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Environmental Impact of the Use of Surfactants and Oxygenates in the Petroleum Industry

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Additional information is available at the end of the chapter

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Abstract

The role of surfactants and hydrophilic additives in gasoline fuel was demonstrated. The impact of anionic surfactant sodium bis-(2-ethylhexyl)sulfosuccinate (AOT) and hydrophilic oxygen containing additives, such as alcohols (methanol, ethanol, propan-2-ol, butanol, 2-methylpropanol) and methyl t-butyl ether (MTBE) on solubility of water, electrolytic conductivity in gasoline and interfacial tension in the water/gasoline system was studied. Small amounts of amphiphilic components improve the solubility of water in gasoline as a result of the occurrence of association phenomena with the formation of reverse micelles. The formation of surfactant aggregates and droplet clusters results in an increase in the solubility of water in gasoline, electrolytic conductivity, and a decrease in interfacial tension. The changes depend on concentration of the surfactant and type of applied biocomponents. Gasoline fuel in the form of microemulsion has a positive impact on the natural environment. The presence of water causes the almost complete combustion of hydrocarbons to the low toxic gases and the absence of carbon black among combustion products reduces fuel consumption, enhances engine power and decreases its temperature, reduces emissions of volatile organic compounds (VOCs), NO_x, SO₂, CO, and particulate matter. The alternative fuel may have a potential use in spark-ignition engines in the future.

Keywords: environmental protection, surfactants, fuel oxygenates, exhaust emissions, solubility of water, association phenomena, electrolytic conductivity, interfacial tension

1. Introduction

Energy consumption and the standard of living of a society are interrelated constantly growing. Nowadays, there are various sources of energy, such as solar, wind, geothermal, hydrogen, tidal, wave, hydroelectric, biomass, nuclear power, and fossil fuels (coal, oil, and natural gas). Among all the sources, crude oil still plays an important role in providing the

energy supply of the whole world. It is the most readily available source of energy to humanity, but also a rich source of raw materials for a lot of chemical industries of any kind. The field of surface chemistry is linked to technological processes of crude oil, including the drilling, petroleum refining, and petrochemical processing, and also other related applications and industries. All the processes are associated with interfacial phenomena and surface chemical interactions, as well as have an impact on the environment.

Crude oil is processed into many products (**Figure 1**) and most of them are fuels used for transportation (**Figure 2**). Among the sources of energy, gasoline is the most commonly used fuel in the transportation industry (**Figure 3**). The global production of the fuel presents an upward trend and, in 2012, amounted to approximately 22,377,200 barrels per day [bbl/d]. Taking the regional production into account, the largest amount of gasoline is manufactured in North America (10,017,000 bbl/d in 2012). The next regions are Asia, Europe, South America and Africa. In Europe, gasoline production had continually increased up to 2006 (4,742,000 bbl/d), after the time it started to slowly decrease (**Figure 4**). The largest producer in the world is the United States, with a production of about 9,058,630 bbl/d. Other most productive countries are China, Japan, Russia, Canada, India, Germany, and others (**Figure 5**).

Gasoline is a petroleum-derived liquid that consists of mostly of organic hydrocarbons obtained by the fractional distillation of crude oil, such as paraffins (saturated and unsaturated), naphthenics, aromatics, and their derivatives. The fuel composition also includes other additives that help attain valuable physicochemical properties [1, 2]. The composition is continually improved by producers in order to achieve better performance and meet the requirements of today's advanced engine technology and environmental institutions. Vapor pressure, distillation curves, or octane rating are features closely associated with the fuel composition and the characteristics of its components. The appropriate additives should ensure antidetonation combustion, good and quick evaporation, high octane number, chemical

