Supporting Information

Advanced progress and prospects for producing high-octane gasoline fuel toward market development: State-of-the-art and outlook

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Summary of Supporting Information (30 pages, 14 Figures, and 9Tables)

Supplement material

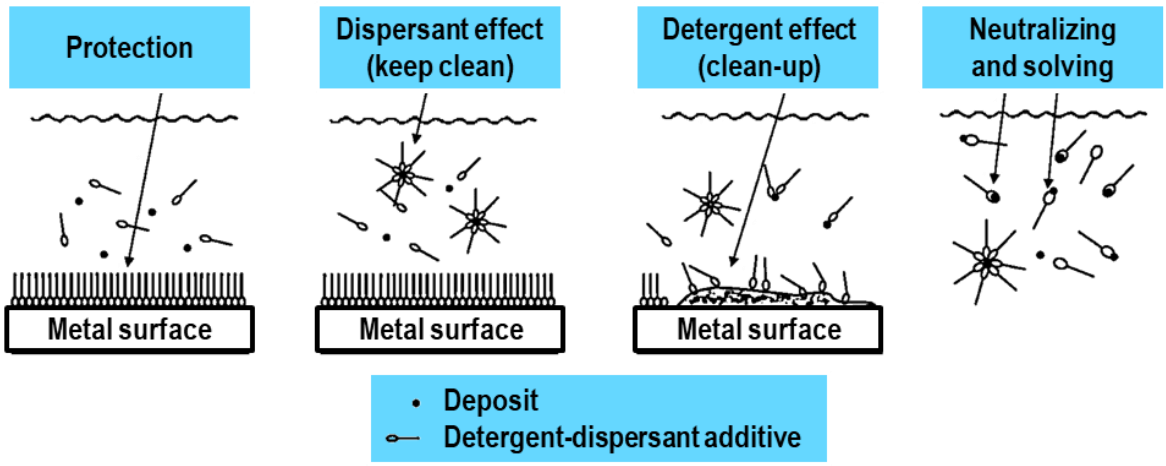


Fig. S1. The principle of action of the detergent additive. Detergent-Dispersant forms a solubility, and ,protective film on metal surfaces, besides their dispersant, detergent neutralization of acids activities.

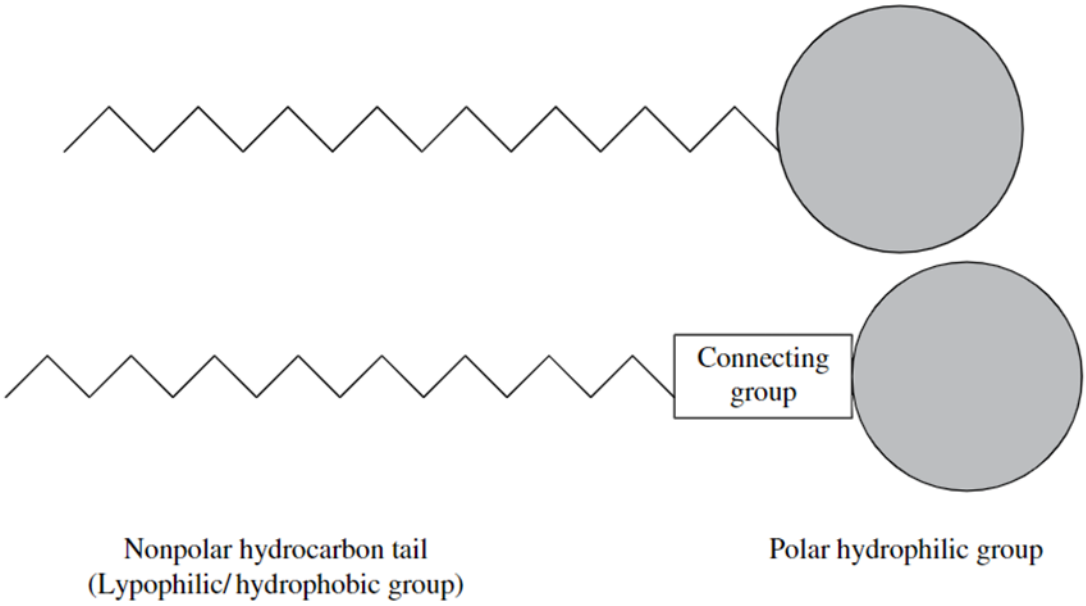


Fig. S2. Typical detergent/dispersant molecule for deposit control. All detergent and dispersant (DD) additives have a polar hydrophilic and a nonpolar hydrophobic group in their structure.

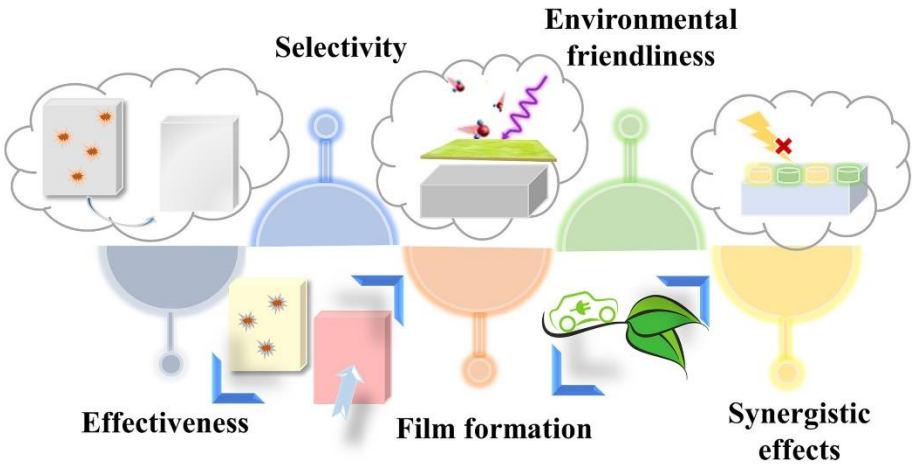


Fig. S3. The mechanism of corrosion inhibitor in a metal surface corrosion prevention. The corrosion inhibitors change the potential at the interface by adsorbing themselves at the double layer as ions or dislodging the ions originally present there.

