engel *et al.*, 2010). However, the cellulases incubated in the presence of 10% of 1-butyl-3-methylimidazolium chloride [Bmim][Cl] again exhibit catalytic activity after dilution of the reaction medium (Salvador *et al.*, 2010), demonstrating reversible deactivation of cellulase in this IL (Turner *et al.*, 2003).

Furthermore, the effects of ILs on enzymatic hydrolysis are more or less important depending on the anion of the IL. In the case of the 1-ethyl-3-methylimidazolium methylphosphonate ([Emim][$MeO(H)PO_2$]), the glucose yield was maximum for a concentration of 10% of IL (Auxenfans *et al.*, 2012). Beyond this concentration, deactivation of cellulases occurs. At high concentrations of [Emim][$MeO(H)PO_2$], inactivation of cellulases could be the consequence of the establishment of hydrogen bonds with the anion of the IL. On the other hand, the improvement in hydrolysis yields in the presence of 10% of this IL is suggested as due to a compromise between a better accessibility to cellulose due to its partial dissolution and a minimised inactivation of enzymes (Kamiya *et al.*, 2008; Jones and Vasudevan, 2010; Auxenfans *et al.*, 2017).

Thus, depending on the nature of the constitutive anion of the IL and depending on the concentration of the IL, the presence of the latter could contribute to an increase in enzymatic activity. The fact that the enzymatic hydrolysis yields of cellulose could be enhanced in the presence of specific concentrations of an IL in the reaction medium has encouraged researchers towards an *in situ* enzymatic hydrolysis in IL systems (Noriho, 2008;

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Zhang and Zhao, 2009; Auxenfans *et al.*, 2017). Combining the IL-pretreatment and the enzymatic hydrolysis step of LCB (*in situ* hydrolysis) is not only time saving, but also allows to simplify the overall valorization process of LCB. Nonetheless, how to increase the yield of fermentable sugars released from the enzymatic hydrolysis of polysaccharides still needs further studies and optimisation.

ILs are recognised as effective solvents for the dissolution and pretreatment of (ligno)cellulose and to some extent exhibit compatibility with several enzymes, as discussed previously. Due to their interesting characteristics, they represent a good alternative to conventional organic solvents, more promising from an environmental viewpoint. However, the residual IL that remains entrapped in the pretreated biomass would have a toxic effect on fermentative microorganisms and the mechanism of its toxicity on yeasts and bacteria is still lacking of knowledge (Dickinson *et al.*, 2016; Cao *et al.*, 2017). The impact of ILs has been the topic for a few contradictory studies where some attributed the deleterious effect on the constitutive anion of the IL or on the cation and others noted that both at the same time are involved (Badgujar and Bhanage, 2015; Mehmood *et al.*, 2015).

In this context, Pernak *et al.* (2003) and Ranke *et al.* (2004) reported an antimicrobial activity of the IL, which is increasingly important when the alkyl chain of the imidazolium cation is longer. The authors attributed the observed toxic effect on many microorganisms including fungi and bacteria, cockles and bacilli, only to the length of the alkyl chain without any effect of the constitutive anion of the IL.

The work of Mehmood *et al.* (2015) showed that [Emim][OAc] and [Emim][MeO(H)PO_2] affect, or even inhibit, the growth of the yeast *Saccharomyces cerevisiae* for a concentration ≥1% of [Emim][OAc] or ≥ 2% of [Emim][MeO(H)PO_2]. Furthermore, the yeast *Kluyveromyces marxianus* was shown to be more tolerant than *S. cerevisiae* towards these two ILs: 2% [Emim][OAc] and 6% [Emim][MeO(H)PO_2] (Mehmood *et al.*, 2018).

The detrimental effect of the IL on microbial cells could be explained by the interaction of the latter with polysaccharides of the cell wall of the yeasts as it interacts with polysaccharides of LCB. Furthermore, the ILs [Emim][OAc] as well as [Emim][Cl] and [Bmim][Cl] appear to mainly alter the mitochondrial function of the yeast *S. cerevisiae* by inducing hyperpolarisation of the membrane of mitochondria (Dickinson *et al.*, 2016). The alteration of the membrane potential of the mitochondria induces the production of reactive oxygen compounds and leads consequently to apoptosis (Pereira *et al.*, 2008).

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The effect of the IL cannot be generalised, so it depends on the nature of the IL, the ions that constitute it, the concentration of the IL, but also on the type of the tested microorganism.

9.6 Concluding Remarks: Challenges Facing the Development of Ionic Liquids Use at Large Scale and Future Directions

The use of ILs appears to be promising both in terms of LCB pre-treatment and in terms of its fractionation. However, there are still many challenges facing the development and the application of IL-pre-treatment at industrial scale. The cost of ILs used to date for pre-treatments remains relatively high, which is the main constraint for the development of this process at an industrial scale. For instance, the prices of [Bmim][Cl] (>98%) and [Emim][OAc] (97%) are nowadays very high, $152.50 and $961.00 USD per 50 g from Sigma-Aldrich, respectively for fundamental studies (Hanabusa *et al.*, 2018). Consequently, the current and future works should be focusing on synthesising low-cost ILs with high pre-treatment and dissolution efficiency. However, the current cost of ILs could decrease with the development of their use in many applications. Furthermore, ILs can be easily recovered while still keeping efficient dissolving ability (Xing *et al.*, 2014). Conversely, a few researches noted that recovered ILs exhibit significant reduction of their solvation capacity over cyclic operation. Therefore, some efforts should be devoted to study the cyclic operation in the mechanism of solvation and to identify a promising solution to overcome it.

Moreover, blending IL with other solvents mainly water or other ILs represents another possible solution to lower IL cost. However, several factors should be taken into consideration when using IL-water mixture, including thermal stability and degradation particularly at high temperature, pre-treatment performance, dissolution of LCB and reuse of ILs. Additionally, the presence of water in ILs has been the focus of contradictory studies in the literature. For some authors, blending ILs with water has a similar pre-treatment effect compared to IL without water, whereas others noted a reduction in lignin dissolution and separation.

In order to reduce the cost of pre-treatment, other, cheaper ILs are also being developed. In this context, the synthesis of protic ILs is achieved by a simple proton transfer reaction from an acid to a base, thus resulting in their high yield and low cost (Hanabusa *et al.*, 2018). Protic ILs exhibit

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similar properties to those of imidazolium-based aprotic ILs such as negligible vapour pressure, high termo-chemical stability and ability to form hydrogen bonds but they are less expensive than conventional ones (Rashid *et al.*, 2016). Recently, a few studies have developed the use of protic ILs for the dissolution and subsequent regeneration of cellulose and kraft lignin for further utilisation (Rashid *et al.*, 2016; Achinivu, 2018; Hanabusa *et al.*, 2018).

On the other hand, it is worthy to mention that despite the proven efficiency of conventional ILs to deconstruct/fractionate LCB under mild conditions, their use at industrial scale is still hindered by their debatable eco-cytotoxicity concerns, particularly with enzymes and cells used in the downstream processes (Gomes *et al.*, 2019). Consequently, the limited compatibility of conventional ILs with the biological tools requires the use of a large amount of water to wash the pre-treated biomass in order to remove as much as possible the residual IL. However, the washing step remains most often insufficient because the presence of ILs in the pre-treated biomass is extremely delicate and can affect deeply the activity of enzymes and cells (Gomes *et al.*, 2019). Altogether, these aforementioned drawbacks of conventional ILs have encouraged the development of novel biologically friendly ILs with enhanced biodegradability and biocompatibility features. These biologically friendly ILs are synthesised from renewable and biocompatible resources, unlike conventional imidazolium-based ILs (Gomes *et al.*, 2019; Huet *et al.*, 2020). The employment of these bio-derived low-cost ILs will overcome several challenges related to IL cost and toxicity, liquid-solid separations, the excessive use of water and the corresponding water treatment.

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10

Septage Characterization and Sustainable Fecal Sludge Management in Rural Nablus – Palestine

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Abstract

Exploding urbanization and the rapidly growing population has made the management of sanitation a major concern. One example is Palestine, a country where most of the citizens (more than 70%) rely on cesspits for disposal of wastewater (WW). Into this gap, this study aims at characterizing the septage and the quality of WW collected in cesspits, and proposing a sustainable treatment process for rural WW. Septage samples were collected directly from cesspit-emptying vacuum tankers and analyzed for different quality parameters. Quality parameters were compared with the EPA guidelines, and other countries.

A model based on Sequencing Batch Reactor technology was built and tested by GPS-X 7.0 simulator. The proposed model achieved removal efficiencies higher than 98% for BOD, 94% for COD, and 98% for TSS.

The produced models were feasible for construction and operation and seen as sustainable solution for septage treatment.

***Keywords*:** Activated sludge, characteristics, modeling, pre-treatment, SBR, septage, sustainable solutions

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Nour Shafik El-Gendy (ed.) Sustainable Solutions for Environmental Pollution Volume 1: Waste Management and Value-Added Products, (375–416) © 2021 Scrivener Publishing LLC

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List of Abbreviations

ASP	Activated Sludge Process	pH	Potential Hydrogen
BOD	Biological Oxygen Demand	PO_4	Phosphorous
CI	Confidence Interval	PWA	Palestinian Water Authority
COD	Chemical Oxygen Demand	SBR	Sequence Batch Reactor
CoM	Council of Ministers	SLR	Solid Loading Rate
CW	Constructed Wetland	SPSS	Statistical Package for Social Sciences
CWs	Constructed Wetlands	TC	Total Coliform
EC	Electrical Conductivity	TDS	Total Dissolved Solids
EPA	Environmental Protection Agency	TKN	Total kjeldahl Nitrogen
FAO	Food and Agriculture Organization	T-N	Total Nitrogen
FC	Fecal Coliform	TP	Treatment Plant
FS	Fecal Sludge	TS	Total Solids
FSM	Fecal Sludge Management	TSS	Total Suspended Solids
MCM	Million Cubic Meter	U.S.	United States
MEDRC	Middle East Desalination Research Center	VBST	Vertical Baffled Septic Tank
MoH	Ministry of Health	VBST	Vertical Baffled Septic Tank
MoLG	Ministry of Local Government	VDS	Volatile Dissolved Solids
NO_3	Nitrate	VFEW	Vertical-Flow Engineered Wetland
NWWTP	Nablus West Wastewater Treatment Plant	VS	Volatile Solids
O&M	Operation and Maintenance	VSS	Volatile Suspended Solids

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PCBS	Palestinian Central Bureau of Statistics	WESI	Water and Environmental Studies Institute

10.1 Introduction

10.1.1 Background

In many countries water is becoming an increasingly scarce resource and specialists are forced to consider any sources of water that might be used economically and effectively to raise further development (FAO, 2018). One example is the Palestinian territories where people are suffering from water shortage due to limited water resources and increasing demand on potable water because of the rapid population growth, which in turn generates a large amount of wastewater (WW). With lack of suitable sanitation services, WW may lead to pollution in soil, surface water and groundwater, and cause diseases related to the pollution of drinking water and agricultural land. Thus, it's a necessity to control the pollution resulting from WW to save the limited water resources and face the growing demand on fresh drinkable water (World Bank, 2008).

The WW situation in Palestine is not quite as bad as the situation of the existing sewerage system which is extremely critical. Approximately, 53.9% of the households in Palestine disposed their WW through the sewage network (34.2% in the West Bank), 33.6% of households in Palestine use cesspits (46.7% in the West Bank), 11% of the households use cesspits (16.6% in the West Bank), as a means of disposal of WW, and 1.6% of the households use other methods of disposal of WW (2.5% in the West Bank) (PCBS, 2019). Roughly, 94.5% of the rural population in the West Bank relies on cesspits and septic pits for temporary storage of WW, as they are not served by sewer networks, none of which is treated (PWA, 2013).

The definition of septage was conducted by the federal regulations as the liquid or solid material removed from a septic tank, cesspits portable toilet, type III marine sanitation device, or similar treatment works that receive only domestic WW (Dutin, 2001; EPA, 1994; EPA, 1993). The majority of these pits are emptied through private-sector vacuum trucks which discharge their contents (septage) into the nearby located sewage treatment plants, if any, and most likely they are overloaded, or

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in an irregular manner (in valleys or agricultural lands), which is a real threat to the environment and public health. Septage will mix with the non-perennial streams and wadis during winter season, while during dry season it mixes with natural springs (Al-Saèd, 2000). However, limited technical data is currently available on urban and rural WW characteristics (Tahboub, 1999; Mahmoud *et al*., 2003).

10.1.2 What is Fecal Sludge?

Fecal Sludge (FS) comes from on-site sanitation technologies, and it is not being transported through a sewer collection network. It is raw or partially digested, a slurry or semisolid, and results from the collection, storage or treatment of a combination of excreta and black water, with or without grey water. Sustainable Fecal Sludge Management (FSM) includes the storage, collection, transport, treatment, and safe end use or disposal of FS (Strande *et al*., 2014; Boot and Scott, 2015).

Solutions for effective and FSM present a significant global need; FSM is a relatively new field. However, it has been rapidly developed and has gained acknowledgement (Strande *et al*., 2014).

Knowledge of the waste that enters treatment systems is a basic prerequisite for the design and development of any wastewater treatment technology. The information is available on conventional sanitary sewage (Henze *et al*., 2001; Tchobanoglous *et al*., 2003) which has a different composition of fresh feces and urine that has not undergone any degradation processes and will have substantially less water or gray water addition. The generation rates and the chemical composition of sewage are key factors to be understood by on-site sanitation technology developers (Henze *et al*., 2001; Tchobanoglous *et al*., 2003).

10.1.3 Legal Considerations

In 2013, a decision was issued by the Palestinian Council of Ministers (Decree No. 16 of the year 2013) on publishing the system for connecting housing and facilities to the public sewer network (CoM, 2013). Also, the concept of "polluter-pays-principle" published by the Applied Research Institute – Jerusalem (ARIJ) has put WW as one of the major pollutants that should be controlled and monitored (ARIJ, 2015).

Moreover, in Palestine, there are places that do not have sewage networks. So the owners of the houses construct cesspits or septic pits to store their WW and then dispose of it without considering the effects

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on health and environment. Most of the cesspits and septic pits are not constructed according to the Central Public Health and Environmental Engineering Organization (CPHEEO) standards and Ministry of Local Government standards (Raj, 2013; MoLG, 2013). Additionally, they are not well maintained. Moreover, the practice of septage collection and disposal is neither scientific nor safe; septage which is collected from on-site systems during cleaning is invariably dumped in drains and open areas, posing considerable health and environmental hazards (Baetings, 2014).

Many laws and regulations concerning the practice of sewage collection and disposal have been enacted in the country, such as Water Resources Management Strategy drafted in 1997; the Study of strategic planning for the water sector in 2000; and the national water policy and the water and sanitation sector strategy for 2011-2013.

Despite the existence of such laws and regulations, there is a lack of technical studies that determine the mechanism of application of these laws and regulations. So, this study was conducted to characterize septage, and design a model to use for treating the characterized septage (D'Amato, 2008).

10.1.4 Study Area

The Nablus Governorate has urban and rural areas. Of these rural areas, 94.5% are not connected to a WW collection system, and almost all the house owners have cesspits or septic pits. Three villages near the City of Nablus were chosen as a case study. Figure 10.1 shows the location of each village and Table 10.1 shows the approximate number of houses in 2018 in each village of the study area.

These villages lack a sanitation network; as a result, they are suffering from other issues related to the pits such as:

- Unpleasant odor when the vacuum trucks empty their cesspits.
- Environmental risks and pollutions to crops and lands.
- High cost of septage disposal due to lack of vacuum trucks.

Factors of selection of the study area

In this study, many factors were considered to specify the study area. These factors are: (i) is there a WW collection network in the area?; (ii) water consumption; (iii) septic pits and cesspits availability; (iv) septic pits and cesspits accessibility; (v) culture; and (vi) location.

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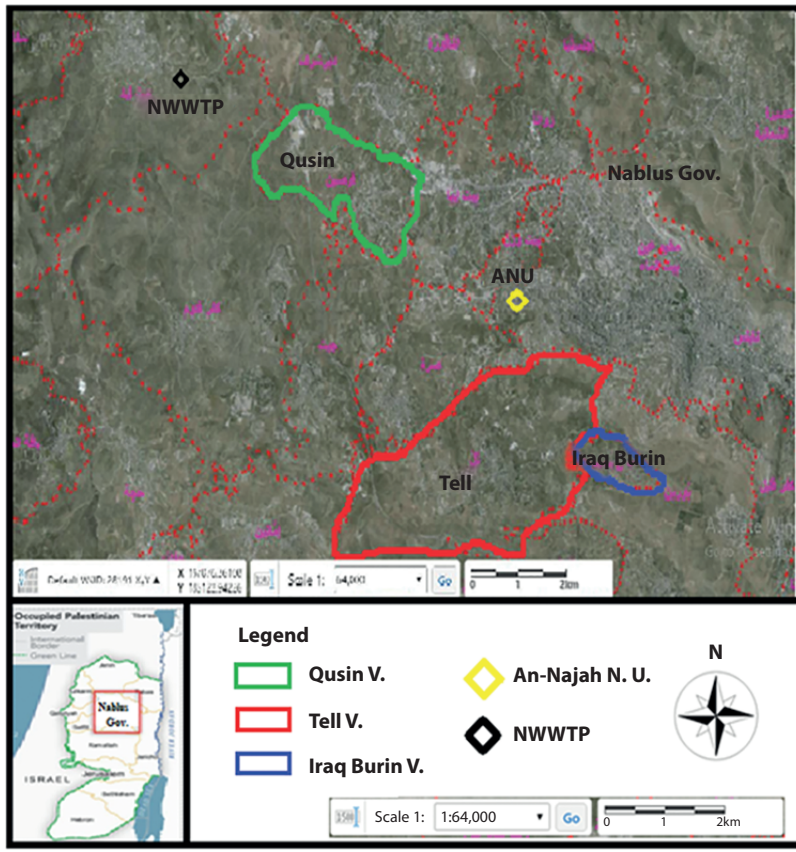

Figure 10.1 Location of the study area (ARIJ, 2018).

Table 10.1 Population and no. of houses in 2018 for the villages of the study area (PCBS, 2019).

Item/Village name	Tell	Qusin	'Iraq-Burin
Population	5216	2275	1019
No. of Houses (approximation)	1023	446	200

Based on the previous factors, three villages were selected to be the study area of this research: Tell, 'Iraq-Burin, and Qusin. These villages are located in the west and northwest of Nablus city, Palestine. Moreover, none of the three villages have a WW collection system as they are located in a rural region. The median water consumption at the study area is around

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66 l/c/d. In the three regions, cesspits are used to store the sewage, and the septage is disposed of in a timely manner by vacuum trucks or tractors at natural wadis or streams.

10.2 Septage Characteristics

10.2.1 Introduction

The rationale for this study is to fill the gap in knowledge about the fecal sludge which limits scientific decision making and implementation of the appropriate method of fecal sludge management practices in the study area.

This chapter summarizes the relative topics on characteristics and pre-treatment of septage, some of fecal sludge management studies, and the relation between the current work and previous literature.

This will feed into Environmental Sanitation Policy which seeks to develop a platform for adequate data collection to improve the planning and management of environmental sanitation (Ghana, 2010; Wilson, 2014).

10.2.2 General Background of Septage Characterization

In general, the main sources of septage are the following sanitation systems (Gracia-Dias and Carlos, 2005): Septic tanks, Cesspools, Privies/portable toilets, Aerobic tanks, holding tanks (septic tanks with no drain field), and Dry pits (associated with septic field).

Table 10.2 below shows the sources of septage, the rate at which these sources are emptied through pumping and the general trends of their characteristics.

Cesspit systems are simply an underground tank that collects and stores sewage upon its removal from the property. This system is the most common treatment unit at household level in rural areas of the West Bank and Gaza Strip. About 65-70% of the annual domestic WW in Palestine is currently collected in cesspits, where inadequate disposal might cause cumulative public health risks and annual environmental degradation.