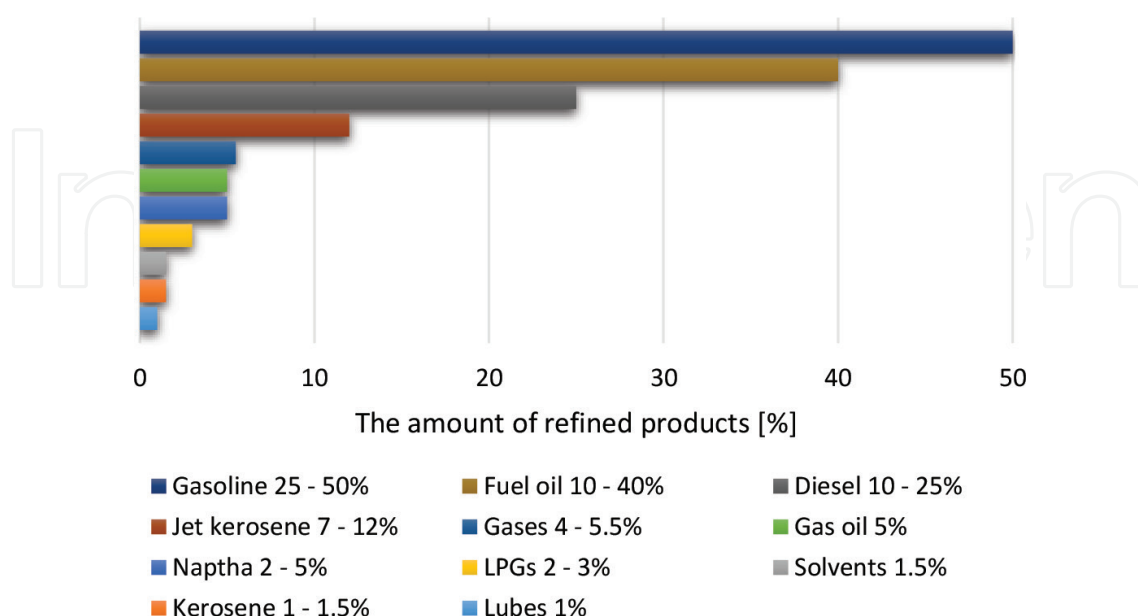


Figure 1. Global refined petroleum products attributable to one barrel [94]. Source: United States Energy Information Administration, 2017.

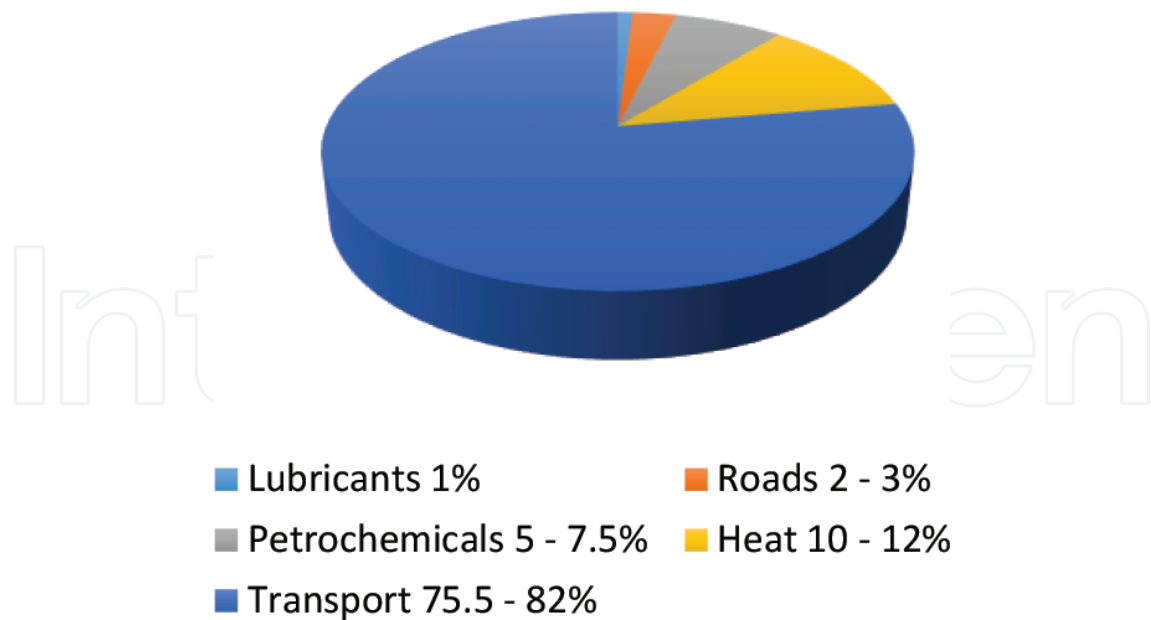


Figure 2. The global application of petroleum products attributable to one barrel [95]. *Source:* United States Energy Information Administration, 2017.