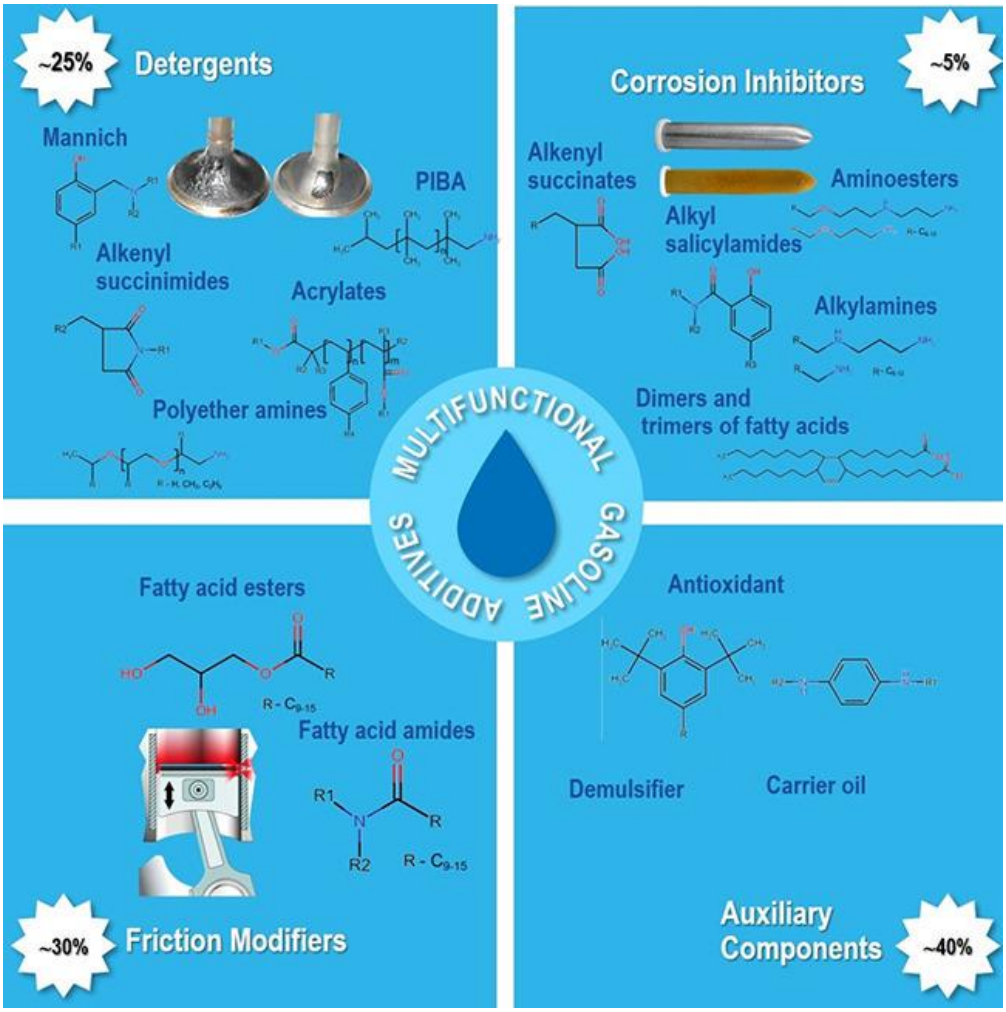


Fig. S4. Principle of the corrosion inhibitors additive and other gasoline additives. Friction modifiers are mild anti-wear additives used to minimize light surface contact, such as sliding and rolling. The corrosion inhibitor slows down the rate at which a metal in that environment corrodes. Passivation, poisoning, precipitation, and adsorption on the surface are the ways by which corrosion inhibitors prevent metal corrosion. Detergents are additives that adhere to dirt and oil insoluble products formed as oxidation by-products during equipment operation.

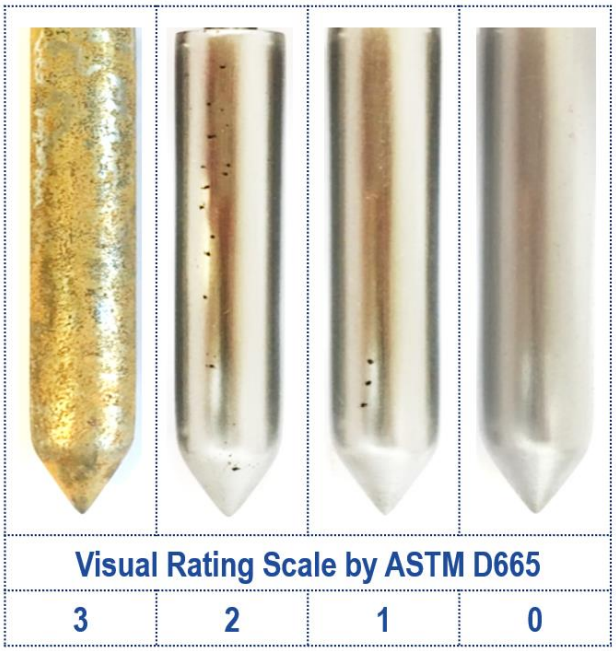


Fig. S5. Appearance of steel bars after testing by the method of ASTM D665. The surface of the rod is free from traces of corrosion. Thus, 20 ppm of this anti-corrosion additive will also be .included in the optimal fuel composition.

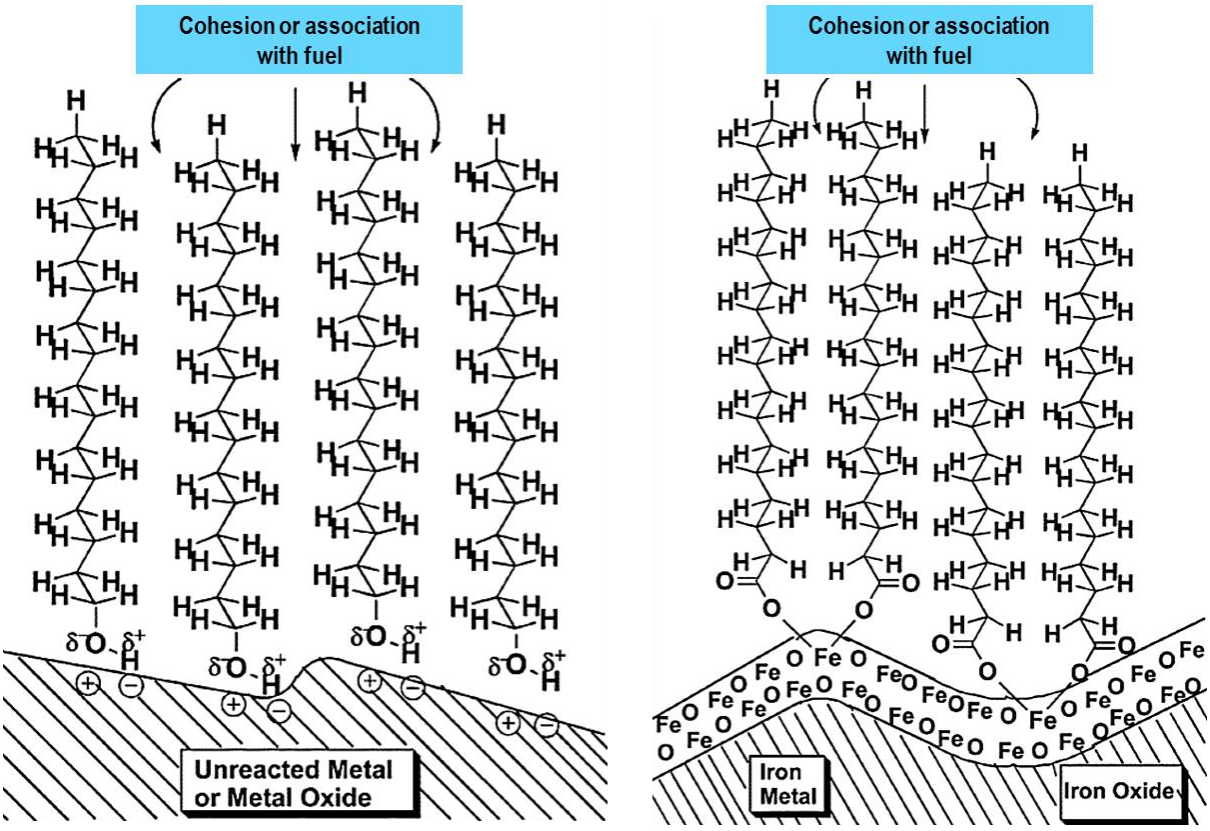


Fig. S6. Principle of operation of the friction modifier. Friction modifiers are mild anti-wear additives used to minimize light surface contact, such as sliding and rolling.