It was estimated that around 41.17 MCM of WW is collected in cesspits that serve 68% of the Palestinian population in the West Bank (PWA, 2012). Signals of groundwater pollution in Palestine have already been reported, e.g., the concentration of NO_3 in the groundwater is more than 50 mg/L within shallow aquifers. Adequate treatment and disposal of domestic septage are crucial to protect public health and the environment.

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Table 10.2 Septage sources, removal pump-out rate, and the characteristics (EPA and ORD, 1994).

Description	Removal pump-out rate	Characteristics
Septic tank	2-6 years, but can vary with location local ordinances	Concentrated BOD, solids, nutrients, variable toxics (such as metals), inorganic (sand), odor, pathogens, oil, and grease
Cesspool	2-10 years	Concentrated BOD, solids, nutrients, variable toxics, inorganic, sometimes high grit, odor, pathogens, oil, and grease
Privies/portable toilets	1 week to months	Variable BOD, solids, inorganic, odor, pathogens, and some chemical
Aerobic tanks	Months to 1 year	Variable BOD, solids, inorganic, odor, pathogens, and some chemicals
Holding tanks (septic tanks with no drain field)	Days to weeks	Variable BOD, solids, inorganic, odor, and pathogens, similar to raw wastewater solids
Dry pits (associated with septic field)	2-6 years	Variable BOD, solids, inorganic, and odor

The present practice of septage disposal in Palestine is mainly via an uncontrolled discharge in nearby wadis and open fields. This type of disposal is uncontrolled and has several negative effects on both the sewerage system and the treatment processes (Al-Atawneh *et al*., 2014).

A study by Al-Atawneh *et al*. (2014) of WW Characteristics in Partially Sealed Cesspit revealed that raw wastewater was of medium strength according to the US-EPA classifications, and was more concentrated than Palestinian municipal sewage. The study characterized the composition of modern single residential source on-site raw WW and primary treated effluent (cesspits). The mentioned research – Al-Atawneh *et al*. (2014) – presented the results for the characterization of household raw domestic WW, and quantification of specific pollution load (g/c/d) and assessing the course of WW quality alteration in terms of BOD_5, COD, TKN, PO4-P, TS, TSS, TDS, pH, EC and heavy metals (Zn, Cu, Ni, Pb, Mn, Fe, Cr), in

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a partially sealed house on-site cesspit during the whole filling period of four months. The recommendation was to replace cesspits by proper WW treatment systems (Al-Atawneh *et al*., 2014).

The characterization of fecal sludge to make it a viable feedstock for the production of biodiesel, a renewable energy fuel, was the subject of a 2014 study. Fecal sludge from households was analyzed for its lipid content, moisture content, total solids and pH (Wilson, 2014).

Physical characteristics of septage are affected by climate, user habits, septic tank size, design, water supply characteristics, pumping frequency, piping material, and household chemicals (Brown and White, 1977). Moreover, the characteristics of septage vary depending on daily practices, water consumption, whether the kitchen food waste grinder is used or not, and frequency of emptying the pits (EPA and ORD, 1994). Tables A.1, A.2, and A.3 in appendix A show the different characteristics of septage according to the United States Environmental Protection Agency (US-EPA).

In regions where dry and wet seasons exist, seasonal changes in septage characteristics are thought to be significant but are usually not taken into account mainly due to the time of septage characterization before septage management options are discussed (Halalsheh *et al*, 2010; Thaher, 2012).

Septage generation rates vary widely from month to month due to weather and geography. Daily and weekly variations in septage generation rates also arise due to inhabitants' habits and attitudes. There are several approaches that could be used to estimate septage generation rate (Rai *et al*., 2012).

According to the Food and Agriculture Organization (FAO), the main constituents in the municipal WW are total solids, nitrogen, phosphorous, chloride, grease, BOD, pathogens, trace and heavy metals (FAO, 1992).

Heavy metals (Zn, Cu, Pb and Ni) are a worldwide problem because these metals are indestructible and most of them have toxic effects on living organisms, accumulate in reservoirs and enter the food chain (Farlane and Burchett, 2000; Loska and Wiechula, 2003). Heavy metals in household sewage might originate from feces, cleaners, paints, wear and tear of utensils and equipment, eroding pipes, and runoff from roofs (Dudka and Miller, 1999; Sorme and Lagerkvist, 2002).

Development of on-site sanitation facilities that treat excreta at, or close to, its source requires knowledge of the waste stream entering the system, and data regarding the generation rate and the chemical and physical composition of fresh feces and urine. In a study by Kanbara 2012 and Rose *et al*. (2015), the data was collected from medical literature and treatability sector, then summarized and statically analyzed to quantify

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the major factors that were a significant cause of variability of feces and urine characteristics. The impact of this data on biological processes, thermal processes, physical separators, and chemical processes was then assessed. Results showed that the median fecal wet mass production was 128 g/c/d, with a median dry mass of 29 g/c/d. Fecal output in healthy individuals was 1.20 defecations per 24-hour period and the main factor affecting fecal mass was the fiber intake of the population (Rose *et al.*, 2015; Kanbara, 2012).

In Jordan during 2007, composite samples of septage discharging at the Khirbit As-Samra municipal WWTP were analyzed during the period from February to the end of October 2007. Septage samples showed difference in concentrations of pollutants between summer and winter as illustrated in Table A.4, A.5, A.6, A.7 and A.8 in Appendix A. The average total COD was 6,425 mg/L during summer, which is double the COD in winter (2,969 mg/L) (Halalsheh *et al.*, 2010).

Moreover, the total BOD_5 represented 45% of total COD in both winter and summer seasons. Anaerobic biodegradability was 75% after 81 days of digestion at 35°C with a biodegradation rate constant (k) of 0.024 d^{-1}, which was lower compared with 0.103 d^{-1} calculated for WW with domestic origin in Jordan. Aerobic biodegradability for septage was 48% – COD basis – after 7 days of digestion at 35°C. The lower anaerobic biodegradation rate of septage compared with that of raw WW of domestic origin suggested that septage could have a negative effect on the performance of a domestic WWTP if septage discharges were not taken into account in the original design of the treatment plant (Halalsheh *et al.*, 2010).

Mahmoud *et al.* (2003) collected samples of raw WW and septage from Beit Dajan in Palestine. The samples were analyzed for TSS, TS, TDS, kjeldahl-nitrogen (Kj-N), COD, BOD and total PO4-P according to standard methods of American Public Health Association (APHA), 1995. The samples were analyzed for temperature, Electrical conductivity (EC), heavy metals (Cu, Ni, Pb, Mu, Fe, Cr, Zn) and pH. Heavy metal concentrations were determined by ICP according to the standard method (ICP multi-element stander solution 4 certiPUR lot- No. HC957274) atomic emission spectrometry (AES) (ICP OPTIMA 3000 Perkin Elemer), following acid digestion and using appropriate certified reference materials in addition to intra-laboratory standards. Tables A.9, A.10, A.11, A.12 and A.13 in Appendix A show the detailed results of the study (Mahmoud *et al.*, 2003). Mainly, the raw WW characteristics of an individual home in Beit Dajan was of medium strength and it was relatively less concentrated than municipal WW.

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10.2.3 General Treatment of Fecal Sludge

Fecal sludge (FS) needs adequate treatment and disposal to safeguard public health and the environment (Sandec, 2006; Cosgrove and Rijsberman, 2000). Fecal sludge treatment can be a complicated process; several different designs could be used, utilizing mechanical, biological, and chemical methods, in different combinations (Metcalf and Eddy, 2003; Wilson, 2014).

Sludge treatment is required in order to render the sludge safe for either disposal to the environment or reuse in agriculture or aquaculture. This requires the treatment plant or facility to be managed in a way that ensures the pathogen levels in the sludge are reduced to safe levels. In Indonesia, the Tegal city treatment plant consists of an Imhoff tank and collector, one anaerobic pond, one facultative pond, one maturation pond, and a sludge drying bed. The total area of the site is about 3,000 m^2. This is being replaced by a new similar plant, with three ponds and a sludge drying bed. The new Jombang city – Indonesia facility has a reported capacity of 200 m^3/day and consists of an intake, a covered and vented stabilization lagoon, roofed drying bed, a filter and a maturation pond (Sandra *et al.*, 2012).

The purpose of the secondary ponds is to treat the liquid component of the sludge. The solid component is separated in the primary tank or pond and then dried on the drying beds. When separated from the liquid fraction of the septage, the solid sludge will contain a large number of pathogens and these must be removed to be safely used. Detailed assessment of sludge treatment options to remove pathogens is beyond the scope of this research but as a general rule pathogen removal can be achieved by composting or by drying sludge for several weeks.

On-site sanitation facilities (especially septic tanks) can be efficient to remove biological contamination (bacteria, viruses); however, the exact level of efficiency depends on both the facility's design and the final infiltration device. If the tanks are not waterproof, WW can contaminate groundwater resources, especially in limestone and sand areas. Moreover, septic tank efficiency for removing nitrogen and phosphate is generally very low. This means that most nitrogen and phosphate will ultimately infiltrate the groundwater (Sandra *et al.*, 2012).

In areas where sewer networks are not available, WW is discharged into percolating pits. Cesspits are emptied by vacuum tankers, which usually dump their contents in open areas, valleys, sewage networks and/or dump sites (PHG *et al.*, 2011). The existing WWTPs in the West Bank have not been designed to specifically treat the sludge collected from cesspits,

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but some treatment plants accept these trucks, e.g., Al Bireh WWTP. Most vacuum trucks are owned by small private companies (PWA, 2013, PWA and Al-Quds Univ., 2016).

There are many approaches to septage's treatment and disposal, which include private or public ownership. Larger municipalities are capable of managing the whole process from handling and treatment to disposal, while other municipalities prefer to use privately owned facilities that alleviate some of the responsibilities of operating a facility. Land disposal of septage after adequate treatment is also a popular option (Brown and White, 1977). But in Palestine, there is a lack of such responsibility to deal safely deal with septage. So, this study will take in consideration the appropriate and best practice to deal with septage.

Knowledge on sewage "treatment" in cesspits as anaerobic reactors is extremely limited. The degree of digestion of the solids in the cesspits most likely depends on the frequency of pumping. Published literature (ATV, 1985; EPA and ORD, 1994) indicated that septage quality could strongly differ from one place to another as many factors influence the physic-chemical characteristics of septage. In Palestine, emphasis was given to characterize and quantify sewage collected in sewer networks (Tahboub, 1999; Mahmoud *et al.*, 2003). But so far very little effort has been made to quantify the cesspits septage generation rate, characteristics and environmental impact in terms of emanated pollutants fluxes to the surface and under surface environments.

Rrtu and Anand (2016) investigated the effect of a modified septic tank system for treating domestic WW. A modified septic tank system was a simple means of treating domestic WW using the treatment mechanisms such as anaerobic digestion and disinfection. The effect of vertical baffles coupled with an anaerobic reactor on septic tank system was analyzed. The reactor selected for the study consists of copper modified zeolite as an adsorbent which will also act as filter media on which attached growth process takes place. The results showed that Vertical Baffled Septic Tank (VBST) coupled with zeolite filter formed a good treatment system. The vertical baffled septic tank had a removal efficiency of 99.99% total coliforms, 99.57% of TSS, 46.83% Ammonia nitrogen, 31.08% of nitrate nitrogen, 48.39% of total kjeldahl nitrogen (TKN), 94.4% of BOD and 71.74% of Phosphates. This study focused on an economical and efficient decentralized treatment method for treating domestic WW (Rrtu and Anand, 2016).

Koottatep *et al.* (2005) research presents lessons that had been learned from the operation of pilot-scale constructed wetlands (CWs) for septage treatment since 1997. The experiments were conducted using three CW units planted with narrow-leave cattails (Typha augustifolia) and operating

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in a vertical-flow mode. Based on the experimental results, the optimum solids loading rate was 250 kg TS/m^2. yr and 6-day percolate impoundment. At these operational conditions, the removal efficiencies of CW units treating septage were at the range of 80–96% for COD, TS and TKN, respectively. The biosolid accumulated on the CW units to a depth of 80 cm and had never been removed during seven years of operation, but bed permeability remained unimpaired. The biosolid contained viable helminth eggs below critical limit of sludge quality standards for agricultural use. Subject to local conditions, the suggested operational criteria should be reassessed at the full-scale implementation (Koottatep *et al*., 2005).

During 2012, a series of pilot-scale freezing bed experiments were conducted to evaluate and model the freeze–thaw treatment of septic tank sludge (septage). Filtrate quality was similar to a low-strength domestic WW and the sludge cake had a dry matter content of 25% with E. coli numbers below 2.0×10^6 CFU/g dry solids. Experimental results showed no impact of snow cover on bed performance in a region with moderate snowfall (1.3–1.6 m) as new layers of sludge effectively melted any accumulated snow; suggesting that it was not necessary to cover the bed or remove the snow in areas where sludge dosing exceeded snowfall. Both freezing and thawing processes were successfully modeled with readily available climatic data. Model output for North American climatic conditions indicated that the freezing bed technology can be widely applied throughout the northern United States and Alaska and most of Canada with the exception of coastal areas and southern Ontario (Kinsley, 2012).

However, only a tiny proportion of this WW is currently treated, and the portion which is safely reused is significantly smaller than the existing directly and indirectly used untreated WW, which is posing significant potential health risks. The research ended with a call for standardized data collection and reporting efforts across the formal and informal reuse sectors to provide more reliable and updated information on the WW and sludge cycles, essential to develop proper diagnosis and effective policies for the safe and productive use of these resources (Mateo-Sagasta *et al*., 2015).

Predicting this request, the Service of Public Works assessed the plan and execution of numerous existing septage offices in planning for recovery and unused development. The assessments concluded that in numerous cities there was sub-optimal possession of the septage treatment offices by neighborhood governments, the regulation courses of action for working the offices and the operation and support budgets were destitute, and the staffing and staff capacity was poor. Moreover, later in 2011, the Ministry of Public Works asked specialists to support national speculations in septage

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infrastructure, focused on helping neighborhood governments develop urban septage administration. In specific, the help was pointed at creating maintainable administration models for working and keeping up septage frameworks (Sandra *et al*., 2012).

10.3 Study Methodology

10.3.1 General

As the septage is inhomogeneous, consists of a liquid phase, settled and partly settled solids, scum and dissolved solids, thus representative sampling from cesspits is very difficult. The development of a standardized sampling method appears nearly impossible due to the fact that conditions of sampling vary from one place to another, and there are different vacuum trucks and variable construction design of the septic tank (Hithnawi, 2004).

This chapter presents the sampling procedure, various lab analyses including the assumptions and calculations. All the analyses were carried out in the laboratories of the Water and Environmental Studies Institute, An-Najah National University, Nablus.

10.3.2 Research Methodology and Methods of Laboratory Analysis

10.3.2.1 Data Collection

- The required data related to water and WW sources, type of pits, and disposal methods of septage were collected from several sources like previous reports, PWA, municipalities, interviews, field visits, and published work.
- Scientific data such as: definition of process parameters was collected from literature.

10.3.2.2 Sampling and Storage

The objective of sampling is collecting a portion of material small enough in volume to be transported conveniently and handled in the laboratory while still accurately representing the material being sampled. This objective implies the relative proportions or concentrations of all pertinent components will be the same in the material being sampled, and that the

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sample will be handled in such a way that no significant changes in composition occur before the tests are made (APHA, 2001).

The sampling techniques used for a WW or septage survey must ensure that representative samples are obtained, because the data from the analysis of the samples will ultimately serve as a basis for designing treatment facilities. Special procedure is necessary to handle problems when sampling wastes that vary considerably in composition. Thus, suitable sampling locations must be selected, and the frequency and type of sample to be collected must be determined (Metcalf and Eddy, 1991).

Data obtained from sampling analysis are valuable for selecting treatment technology and properly operating the system (APHA, 2001). A good sampling program should: ensure that the sample is representative, use proper sampling technique, and protect the samples until they are analyzed.

In this research, samples were collected from different trucks, different places at different times. The samples were preserved at 4°C in special insulated boxes during transportation to laboratory at An-Najah University (See Figure B.1 in appendix B).

The sampling process followed these steps:

1. Preparing clean sampling bottles.
2. Identifying the sources of septage, which is three cesspits in three different locations as mentioned in the section of the study area.
3. Identifying the sources of stools and urine, which is two houses in two different locations in one of the villages of the study area which is Tell Village.
4. Collecting representative samples from a truck during emptying the septage by mixing the amount taken at the beginning of the evacuation process, at the middle and at the end to form a homogeneous sample.
5. Analyzing samples immediately. Otherwise, stored at a low temperature (less than 4°C) immediately after collection to preserve samples.

10.3.2.3 Sampling of Septage

Sampling was done for three continuous months in the summer season. During this period, eighteen samples from nine different locations were collected; these locations were in the study area of the three mentioned

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villages. Two homogeneous samples were taken from each location at monthly basis.

10.3.2.4 Sampling of Stools and Urine

Stools and urine samples were collected from two houses in Tell village for five different persons. The age ranges of the individuals from whom the samples were taken varied over the periods of each estimated period of ten years, starting from the first decade ang going up to the fifth decade. Sampling was done in two different times: one for stools and one for urine during two weeks. See Figure B.2 and B.3 in Appendix B.

The stools samples were composite samples that included the pure feces, urine, and 4 liters of tap water, as (60–70%) of people flushing 4 liters after they used the toilet in the study area.

10.3.2.5 Storage of Samples

APHA (2001) recommend immediate analysis after collection, if possible, analyzing samples immediately after the collection, because preservatives often interfere with the test. Otherwise, store at a low Temperature (< 4°C) immediately after collection to serve most samples. Preservation types are shown in Table A.14 in appendix A.

10.3.3 Characterization of Fecal Sludge (FS)

In characterizing the samples, a number of parameters were considered. All parameters listed in Table 10.3 were taken in characterization of the septage.

Lab analysis was conducted according to the Standard Methods (APHA, 2001). Heavy metals analyses were done by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) device. See Figure B.4 in Appendix B.

The pH and EC tests were done on-site just after sampling to avoid as much as possible degradation of the FS that may not be accounted for. A digital measuring kit with a probe was used. Figures B.5, B.6, B.7 in Appendix B show some process of analysis.

10.3.4 Statistical Analysis of Data on Characterization of FS

A statistical approach was used to analyze the data on characterization of fecal sludge, to determine the variation in the means of the data obtained based on the sources and the months of sampling.

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Table 10.3 Parameters considered for characterizing the collected samples.

Type of analyses	Parameter names
Physical analysis	pH, Torpidity (NTU), Temperature, TS, TSS, TDS, VS, VSS, VDS.
Chemical analysis	BOD_5, COD, NH_4-N (Ammonia), NO_3-N (Nitrate), TN, TKN, PO_4-T, PO_4-P, Alkalinity (as $CaCO_3$), EC, Fat & Grease
Heavy metals analysis	Ag, Al, Ba-1, Be, Bi, Cd, Cr, Co, Cs, Ga, In, Li, Mn, Mo
Microbial analysis	Total Coliform Count TCC (/1ml), Fecal Coliform Count FCC (/1ml)

10.4 Septage Pre-Treatment Process

10.4.1 General Treatment Options

The potential treatment processes that were identified as suitable for developing countries were: Planted drying beds (constructed wetlands), Waste Stabilization Pond (WSP), combined composting ("co-composting") with organic solid waste, Anaerobic Digestion with biogas utilization and Unplanted Drying Beds (Cofie *et al*., 2006; Heinss *et al*., 1998; Klingel *et al*., 2001; and Koottatep *et al*., 2005). The treatment processes above can be used alone or in combination to achieve the required standards of the sludge and leachate. Usually, there is a high content of coarse wastes such as light plastics, tissues and paper in the fecal sludge discharged by collection and transport trucks, thus, a preliminary screening is needed for most treatment technologies (Strauss and Montangero, 2002).