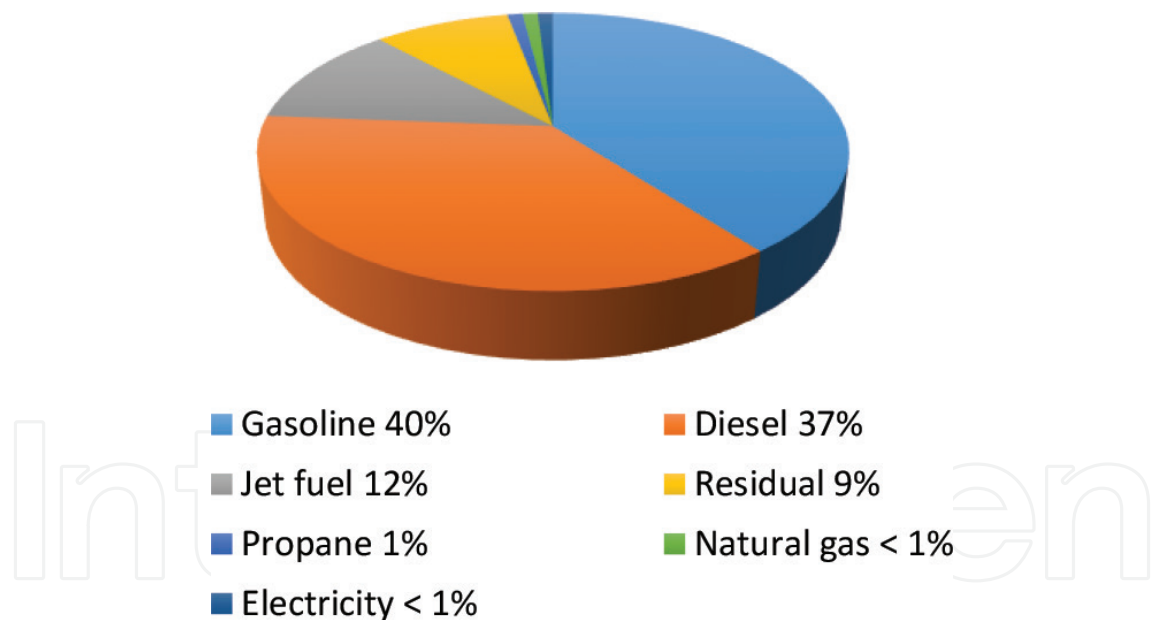


Figure 3. Various fuels used for global transportation in 2012 [96]. *Source:* U.S. Energy Information Administration, International Transportation Energy Demand Determinants (ITEDD-2015) model estimates.

stability, reducing emissions. Furthermore, fuel cannot be corrosive to metals and should not make deposits that interfere with the engine operation [3]. Most of additives belong to a few main functional groups, such as oxygenates (alcohols, ethers, esters, ketones, and others), complex binders, metalorganic compounds, heterorganic compounds, oxidizing organic compounds, petroleum fractions (aromatics, and light and heavy aliphatic hydrocarbons), surfactants, and polymers. Among the various types of components, high octane oxygen-containing