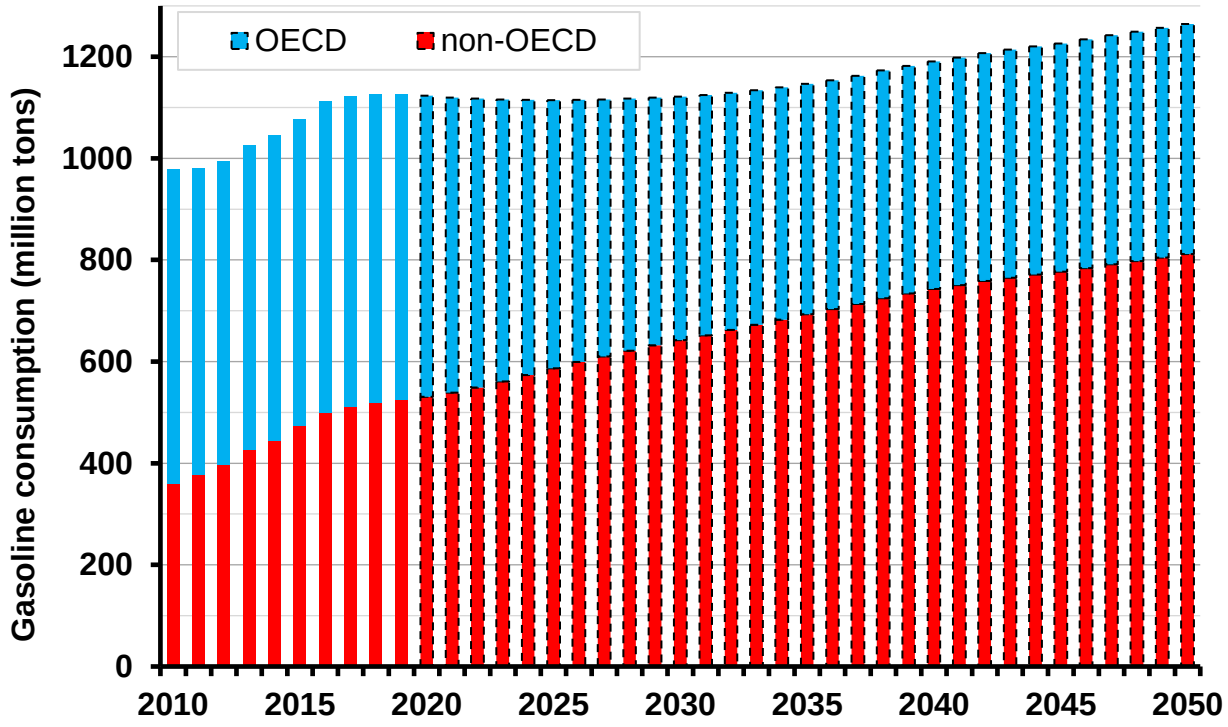


Fig. S7**.** World demand for motor gasoline. intensive decline in demand for gasoline in the countries of the Organization for Economic Cooperation and Development (OECD) is predicted due to the implementation of decarbonization programs for transport in accordance with the European Green Deal adopted in 2019 and other agreements to achieve carbon neutrality by 2050-2060.

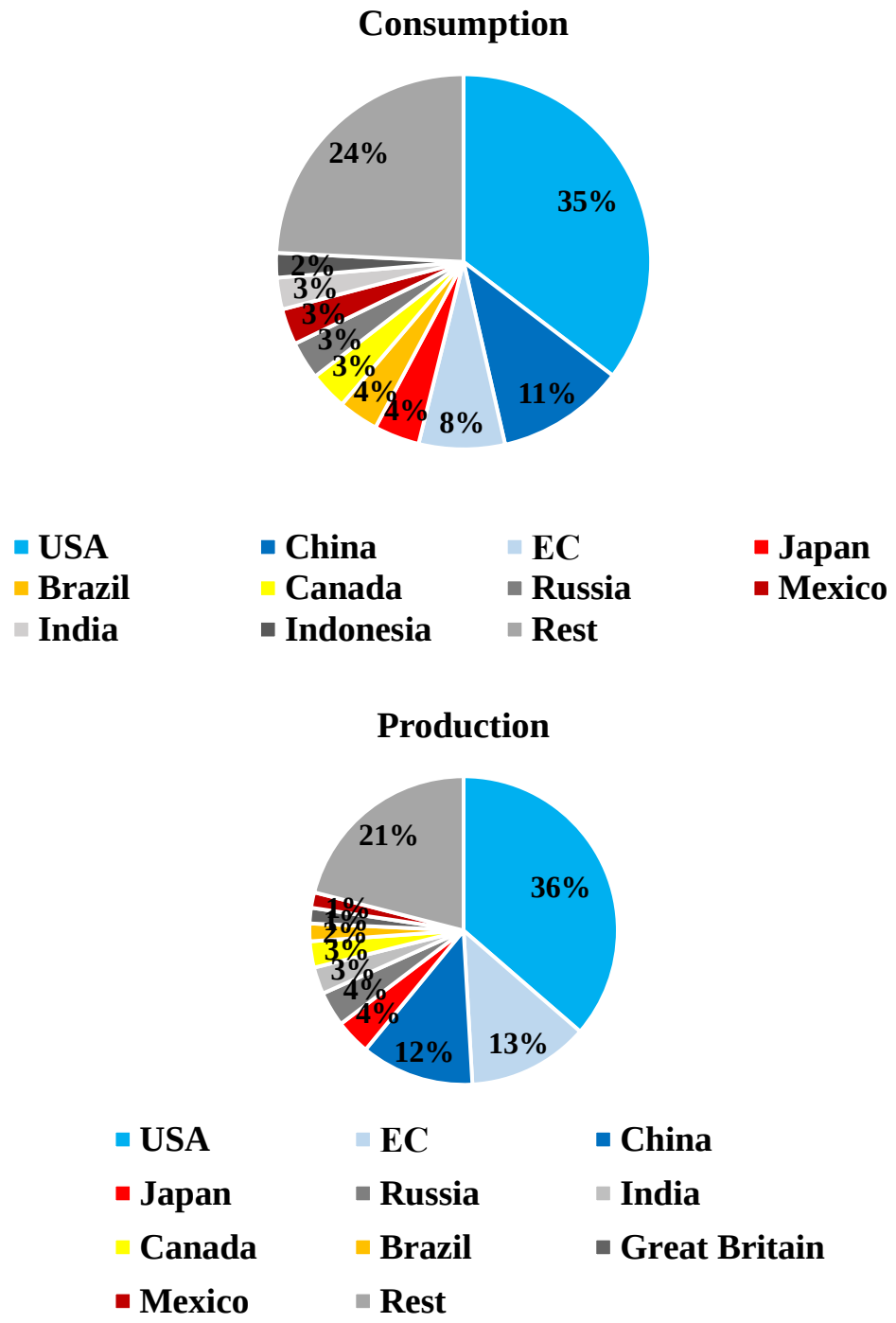


Fig. S8. Structure of world production and consumption of motor gasoline in 2019. The largest world markets for motor gasoline at the moment are the markets of China, the USA and the EU. The volume of production in the USA in 2019 amounted to about 400 million tons, while consumption turned out to be at the level of 390 million tons