10.4.2 Selection of Treatment Options

The selection of a feasible treatment option is always decided according to a set of factors that requires careful analysis. The first step is to pre-screen the technology options and exclude unfeasible technologies; for example, co-treatment with WW is not feasible for a city without a sewer system. Secondly, the preselected potentially feasible options are compared based on the selected criteria as shown in Table A.15 and Table A.16 in appendix A. The final step is for decision-makers to evaluate and weigh the different

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options against the same criteria and select the most suitable option(s) for the fecal sludge management concept (Montangero and Strauss, 2002).

10.4.3 Septage Quality Determination

Quality parameters are needed as input to the proposed treatment model, they were determined based on the results of septage characterization. These parameters include: pH, BOD_5, COD, TS, TSS, TDS, Ammonia, Total Nitrogen, and Total Phosphorus.

10.4.4 Software Selection

Many programs deal with WWTP modeling. GPS-X 7.0 program was chosen because it is free, and capable of achieving the objectives of this research. GPS-X 7.0 can deal with two sides: WW and sludge treatment.

10.4.4.1 Modeling by GPS-X 7.0

The septage treatment plant modeling is a critical point in this research, so the following points were considered:

1. Treatment plant modeling steps:
- Determining model's goal.

The main objective is to build a treatment model and to study the fit of proposed treatment plant effluent with the local treated WW specifications by EQA.

2. Data analysis:

The data needed and relevant information to the treatment plant were analyzed, and the missing data were identified from literature or from laboratory experiments.

3. Model setup:

The treatment plant was represented using GPS-X 7.0 program, an academic licensed version for An-Najah National University. The model type ASAL1 option was chosen which meets septage treatment properties. ASAL1 requires sewage retention time greater than 2-4 hours, and the modeling effort was directed at effluent quality. This model incorporates oxidation, nitrification and denitrification processes.

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4. Data Management:
The results obtained from the modeling of treatment plant were discussed, and an executive plan was recommended to build the simulated cases.

10.4.5 End-Use and Disposal

End products of the treated sludge (for example dried or partially dried sludge, compost, leachate, and biogas), have an intrinsic value, which can turn treatment from merely a method for environmental and public health protection to resource recovery and value creation (Weemaes and Verstraete, 2001). Historically, the most common resource recovery from sludge has been as a soil conditioner and organic fertilizer, as fecal sludge contains essential plant nutrients and organic matter that increases the water retaining capacity of soils. Researches are underway to recover end products as a bio-fuel (Diener *et al*., 2014; Muspratt *et al*., 2014), for example, pyrolysis, gasification, incineration and co-combustion or as resource recovery of organic matter through the growth of Black Soldier flies for protein production. With the implementation of resource recovery, it is important to evaluate constituents that may impact both humans and the environment. These include the presence of pathogens and heavy metals. Social factors such as acceptance in using products from fecal sludge treatment and market demand also need to be taken into account in order to ensure uptake of the intended end use (Diener *et al*., 2014).

10.5 Results and Discussion

10.5.1 Measured Parameters for Fecal Sludge

10.5.1.1 Septage Characteristics

Physical, chemical and bacterial septage characteristics

All the characteristics from the study area are presented in Table 10.4, where N*: number of samples analyzed and C/1ml: Colony per one milliliter.

Heavy metals septage characteristics

The heavy metals Septage characteristics from the three villages are presented in Table 10.5.

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Table 10.4 Physical, chemical and bacterial septage characteristics for rural Nablus.

Parameters	Unit	N*	Range of values		AVG.	STD
			Min.	Max.		
Physical septage characteristics						
pH		18	7.15	8.14	7.74	0.38
Turbidity (NTU)	NTU	12	150	820	438	242.26
Temperature	(mg/l)	18	20.6	24.5	22.1	1.4
TS	(mg/l)	14	1030	2245	1620	368
TSS	(mg/l)	12	143	573	328	162
TDS	(mg/l)	12	786	1498	1001.08	234.1
VS	(mg/l)	14	732	1244	965.5	171.86
VSS	(mg/l)	10	132	400	203.5	90.09
VDS	(mg/l)	14	447	944	652	141
Chemical septage characteristics						
EC (ms/cm)	(mg/l)	14	2.3	2.83	2.59	0.16
BOD_5	(mg/l)	14	150	900	371	239

(*Continued*)

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Table 10.4 Physical, chemical and bacterial septage characteristics for rural Nablus. (*Continued*)

Parameters	Unit	N*	Range of values		AVG.	STD
			Min.	Max.		
COD	(mg/l)	14	540	1690	1087	376
NH_4-N (ammonia)	(mg/l)	18	74	192	149	39
NO_3-N (nitrate)	(mg/l)	18	0	1.40	0.29	0.46
N-T	(mg/l)	12	80	255	178.33	69.04
TKN	(mg/l)	18	80	254.09	188.96	69.03
PO_4-T	(mg/l)	12	8.3	15.6	12.1	2.86
PO_4-P	(mg/l)	14	7.6	14.9	11.2	2.9
Fat & Grease	(mg/l)	18	32.5	109.5	71.7	24.2
Alkalinity (as $CaCO_3$)	(mg/l)	16	800	1500	1178	221
Bacterial septage characteristics						
TCC	(C/1ml)*	7	1960000	48300000	19500000	18000000
FCC	(C/1ml)*	14	3600	38000	11200	8590

N*: number of samples analyzed. All units are (mg/l), except pH(-) and which specified.

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Table 10.5 Heavy metals septage characteristics for rural Nablus (2018).

Parameters	Unit	N*	Range of values		AVG.	STD
			Min.	Max.		
Ag	(mg/l)	4	0.04	0.12	0.07	0.04
Al	(mg/l)	4	3.93	5.82	4.64	0.87
Ba	(mg/l)	6	0.41	0.67	0.51	0.11
Be	(mg/l)	6	0	0	0	0
Bi	(mg/l)	6	0	0	0	0
Cd	(mg/l)	6	0	0	0	0
Cr	(mg/l)	6	0.1	0.12	0.11	0.01
Co	(mg/l)	6	0	0.01	0.01	0
Cs	(mg/l)	6	0	0	0	0
Cu	(mg/l)	4	0.31	0.38	0.35	0.03
Fe	(mg/l)	5	11.88	22.74	17.52	5.04
Ga	(mg/l)	6	0	0.01	0.01	0
In	(mg/l)	6	0	0	0	0
Li	(mg/l)	4	0.01	0.02	0.01	0
Mn	(mg/l)	6	0.26	0.47	0.37	0.1
Mo	(mg/l)	6	0.01	0.05	0.03	0.01
Ni	(mg/l)	6	0.08	0.1	0.09	0.01
Pb	(mg/l)	6	0.04	0.12	0.08	0.03
Rb	(mg/l)	6	0.03	0.11	0.08	0.03
Sr	(mg/l)	6	0.35	0.59	0.41	0.1
V	(mg/l)	6	0	0.03	0.01	0.01
Zn	(mg/l)	6	3.95	4.83	4.37	0.41

N*: number of samples analyzed. All units are (mg/l), except pH(-) and which specified.

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Table 10.6 shows a comparison of constituents present in septage data from rural area and EPA. The values of septage parameters in EPA were higher than those presented in the study area. This could be due to the following: cultural and behavioral differences between the study area and the United States where EPA specifications were developed; cesspit design and pump out interval in rural areas or in the study area is different from the United States where EPA specifications were developed.

Kitchen grinders are seldomly used in Palestine (which is used to reduce the volume of kitchen waste through sewers), thus increasing the concentrations of organic matter in the septage. Also, the lifestyle and hygiene approaches are different, where soiled toilet papers are partly discharged through sanitary facilities in the U.S., while tap water is used for hygienic cleaning purposes in Palestine. Additionally, the source of septage is from central unsewered urban dwellings, where short hydraulic retention time prevailed in most cesspits, leading to weak anaerobic transformation processes.

Table 10.6 Comparison of domestic septage between rural Nablus (this study) and the USA (EPA, 1994).

Parameter	Septage range	Septage range (EPA, 1994)
BOD_5	150–900	440–78,600
COD	540–1,960	1,500–703,000
NH_4-N	73–192	3–116
PO_4-P	7.6–14.9	–
Alkalinity	800–1,500	522–4,190
TKN	80–254.1	66–1,060
Oil & Grease	32–109.5	208–23,368
TS	1,030–2,245	1,132–130,475
TSS	142.5–1,498	310–93,378
VS	732–1,244	353–71,402
pH	7.15–8.14	1.5–12.6

All units are in mg/L except for pH.

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10.5.2 Stools Characteristics

Feces characteristics from five persons in Tell village are presented in Table 10.7. The results revealed that the parameters value in stools were higher than in septage, which could be attributed to the dilution of septage with other sources of water such as spring water, and the treatment of septage inside the cesspit while the cesspit is not being emptied.

10.5.3 Urine Characteristics

Urine characteristics from five persons were analyzed and presented in Table 10.8. It is obvious that none of the samples contain any type of solids (TS, TSS, TDS, VS, VSS and VDS), oil or grease.

10.5.4 Specific Parameters in Details

10.5.4.1 pH and EC

Measurement of pH and EC is essential for the understanding of water chemistry processes, such as acid-base chemistry, alkalinity, neutralization, biological stabilization, precipitation, coagulation, disinfection, and corrosion control (APHA, 2001).

From Figure 10.2 (a) below, the average value of pH of septage from cesspits in rural Nablus was (7.74±0.38). Also, the average of EC of septage from cesspits in rural Nablus was (2.59±0.16 ms/cm). Moreover, the average of the septage pH was within the average of pH in the inlet of Nablus WWTP for municipal wastewater (7.84±0.15); on the other hand, the average of the EC was more than the average of EC in the inlet of Nablus WWTP (1.63±0.18 ms/cm). This variation is related to the absence of wastewater in the cesspit for a period of time (NWWTP, 2018).

10.5.4.2 Turbidity

The measurement of Turbidity is one of the important tests when trying to determine the characteristics of wastewater to measure the level of turbidity. From Figure 10.2 (b) below, the average value of turbidity of septage from cesspits in rural Nablus was (483.0±242.26 NTU). The big variation between these locations is related to the water consumption, frequency of emptying the cesspit, and to soil content. The lower readings were in 'Iraq Burin, which is due to the nature of this village as it is located on a rocky mountain.

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Table 10.7 Stools characteristics for rural Nablus (2018).

Parameters	N*	Range of values		AVG.	STD.
		Min	Max		
pH	5	6.07	8.62	7.32	1.02
EC (µs/cm)	5	1575	2700	2089.8	560.8
Turbidity (NTU)	3	204	595	363.67	205.12
Temp.	5	21.5	23.4	22.46	0.78
BOD5	5	700	2500	1840	745
COD	3	1240	5390	31567	2093
NH4-N (ammonia)	5	50	155	97	44.94
NO3-N (nitrate)	3	0.1	0.2	0.17	0.06
N-T	5	350	480	408	52
TKN	5	349.9	479.8	402.4	56.9
PO4-T	4	13.7	19.9	16.6	2.6
PO4-P	4	16.4	23.40	19.08	3.16
TS	3	3096	3838	3389.33	394.64
TSS	4	1260	3147	2228	914
TDS	5	922	4220	1756	1397
VS	3	566	928	701	198
VSS	3	86.67	130	109	22
VDS	3	426	553	491	64
Fat & Grease	3	21.5	115.50	67.17	47.06
Alkalinity (as $Caco_3$)	3	1800	2000	1900	100
TCC (C/1ml)	5	3000000	16000000	6640000	5360000
FCC (C/1ml)	4	10000	150000	62500	67000

N*: number of samples analyzed. All units are (mg/l), except pH(-) and which specified.

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Table 10.8 Urine characteristics for rural Nablus (2018).

Parameters	N*	Range of values		AVG.	STD.
		Min	Max		
pH	5	5.15	5.79	5.57	0.3
EC (µs/cm)	4	7.2	16.12	12.08	3.84
Turbidity (NTU)	4	3.24	7.71	5.2	2.04
Temp.	5	20.90	21.20	21.04	0.13
BOD5	4	1150	1950	1551.5	452.2
COD	4	4285	9300	6645	2435.72
NH4-N	4	86	165	129	38.17
NO3-N	3	1	1.5	1.33	0.29
TN	4	1080	1850	1447.5	317.63
TKN	4	1078.5	1849	1446.4	317.77
PO4-T	5	49.2	56.3	52.66	2.53
PO4-P	5	38.2	48	42.54	4.62
TS	0	0	0	0	0
TSS	0	0	0	0	0
TDS	0	0	0	0	0
VS	0	0	0	0	0
VSS	0	0	0	0	0
VDS	0	0	0	0	0
Fat & Grease	0	0	0	0	0
Alkalinity (as $Caco_3$)	4	500	600	550	57.74
TCC (/1ml)	5	0	0	0	0
FCC (/1ml)	5	0	0	0	0

N*: number of samples analyzed. All units are (mg/l), except pH(-) and which specified.

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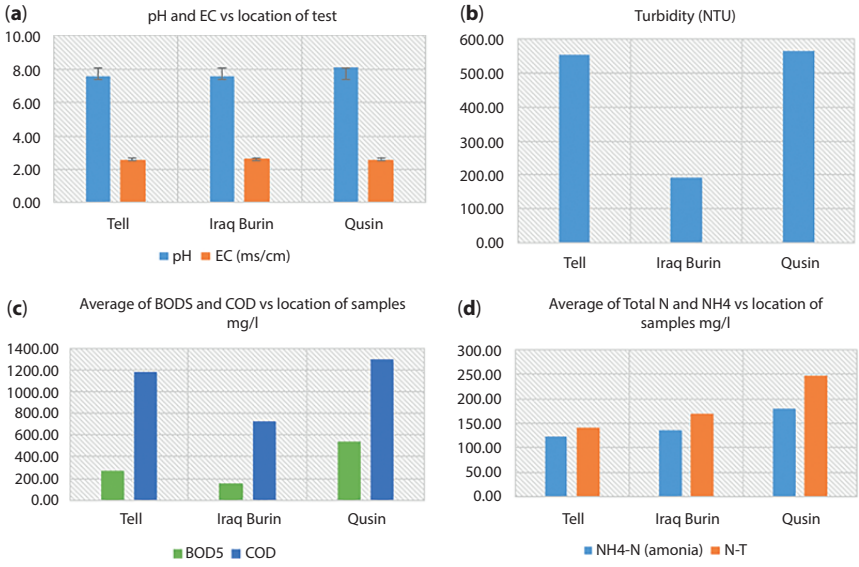

Figure 10.2 Average values for septage analyzed at rural Nablus; (a) pH and EC, (b) Turbidity, (c) BOD_5 and COD, (d) Total N and NH4.

10.5.4.3 COD/BOD5

The measurement of COD and BOD5 are important when trying to determine the characteristics of wastewater as these parameters determine the degree of pollution and the biological and chemical demand for oxygen. It can be noticed from Figure 10.2 (c) below that the average values of COD and BOD5 of septage from cesspits in rural Nablus were (1086.86±376.23) and (371.43±239.16) respectively in mg/l. The large variation between these locations is related to the water consumption, frequency of emptying the cesspit, soil context and for the other factors mentioned in section 2.2.

Also, it can be noticed in Figure 10.3 that the factor of COD/BOD5 was around 3.4 and it was greater than the average ratio of raw wastewater at inlet of Nablus WWTP in the same period which equaled 2.0 (NWWTP, 2018), this is due to the high dilution factor of municipal wastewater, and the context of septage as it contains chemical solutions at the household level more than at the municipal level.

10.5.4.4 Total Nitrogen and Ammonia

As noticed in Figure 10.2 (D) below, the average value of TN of septage from cesspits in rural Nablus was: 178.33±69.04 mg/l.

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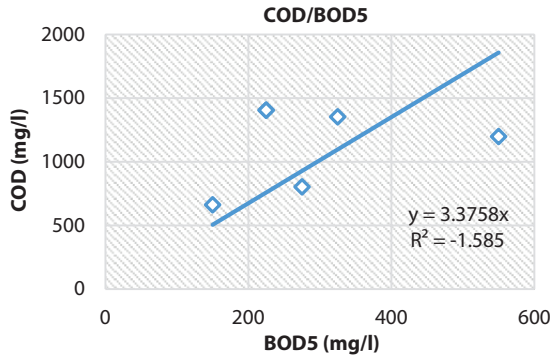

Figure 10.3 COD/BOD5 ratio for septage analyzed at rural Nablus.

The measurement of TN is an important test when trying to determine the characteristics of wastewater. And if the average of TN in septage is compared with the average of TN at the inlet of Nablus WWTP for municipal wastewater (84.67±7.57 mg/l) it could be concluded that the average TN in septage was larger (NWWTP, 2018).

10.5.4.5 TS, TDS, and TSS

Samples from the cesspits have high TS, TSS, and TDS compared with raw wastewater (Hithnawi, 2004). Figure 10.4 (a) shows the average values of the TS, TSS and TDS respectively.(1620.54±368.46), (328.25±162.25), (1001.08±234.10), all in mg/l.

For example, the TSS at the inlet of Nablus WWTP for municipal wastewater (474.67±69.62 mg/l) was less than the average of TSS in the septage in rural Nablus (NWWTP, 2018). The concentration of TSS becomes higher as the septage dense due to leaking the water content through the soil.

The large variation in these tests among the results is due to several reasons in addition to the factors mentioned in section 2.2, such as the error in balancing after burning the samples on 105°C and due to the dilution of the samples as they were very dense of solids.

10.5.4.6 VS, VDS, and VSS

Samples from the cesspits will have high VS, VSS, and VDS compared with raw wastewater (Hithnawi, 2004). Figure 10.4 (b) shows the average values of the VS (965.50±171.86), VSS (203.50±90.09), and VDS (651.68±141.35) all in mg/l.

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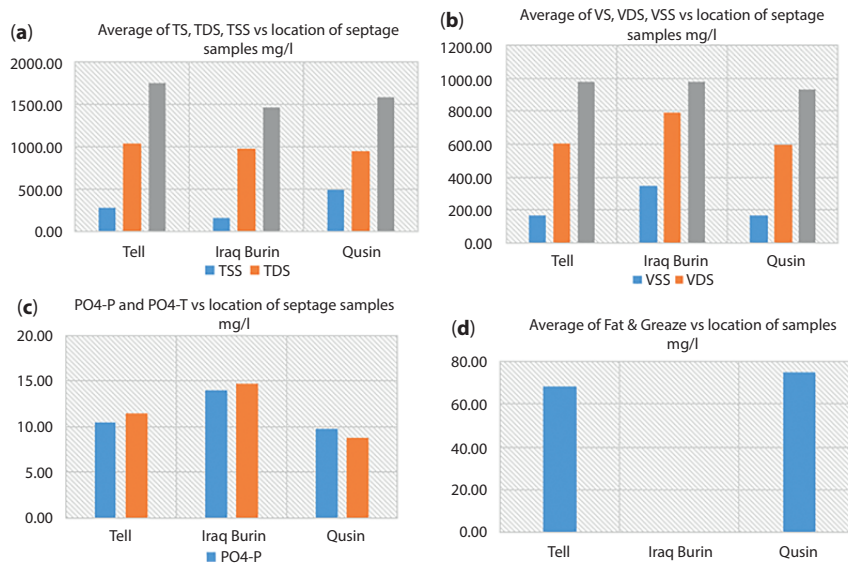

Figure 10.4 Average values for septage analyzed at rural Nablus; (a) TS, TDS, and TSS, (b) VS, VDS and VSS, (c) PO4 and PO4-T, (d) Fat and grease.

The huge variation in these tests among the readings is due to several reasons in addition to the factors mentioned in section 2.2, such as the error in balancing after burning the samples on 550°C and due to the dilution of the samples as they were very dense of solids.