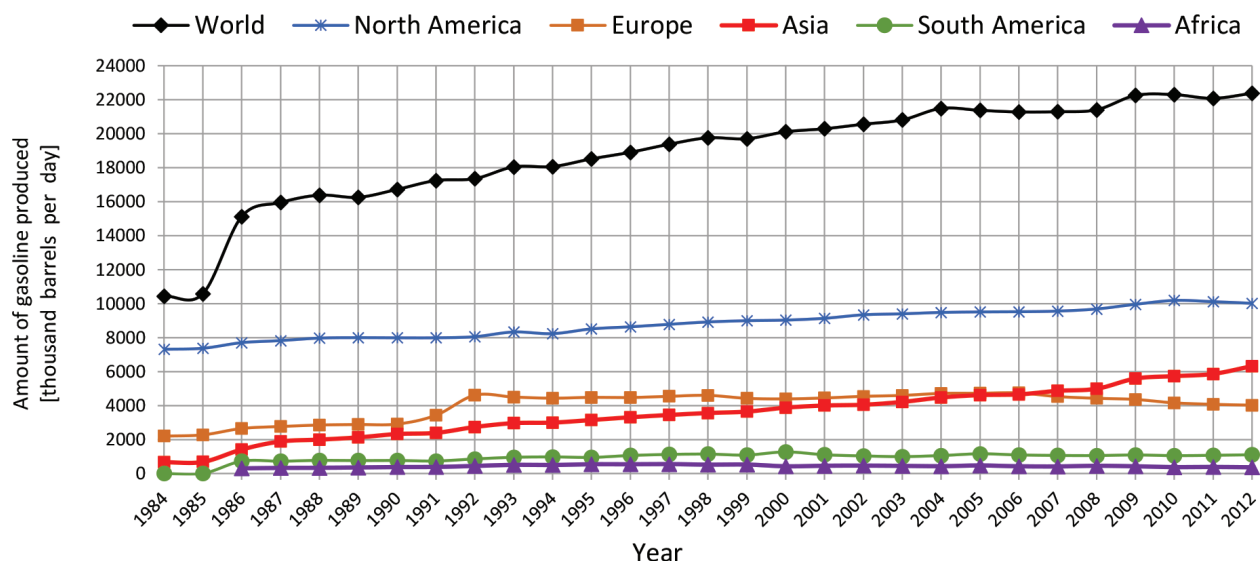


Figure 4. Global motor gasoline production by year [97]. Source: United States Energy Information Administration, 2016.

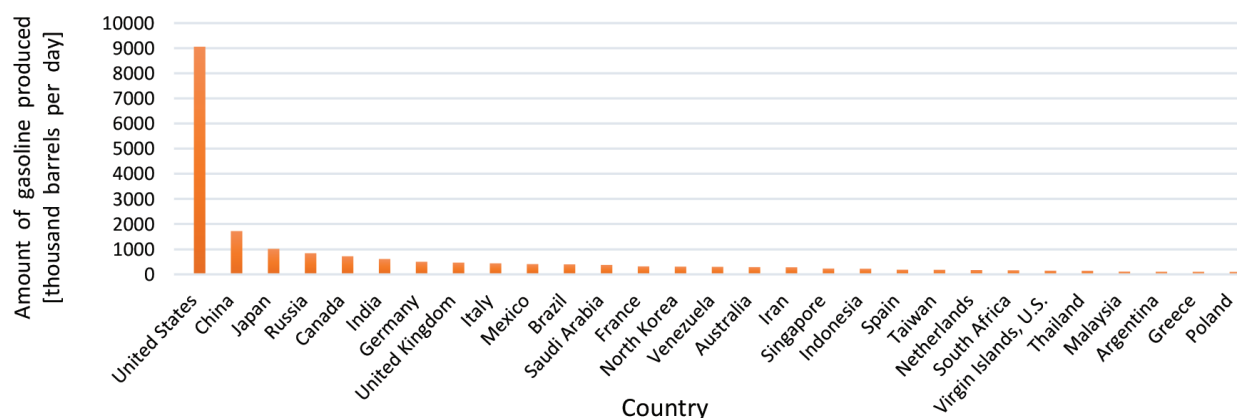


Figure 5. Motor gasoline production by country in 2012 [98]. Source: United States Energy Information Administration, 2016.

compounds, such as alcohols and ethers, are able to reduce pollutants from vehicle exhaust gases, increase the octane number [4], have antiknock properties, they can be obtained from renewable agricultural raw materials instead of fossil sources, they reduce carbon monoxide (CO), volatile organic compounds (VOCs), and unburned hydrocarbons emission [5–8].

A very important property of gasoline fuels is their hygroscopicity, which has a considerable effect on the reliability of vehicles and equipments. Operational experience showed that the permanent addition of a small amount of water to hydrocarbon fuel has a positive effect on a combustion process, provided that water in gasoline is in the form of an emulsion. Therefore, studies to determine physicochemical properties of microemulsions have significant practical importance. The emulsion, with the addition of 5 and 10% water, insignificantly increases engine torque, but a mixture with an addition of 15% water decreases engine torque. Water-in-gasoline emulsions (WiGEs) cause an increase in brake-specific fuel consumption (BSFC) and a decrease in exhaust temperature. Compared to basic gasoline, the WiGE fuel reduces NO_x and CO and enhances O₂ emissions [9].