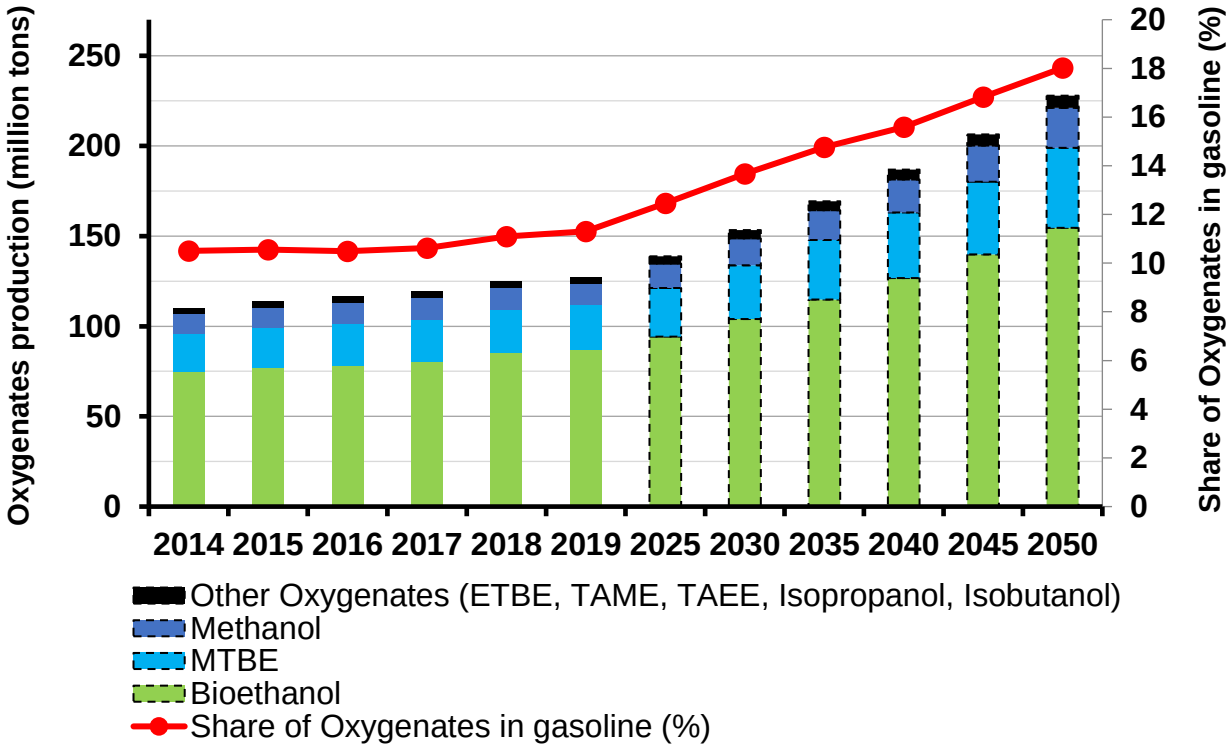


Fig. S9. Market structure of high-octane oxygenates. high-octane oxygenates are used to increase the octane number of motor gasoline. The most large-scale high-octane oxygenate used as a component of motor gasoline is ethanol.

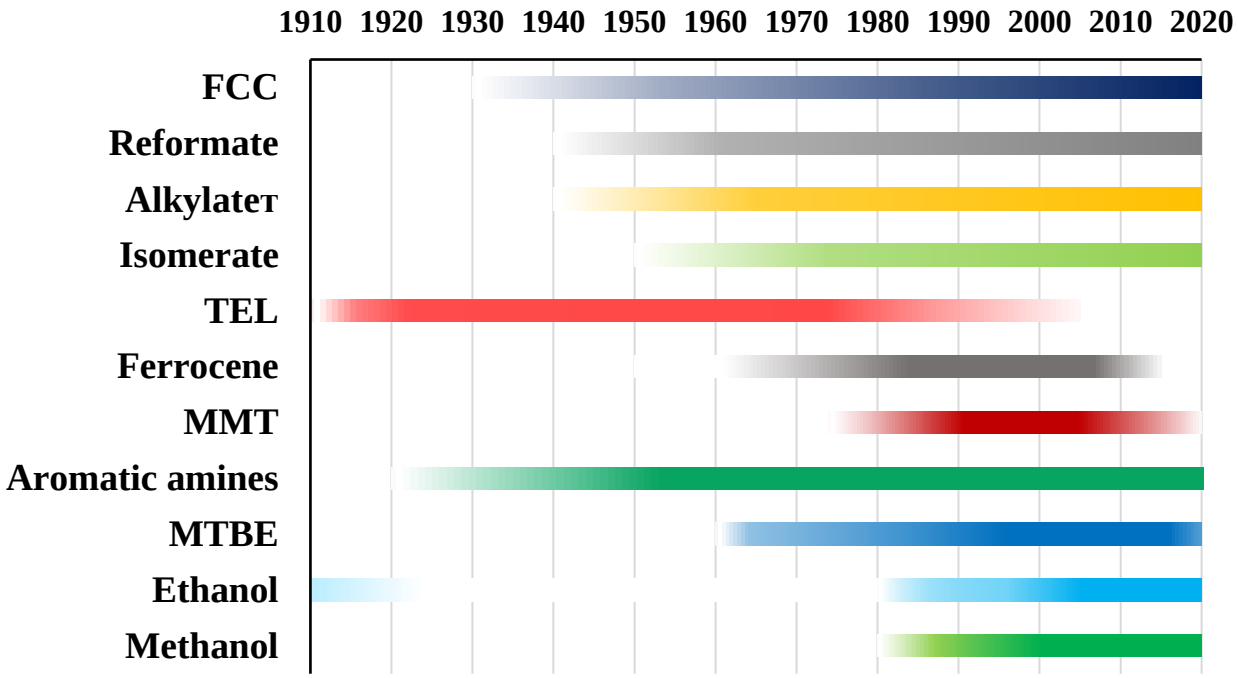


Fig. S10. Periods of use of the main high-octane components of motor gasoline in the world. properly blended M15 fuel with appropriate levels of co-solvents (for low temperature phase stability) and corrosion inhibitors provides satisfactory performance.