10.5.4.7 PO_4-P and PO_4-T

As noticed in Figure 10.4 (c), the average value of PO4-P and PO4-T of septage from cesspits in rural Nablus were (11.22±2.89) and (12.10±2.86) respectively in mg/l.

The measurement of PO_4 is an important test when trying to determine the characteristics of wastewater. The presence of washing machines, wash-basins, and industries that are connected to Nablus WWTP are significant contributors of phosphate in domestic wastewater.

This leads to note that the average of PO_4-P at the inlet of Nablus WWTP (26.57±5.43 mg/l) was more than the average of PO_4-P in the rural Nablus septage (NWWTP, 2018).

10.5.4.8 Fat and Grease

Figure 10.4 (d) shows Oil and Grease average value for septage at rural areas in Nablus was (71.67±24.15) mg/l.

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10.5.4.9 Alkalinity

The high value of alkalinity affects nitrification and denitrification process. The average value of alkalinity in this study was (1178.13±220.58) mg/l. Figure 10.11 shows the $CaCO_3$ average values for septage extracted from cesspits at the three locations of this study.

10.5.4.10 TC and FC

Figure 10.5(b) below shows, the average of the TC and FC per 1 ml of the septage analyzed in this study were (1.95E+07±1.8E+07) and (1.12E+04±8.59E+03) respectively. The high variation in the averages is related to high dilution during the testing processes and the value itself.

10.6 Pre-Treatment of the Fecal Sludge – Results and Discussions

The second objective of this study was to enhance the quality of septage by on-site (pre)-treatment model. To achieve this objective; the following assumptions were made: (i) all the fecal sludge produced will be sent to the treatment plant, (ii) the fecal sludge was not diluted by water during desludging, (iii) the average household Size is 5.1 (PCBS, 2019), and (iv) the peak factor for design of septage TP is 2.0. The sludge production method was used to estimate the quantity of sludge that would be generated.

10.6.1 Quantification of Domestic Septage

The proposed model here is for Tell and 'Iraq Burin. The same methodology could be followed for Qusin area septage. This model is applicable and

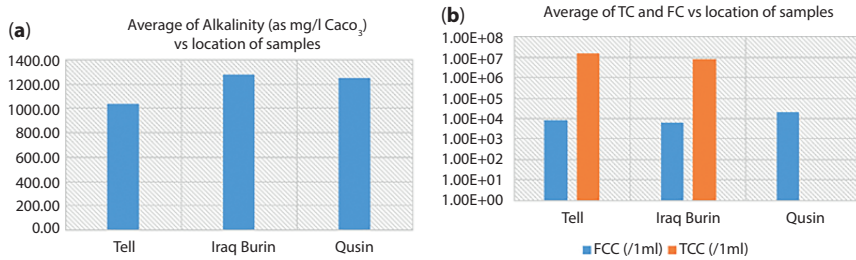

Figure 10.5 Average values for septage analyzed at rural Nablus; (a) Alkalinity, (b) TC and FC.

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expandable. The quantification and the capacity of the TP are: nNumber of households not connected to sewer network = 1,223; percentage of households which disposed of sewage by vacuum truck = 40%; annual increase in the percentage of households which used avacuum truck to dispose of the septage = 5%; average amount of septage per month produced by households = 12 m^3/month; number of years to use this TP as pretreatment plant = 5 years; the peak factor = 2.

Capacity (m^3/day) = no. houses × % of vacuuming houses × % of expansion of study area × the Average of households septage production × peak factor = 1223×{0.40+(0.05×5)}×12×2 = 19,078.8 m^3/month = 635.96 m^3/day.

10.6.2 Design Septage Characteristics

10.6.2.1 Untreated Septage Characteristics

Table 10.9 shows the design values of influent septage characteristics at the proposed septage treatment plant. As shown in this table, the 85% Confidence Interval (CI) was obtained for the characterized samples in the study area. And then the maximum value of 85% of CI were taken as a design value for the treatment plant model.

Table 10.9 Design values of parameters for septage treatment plant model (Rural Nablus).

Parameter	85% CI	Design value
pH	7.74 ± 0.13	7.87
BOD_5	371.43 ± 84.99	456.42
COD	1086.86 ± 133.69	1220.55
TS	1620.54 ± 130.94	1751.47
TSS	328.25 ± 57.66	385.91
TDS	1001.08 ± 83.19	1084.27
VS	965.50 ± 171.86	1026.57
VSS	203.50 ±90.09	293.59
TN	178.33 ± 24.53	202.87

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10.6.2.2 Treated Septage Characteristics

The effluent of the septage treatment plant should be less than the upper limit of treated WW based on the Palestinian specifications, see Table 10.9.

10.6.3 Software Design

10.6.3.1 Treatment Plant Modeling

GPS-X 7.0 (under An Najah-National University License) program was chosen to simulate different treatment-processes' options that were capable of sustainably treating septage under variable flow and feed options, and under varying temperature conditions. Also compared to the Palestinian Guidelines for treated wastewater reuse in restricted irrigation according to the Palestinian Standards Institute (PSI) (Table 10.10). Only the

Table 10.10 Classification of treated wastewater for agricultural purposes in Palestine (PSI, 2015).

Maximum limits of chemical and biological properties (mg/l) unless otherwise indicated	**Treated water quality**			
	High quality	**Good quality**	**Medium quality**	**Poor quality**
	(A)	**(B)**	**(C)**	**(D)**
pH	43991	43991	43991	43991
EC (ms/cm)	-	-	-	-
BOD_5	20	20	40	60
COD	50	50	100	150
TS	-	-	-	-
TSS	30	30	50	90
TDS	1200	1500	1500	1500
VS	-	-	-	-
TN	30	30	45	60
PO4-T	-	-	-	-
PO4-P	30	30	30	30
FC (colony 100ml)	200	1000	1000	1000

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sequencing batch reactor (SBR) process was found suitable for septage treatment under Palestinian rural conditions as previously described.

This research focused on the long-term simulation because the effects of the initial conditions were ignored. Also, during this long period the model may receive a shock of high or low concentration septage or WW; this shock will be directly considered and the behavior of the TP will be presented in the simulation figures.

Basically, the SBR system is a set of filling and evacuation tanks. Each tank in the SBR system is filled over a period of time and then functions as a discontinuous reactor. After the desired treatment, the mixed liquid is allowed to settle and the clarified supernatant is then discharged from the reservoir. The cycle for each tank in a typical SBR is divided into five distinct periods: filling, reaction, sedimentation or settling, evacuation or flushing, and idle.

Figure 10.6 presents on-site septage TP scheme represented by GPS-X 7.0 simulator, which comprises: the fine bar screen, a Grit removal, SBR, wastewater outlet pipe and excess sludge dewatering and outlet pipe.

There are several models proposed by the International Water Association (IWA), describing the biological process in the activated sludge plant (ASM1, ASM2, ASM3) (Serdarevic and Dzubur, 2016). The ASM1, ASM2 and ASM3 models incorporate carbon oxidation, nitrification and denitrification, and ASM2 also describes the biological and chemical phosphorus removal. The models are based on COD units (use chemical oxygen demand to define organic pollution) and ASM3 has a Total Organic Carbon (TOC)–based version as well. In this study, ASM3 process modeling was used as the characterized septage fit with ASM3 specific limitations such as temperature within (8 - 23) °C, pH in the range of (6.5–8.3) (Heryk Melcer *et al*., 2003).

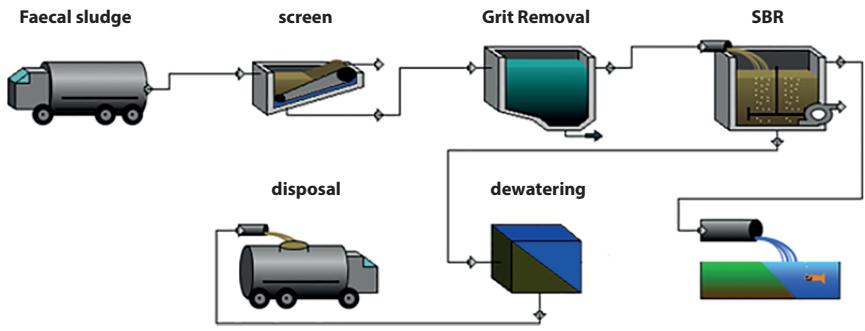

Figure 10.6 Designed wastewater treatment plant unit scheme for septage pretreatment represented by GPS-X7.0 simulator.

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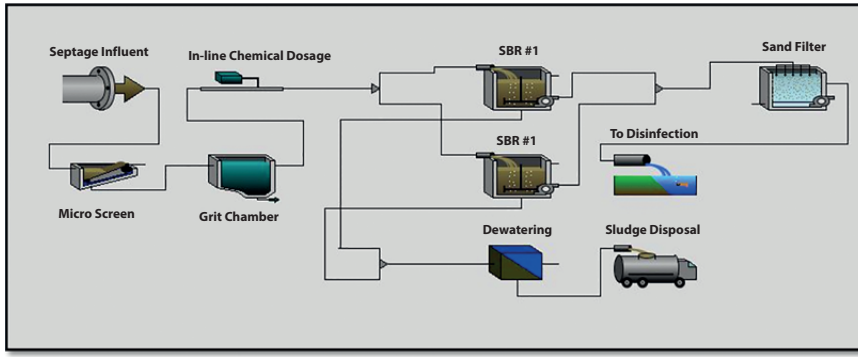

Figure 10.7 Septage treatment plant model scheme designed by GPS-X 7.0 simulator.

10.6.3.2 Optimizing the Appropriate Model

The scheme of the optimized model is shown in Figure 10.7 below. The volume of each SBR is 200 m^3 with surface area of 40m^2.

The proposed TP consisted of two in parallel SBRs. The first one will be filled and start its operation cycle 3 hours before the other SBR. Each cycle will take around 3 hours by one-fourth of daily designed volume (160.2 m^3) for both. The percentage of cycle time among the SPR units are: 3.0 hr filling, 1.5 hr react (Aeration), 0.75 hr settling, 0.5 hr decanting and 0.25 hr for idle.

After modeling the influent flow for the proposed treatment plant, the effluent characteristics are illustrated in Table 10.11.

The results showed that the TP had a 98% removal efficiency for BOD and 94% for COD. Moreover, the removal efficiency for SS and TN were 98% and 78%, respectively. All the affluent parameters fitted with Palestinian regulations and limits for treated WW for type C.

10.7 Treatment Plant Estimated Cost Breakdown

The construction and operation of a wastewater treatment plant is an economic activity, specific in any case. Several resources are required in order to achieve an increase in services, within a definite time margin, that will result in meeting the needs of the population.

A sophisticated examination of the cost elements that derive from the construction and operation of a WWTP is consequently required. The principal cost components that determine the total cost of a WWTP

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Table 10.11 Effluent characteristics of septage TP using GPS-X 7.0 vs. Pal. Treated WW type-C limits.

Parameter	Influent value	Effluent value	Palestinian regulations (Type C) (PSI, 2015)	Efficiency %
BOD_5	456.42	7.91	40	0.983
COD	1220.55	73.93	100	0.939
TS	1751.47	29.27	-	0.983
TSS	385.91	6.45	50	0.983
VS	1026.57	15.12	-	0.985
VSS	293.59	4.32	-	0.985
TN	202.87	44.28	45	0.782

depend on the daily flow rate of septage, as well as the system of treatment, the costs of land, design, construction, operation and maintenance. The main elements of analysis are the direct and indirect expenditure of the economic resources such as the use of land, materials and instruments, man-hours of design and construction.

The cost estimation breakdown for the modeled TP is as follow:

1) The cost of land: the cost of land required for the purpose of serving the facilities depends on the required surface and the unit price of the land surface in the specific area of the facility. In our case, around 750 m^2 is required for such a plant. And the unit price is around 21 USD$/$m^2$ in the selected area, as this area is already classified as agricultural area. The total cost of the land is updated for the period of time as construction take place.
2) The construction cost: The cost is mainly a function of the cost estimate for the construction of the treatment plant, the size of the plant, the type of soil and the topography of the facility's area, the distances for the transportation of materials. In this case study, the construction cost defined as civil works and the cost of the arrangement of the space, roads, etc., as far as conventional systems are concerned, the percentage of the construction cost of the building

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works of the main installation makes up 65%, the main network cost makes up 12.5%, and the cost of the arrangement of the space makes up 22.5%. The total estimated cost for the civil works for 1 HH is around 35 USD.

3) The material costs: the term material corresponds to the various parts of the WWTP mechanical equipment and control panel for the operation steps. In our case study, the equipment and control panel costs are around 35,000 USD.
4) The energy cost: the financial cost of the electric power construction of the WWTP is a function of the quantity of electric power consumed for the purpose of the WWTP's operation. In this case study, the estimated daily average electric consumption is a round 1.8 USD.
5) The operation and maintenance cost: The core individual elements of the maintenance and operation cost are the salaries and wages cost, and the spare parts expenditure. In this case study, the operation and maintenance cost depend on the performance and working hours. The spare parts and available in the markets and the useful life of the installed material is around 10 years. So, this item is to be identified when operation and maintenance take place. The energy cost was extracted from the O&M cost.

10.8 Conclusion

This study aimed to characterize the septage, fresh feces and urine in three villages in the rural area of Nablus Governorate, where the septage was disposed in an open area (such as agricultural lands) by vacuum pumps. The other objective of this study was to make an evaluation of the performance of SBR model dealing with Septage characterized by high organic loadings. The study findings revealed the following;

- Almost all values of septage parameters in rural Nablus were within the values of EPA and U.S. septage parameters except BOD and COD which were less than the ranges.
- The values of septage parameters in EPA were higher than those of rural areas in Nablus. This could be due to variation in septic tank design and pumping out intervals between the study area and the U.S., in addition to the difference in

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soil profile from one place to another. Moreover, the lifestyle and hygiene approaches in Palestine are different from other countries, where soiled toilet papers are partly discharged, and water is used for hygienic cleaning purposes. And the source of septage in rural areas is from unsewered rural dwellings, where short hydraulic retention time prevailed in most cesspits leading to weak anaerobic transformation processes

- The rural Nablus septage characteristics were higher than the municipal wastewater received to NWWTP. Also the septage parameters were higher than the design value in NWWTP. So as was expected, septage needs an independent treatment facility.
- The parameters of Turbidity, TN, PO4-T, TS, VS, TSS, VSS, Alkalinity, and FC had the highest values for septage in Qusin village and the lowest in Tell village. The differences were mainly due to behavior of people in households, the soil context, cesspit criteria, and frequency of emptying.
- Variation in the chemical and physical composition of feces and urine was widespread throughout the study. This means that technology developments must be robust and flexible in order to deal with this uncertainty.
- The determined time intervals between cleanings of cesspits in rural area depended on the water consumption, soil index, and capacity of cesspits. In this study almost all of the sampled cesspits were cleaned once or twice per month.
- Heavy metals concentration in the rural septage were within the acceptable rang according to the previous studies, EPA and U.S. septage specifications; the Fe, Aland Zn had the highest concentration. 'Iraq Burin had the highest values for Fe and Al while Qusin had the lowest. In contrast, Tell village had the highest value for Zn. These parameters depend directly on the soil index for each location.
- Septage content of the heavy metals were not in compliance with heavy metals concentration limits according to the Palestinian regulations for wadi disposal and effluent reuse in agriculture. This indicates that septage disposal in wadi and agricultural fields was not safe.
- The removal efficiencies of COD, BOD_5, TSS and TKN in the proposed TP model were acceptable according to the process guide lines that reached to 94%, 98%, 98%, and 78%,

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respectively. And the effluent from run are within with the Palestinian limitations of 2017 regulations for type C, which made the treated water suitable for irrigation of Almond, Olive, Citrus and Forest trees. Also, for Industrial crops, grains, Dry feed. Moreover, and the most important, it can feed the aquifer by filtration.

10.9 Recommendations

The following recommendations will be requested for any future developing of this study, in order to build on the achieved results:

- Increasing the proportion of sludge transported to the treatment facilities should be the immediate priority. This will require better fecal sludge management, starting with improved record keeping, and enforcement of legislation prohibiting indiscriminate dumping of fecal sludge.
- In other to gain a better overall understanding of the composition of FS, there is the need to conduct further studies in different locations at different seasons.
- Due to the large variability in the results obtained for the characteristics of fecal sludge, a more specific sampling approach, targeting smaller communities or groups of people, is also recommended.
- It is recommended to implement the modeled TP to examine the operation and efficiency of such TP on the ground and to make calibration for the model if needed.
- Flow which enters the treatment plant should be measured and logged continuously; classification of that flow will be helpful in the simulation process.
- It is recommended for operation of SBR a full control of the factors which affect the system efficiency such as temperature, organic loading rates, ph and oxidation reduction potential.
- Further researches should be carried out to improve this technology and enhance the effectivity of such TP.
- In order to benefit from operating of the treatment plant, a feasible strategy for effluent water reuse should be elaborated.

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11

Lipase Catalyzed Reactions: A Promising Approach for Clean Synthesis of Oleochemicals

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Abstract

Oleochemicals are chemicals derived from oils and fats. Several industrial processes, such as splitting, distillations, and fractionation, are carried out to convert oils and fats into basic oleochemicals such as fatty acids and glycerin. These fatty acids can be further esterified to produce value-added oleochemicals. Usually, the esterification reaction is carried out using chemical catalysts such as mineral acids. Such chemicals pose threats to the environment owing to their trace presence in effluents. Furthermore, the chemically catalyzed esterification reaction is an energy-intensive reaction that harms the environment. Recently lipase-catalyzed hydrolysis/esterification reaction has received much attention. Besides the biodegradability nature of lipases, they can catalyze the reaction at milder temperatures and produce no toxic by-products. The techno-economic assessment has proved the feasibility of enzyme technology compared to replace chemistry-based routes. This chapter focuses on oleochemicals' sustainable production through various processes. The processes include esterification, transesterification, and interesterification.

***Keywords*:** Lipase, esterification, environmental impact, pollution, energy consumption

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Nour Shafik El-Gendy (ed.) Sustainable Solutions for Environmental Pollution Volume 1: Waste Management and Value-Added Products, (417–448) © 2021 Scrivener Publishing LLC

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11.1 Introduction to Oleochemicals Industry

Oleochemicals are commonly known as the chemicals derived from oils and fats. The history of oleochemicals is as old as the history of humans. Soap was the first produced material based on goat fat and fire ashes by the Phoenicians. The ancient Egyptians utilized lubricating grease from calcium hydroxide and olive oil for their chariots' wheels. It is reasonably acceptable to assume that the industrial identity of the oleochemicals industry started because of the development of oils and fats (Food sector) and personal care products markets (Abdelmoez and Mustafa, 2014). In 1833, triglyceride hydrolysis to fatty acids and glycerol under high pressure and temperature was reported for the first time by A. de Mill and A. Motard but with technical limitations. In 1930, the high-pressure hydrolysis process based on high-pressure autoclave became the most available and convenient hydrolysis (splitting) process for fatty acid production, as it is today. The resulting fatty acids can be esterified with alcohols such as glycerol, isopropyl alcohol, 2-ethyl hexyl alcohol, pentaerythritol, sorbitan, and others to produce a wide range of technical (non-food) esters (Abdelmoez *et al.*, 2013). The transesterification process can also produce the same esters, where oils and fats react with alcohol at high temperatures with the presence of a catalyst. Hydrogenation and Interesterification are also processes used to modify triglycerides structure and produce high-quality structured fats that find many food applications. Hydrolysis, esterification, transesterification, hydrogenation, and Interesterification processes produce high-quality and cost-wise oleochemicals. On the other hand, they are energy-intensive processes and produce side products and gas effluents that harm the environment (Mustafa *et al.*, 2016a). Figure 11.1 shows the hierarchy of oleochemicals production processes.

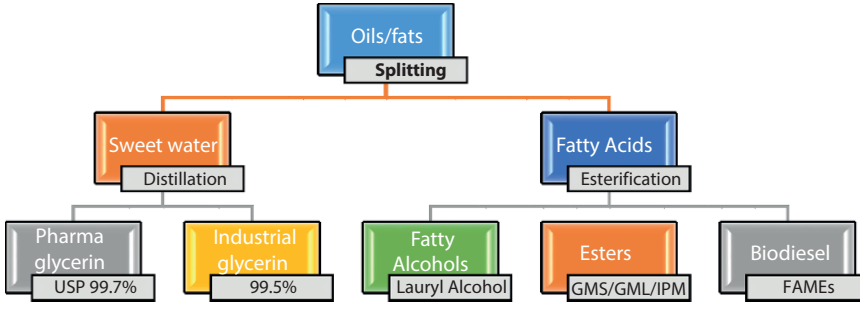

Figure 11.1 Hierarchy of oleochemicals production processes.

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Table 11.1 Historical progress of enzymes utilization for oleochemicals production.

#	Year	Key enzyme	Application	Reference
1	1903	Lipases	hydrolysis of fats	(Lewkowitsch and Macleod, 1904)
2	1985	Immobilized lipase Lipozyme® RM IM	for production of CBEs and infant milk fat	(Holm and Cowan, 2008)
3	1994	Porcine-based phospholipase A2 Lecitase® 10L	degumming of vegetable oils	(Clausen, 2001)
4	1999	Novozyme® 435	Triacylglycerides (TAGs) enriched in PUFA	(Haraldsson, 1999)
5	2001	Microbial-based phospholipase A1 Lecitase® Novo	for degumming	(Clausen, 2001)
6	2001	Immobilized lipase Lipozyme® TL IM	enabling bulk fat modification	(Husum *et al.*, 2004)
7	2004		Desmet and Alfa Laval start offering plants dedicated to enzyme processing	(Kellens, 2000)
8	2008	Phospholipase C Purifine® PLC	for enzymatic degumming	(Hitchman, 2009)
9	2013	Lipases Callera® Trans	for production of biodiesel	(Cesarini *et al.*, 2013)
10	2017	Hemicellulases Palmora®	for improving extraction yield in palm oil plants	(Holm *et al.*, 2018)

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Recently, the utilization of lipases has received much attention due to their biodegradability and selectivity. The enzymatic processes are carried out using lower temperatures and produce no side products. Unlike chemically catalyzed processes, a high temperature that reaches more than 200 °C requires high-pressure steam or thermal fluid for the heating purpose. Both heating elements need special boilers that consume a considerable amount of fuel during the combustion process. The carbon footprint results from the chemically catalyzed process are much higher than enzymatically biocatalyzed processes (Mustafa *et al.*, 2016b; Hosney *et al.*, 2020; Hosney and Mustafa, 2020). Now lipases are used for synthesizing many oils and fats–based products such as specialty fats (i.e., high omega-2 fish oils, cocoa butter equivalent and infant formulas) (Hosney *et al.*, 2020). In addition, lipases are successfully used to modify fats' melting properties to produce trans-free fat shortenings and margarine without hydrogenation. They are used to synthesize specialty esters with reduced energy consumptions and lowered by-products formation. Lipases are also used to catalyze the transesterification reaction of biodiesel production, where fatty acids methyl esters "FAME" could be produced from low-quality feedstocks such as spent cooking oils (Abdelmoez *et al.*, 2016; Holm *et al.*, 2018). Recently, enzymes are used in palm oil extraction, where selected structured component hydrolysis in the fruit of palm increases the overall process yield. Table 11.1 reports the historical progress of enzymes utilization for oleochemicals production.

11.2 Sources of Lipases

Lipases are commonly distributed in plants, animals and microorganisms (Bharathi *et al.*, 2019; Bornscheuer, 2002). Microbial lipases have received much attention from the commercial point of view because of their ease of genetic manipulation and cultivation, ease of their production and isolation and because of their high biochemical activities (Hasan *et al.*, 2006). Lipases play an important role in cutting down the energy consumption for the reactions that naturally need high temperature, thus cutting down the carbon emissions (Tyndall *et al.*, 2002). Table 11.2 shows various lipase-producing microorganisms.

11.2.1 Bacterial Lipases

Extracellular bacterial lipases are lipoprotein that find great interest and are well studied compared to animals and plant lipases. The microorganism

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Table 11.2 Lipase-producing microorganisms.

Lipase producing microorganism	**Reference**
Bacillus sp	(Kumar *et al.*, 2012)
Bacillus subtilis	(Ruiz *et al.*, 2005)
Penicillium simplicissimum	(Stöcklein *et al.*, 1993)
Penicillium cyclopium	(Chahinian *et al.*, 2000)
Bacillus thermocatenulatus	(Lee *et al.*, 1999)
Fusarium solani	(Knight *et al.*, 2000)
Acinetobacter sp.	(Snellman *et al.*, 2002)
Pichia burtonii	(Sugihara *et al.*, 1995)
Lactobacillus plantarum	(Lopes *et al.*, 1999)
Rhizomucor miehei	(Herrgård *et al.*, 2000)
Trichosporon laibachii	(Liu *et al.*, 2004)
Rhizopus sp.	(Alves Macedo *et al.*, 2003)
Pseudomonas fragi	(Nishio *et al.*, 1987)
Staphylococcus aureus	(Götz *et al.*, 1998)
Staphylococcus haemolyticus	(Oh *et al.*, 1999)
Aspergillus oryzae	(Toida *et al.*, 1998)
Trichosporon asteroides	(Dharmsthiti and Ammaranond, 1997)
Candida cylindracea	(Muralidhar *et al.*, 2001)
Streptomyces flavogriseus	(Mostafa and Ali, 1979)
Botrytis cinerea	(Comménil *et al.*, 1995)
Aspergillus niger	(Namboodiri and Chattopadhyaya, 2000)
Geotrichum candidum	(Jacobsen and Poulsen, 1995)
Chromobacterium viscosum	(Taipa *et al.*, 1992)
Staphylococcus warneri	(Simons *et al.*, 1996)
Enterococcus faecalis	(Kar *et al.*, 1996)
Pseudomonas fluorescens	(Kojima *et al.*, 1994)
Pseudomonas aeruginosa	(Chartrain *et al.*, 1993)

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is generally grown on a medium containing nutrients of carbon sources (sugar, oil, and combined carbon sources), phosphorus, and mineral and nitrogen source. The oil nutrient is considered the master substrate that induces lipase production. Lipases from Bacillus sp. and Pseudomonas can be regarded as the first reported lipase-producing bacteria. Later on, *Alcaligones sp., Achromobacter sp,* and *Chromobacterium sp.,* have been proposed for lipase production (Dunhaupt, Lang, & Wagner, 1991).

11.2.2 Fungal Lipases

Due to their low extraction cost, stability in organic solvents, substrate specificity and good pH and thermal stability, fungal lipases have received much attention from many lipases producers. Examples of fungi-producing lipases are *Rhizopus sp, Aspergillus sp,* and *Mucor sp* (Aguieiras, de Barros, Fernandez-Lafuente, & Freire, 2019).

11.2.3 Plant Lipases

Plant lipases are present in the reserve tissues of foods growing seeds that contain a significant amount of triacylglycerides. The activity of lipase in seeds of plant increases through the period of germination as lipases consume the triacylglycerides and converts it to sugars. Such sugars are then transported to the tissues of growing in order to supply energy and structural carbon for supporting the young plants' growth.

11.2.4 Animal Lipases

Animal lipases can play a leading role in lipid digestion in the biological system by hydrolyzing the animal fats before absorption by lymph and blood. Although animals are rich sources of lipases, they are rarely studied because of the low cost, ease of production, and availability of microbial lipases. Animal lipases have been derived from lots of fishes, insects, and mammals (Walton, Cowey, & Adron, 1984).

11.3 Application of Lipases

Lipases have received much attention recently. The main benefit of lipases is that they can effectively catalyze industrial processes using milder conditions. Examples of processes are hydrolysis, transesterification, esterification, and intraesteification. Such reactions produce a wide range of product

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categories: margarine and shortening, structured fats, biodiesel, cosmetics, lubricants and metalworking, detergents, personal care, textile, plastics, food, and feed, and others (Houde *et al.*, 2004; Loli *et al.*, 2015; Tomke *et al.*, 2017). As lipases could effectively replace the chemical catalysts, therefore unwanted by-products could be reduced. In most of reported enzymatic reactions, the reaction temperature does not exceed 60°C, which is a mild low-temperature reaction compared to chemicals catalyzed reactions. Thus, the oleochemicals industry based on enzymatic reaction contributes to clean reactions and reduced carbon footprint (Abdelmoez and Mustafa, 2014). Due to the vast and worth noting applications of lipases, efforts are still being done to screen newer microbes that can produce active lipases (Verma *et al.*, 2012).

11.3.1 Monoglycerides Production

Monoglycerides are a significant and specific product category that find several applications in the food and cosmetics sectors. They are commonly produced by oils/fats transesterification (glycerolysis) and fatty acids esterification. The former is the most widely produced industrial method, because generally oils and fats are cheaper than their corresponding fatty acids. Furthermore, glycerolysis of triglycerides produce glycerol as by-product; such product is a credit and contributes to raising the product profit margin. The esterification and transesterification processes are carried out using catalyst/biocatalyst. They can also be performed in an autocatalytic approach without catalyst but under elevated temperature. Not surprisingly, the cleanest process among them is the enzymatic method; however, the high cost of enzymes is restricting the ease of commercialization. The detailed discussion of monoglycerides production using chemical technology and biotechnology is presented below (Mustafa *et al.*, 2016a).

11.3.2 Oil/Fats Glycerolysis (Chemically Catalyzed)

Chemically catalyzed glycerolysis reaction is carried out at high temperature between triglycerides and glycerol using alkali catalyst. In this reaction, the glycerol breaks the triglycerides and substitutes its location mostly in the sn-1 position. Glycerol is a polar nontoxic material. Natural glycerol is commercially produced as by-product from three reactions: fat splitting, transesterification of triglycerides and methanol (biodiesel production) and fats saponification (Abdelmoez *et al.*, 2013). Glycerol utilization as raw material for monoglycerides production contributes to further

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raise its value as by-product. This also helps in avoiding the glycerol accumulation and environmental pollution. Triglyceride and glycerol structure and base catalyzed glycerolysis of triglycerides are shown in Figure 11.2a, 11.2b and 11.2c, respectively.

Although the base catalyzed transesterification is the most used commercial method for monoglycerides production, it has many disadvantages. The high temperature reaction of more than 200 °C results in very dark product and trace by-products. This requires further downstream processes steps in order to eliminate such undesirable materials as washing, bleaching and distillation. Thus, with every purification step liquid, gas and solid effluents are being generated which pollute the environment. Strong homogeneous base catalysts, such as sodium hydroxide and potassium hydroxide, are normally used to accelerate the reaction. However, the presence of such catalysts in the final product in trace levels results in low-quality product. Furthermore, sodium and potassium hydroxide cannot be considered selective catalyst toward monoglycerides formation. The reaction produces a random mixture of mono, di and triglycerides with low yield of monoglycerides; as a result the energy-intensive molecular distillation process is usually used to produce high content of monoglycerides (Abdelmoez and Mustafa, 2014). The production yield of 48.3% of monoolein and monolinolein from sunflower oil was achieved by Galucio *et al.* (Galúcio *et al.*, 2011) using heterogeneous catalyst $Ca(OH)_2$. Monoglycerides could also be obtained by reacting neem oil with glycerol with a molar ratio of 1:2 respectively, heterogeneous catalyst of CaO with load of 0.05% at temperature of 220 °C with aid of nitrogen purging. The reaction was monitored by periodically drawing samples and dissolving

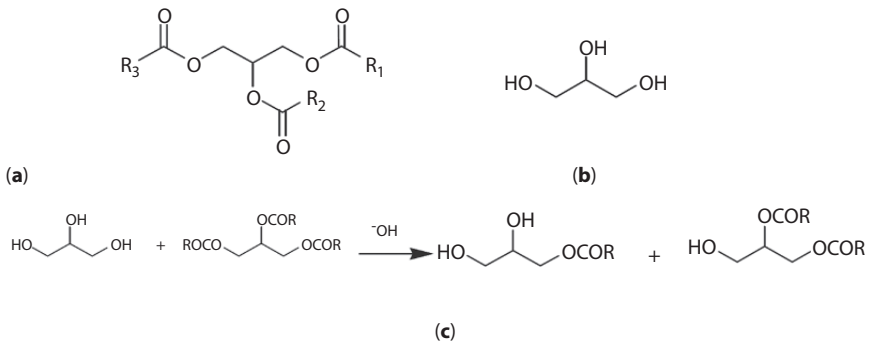

Figure 11.2 Triglyceride structure: (a) glycerol structure (b) triglyceride glycerolysis reaction (c).

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them in anhydrous methanol until obtaining clear solution (Chaudhari *et al.*, 2015).

The main advantages of using heterogeneous catalysts are the ease of their separation. However, the high reaction temperature employed produces products with charred odors which need an additional distillation step to remove the odor and color. Such sequence requires high capital investment. Furthermore, such elevated temperature is not suitable for the heat sensitive monoglycerides production.

11.3.3 Oil/Fats Glycerolysis (Enzymatically Catalyzed)

Selective sn-1,3 lipase finds many applications in the oils/fats sectors. Unitization of lipases as alternatives to chemical catalysts contributed in reducing many of the environmental disadvantages caused by the chemically based glycerolysis reaction. The low reaction temperature employed not only increase the purity and yield of the produced monoglycerides, but also it serves in producing the heat sensitive monoglycerides. Lipases showed good activity in solvent systems and solvent free systems. The most commonly used lipases for monoglycerides production are Novozym 435, Lipozyme RM, and Lipozyme TL IM. All three lipases are produced by the global enzymes producer Novozymes A/S, Denmark. Of these, Novozym 435 is the most expensive, and it has vast applications in oleochemicals production. Lipozyme RM and Lipozyme TL IM are cheaper and they find many applications in oils glycerolysis. They also cannot work on a temperature of more than 60 °C. Other reported lipases used in glycerolysis catalysis along with the reaction conditions and results are shown in Table 11.3. Enzymatic glycerolysis of vegetable oil was carried out by McNeill *et al.* (McNeill *et al.*, 1992) where 90% of monoglycerides were obtained. On the other hand, enzymatic glycerolysis of heat sensitive oils containing high order of polyunsaturated fatty acids has been reported, such as tuna anchovy oils.

Despite the benefits of using lipases such as selectivity and specificity, their utilization is usually accompanied by disadvantages. Such disadvantages can include their cost. The common active commercial lipase is expensive, which restricts their path to commercialization. Another disadvantage is that in some reactions, when the reaction is carried out at low temperature, the medium viscosity becomes high and mass transfer limitations occur, resulting in lower conversion and yield. That is why performing such reactions in the presence of solvent can remarkably reduce the medium viscosity and increase the access of substrates to the enzyme (Abdelmoez & Mustafa, 2014).

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Table 11.3 Lipase catalyzed glycerolysis reactions.

Oil/fate	Ljpase type	Reaction conditions	Yield	Reference
Olive Oil	Novozym 435	Molar ratio of 2:1 glycerol to olive oil; Temperature of 30 °C; 3 h; water content of 3.5% (w/w)	MAG (26%); DAS (30%)	(Singh and Mukhopadhyay, 2012)
Babasu Oil	*Burkholderia Cepacia* lipase	6 h; molar ratio of babasu oil: glycerol, 1:15; Temperature 55°C and 10 wt% *B. Cepacia* lipase, solvent free	25 wt% MAG	(Freitas *et al.*, 2010)
Palm Oil	Immobilized lipase PS on Accurel EP-100 (IMPS)	Molar ratio of glycerol : palm oil, 8:124 h; and 50 wt% IM-PS loading (based on oil), Temperature 45°C; 10% (w/v) of palm olein in acetone/isooctane mixture	56 wt% MAG	(Kaewthong and Aran, 2004)
Olive Oil	Novozym 435	Novozym 435 load; Molar ratio of 6:1 glycerol to olive oil; 9% 16% wt tween 60; Temperature of 70 C; solvent free	MAG (26%); DAS (17%)	(Valerio *et al.*, 2009)
Tuna oil	Novozym 435	Weight ratio of *t*-butanol to oil 2:1; Temperature 40°C; 3 h; The molar ratio of glycerol : tuna oil, 4:1; and 15 wt% Novozym 435.	90% crude MAG	(Pawongrat *et al.*, 2008)

(*Continued*)

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Table 11.3 Lipase catalyzed glycerolysis reactions. (*Continued*)

Oil/fate	Ljpase type	Reaction conditions	Yield	Reference
Sun flower oil	Fermase CALB 10000 produced from *candida antarctica Lipase*	Temperature 50°C; 5 h; a stirring rate of 200 rpm; The molar ratio of glycerol : sun flower oil, 5:1; and 15 wt% Fermase CALB 1000 loading (based on total mass of reagent), solvent free	70-80 wt% MAG	(Naik *et al.*, 2014)
Soybean Oil	Novozym 435	Temperature 40°C; 24 h; The molar ratio of glycerol : olive oil, 4:1; 3.5% (w/w) water content in glycerol and 10% of enzyme loading (wt% of oil mass), solvent free	32 and 48 wt% of MAG and DAG	(Fregolente *et al.*, 2008)
Soybean Oil	Novozym 435	stirring rate of 900 rpm; Temperature 70°C; 1.5 h; a; 10% (w/w) Novozym 435 loading; The molar ratio of glycerol : canola oil, 0.1:1 solvent free; 40 % of ultrasound intensity (52.8 W cm^{-2})	65 wt% (MAG + DAG)	(Remonatto *et al.*, 2015)
Anchovy Oil	Lipase PS-DI from *Burkholderia cepacia*	Temperature 45.8°C and 54.7°C; over 4 h; a stirring rate of 200 rpm; The molar ratio of glycerol : anchovy oil, 3:1; 3.5% (w/w) Lipase PS-DI loading, solvent free	24.58 and 28.34 wt% of MAG rich with EPA and DHA	(Palacios *et al.*, 2019)

(*Continued*)

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Table 11.3 Lipase catalyzed glycerolysis reactions. (*Continued*)

Oil/fate	Ljpase type	Reaction conditions	Yield	Reference
High Oleic Sun Flower Oil	Novozym 435	Temperature 50°C; 8 h; The molar ratio of glycerol : high oleic sun flower oil, 3:1; and 3 wt% Novozym 435 loading (based on oil), *tert*-butanol and *tert*-pentanol (80/20, v/v)	75 wt% Crude MAG and 93.3% GMO	(Zhu *et al.*, 2011)
Canola Oil	Novozym 435	Temperature 70°C; 2 h; a stirring rate of 900 rpm; The molar ratio of glycerol : canola oil, 0.1:1; 10% (w/w) Novozym 435 loading, solvent free; 40 % of ultrasound intensity (52.8 W cm^{-2})	75 wt% (MAG + DAG) 75 wt% (MAG + DAG)	(Remonatto *et al.*, 2015)
Soybean Oil	Lipozym TL IM	Temperature 45°C; 4 h; The molar ratio of glycerol : olive oil, 3.5:1; and 15 wt% Lipozyme TL IM loading (based on oil and glycerol), *tert*-butanol:isopropanol at ratio 80:20 and weight ratio of solvent to oil 4:1	72% MAG	(Zhong *et al.*, 2009)
Tuna Oil	*Pseudomonas fluorescence* Lipase	Temperature 45°C; 24 h; The molar ratio of glycerol : tuna oil, 3:1; water added 4 wt% in glycerol; and 30 wt% IMAK (based on tuna oil), and weight ratio of *t*-butanol to oil 2:1	25% MAG but containing 56 wt% PUFA (EPA and DHA)	(Pawongrat *et al.*, 2007)

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11.3.4 Biodiesel Production

The feedstock price and availability can be considered the major challenge that affects biodiesel economy. That is why low-quality, cheap and low-cost feedstock is probably the target of producers. Most of such economic feedstocks contain high order of free fatty acids. Such kind of feedstocks require a refining process step before being used as starting material in the methanolysis reaction; this is important in order to avoid harming the chemical catalyst. In addition, the chemically catalyzed biodiesel production is carried out at high temperature and uses excess of methanol to oil molar ratio, which therefore affects the fixed and running cost of the biodiesel production process (Abdelmoez *et al.*, 2016).