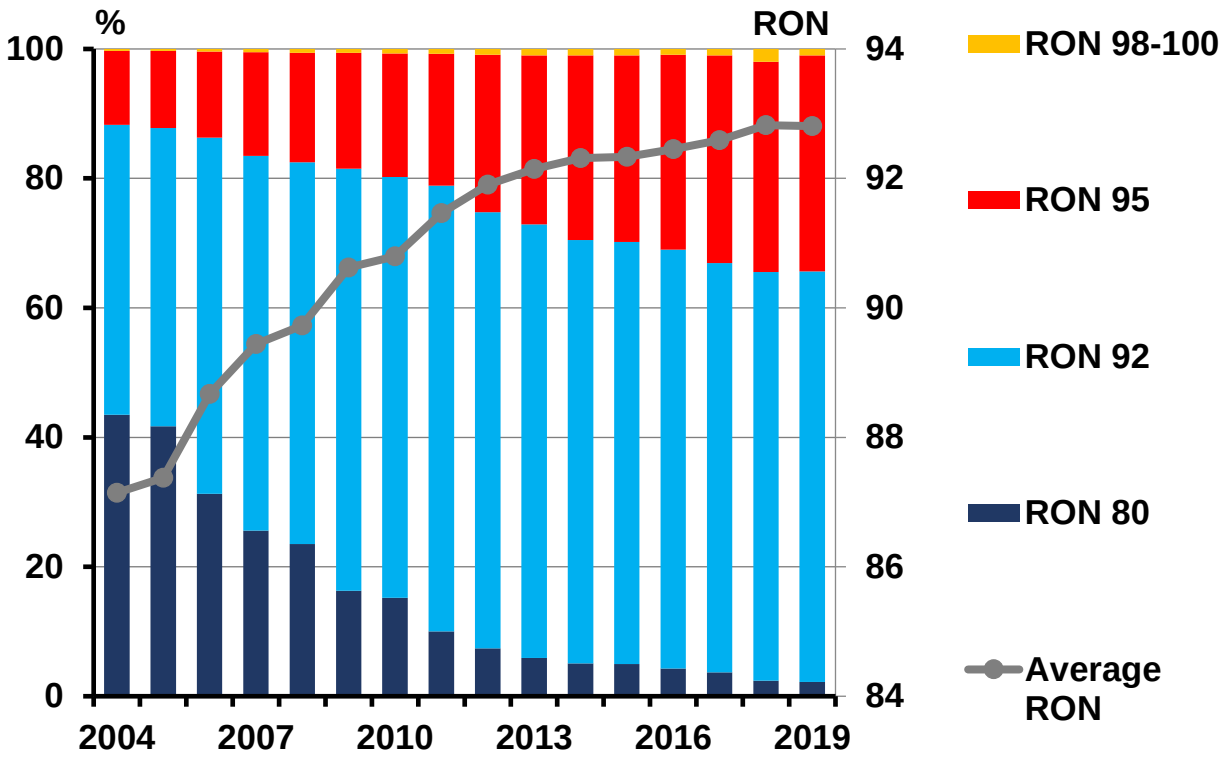


Fig. S11. Brand structure of motor gasoline production in Russia. The average octane number of the gasoline pool has increased over the past 15 years from 87.1 in 2004 to 92.8 in 2019.

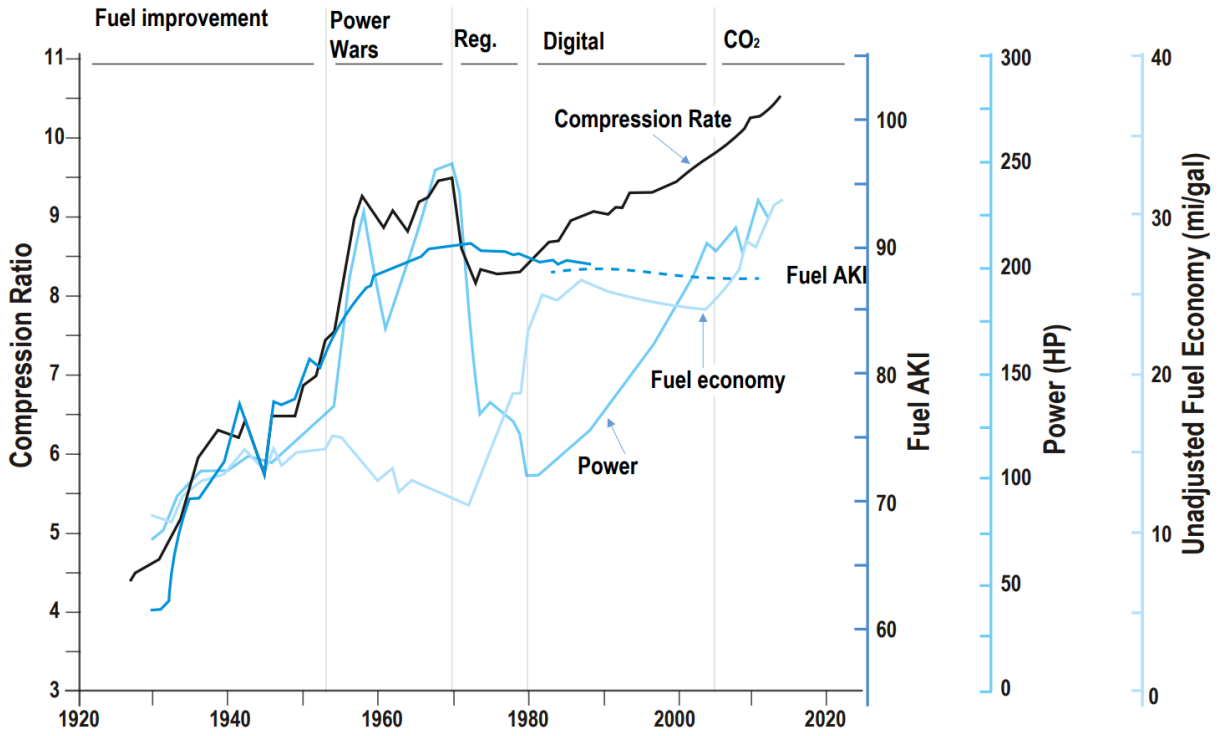


Fig. S12. Historical data on compression ratio, fuel RON and fuel economy in the USA. RON increased from 80.5 in 1953 to 90 in 1970, while the concentration of TEL remained unchanged. The increase in the RON of produced gasoline during this period made it possible to significantly increase the compression ratio of engines, which made it possible to increase the performance of internal combustion engines.