Watanabe *et al.* (2000) was the first to report the enzymatic production of biodiesel from low-quality feedstock. Nowadays, there are dozens of publications that have addressed the enzymatic production of biodiesel using different enzymes preparations and different feedstocks. One of the most studied aspects in biodiesel production is the production cost. An optimized use of lipases is a must in order to have an economically feasible process. This is achieved by using the less amount of lipase against highest productivity through enzyme reusability. Immobilized enzymes are most suitable to be reutilized several times; however, maintaining the activity of lipases through the reusability for many cycles is also problematic. This becomes more troublesome when low-quality feedstock is used. The presence of soap and acids residues is enough to deactivate the lipase.

The reactor configuration has been extensively reported, such as mechanically stirred tank reactor, packed bed reactor and air/nitrogen stirred tank reactors. However, an optimal operation for every reactor configuration is required. For example, high shear mixers are not suitable with immobilized enzymes as they damage the immobilization system of lipase, leading to lipase deactivation. Therefore, a gentile mixing by air or nitrogen can result in calm mixing. Utilization of a packed bed reactor has an advantage against a stirred tank reactor, since it reduces the downstream processes related to lipase separation from final product because they are already separated in the bed. However, a non-optimal operation of such kind of reactor causes glycerol accumulation and then blocks the active site of lipase and reduces the substrates access to the active site, which reduces the conversion. Utilization of free diffusing lipases instead of immobilized lipases had also been considered to avoid the limitations caused by glycerin attachment to the enzyme particles. It also offers in reducing the overall cost of process and it is cheaper than immobilized lipases (Cesarini *et al.*, 2013).

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11.4 Lipase Catalyzed Production of Biodiesel

In 2012, Novozymes A/S developed a biodiesel production process based on free diffusing lipase Eversa® Transform. In this process, an enzyme separation step is required after the methanolysis reaction. As enzymes are hydrophilic in nature, they create an emulsion phase that is located in the interface between upper layer (biodiesel phase) and bottom layer (glycerin phase). The process is shown in Figure 11.3. The process conditions are temperature of 40 °C, water of 1.5%-2% (w/w); enzyme load of 0.3%-0.4%; methanol of 1.2-1.5 equivalent; reaction time 24, 48h and proper agitation.

This process has suggested a gradual addition of methanol to avoid lipase inhibition due to excessive ratio of methanol. It also suggested that at least methanol could be added hourly by dividing the whole amount into portions. When this process was developed in 2012, the Novozymes team recommended lipase reutilization (free diffusing). However, due to the low quality of starting feedstock that affects also the activity of enzyme and the low enzyme load is employed with moderate cost, it is preferred to use enzyme in this process only one time (Holm *et al.*, 2018). When it comes to using low-quality feedstock for biodiesel production, a pretreatment step is required in order to have smooth and stable operation. Mineral acidity probably exists in most low-quality oils feedstocks, regardless of its origin. This acidity comes because of many reasons, such as adding phosphoric acid in the oil refinery steps. Such acid traces should be neutralized before

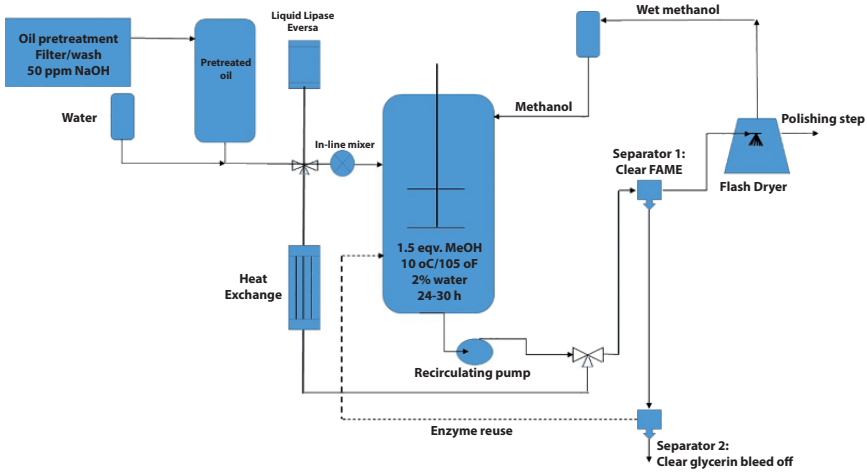

Figure 11.3 Lipase catalyzed production of biodiesel using low-quality feedstock (Holm *et al.*, 2018).

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stating the enzymatic methanolysis reaction to avoid affecting the performance of enzyme due to pH variation.

The first commercial unit for enzymatic production of biodiesel with capacity of 50,000 tons per year was constructed in 2008. The process was based on immobilized lipase and was pioneered by a Chinese expert professor, Dehua Liu, of the University of Tsinghua. A few years later, Stuart Company, United States, developed a continuous enzymatic process for biodiesel production based on liquid lipase for the first time. The plant was designed to process low-quality feedstocks such as used brown grease and cooking oil that enabled low running cost. Today there are more than 10 industrial plants that use lipase technology with different feedstocks for biodiesel production (Holm *et al.*, 2018).

11.4.1 Production of Biodiesel from Oil Extracted from Spent Bleaching Earth (SBE)

Spent bleaching earth is an oily waste generated from oil refineries and oleochemical plants in the step of bleaching. The annual world generation of SBE is about 2 million tons (Huang and Chang, 2010). Such a very large quantity contains from 20% to 30% oil as on a weight basis. The spent bleaching earth disposal is a serious problem for most refineries. This is because of the hazard of fire if it is stored or disposed of incorrectly.

Many studies have been made in order to recover the residual oils adsorbed on BE in several methods such as solvent extraction, supercritical CO2 and others (Demirbas & Balat, 2006; Fattah, Mostafa, Mahmoud, & Abdelmoez, 2014; Haas, McAloon, Yee, & Foglia, 2006; Lam, Tan, Lee, & Mohamed, 2009). These researches succeeded in recovering the residual oils. However, the economic benefits for the oil regeneration process are unconvincing for the plant owners until now. Furthermore, the regenerated bleaching earth did not have its original activity that could bleach the edible oils efficiently. Hung and Chang (2010) indicated that the reactivated spent bleaching earth exhibited poor removal of chlorophyll pigment (27% w/w) and negligible removal of the ß-carotenoids and phosphorus from the processed oil, while the virgin BE showed effective removal for chlorophyll, ß-carotenoids and phosphorus with percentages 98%, 100%, 71% w/w, respectively. That is why the current direction in oil refineries and oleochemical plants is to get rid of it by landfill or by incineration without any treatment that would protect against a threat to the atmosphere.

Utilization of the recovered oils from the SBE for producing value-added products is thus a subject of great interest currently. Many researchers have used the recovered oils for production of valuable products such

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as biodiesel, fatty acids, bio lubricant, animal feed, and different alkyl esters (Haas *et al.*, 2006). Also, current studies have a significant interest in using the SBE in the fermentation processes as a substrate for enzyme and surfactant production. The oils recovered from spent bleaching earth can be considered as a promising low-cost feedstock for biodiesel production.

Nowadays the principal concern of biodiesel production is the cost feasibility (Demirbas and Balat, 2006). The total cost of biodiesel production by chemical technology consists of feedstock cost, catalyst cost, utilities (steam, electricity) and labor (Haas *et al.*, 2006). It should be noted that most biodiesel producers are now using plant origin oils as feedstock. Lam *et al.* (Lam *et al.*, 2009) reported that utilization of refined plant origin oils as a feedstock for biodiesel production represents about 80% of the total production cost. Therefore, selection of an appropriate feedstock is an important issue that has to be considered.

SPE Utilization for biodiesel production, whether by chemical technology or by biotechnology, has been discussed in several papers and books. Abdel Fattah *et al.* (Fattah *et al.*, 2014) mention that the free fatty acids content in the recovered SBE oil is considerable, which in turn make its utilization as an edible oil source not practical. Therefore, these oils can be converted to methyl esters such as biodiesel or other non-food applications.

One of the important studies that considered both technical and economic aspects was by Huang and Chang (2010). They extracted the oils from the bleaching earth by hexane then developed a two-step esterification reaction. The first one was to reduce the free fatty acids content by reacting the highly free fatty acid oil with methanol to avoid the saponification with caustic soda. The second reaction was reacting the esterified oil with further methanol at 60 °C for about 1h. Huang and Chang proved that the production cost of fossil diesel or biodiesel made of refined oil or waste cooking oil was higher than what was obtained by using the spent bleaching earth.

Enzymatic production of biodiesel from spent bleaching earth is well known. The enzymatic route has several advantages over the chemical route; however, the two main concerns of long enzymatic reaction—time and enzyme cost—remain the major reasons for not taking this route. Furthermore, lack of research in scaling up the enzymatic process maybe delays its industrial implementation.

The first pilot plant of lipase catalyzed FAME production was conducted in the research of Park *et al.* (Park, Sato, & Kojima, 2008). Park and colleagues developed a very simple way for producing FAME in 50 liters reactor. The reactants were SPE, *Candida cylidraca* lipase, Kerosene (as a

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solvent) and methanol. The maximum conversion obtained was 97% after 12h at 25C and 1% (w/w) lipase. The main drawback of this research was the long reaction time as well as the impossibility of lipase powder recovery from the spent bleaching earth at the end of the process after the filtration step. It was found in the research that the enzyme cost accounted for 80% of the total production cost. Park *et al.* mentioned that the main inhibitory factor of enzymatic synthesis of methyl ester from spent bleaching earth is the presence of chlorophylls pigments. It was found that adding a small quantity of alkali in the reaction medium would eliminate the inhibitory effect and accelerate the methyl ester production rate compared to that without addition of KOH. The conversion obtained was 100% within 3h with only 0.05% (w/w) lipase.

All the previous studies used different organic solvents to recover the adsorbed oil. On the other hand, oil extraction by supercritical (SC-CO_2) is a promising approach. Kheang *et al.* (2006) compared between both oil recovery by hexane and by SC-CO_2. They observed that the residual oils recovered by SC-CO_2 had higher quality in terms of color and copper-iron presence. The biodiesel yield obtained was more than 98% after using RH-resin as a catalyst during the transesterification process.

11.5 Esterification of Fatty Acids with Glycerol

Monoglycerides production can also be done by esterification. In this reaction, free fatty acids are reacted with glycerol in the presence of chemical acid catalyst or enzymatic catalyst. When targeted fatty ester is required, pure fatty acid must be used as starting materials instead of triglycerides, like the case in transesterification. Unlike transesterification, esterification reaction does not generate glycerol as by-product.

11.5.1 Chemically Catalyzed Esterification

The acid catalyzed esterification reaction is carried out at high temperature of around 200 °C. Water is generated, as by-product from this reaction; such waters should be removed from the reaction mixture as it encourages the reversible hydrolysis reaction. Usually water is removed by purging nitrogen in the main reactor and/or by applying vacuum. Efficient removal of water plays a major role in driving the reaction toward esterification rather than hydrolysis, thus increasing the conversion and reducing the reaction time. Figure 11.4 is a schematic diagram showing a simple esterification reactor with water removal system.

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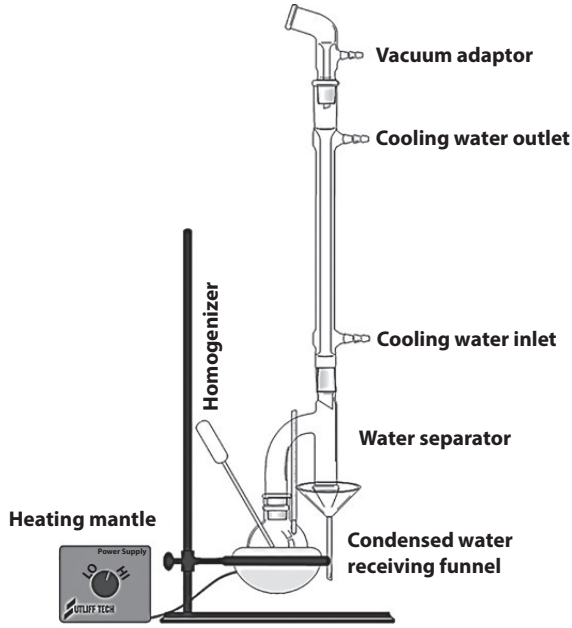

Figure 11.4 Schematic diagram of a simple esterification reactor with water removal system.

Using a homogeneous catalyst such as sulfuric acid or phosphoric acid is quite common in the esterification reaction industrially. The challenge associated with such type of catalysts is the difficulty of their separation from the final product. Even after separation, they pose a threat to the environment. Furthermore, when a homogeneous catalyst is used, care should be paid to optimize the reaction conditions as the acid catalyst is not selective and causes formation of high order of triglycerides, which is not the targeted product. Usually higher molar ratio of glycerol to fatty acid is used in order to avoid the formation of triglycerides instead of mono and diglycerides (Mustafa *et al.*, 2016a).

In order to avoid the problems caused by the homogeneous catalysts, heterogeneous catalysts have recently received much attention due to their ease of separation, which reduce the downstream processes steps and avoid the entrainment of catalyst in the final product. Also, this type of catalyst can be reused several times, which positively influences the process economy. Bossaert *et al.* (Bossaert *et al.*, 1999) used MCM-41-SO_3H as heterogeneous catalyst and they obtained 53% of monoglycerides. Diaz *et al.* (2003) also synthesized 63% of monolaurin and 45% of monoolein using the supporting material MCM-41 based heterogeneous catalyst. Monolaurin

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with a parentage of 50% was also synthesized by Hoo and Abdullah (2014) using mesoporous 12-tungstophosphoric acid SBA-15 catalyst. Kotwal *et al.* (Kotwal, Deshpande, & Srinivas, 2011) reacted different individual fatty acids with glycerol to study the selectivity of Fe-Zn double metal cyanide catalyst. The monoglycerides obtained were Monolaurin with yield of 66%, monomyristin with yield of 75.9%, monostearin with yield of 62.2% and monoolein with yield of 63.4%.

11.5.2 Lipase Catalyzed Production of Monoglycerides

In order to reduce the energy consumption and pollution caused by the chemical catalyzed method, lipases have received much attention. The esterification reaction is carried out at milder temperatures and produces almost zero water. Furthermore, lipases are more selective and specific towards monoglycerides formation. In this regard, immobilized lipases had been studied extensively in the literature as a candidate for production of esters. Immobilized lipases are favored as they can be separated easily from the reaction mixture and reused. Sn-1,3 selective lipases are commonly used in the production of monoglycerides. Most of active lipases are produced by Novozymes, A/S, Denmark. Novozymes, A/S, has the largest enzymes market share globally. Examples of these enzymes are Lipozyme RM, Lipozyme 435 (previously named Novozym 435) and many more. Table 11.4 reports some published work related to enzymatic production of monoglycerides.

11.6 Interesterification

The interesterification process is used to modify the oils and fats melting properties. This modification might be a decrease or increase in melting point (Gunstone, 2004). This technology is extensively used in the production of margarine and shortening. In this industry, vegetable oils and fats are hardened to obtain a final product with specific melting profile. Adjusting the melting point is of great importance; for example, high-quality chocolate melts in the mouth sharply. On the other hand, poorer-quality chocolate gives a waxy mouth-feel. The existing technologies utilized to modify the oils/fats melting point are hydrogenation, blending, dry fractionation, chemical interesterification and enzymatic interesterification (Holm *et al.*, 2018). Mixing two or more types of fats is not necessary enough to give the sharp melting profile that gives the required functionality in many end products. Dry fractionation is

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Table 11.4 Enzymatic production of monoglycerides from fatty acid and glycerin.

Reactants	Lipase	Conditions	Yield	Ref
palmitic acid with glycerol	Novozym 435	Temperature 50°C, the molar ratio of glycerol: palmitic acid, 6:1; 25% Novozyme 435 related to the amount of dissolved palmitic acid	77.9 wt% MAG	(Tai and Brunner, 2011)
Myristic acid with Glycerol	Lipase G (*Penicillium camembertii*)	Temperature 60°C; 6 h; a stirring at 200 rpm; the molar ratio of glycerol: myristic acid, 8:1 mol; 5% (w/w) Lipase G immobilized on SiO2-PVA loading; solvent free	47.92% MAG, 79.92% selectivity	(Freitas *et al.*, 2010)
Palmitic acid with glycerol	*Candida antarctica lipase B* (CALB)	Temperature 50°C; a stirring rate of 300 rpm; the molar ratio of glycerol: palmitic acid, 7:1.76 mmol; 50 μL enzim loading; 1% (v/v) water; 20 mg molecular sieves; 4 mL acetone	87 wt% MAG	(Kapoor and Gupta, 2012)
Palmitic acid with Glycerol	Lipase G (*Penicillium camembertii*)	Temperature 60°C; 6 h; a stirring at 200 rpm; the molar ratio of glycerol: palmitic acid, 8:1 mol; 5%(w/w) Lipase G immobilized on SiO2-PVA loading;	45.86% MAG, 83.80% selectivity	(Freitas *et al.*, 2010)
Caprylic acid with Glycerol	Novozym 435	caprylic acid, 1.1:1 mol; 2 g Novozym 435 loading; 4% (w/w) water content in glycerol; enzyme packed bed reactor (EPBR); space velocity 2.5 min^{-1}	92.02 wt% MAG	(Wang *et al.*, 2012)
Oleic acid with glycerol	Lipase GH1	Temperature 35°C; a stirring rate of 250 rpm; the molar ratio of glycerol: oleic acid, 11:1; solvent free; Lipase GH1 fermentation broth (water content 1.5 wt%; enzyme content 80 U per g)	84 wt% MAG	(Huang *et al.*, 2013)

(*Continued*)

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Table 11.4 Enzymatic production of monoglycerides from fatty acid and glycerin. (*Continued*)

Reactants	Lipase	Conditions	Yield	Ref
Lauric acid with Glycerol	Lipase G (*Penicillium camembertii*)	Temperature 60°C; 6 h; a stirring at 200 rpm; the molar ratio of glycerol: lauric acid, 8:1 mol; 5% (w/w) Lipase G immobilized on SiO2-PVA loading; solvent free	59.45% MAG, 62.91% selectivity	(Freitas *et al.*, 2010)
Stearic acid with Glycerol	Lipase G (*Penicillium camembertii* lipase)	Temperature 60°C; 6 h; a stirring at 200 rpm; the molar ratio of glycerol: stearic acid, 8:1 mol; 5% (w/w) Lipase G immobilized on SiO2-PVA loading; solvent free	42.16% MAG, 70.58% selectivity	(Yadav *et al.*, 2017)
Lauric acid with Glycerol	Lipozyme RM IM (*Rhizomucor miehei* lipase)	Temperature 60°C; 3 h; the molar ratio of glycerol: lauric acid, 4:1 mol; 4% (w/w) Lipozyme RM IM (*Rhizomucor miehei* lipase); solvent free	Conversion values 93.23%, 53.67% MAG	(Mustafa *et al.*, 2016a)
Oleic acid with Glycerol	Lipase G (*Penicillium camembertii* lipase)	Temperature 60°C; 6 h; a stirring at 200 rpm; the molar ratio of glycerol: oleic acid, 8:1 mol; 5% (w/w) Lipase G immobilized on SiO2-PVA loading; solvent free	32.92% MAG, 75.02% selectivity	(Freitas *et al.*, 2010)
Lauric acid with Glycerol	Lipase from *Rhizomucor miehei* (Lipozyme IM)	Temperature 70°C; 8 h; the molar ratio of glycerol: lauric acid, 5:1 mol; 10% (w/w) Lipozyme IM from lauric acid; *n*-hexane/*tert*-butanol (1:1, v/v)	Conversion values of lauric acid 65%	(Monteiro *et al.*, 2003)
Lauric acid with Glycerol	Immobilized lipase (Lipozyme IM-20)	Temperature 50°C; 6 h; the molar ratio of glycerol: lauric acid, 5:1 mol; 3% (w/w) Immobilized lipase (Lipozyme IM-20)	45.5% Monolaurin	(Pereira *et al.*, 2004)

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also clean technology that depends on fats crystallization flowed by filtration to separate the unsaturation fatty matters from saturated. The degree of crystallization and filtration depend on the final required melting profile and functionality. This process is completely physical and produces no wastes. The disadvantage of this process is its high capital investment due to the high cost of membrane filter press.