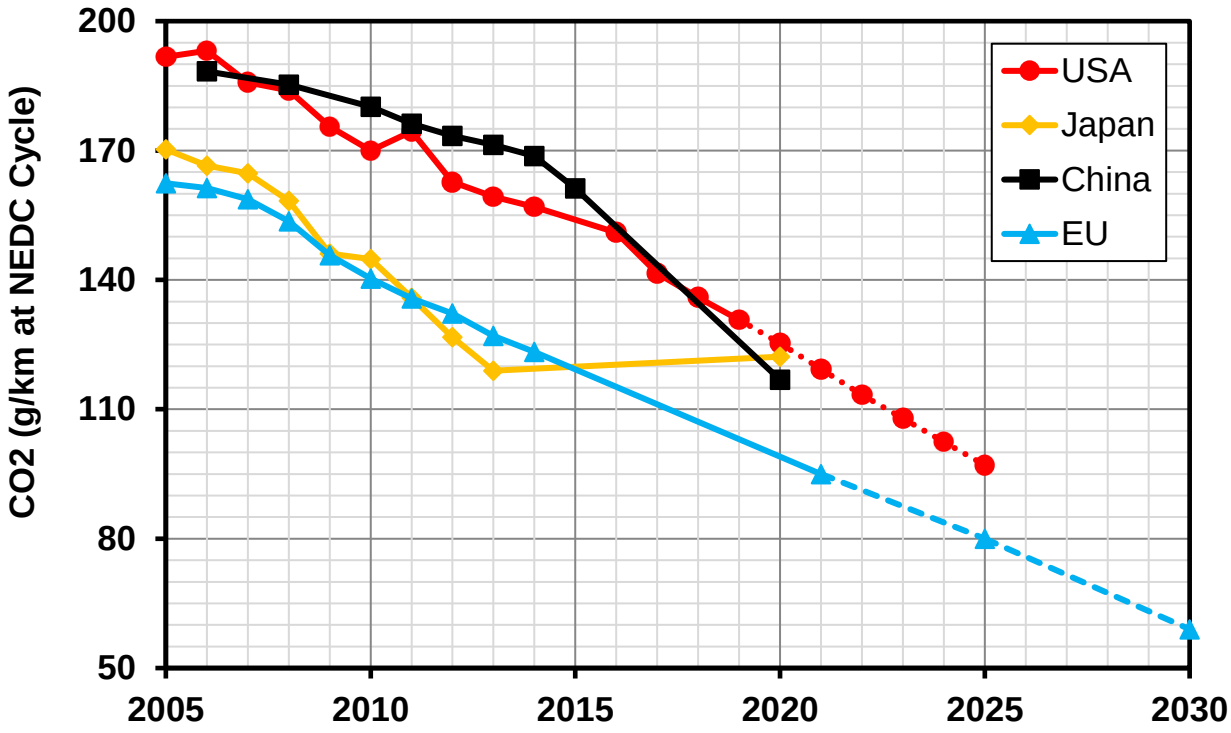


Fig. S13**.** Forecast of changes in CO_2 emission standards for passenger cars. The transition to the current stage of development - the era of decarbonization is associated with the introduction of legislative standards for fuel economy and CO_2 emissions.

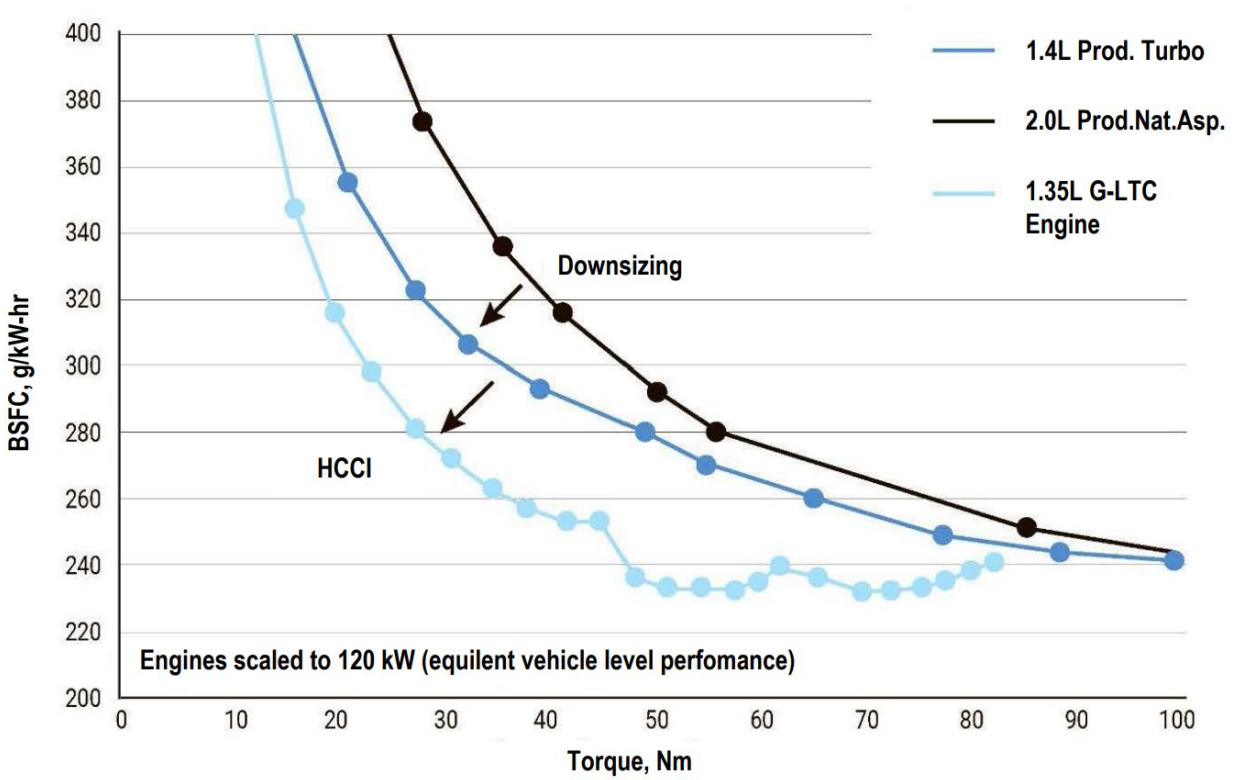


Fig. S14**.** load characteristics of gasoline internal combustion engines of three different designs. Due to the over-leaning of the mixture, it is possible to avoid detonation during operation in the HCCI mode even with a significantly increased engine compression ratio, as a result of which the efficiency and fuel efficiency of the HCCI can be significantly increased relative to the classic gasoline internal combustion engine.

Table S1. Global gasoline brands and their marketing claims

Company	Key marketing statements
Shell	✓ Remove an average of 70% of baked-in deposits left by lower-quality premium gasoline, starting with the very first tank. ✓ Formulate with a unique agent to provide unbeatable protection against corrosion. ✓ Provide our best protection against wear and tear in engine. ✓ Reduce friction at interior engine surfaces.
Exxon Mobil	✓ Fuel detergents provide outstanding cleanliness in port fuel injection and direct injection engines. Cleaner engine parts can lead to better gas mileage, engine protection and performance. ✓ Friction modifier protects engine by reducing wear and tear by 30%. ✓ Corrosion inhibitor helps prevent rust in fuel distribution systems and/or key engine parts the fuel comes into contact with, such as the gas tank and the intake valves.
Chevron Texaco CALTEX	✓ Gasoline with Techron clean up grimy deposits (remove up to 50% of harmful carbon deposits) that can interfere with fuel combustion—which can boost miles per gallon. Also, Techron helps to minimize the harmful combustion chamber deposits that can lead to knocking.