Fats/oils melting profile can be also achieved by hydrogenation or partial hydrogenation. The hydrogenation technology is old and well established. In this process, hydrogen is added to react with the unsaturated double bonds and therefore converts the unsaturated bonds to saturated. Despite that partial hydrogenation process gives accurate properties, it also creates trans fatty acids that can increase the risk of coronary heart diseases (Ascherio *et al.*, 1999). The chemical interesterification is another choice that manufacturers use to produce high-quality shortening and margarine. On the other hand, the sustainable enzymatic technology has also put itself in competition with all previous technology.

11.6.1 Chemical Interesterification

Interesterification catalyzed by chemicals is used to reorder the position of fatty acids in the glycerin backbone between saturated and unsaturated blend in the presence of chemical catalyst such as sodium methoxide in short reaction time (about 30 min). Such chemical catalysts are toxic and the process produces side reactions, which means that downstream processes such as washing, bleaching, and deodorization are required. Such process steps generate pollutants to the environment and cause loss of yield (Lampert, 2000).

11.6.2 Enzymatic Interesterification

Enzymatic Interesterification has been reported in many books and journals, but the process was only limited in lab research due to the high cost of lipases compared to the chemical catalyst. Now after optimizing the process and offering cost advantage enzymes the full commercialization of this process has become possible. Like the chemical Interesterification, the enzymatic process rearranges the fatty acids on the glycerin backbone using selective and specific lipases. Unlike chemical Interesterification, the final product is pure and ready for selling without treatment. The process economy needs to be further optimized in order to have higher profit margins (Holm *et al.*, 2018).

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11.7 Environmental Benefits of Enzymatic Process Against Chemical Process

Enzymes have succeeded in replacing the chemical catalyst in full industrial scale in some applications. The environmental benefits of using enzymes over chemical catalyst have been discussed in many journals, conferences and books. All agree that utilization of lipases is a sustainable choice. The lower reaction temperature and higher purity and yield of product are the main advantages of using enzymes. Table 11.5 shows the net savings obtained though operating enzymatic process against chemical process, enzymatic intresterification process, and ester synthesis. Such savings demonstrate the sustainability and environmental benefits of using biocatalyst instead of chemical catalyst (Cowan, Willits, & Pearce, 2008).

When comparison between chemical method and enzymatic method is discussed, different prospective should be highlighted. Despite the technical and environmental benefits of using enzymes, the chemical method is now the most commercialized method in the world. Without doubt, the enzymatic process is favorable to the environment, but to make this process more attractive and complete with the chemical one, optimum utilization of enzymes must occur. In other words, fewer amounts of enzymes must be used in achieving high productivity. Table 11.6 shows a comparison between chemical methods and enzymatic method from different perspectives.

Table 11.5 Net savings due to implementing enzymatic process (per 1000 kg processed/produced).

	Enzymatic interesterification	**Enzymatic ester synthesis**	**Enzymatic degumming**
Global warming (Kg CO_2)	23	187	44
Smog formation, C_2H_4	49	74	18
Energy requirements, MJ	280	2,760	400

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Table 11.6 A comparison between chemical methods and enzymatic method from different perspectives.

Item of comparison	Enzymatic	Chemical
Odor (before distillation)	Fatty	Charred
Color	Same as starting material	Dark
Profit	Less profitable	Profitable
Environment	Friendly	Not friendly
Solvent	Sometimes free	free
Temperature	Not exceeding 60 °C	Exceeds 200 °C
Reaction Selectivity	Selective	Not selective
Investment	Cheap	Expensive
Catalyst degradability	Degradable	Not
Needs for distillation	Sometimes	must
Price of catalyst	Expensive	Cheap
Availability of catalyst	Available	Available

11.8 Conclusion

Oleochemicals production by chemical technology is an energy-intensive process; thus, it produces a high quantity of greenhouse gases and has a negative effect on climate change. On the other hand, the enzymatic technology strongly placed itself in competition with the chemical technology. The higher product yield, less process steps, cleaner product and less process investment are the major benefits of the enzymatic technology, which offers many benefits over the chemical technology. The environmental pressure and restrictions that local and global environmental policies apply seem to accelerate the implementation of the enzymatic technology in the near future in larger scale. Now there are many available commercialized enzymatic processes in the world, especially in the biodiesel sector. The process has become more profitable than in the past due to the research efforts that are being done globally.

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12

Seaweeds for Sustainable Development

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Abstract
Seaweeds is a term that refers to macroalgae that grow in marine water bodies. They grow in the sublittoral, littoral and supralittoral zones of the coast. They usually belong to Chlorophyta (green algae), Rhodophyta (red algae) and Phaeophyta (brown algae). They usually grow in mass quantities depending on the environmental conditions. They contain a diverse array of chemical constituents including, for example, polysaccharides, growth-stimulating substances, minerals, vitamins, antioxidants and many other bioactive compounds. Seaweeds can mitigate and sometimes be a remedy for the hazardous effects of pollution. The mass growth of seaweeds on polluted beaches not only sequesters carbon, nitrogen and phosphorus but also provides a sink for heavy metals and toxic substances. We can capitalize on this for the purpose of sustainable development in which we use the biomass in many applications including generation of biofuel, bioplastics and biopolymers as well as using the residual biomass as biofertilisers and animal feed. Thereby we make the best of a bad situation. However, growing seaweeds and bioprocessing must be performed in a cost-effective manner.

***Keywords*:** Biofertilisers, bioplastics, bioprocessing, pollution, seaweeds

12.1 Introduction

There are more than 300,000 algae species, a great proportion of which live in marine water bodies. Algae are thought to be a polyphyletic group of

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Nour Shafik El-Gendy (ed.) Sustainable Solutions for Environmental Pollution Volume 1: Waste Management and Value-Added Products, (449–470) © 2021 Scrivener Publishing LLC

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organisms where a great degree of diversity is observed on the structural, functional and size levels (Van den Hoek *et al*., 1995). They all have in common the presence of Chlorophyll a as the main pigment in photosynthesis. During photosynthesis, oxygen is produced and carbon dioxide is fixed, which results in the formation of organic matter and the release of oxygen. Oxygen is used in respiration and that is why algae are an essential and important part of the life cycle of aquatic organisms. Photosynthetic products in algae can vary among algal groups but in most cases carbohydrates are the main photosynthetic product and algae are therefore called primary producers. Carbohydrates are either used in the breathing process or in building cell materials or are stored in the form of starch and sometimes in the form of oils, while other aquatic organisms are unable to produce these substances so they depend on algae and other plants in the process of obtaining organic materials. There are other benefits for other species, including being part of human food where there are more than 70 types of edible seaweed, such as *Porphyra*, which is widely used in the field of nutrition. In Asian countries, the beneficial use of it began commercially in the production of large quantities of proteins, fats, carbohydrates and vitamins used by humans, and there are types that are used as food for animals after being dried (Heuzé *et al*., 2017). Other types are used as fertilizer for private agricultural land, which is widely used in bacteriological farms and food industries, and in many different medical purposes, such as the manufacture of medicine and medicinal herbs, and can also be used in many beneficial areas, including bioremediation and pollution control. There are many taxonomic treatments for algal categorization. However, the most commonly used systematic division of algae is according to the types of dominant pigments present where the algae is composed of the following divisions (Van Den Hoek *et al*., 1995):

- Division of Green Algae (Chlorophyta)
- Division Brown Algae (Phaeophyta)
- Division of Red Algae (Rhodophycophyta)

Algae chemical composition is variable even within the same organism during different developmental stages and growth conditions. According to the Food and Agriculture Organization (FAO), protein content of green and red macrophytes is 6–26% and 3–29%, respectively. Lipid content of red algae is in the range (0.1–1.8%) whereas that of green algae is (0.3–3.2%). Ash content of green macrophytes is in the range of (12–31%) whereas ash content of red algae is in the range (4–47%) (http://www.fao.org/docrep/012/i1141e/i1141e01.pdf). Green algae-free walls are mainly

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cellulosic (Van den Hoek *et al*., 1995) with associated sugars. Red algae walls are formed of cellulose (structural support), agarocarginates. Brown algae generally contain cellulose or structural support in addition to alginic acid and fucoidans and sulfate.

12.2 Types of Seaweeds

12.2.1 Green Algae

Green algae are the largest and most widespread group, and most marine species live on the beaches, while some species live in the soil and on the rocks. These algae differ greatly in shape and size. Green algae are distinguished by their cells consisting of a protoplast and cell wall that contains cellulose and pectin, eukaryotic nucleus, a chromatin network. Green algae contain several pigments, including chlorophyll A, chlorophyll B, carotenoids and xanthophyll. Food is stored in the form of starch, and the optimum temperature range for the growth of green algae is between 30-35 m (Van den Hoek *et al*., 1995).

12.2.2 Red Algae

Red algae is considered the most abundant seaweed, especially in the temperate and tropical seas. Thalli are typically in the form of delicate branched filaments and in the form of membranous or lubricated leaf-like. None of them is floating. Red algae usually grow on rocks close to the beaches, attached to them and in some cases live as Epiphytes on large aquatic plants. Red algae profusely grow at far depth from the surface of the water where other algae or plants cannot grow with this density. This is due to the ability of red algae to absorb wavelengths that penetrate deep water, whereas this radiation is difficult to absorb by the rest of the photosynthetic organisms. The red algae contain another accessory pigment, chlorophyll D, in addition to phycobilins proteinaceous pigments mainly red pigments (phycoerythrin) and blue pigment (phycocyanin), which gives these algae the ability to absorb light rays of different wavelengths t and then the light energy is transferred to chlorophyll A. This feature enables red algae to grow in the depths of the sea far from the surface of the water. The vegetative body of these algae is mostly multicellular. Nevertheless, there are a few species present as single cells. The main food reserve is floridean starch and the cell wall is mainly rich in polysaccharides such as agar and carrageenan (Van den Hoek *et al*., 1995).

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12.2.3 Brown Algae

It includes genera of different shapes and sizes; they may be microscopic, or some of them reach a length of 7.0 meters, and they are called kelps. And their shapes are mostly real parenchymatous or pseudoparenchymatous, where they appear as threads intertwined with each other. The majority contains a fixed base part connected to a narrow part that represents the neck and a blade that differs in shape and size according to species; all are multicellular forms. The cells are surrounded by a three-layer inner wall, made of cellulose, and the outer ones are gelatinous materials from algin acid (present as alginates) and Fucinic acid in addition to the substance Fucoidae that spreads between cells and may be 24% of the dry weight of the thallus. Cells in some species may contain calcium carbonate. Pigments are mainly chlorophylls a, cl, c2, ch1 and B-carotene and a number of xanthophyll dyes including violaxanthin, fucoxanthin, dinoxanthin and diatoxanthin, and these pigments give the brown color of thallus and Fucoxanthin is the prevailing pigment. The stored food is in the form of soluble carbohydrates called laminarin starch. The food is also stored in the form of mannitol which is a hexa alcohol (Van den Hoek *et al*., 1995).

12.3 Bioremediation

12.3.1 Pollution

Pollution is defined as the process that makes the land, air, or water unsafe to use, and this can happen by inserting a pollutant into a natural environment. Water pollution is defined as any substance that enters the water and changes its nature, characteristics or components, and therefore some of the chemicals may enter into the water, through which it works to change the water in terms of chemical change or biological change, and this can result in negative health, economic, and ecological effects and in severe cases devastating damage.

12.3.2 Bioremediation of Polluted Water

Bioremediation denotes the removal/conversion of hazardous pollutants such as heavy metals by biological entity whether dead or alive biomass. This can be by converting them into less harmful form; or by removing, for example from groundwater or wastewater via immobilization. With regard to organic hazardous substances, they can be degraded and mineralized into organic substances such as carbon dioxide, water, nitrogen

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gas, and other mineral constituents. Heavy metals can contribute to the pollution deterioration of aquatic ecosystems by unbalancing and reducing biodiversity and through the accumulation of metals in living organisms and food web (Hosono *et al*., 2011). The human sources of this pollution are the petroleum industries, mining, municipal waste and wastewater (Fu and Wang, 2011). The process of bioremediation can be applied in different water bodies via *in situ* and *ex situ* techniques like biosorption, bioaccumulation, bioconversion and/or inter/intracellular precipitation (as oxalates of Zn, Cu, Co, Cd, Ni) (Kapahi and Sachedeva, 2019). In case of microbial biomass, immobilization in matrices such as alginate and silica might be required to develop biosorbents with suitable strength and porosity (Velkova *et al*., 2018). A relatively recent revelation is that another strategy for marine algae in dealing with pollution is through detoxifying them by converting them to nanopforms; the polysaccharide sheath is thought to be involved in the process (Bakir *et al*., 2018; Younis *et al*., 2019).

Several factors can affect bioremediation. For example, pH can affect processes such as complexation, hydrolysis, redox and precipitation involved in bioremediation (Esposito *et al*., 2001; Qiang and Jeremy, 2015; Kapahi and Sachedeva, 2019). Protonation and deprotonation of functional groups is controlled by the pH of the medium, which affects the biosorption capacity (Bilal *et al*., 2018): at low pH, carboxylic groups, being acidic, exist in a protonated state due to the presence of excess H^+ and H_3O^+; therefore, repulsive forces of these protonated groups with positively charged heavy metal ions are responsible for the lower biosorption capacity at low pH (Ahmad *et al*., 2018). With the increase in pH, functional groups such as amine, carboxyl, and hydroxyl groups are exposed by deprotonation, which enhances electrostatic attraction with heavy metal ions due to a negative charge on algal surface. The high increase in pH leads to the formation of hydroxide anionic complexes and precipitation is a reported reason for the low biosorption capacity (Ahmad *et al*., 2018). Temperature is also an important parameter influencing the biosorption processs (Bilal *et al*., 2018).

Biological absorption processes are complex. The overall results of the mineral absorption mechanism is a mixture of different primary mechanisms, such as electrostatic reactions, complexity, ion exchange, and chelation adsorption (Raize *et al*., 2004; Bilal *et al*., 2018; Ahmad *et al*., 2018). The initial operations involved in the process of biological absorption are chemical, which involves chemical reaction and physical, which involves retention of metal ions via Van der Waals attraction.

Algae play their role in reducing environmental pollution for the process of accumulation and bio-removal while detoxifying heavy metals

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and maintaining metal homeostasis. This type of bioremedication has the advantages of being cost-effective and ecofriendly (Romera *et al*., 2006; Romera *et al*., 2007), unlike chemical or physical remediation. Also the biomass of algae can be exploited in so many different industrial and agricultural aspects. It was found that most algae that live in water containing heavy elements tend to concentrate those elements in their bodies at higher concentration than that found in the environment in which they are living (Murugesan *et al*., 2008).

The use of naturally abundant renewable biomaterials have the following advantages according to (Ismail and Tarek, 2016); their cheap production; their ability to treat large volumes of wastewater; their high selectivity exemplified in their ability for removal and recovery of certain heavy metals; their ability to bioremediate mixed wastes; their high affinity; their cost-effectiveness compared to other bioremediation methods; their activity over a wide range of environmental conditions including temperature, pH, and other ions (e.g., Ca (II) and Mg (II)).

Moreover, Bilal *et al*. (2018) reported that algae possess the following additional attributes and bioredediation agents: 1) different multifunctional groups on their surface, (2) the relatively uniform distribution of binding sites on their surface, (3) the limited preparatory steps needed, (4) the almost null use of harsh chemicals, (5) the naturally renewable, recyclable, and easily available nature of algal biomass that can be present all year round. Therefore, Bilal *et al*. (2018) considered marine algae as a effecient alternative to the conventional methods used for bioremediation.

The way algae remove heavy metals is divided into two main categories:

a) metabolism-dependent processes are termed bioaccumulation which is active biosorption that involves active transport in two stages:

1. Attachment to algal cell and
2. Active transport of metal ions into cell (Flouty and Estephane, 2012).

The amount of metal bioaccumulation is dependent on the toxicity of those elements, the type of heavy elements, the type of algae, algal physiological state, heavy metal concentration as well as the presence or absence of other elements in growth medium (Becker, 2018).

b) The metabolic-independent biosorption which is a passive process (Volesky, 2007; Chojnacka, 2010). Biosorption is faster

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than bioaccumulation. Adsorption, chelation/complexation, ion exchange, and surface precipitation are different processes reportedly involved in biosorption. Nevertheless, ion exchange is considered the main mechanism of biosorption, which occurred through different functional groups present on the surface of algal biomass (Chojnacka, 2010). The mechanism of biosorption usually depends upon functional groups on surface of algal biomass; for example, brown seaweeds have alginate, sulfonated polysaccharides unlike green or red algae. This variation is responsible for the difference in mechanisms (Farooq *et al*., 2010; El Hameed *et al*., 2015). Ion exchange is suggested to be the main mechanism for the biosorption as the algal biomass serves as natural ion exchangers. Calcium and magnesium ions present in the cell wall get replaced by heavy metal ions via ion exchange. However, monovalent ions (H^+, Na^+/K^+) were reported to be more involved in the ion exchange process due to a weak attachment with biomass as compared to divalent ions (Verma *et al*., 2008). It is also reported that sulfate, carboxyl, and hydroxyl groups which can interact with ions and bind them (Ahmad *et al*., 2018). The uptake of ions is facilitated by pores present on the surface (Ahmad *et al*., 2018). Biosorption varies with the type and structure of the algal biomass, charge and chemical constitution of the heavy metal ion but it is suggested that brown algae are best algal biosorbents. Interestingly, heavy elements can associate to algal body, through other ways: e.g., phagocytosis by engulfment within vesicles and adsorption where elements congregate on the surfaces of areas exposed to them (Gaur *et al*., 2014).

Algae can evade the toxic effect of heavy metals through different mechanisms. One method is through phytochelation, which is a mechanism for metal detoxification and tolerance. Examples of phytochellating compounds include protein and peptide-based compounds which are rich in amino acid cysteine, as these compounds are able to bind ions and produce elemental complexes. These compounds are built by the phytochelatin synthetase enzyme (specific γ-glutamylcysteine dipeptidyl transpeptidase) which catalyses the synthesis of these chelating compounds followed by secreting them extracellularly where they bind to elements and convert them to inactive form or reduce their bioactivity (Grill *et al*., 1987; 1989). Some algae have the ability to form organic compounds outside or within cells such as carbohydrates, which in turn tend to bind to those metals (Macfie and Welbourn, 2000).

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Another mechanism in algae is the formation of polyphosphate inside the cells. The anionic nature of polyphosphate allows the sequestration of cations, thereby enabling algal cell to exhibit tolerance to heavy metals and preventing metabolic abnormalities and malfunctioning resulting from elevated intracellular cation concentrations (Sanz-Luque *et al*., 2020). Interestingly, algae can detoxify metal ions through transforming them into none-harmful nano particles both intraceullarly and extracellularly (Bakir *et al*., 2018; Younis *et al*., 2019).