	✓ Carbon build-up from low-quality gasolines can negatively affect engine to the point where acceleration lags. The cleaning power of Techron helps to remove those deposits for a smoother drive. ✓ Techron's cleaning technology bonds to vital engine parts to minimize carbon deposits which helps keep the air and fuel in engine flowing properly. This can limit the harmful emissions that cause air pollution.
BP	✓ Specially formulated to remove existing dirt from critical engine components (intake valves and fuel injectors) and protect against its build up. ✓ Cleaning of engine deposits, thanks to the use of BP Ultimate with active technology can give an additional up to 21 miles per tank. ✓ BP Ultimate Unleaded also contains a friction modifier which improves the upper cylinder lubrication of the engine. This can contribute to improved engine efficiency and therefore improved fuel economy.
Total	✓ Prevent up to 93% of fouling in gasoline engines and cleans up to 24% of existing build-up in gasoline engines. ✓ By eliminating deposits, Total Excellium enables your engine to maintain its performance. Its anti-corrosion technology protects your engine for an extended lifetime. ✓ Total Excellium contains detergents which make for a reduction in your fuel consumption. ✓ By improving the running of your engine, Total Excellium contributes to a reduction in polluting

	emissions. The reduction in consumption directly results in a reduction in CO_2 emissions[15].
Rosneft	✓ Remove up to 84% of the existing deposits on the intake valves after 60 hours of engine operation (when switching from regular gasoline). Provides 100% maintenance of clean injectors in direct injection engines.
Lukoil	✓ The cleanliness of the fuel system ensures maximum atomization and complete combustion of the fuel, provides stable power, fuel economy (up to 5%) and reduces harmful emissions. ✓ Corrosion inhibitors components ensure that the metal surfaces are coated with a protective film, which, in turn, prevents corrosion. ✓ The presence of a friction modifier in the ECTO fuel reduces mechanical friction in the cylinder area and provides excellent maneuverability due to an instant increase in power under various engine operating modes.
Gazprom Neft	✓ The increase in engine power of up to 12 %. ✓ Improve vehicle acceleration dynamics up to 1.8 seconds. ✓ Reduce deposits on the engine exhaust valves by more than 10 times. ✓ Reliable protection of the fuel tank against corrosion and ingress of water-fuel emulsion into the fuel system of the engine.

Table S2. Main groups of detergents compounds of multifunctional packages additives into motor gasoline.

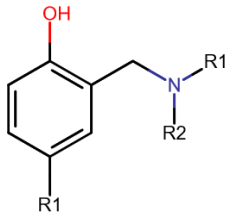
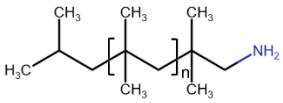
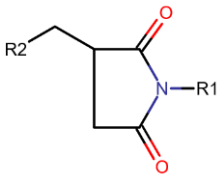
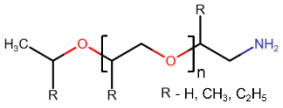
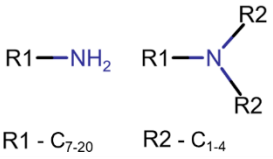
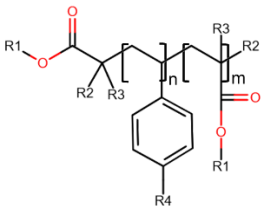
Class of compound	Structural formula	World manufacturers / developers	Effectiveness on various elements fuel system		
			valve	nozzle	chamber
Mannich base		Afton Chemical, Lubrizol, Total, Innospec, Ethyl Corp	High	Low	Moderate
Polyisobutene monoamine		BASF	High	Low	Moderate
Alkenyl succinimides		BASF, ExxonMobil	Low	High	Low
Polyether amines		Shell, China Petroleum	Low	Low	High
Low molecular weight amines		BASF, Lubrizol, Shell	Very low	High	Moderate
Block copolymer of alkyl acrylate and styrene derivatives		Total	-	High	-

Table S3. The requirements of the legislation of various countries and manufacturers of equipment for the cleanliness of the fuel system.

Properties	Engine	WWFC	USA			China	India
		5/6*	EPA	CARB	TOP TIER	(Beijing)	
Fuel injector cleanliness, % flow loss,							
max:	Chrysler	5	5	5	5	5	-
ASTM D5598 -	2.2L	10	-	-	-	-	-
ASTM D6421 -	Chrysler	-	-	-	Max one	-	-
GM 4.3-L V6 -	2.2L				dirty		
	GM 4.3-L				injector		
	V6						
Intake valve cleanliness, mg/valve, max:							
CEC F-05-A-93 -	MB M102	30	-	-	-	-	50
CEC F-20-A-98 -	MB M111	-	-	-	-	70	-
ASTM D5500 -	BMW 318i	-	100	50	-	-	100
ASTM D6201 -	Ford 2.3L	50	-	-	50	130	90
Combustion chamber deposits*, max:							
ASTM D5500, mg/valve -	BMW 318i	-	-	1300	-	-	-
ASTM D5500, % of base fuel -	BMW 318i	-	-	140	-	-	-
ASTM D6201, % of base fuel -	Ford 2.3L	140	-	-	140	-	-

* Standards for categories 5 and 6 of fuel markets according to WWFC.

Table S4. Main groups of compounds of corrosion inhibitors components of multifunctional packages of gasoline additives

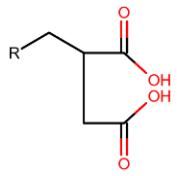
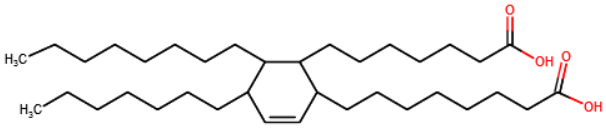
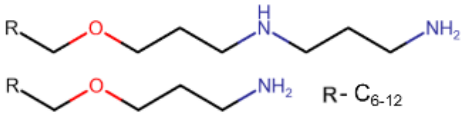
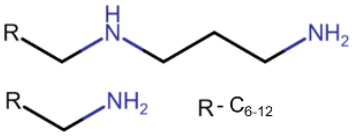
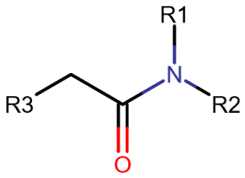
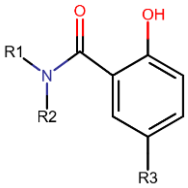
Class of compound	Structural formula	World manufacturers / developers
Alkenyl succinates		Innospec, Petrolite, Nalco, Chevron, ExxonMobil
Dimers and trimers of fatty acids		Innospec, Petrolite, Nalco, Du Pont
Aminoesters and polyaminoesters		Petrolite
Alkylamines and polyalkylamines		Innospec, AkzoNobel
Fatty acid amides		BASF Nalco
Alkyl salicylamides		Rosneft

Table S5. Main groups of compounds of fuel friction modifiers

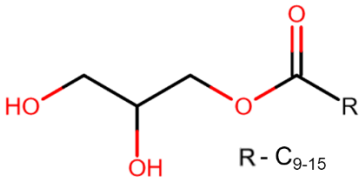
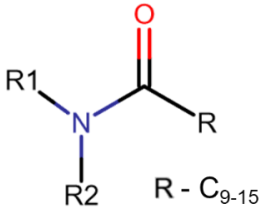
Class of compound	Structural formula	World manufacturers / developers
Fatty acid esters and their derivatives		Total, Ethyl, ExxonMobil
Fatty acid amides and their derivatives		Innospec, Lubrizol, Shell, ExxonMobil, Afton

Table S6. The share of motorization in major consuming countries and producers of motor gasoline.