The bioremediation using algae can be performed on dead algal biomass. For example, dead biomass from marine brown algae *Fucus ceranoides*, *F. vesiculosus* and *F. serratus* were tested for their ability to remove cadmium from aqueous solutions. The metal sorption process was rapid, with most of the metal uptake completed within the first 25 min. The experimental results demonstrated that these seaweeds constitute a promising, efficient, cheap and biodegradable sorbent biomaterial for cadmium removal from wastewaters (Rodríguez *et al*., 2006).

The ability of seaweeds to tolerate and accumulate metals led scientists to use them as bioindicators. Bioindicators are living organisms that thrive in certain living conditions and are used for revealing the presence/abundance of substances/pollutants thereby providing information about the environmental niche studied. For example, *Cladophora* sp. abundance would indicate the presence of massive phosphate concentrations as well as heavy metals (Chmielewská and Medved, 2001). In the Tarut bay in the Kingdom of Saudi Arabia, *Liagora visicidis* abundance is correlated with pollution with heavy metals such as mercury, nickle cadmium, and iron. As *Liagora viscidis* is able to bio-accumulate these metal ions, it can be considered suitable for bioremediation of those elements (Guitouni *et al*., 2016). Kapahi and Sachdeva (2019) listed the marine algae that are capable of accumulating the different types of heavy metals. However, they reported that brown algae such as *Fucus* spp., *Sargassum* spp. are the most efficient heavy metals biosorbents. The authors suggested that alginates in the cell wall immobilize heavy metals such as cadmium, lead, copper and chromium and act as biosorbents.

12.3.3 Algal Bioremediation of Eutrophic Water

Seaweed cultivation can mitigate eutrophication issues due to aquaculture or wastewater discharges (Lüning and Shaojun, 2003; Merrill, 1996). Seaweeds can remove most of the nutrient waste from an intensive fish farm.

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12.4 Seaweeds in Nutrition

12.4.1 Human Nutrition

The widespread of marine macroalgae made it a basic substance in several industries and applications. It is known that seaweeds were used by humans since ancient times, but their uses in the recent period expanded, and they differed from what they were in the past. One type of marine red algae, namely *Porphyra* sp. is thin and paper-like and grows attached to rocks in the lower part of the tidal zone; it has a delicious taste that is quite popular in Japan. The Irish red alga *Condrus crispus* is short and is used as a binder in ice cream, sweets, and toothpastes. Another red alga *Corallina* sp. grows on rocks and on the shells of hermit crabs.

There are a number of edible marine algae as well as algae used in food industries. Examples from green algae include *Caulerpa*, *Entermorpha,* and *Ulva*; examples from brown algae include *Laminaria, Undaria, Alaria, Ecklonia.* Examples from red algae include *Porphyra, Palmaria, Gelidium and Eucheuma* (https://web.archive.org/web/20150721104212/http://www.countrylovers.co.uk/wfs/wfsseaweed.htm; http://www.fao.org/3/y4765e/y4765e0b.htm).

According to an FAO report, the analysis of seaweed has shown that most of them contain important amounts of proteins, vitamins and minerals that are important in applications (http://www.fao.org/docrep/012/i1141e/i1141e01.pdf). They also contain large amounts of multiple sugars and are a relatively good source for protein. Seaweed is also a good source of a large number of vitamins, and the genus *Porphyra* contains vitamin C, lemon-like. Seaweed also contains vitamin A and D, and it is highly concentrated in oils extracted from seaweed. It also contains vitamin B2, B1 as well as vitamin E, and seaweed is a source of vitamins in human food. Dried seaweeds are sold as powder in Denmark, for example (http://www.fao.org/3/CA1121EN/ca1121en.pdf).

12.4.2 Animal Feed and Feed Additive

Seaweed is used as food by wild animals such as rabbits, foxes and polar bears. The red algae used as animal feed for *Chondrus* are *Palondia* and *Palmaria.* The animals can take their food from these weeds directly by feeding them directly in the coastal areas. As for the areas far from the coast, seaweed is dried, ground and added to the animals' daily food. *Ascophyllum* is considered one of the most important species of seaweed

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used in this way. Fish feed cannot be entirely based on algae. However, algae can be used as a valuable fish feed supplement (http://www.fao.org/docrep/012/i1141e/i1141e01.pdf).

12.5 Seaweeds as a Source of Pharmaceutics

Seaweed is used in East Asian countries to treat many diseases such as iodine deficiency and as a source of vitamins and treatment of many intestinal diseases and lowering the level of cholesterol and sugar. Some of those medically important bioactive compounds were reviewed by El Gamal (2005) who collected information on substances discovered by different scientists and their biological action and categorized them as follows.

12.5.1 Pharmaceutics from Green Algae

Examples of pharmaceutics include: Anti-inflammatory3-0-β-D-glucopyranosylstigmasta-5,25-dienefrom *Ulva lactuca;* Immuno-suppresants from *Arrainvilla rawsonii;* Antiviral agent Halitunal43 from *Halimeda tuna.*

12.5.2 Pharamaceutics from Brown Algae

Examples of pharmaceutics include: antifungal agent 1,4-napthaquinone derivative (deoxylapachol)119 from *Landsburgia quercifolia;* anti-inflammatory agent Lopophorian 122 from *Lobophora variegate;* antiviral agent 10, 18-diacetoxy-8-hydroxy2,6-dollabeladiene from *Dictyota pfaffi*; antioxidant 1,1-diphenyl-2-picrylhydrozyl (DPPH) from *Ecklonia stolonifera* and *antidiabetic* agent Fucosterol from *Pelvetia siliquosa.*

12.5.3 Pharmaceutics from Red Algae

Examples of pharmaceutics include: antiviral agent sulquinovosyl diacylglycerol isolated from *Gigartina tenella*; anti-vermin agent Chondriamide and 3-indolacrylamide from *Chondria atropurea*; insecticidals Polyhalogenated monoterpenes from *Plocamium cartilagineum;* and anti-marlaria Snyderol sesquiterpene365 from *Leurencia obtusawas.*

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12.6 Seaweeds Hydrocolloids and Biopolymers

Three major gelling substances are found in seaweeds: agar, carragenaans and alginates.

They are all polysaccharides that dissolve in hot water. They can form gels upon cooling. Their chain is characterized by the presence of OH group that make it a plausible candidate as a future precursor for biodegradable fibres (Rhidwan *et al*., 2018).

12.6.1 Agar

Agar is a sulfated polysaccharide that consists of linear polymer agarose and branched sulfated agaropectin, one of the main components of the cell walls of some red algae, especially members of the family Gelidiaceae and Gracilariaceae. The term agar is now called algal galactans. The agar is dissolved in hot water and it is extracted or evaporated at room temperature. The freezing and thawing process is used to purify it. Agar was used as a food material, then later was used in the growth media of microorganisms. It has become the first derivative of seaweed extracts to be used on a commercial scale instead of using it as food (Atef *et al*., 2014). Atef *et al*. (2014) used additives to increase the meachanical, thermal and physical strength of agar to be used as biopolymer. They added nanocrystalline cellulose to agar and that proved to form rather stable composite.

12.6.2 Carrageenans

The water-soluble carrageenans are linear sulfated polysaccharides and are extracted from red algae, in particular the genera of *Chondorus, Girgartina*, for their gelling properties. They are used in food industry as emulsifiers, stabilisers and thickners. They are formed of D-galactose and D-anhdro galactose that with sulfated ester that makes it anionic that can be neutralized by cations. They are used also in pharmaceuticals, makeup, dyes, ink, and in other industries (Prajapati *et al*., 2014). With regard to biopolymers of carrageenan, it was found that chitin nanofibrils when added to carrageenan film matrix in the presence of glycerol as plasticizer improved mechanical, physical and water vapour barrier properties (Sánchez-García *et al*., 2010).

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12.6.3 Alginates (Alginic Acid)

Anionic polysaccharide of copolymer of alpha D-mannuronic acid and L-guluronic acid can form insoluble polysaccharides by reacting with polyvalent cations. In addition to its use in food, textile, and pharmaceutical industries as gelling agent it is also used as mulching film in agriculture where it binds loose soil particles together (Comaposada *et al*., 2015). With regard to biopolymers of alginates, Rhim (2004) modified sodium alginates through the addition of calcium chloride via two different methods, mixing and immersion. The films modified by immersion showed both greater tensile strength and water resistance through immersion rather than through mixing. Immersion in solutions higher than 2 gm/100 ml of calcium chrolride showed a marked degree of cross linking between calcium and carboxyl group of alginates.

12.7 Seaweeds and Bioenergy

Algae biofuel production is a promising new clean green technology. Algae use simple materials to grow and make their own organic matter by performing photosynthesis that consumes carbon dioxide and releases oxygen, which reduces the greenhouse effect. The biomass of marine algae is a starting organic material that is formed during photosynthesis for the production of renewable energy (Kim, 2012). There are different types of biofuels that can be extracted from algae, including biodiesel, bio-ethanol, ethanol and bio-hydrogen (Parmar *et al*., 2011) and fats are used to produce biodiesel while carbohydrates produce ethanol (Benemann, 2009). And bio-ethanol is used as a fuel for cars and results from the conversion of complex carbohydrates. Those carbohydrates result from photosynthesis or entering the structure of the algal cell wall, such as cellulose, for simple sugars by digesting using mineral acids or enzymes, and then using sugars to produce ethanol using anaerobic fermentation (Nahak *et al*., 2011).

Algae are the preferred candidate for production of biofuel over plants for many reasons. Unlike plants, they do not require large landplots, labour, specific season and expensive fertilisers. Also if crops are grown for the purpose of generating biofuel then there will be shortage in supply of essential crops, which is one of the drawbacks of producing ethanol from food crops. The world is facing a gap between food requirements and energy requirements, and algae represent the optimal alternative for biofuel production. Also, algae do not contain lignin and can be grown in open sea and in rather extreme and polluted habitats. This is the best practice to maximize benefit from algae where they can be grown for biomass

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and biofuel generation and at the same time they reduce pollution and evolve oxygen. Inhospitable habitats for crops like the vast oceans and seas as well as wastewater can be put to use by growing algae in them.

Seaweeds as red and brown algae have diverse types of polysaccharides, whereas green marine algae have starch similar to green plants. That makes them highly plausible candidates for bioethanol generation that uses carbohydrates as a precursor. In red algae, the cell wall contains many polysaccharides, which are cellulose and galactic acid (agar). It does not contain lignin. Galactan is a polysaccharide consisting of (3-linked β-D-galactopyranosyl units and 4-linked α-3,6-anhydrogalactopyranosyl units). A large amount of agar equal to approximately 70%, a polysaccharide is converted into a simple sugar (glucose). The latter is converted to pyruvic acid during glycolysis and under anaerobic conditions, fermentation in the presence of yeast converts it to ethanol. In brown algae, the carbohydrate composition includes two types of sugars in addition to cellulose:

- SFs (Sulfated Fucans) is also called (Fucoidan) and consists of high fucose-containing glycan.
- SGs (Sulfated Galactans). These materials represent 40% of the dry weight of the cell wall. Methods for extracting materials from the cell wall and references are cited in Kim (2012) include extraction in hot water, aid solutions and Enzymatic extraction. With regard to extraction in hot water, the extract is neutralized, purified from any traces of pollutants using several organic solvents and then subjected to Ion-exchange-based Chromatographic separation using a separation column in a cation resin composed of DEAE cellulose and DOWEX. Alternatively, use columns filled with pre-prepared cation materials such as perforated silica or silica gel (Pomin and Victor, 2012). With regard to bioethanol production from green algae which store its photosynthetic product as starch which is a polymer of glucose, sonication proved to be beneficial for releasing glucose from *Ulva rigida* and its subsequent conversion to bioethanol (Gedanken *et al*., 2015).

12.8 Seaweeds as Biofertilizers

Seaweeds can be used as biological fertilizers as a powder or by using liquid extracts from them Farmers already use commercial seaweed extracts

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for enriching the soil and enhancing plant growth. The stimulant effect of the marine algal extracts is attributed to the presence of plant growth regulators (hormones) (Kingman and Moore, 1982) as well as the major and minor mineral elements in addition to different growth stimulants/hormones (Zodape, 2001).

Among the methods of using algae extract are:

1) Sprinkles of paper or mixed with soil
2) As a liquid in which the seeds are soaked before growing them, where germination of seeds increases and increases the nutrient inputs to the plant and gives resistance to cold and fungal diseases (Parekh *et al*., 1989). Just as seaweed extract has a positive effect on fruit production, increasing its life and improving its quality, it also works excellently as a soil conditioner. As the population in the world increases, agricultural products are highly needed. A renewable source for growth stimulants/fertilisers is desperately needed to meet those demands. Expensive, harmful, chemical fertilizers have caused a damaging effect on the environment and on the health of human beings as well. According to Zodape (2001) and references within, the advantages of soil treated with seaweed include increasing plant resistance to pests/pathogens, ease of application, the binding of loose soil particles, and the cost effectiveness of quality instead of commercial soil conditioners.

Seaweed has plant hormones, especially cytokinin (Featonby-Smith and van Staden, 1984) which increases cell division and hence plant growth.

According to Zodape (2001), the method of application of the extracts can vary. It can be used as a foliar spray or by direct application to soil as well as for soaking of seeds before sowing. It increases the germination of seeds, increases uptake of plant nutrients, and gives resistance to frost and fungal diseases. He reviewed many cases in which the seaweed extract had promoting effect on ripening of fruits, increasing shelf-life of the produce serving as an excellent soil conditioner as the alginates and gel particles link the soil particles together, thereby enhancing water retention.

12.9 Seaweeds as Ecological Player in Sulfur Geocycle

Dimethylsulfoniopropionate (DMSP) is one of the most widespread natural products in algae and in marine organisms (Alstyne, 2008). It acts as

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a sulfur detoxifier and an osmoregulator and accumulates both in cytoplasm and vacuoles of marine algae. It also functions in keeping cells from freezing as it works to stabilize proteins and reduce the degree of freezing of cells. It also keeps the enzymes at low temperature and acts as methyl donor. DMSP can be converted by the catalysis of enzyme called (DMSP Lyase) into DMS (dimethylsulphide) which is a greenhouse gas and is thought to be responsible for the sea smell.

The products of DMSP (DMS and acrylic) can act as antioxidants, antibiotics, and grazing inhibitors (algae eating-suppressants), as well as removing excess energy and sulfur, especially under nitrogen deficiency conditions. It is also suggested that DMSP fracture is a method of coping with salinity to maintain osmotic balance (Sunda *et al*., 2002).

Its role in atmospheric sulfur cycle is being the focus of research that looks into the relationship between DMSP, atmospheric sulfur and acid rain. When DMS and DMSP are released from algae bodies during their death or rupture, DMS evolves in the atmosphere; where sulfur builds up in clouds and when rain falls, acid rain may be the result. It also may affect the local climate through dispersion of sunlight, which encourages the formation of liquid water droplets that ultimately lead to decreasing temperature and the formation of clouds leading to rainfall. Therefore, DMSP captures the sulfur in non-volatile form unlike DMS and therefore it acts as sulfur detoxifier.

12.10 Culturing Seaweeds in the Marine Habitat (Algal Maricultures)

In order to allow the renewable production of seaweeds for sustainable development and year-round yield, certain factors are necessary. On top of these factors is the selection of a suitable site for growing algae in the marine water body. It must be away from turbulent water sources such as torrents and floods. The movement of water currents is recommended to be between 20-40 meters per minute. Preferably, the site of the farm can be in a protected bay but avoiding higher salinity than normal sea salinity. Water must be of proper depth and preferably rich in nutrients thereby providing a suitable habitat for mariculture. However, it must be noted that different seaweeds develop under different environmental conditions. Every species has specific salinity level, nutrients, water current, temperature and light requirements. For species propagating vegetatively, seaweed pieces are tied to ropes or nets, or sunk to the bottom of the pond, unattached or held in place by a fork – in sediments or sand-filled tubes

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(in sandy soil). Harvesting is performed either by removing the whole plant or most of it, but leaving small pieces that are the seeds for further cultivation. In brown seaweeds, with alternation of generations, only the large sporophyte form is harvested (McHugh, 2003), http://www.fao.org/3/AC416E/AC416E00.htm.

12.10.1 Mariculture Establishment

According to (http://site.iugaza.edu.ps/elnabris/files/2010/02/6_Algae_3__Culturing.pdf) and http://www.fao.org/3/a-bl759e.pdf to start mariculture, materials used in culture must be prepared, such as ropes, plastic tubes, and styrofoam. The pipes should be fixed in the shallow bottom; algal seedlings are tied with plastic ropes and submerged in sea water. Depending on the purpose of culture and the target yield, different cultures exist.

12.10.1.1 Single Culture

The cultured algae are installed in shallow water with sandy sea floor. Marine algae grow naturally at the site. Water is fertile and pollution-free.

12.10.1.2 Repeated Culture

And in it algal culture is done on the bottom and it is necessary to have on-site the following characteristics: The culture site is protected from high waves, and the movement of water at the site is moderate. Deep water (about 10 meters).

12.10.1.3 Multiple Cultures

Algae is cultured as a secondary crop in fish cages, where fish waste and feed residues are a good fertilizer for marine algae, and algae provide good fish shadows.

12.10.2 Cultured Seaweed Harvest

Seaweeds are harvested 45 - 60 days after rearing, and this is done in three ways:

1. Removing or cutting algae from the culture cord in case of repeated culture within the site.

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2. Dissolving the culture rope from the ends attached to the pipes, then the algae will be removed.
3. Withdrawing the crop, along with it, ropes and pipes, to the work area on the beach, and then the algae is removed.

12.10.3 Processes Following the Algae Harvest

Seaweeds can be inhabited by many invertebrates, which in turn are praise for arthropods and marine birds so they should be cleaned. As harvested seaweeds are rich in water and to prevent them from becoming mouldy they must be dried. The algae are dried immediately after harvesting and the completion of its cleaning. The drying process continues for 2-3 days. The most common method of drying is by laying algae on the ground and spreading them over an outdoor mat or coconut palm as flooring, then exposing them to the sun. Turning them constantly to speed up the drying process and prevent rot is very important. Drying with heat or steam must be avoided as it may lead to the breakdown of carrageenan. Also, covering and protecting the algal mass from rain must be observed. In some practices, algae can be suspended on ropes in the open air for drying. This method helps to quickly dry the algae in a short time. After drying, seaweed is wrapped in large bales for use or export as it is easy to handle and reduces shipping costs. Some issues must be taken into consideration. For example, marine algae crop must be stored for a short period of time. The warehouse should be clean and well ventilated. The stored algae must be dry and it is best not to store algae stacked up on top of each other. However, if a seaweed meal is prepared the moisture must be minimized. Harvested seaweeds are passed through hammer mills with smaller screens to reduce it to fine particles. The biomass is then dried in a drum dryer (McHugh, 2003).

12.11 Conclusion

Seaweeds are prolific sources for all aspects of sustainable development. They can serve as biological sorbents for heavy metals in polluted water bodies, food for humans, feed for animals, and a source of pharmaceuticals, a source for biopolymers and hydrocolloids, and as biofertilizers for plants. They also serve as ecological functions not only as photosynthetic organisms but also as bioindicators and source of DMSP, which is an important natural product sulfur cycle.

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12.12 Recommendations

- The expansion in seaweed farming especially in polluted areas of marine water bodies.
- The application of the bio-refinery in seaweed farming where all the assets of biomass are utilized.
- The development of machineries for bioprocessing and sorting fractions of the biomass for desired applications.
- The screening of more seaweeds for active ingredients/components.
- The expansion in local hydrocolloid industry that is worth billions of dollars commercially.
- The use of seaweed as ecofriendly material in industries for biocomposites and fibers.
- The use of seaweeds in feeding animals, poultry and fish.
- The expansion of use of seaweeds as biofertlisers and soil conditioners.
- The observation of cloud formation and acid rain as a result of evolution of DMS.

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