Country/Region	Number of cars per 1000 person	
	2008	2018
Africa	27.2	39.8
Asia, Far East	53.8	118.8
Asia, Middle East	102.7	155.7
Brazil	140	212.8
Canada	623	656.1
Central and South America	131.9	181.3
China	35.7	167
Eastern Europe	300	399
Western Europe	593.2	619.5
India	13.2	43.6
Indonesia	34.7	102.2
Mexico	230.2	343
USA	838.5	836.3

Table S7. Requirements for motor gasoline in different countries.

Name of indicator	Requirements of regulatory and technical documentation							
	Russia		World Fuel Charter 2019	European Union 98/97/EC	USA, California	Japan	China	Canada
	TR TS 013/2011	GOST 32511-2013			CaRFG Phase 3	JIS K 2202	GB 17930-2016	CAN/CGSB-3.5-2016
Octane number: − RON − MON	≥ 80 ≥ 76	≥ 80/92/95/98 ≥ 76/83/85/88	≥ 91/95/98/102 ≥ 82.5/85/88	≥ 91/95 ≥ 81/85	- -	≥ 89/96 -	≥89/92/95 -	- ≥82/-/-/-
Mass fraction of sulfur, mg/kg	≤ 10	≤ 10	≤ 10	≤ 10	≤ 15*	≤ 10	≤ 10	≤10
Volume fraction of hydrocarbons, %: − aromatic − benzene − olefinic	 ≤ 35.0 ≤ 1.0 ≤ 18.0	 ≤ 35.0 ≤ 1.0 ≤ 18.0	 ≤ 35.0 ≤ 1.0 ≤ 10.0	 ≤ 35.0 ≤ 1.0 ≤ 18.0	 ≤ 22.0 ≤ 0.7 ≤ 4.0	 - ≤ 1.0 -	 ≤ 40 ≤ 1 ≤ 24	 - ≤ 1.5 -
Oxygen concentration, wt. %	≤ 2.7	≤ 2.7	≤ 3.7 + E22	≤ 3.7	1.8-3.5 (3.7)	≤ 1.3-3.7	≤2.7	≤2.7
metal concentration,	Absence Pb, Mn, Fe	Absence Pb, Mn, Fe	≤ 1 mg/Kg or Absence	Absence Pb, Mn	Absence Pb, Mn	Absence Pb	Pb ≤0.005 Mn ≤0.002	Pb ≤0.005 Mn ≤0.0018
Phosphorus content	-	-	≤ 1 мг/кг	-	≤ 5 мг/л	-	-	≤0.0013 г/л
Chlorine content, mg/kg	-	-	≤ 1	-	-	-	-	-
Concentration of washed wax, mg/100 cm^3	-	≤ 5	≤ 5	≤ 5	-	≤ 3	-	-
Concentration of wax, unwashed solution, mg/100 cm^3	-	-	≤ 30	-	-	≤ 20	-	-

Content of mechanical impurities, mg/l	-	-	≤ 1	-	-	-	-	-

Name of indicator	Requirements of regulatory and technical documentation							
	Russia		World Fuel Charter 2019	European Union 98/97/EC	USA, California	Japan	China	Canada
	TR TS 013/2011	GOST 32511-2013			CaRFG Phase 3	JIS K 2202	GB 17930-2016	CAN/CGSB-3.5-2016
Definition of particulate matter, ISO code	-	-	18/16/13	-	-	-	-	-
Induction period of gasoline, min	-	≥ 360	≥ 480	≥ 360	≥ 240	≥ 240	≥ 480	≥ 240
Cleanliness of the nozzle, % reduction in throughput	-	-	≤ 5	-	≤ 5	-	-	-
Inlet valve cleanliness, mg	-	-	≤ 30	-	≤ 50	-	-	-
Deposition in the combustion chamber, mg/cylinder	-	-	≤ 140% ****	-	≤ 1300	-	-	-
PMI	-	-	specify	-	-	-	-	-
Note: * The average annual rate is indicated ** The rate is indicated for a separate batch of gasoline *** The rate is indicated when conducting qualification tests **** The rate is indicated in% of the base gasoline when conducting comparative tests of gasoline with a detergent additive								

Table S8. Component composition of the gasoline pool of the Russian Federation in 2019.

Commercial gasoline components		Production, thousand tons	Share of the component in the gasoline pool, %
Light	Reformate	17126	42.0
	FCC gasoline	10222	25.1
	Isomerate	7607	18.7
	Alkylate	1694	4.2
	Hydrocracking Gasoline	836	2.1
	MTBE	1385	3.4
	TAME	217	0.5
	Low octane fractions:	1684	4.1
	Commercial gasoline	40771	100.0

Table S9. Distribution of automotive technologies.

Year	continuously variable transmission	Cylinder deactivation	Stop-start	Turbocharging	Direct injection
1996	0.0%			0.3%	
1997	0.1%			0.7%	
1998	0.1%			1.4%	
1999	0.0%			2.5%	
2000	0.0%			2.2%	
2001	0.0%			3.3%	
2002	0.1%			3.9%	
2003	1.0%			20.0%	
2004	0.9%			3.6%	
2005	1.1%	1.0%		2,.4%	
2006	1.2%	2.0%		3.2%	
2007	6.7%	0.9%		3.6%	0.3%
2008	7.7%	2.0%		4.5%	3.1%
2009	8.3%	1.8%		4.0%	4.2%
2010	8.4%	2.1%		4.1%	9.2%
2011	8.8%	1.3%		8.2%	18.4%
2012	11.0%	1.7%	1.3%	9.7%	27.4%
2013	13.7%	1.9%	3.5%	15.1%	37.3%
2014	21.3%	2.2%	10.7%	18.1%	42.7%
2015	26.3%	2.2%	12.7%	18.1%	44.0%
2016	27.2%	2.1%	12.1%	23.6%	49.5%
2017	29.1%	3.0%	20.5%	29.0%	52.4%
2018	26.7%	3.3%	26.0%	36.4%	52.6%
2019	29.5%	3.1%	28.7%	39.0%	54.8%