Owing to specific chemical structure, surfactants are commonly used as fuel additives with a range of various functions, such as reduction of surface tension [10], prevention of particle formation, removing deposits, dispersion of water, formation of protective layers on surfaces, and an increase in electric conductivity. The addition of surfactants into gasoline leads to a reduction of the amount of deposits formed in the injectors, intake valves, and combustion chambers of gasoline engines. Deposits cause various performance and emissions problems, so their continuous removal is needed. Surfactants dissolved in nonpolar solvents may undergo association with the formation of reverse micelles. In the aggregates, polar (hydrophilic) groups are directed to the center of the micelle and hydrocarbon chains toward the apolar (hydrophobic) phase [11].

Water-in-gasoline emulsion (WiGE) fuel with an addition of hydrophilic high-octane oxygen components has become the best alternative fuel to substitute gasoline fuel in spark-ignition engines. The growing interest to this type of fuel is due to simultaneous reduction of unburned hydrocarbons and CO, reduction of the formation of atmospheric ozone resulting from gasoline emissions, reduction of emissions of exhaust pollutants, such as volatile organic compounds (VOCs), NO_x, and particulate matters. This occurs as a result of the reduction in peak cylinder temperature and secondary atomization by a further breakup of gasoline spray due to microexplosion. Experimental investigation about the effect of various surfactants present in the WiGE fuel on engine performance and pollutant formation has not been fully known. Studies conducted in this field may constitute the basis for investigation the effects of blends of emulsified fuel with various surfactants and hydrophilic oxygen compounds on the combustion characteristics, emission formation processes, and engine behaviors also to determine the pollution formation suppression capability of the emulsified fuels by in-depth combustion characteristics analysis. It is also equally important to select the suitable emulsification method, optimized speed, agitation time, and suitable chemical stabilizers in order to achieve stable emulsions. It is reasonable to conduct intense studies in order to know the effect of water content on the engine combustion characteristics and to determine an optimum percentage of water content in the WiGE fuel. Systematic studies of the optimization of water content in the emulsion for best engine performance and emission by both experimental and numerical investigations are necessary so that it can give the best recommendations for the commercialization of the WiGE fuel as an alternative source of energy for the future spark-ignition engines.

The aim of this work is to study the effect of chosen hydrophilic additives (alcohols MeOH, EtOH, BuOH, IPA, IBA, and MTBE, 3% v/v) and the anionic surfactant (sulfosuccinic acid bis[2-ethylhexyl] ester (AOT) at various concentrations) upon the solubility of water in basic gasoline, electrolytic conductivity, and interfacial tension isotherms at water/gasoline interfaces.

2. Oxygenates used in gasoline fuel

Oxygenates are chemical substances that contain oxygen in their structure. There are several oxygenates that can be added into gasoline (**Table 2**) and they can be divided into several groups based on their functions in fuel. Antistatic additives are responsible for reducing the potential for static build up by improving electrical conductivity and charge dissipation. The electrolytic conductivity of basic gasoline is very low (25 pS/m). Static electricity can build up

during pumping, filtering, and splash transfer operations within refineries and also at filling stations, so it can be a reason of static discharges presenting an obvious fire hazard due to low conductivity of gasoline. Grounding and bonding during liquid transfer is a need to protect against static discharge. In a container flow discharging back to the walls may happen, thus the rate at which it can discharge depends on the gasoline composition and properties. In the case of walls being conductive, the electric field achieved by the flow can induce a charge on the walls. The external part of the walls can achieve a charge equal to the charge of gasoline, and the internal part can achieve a charge that will be equal and opposite to that of fuel (**Figure 6**). In order to eliminate the possibility of an electrostatic discharge, various antistatic compounds are used for this purpose [15]. Metal deactivators' task is to extend the durability of fuel by reducing the effect of the catalytic metal to its oxidation. The inhibitory action of these additives involves the creation of inactive compounds with metal ions present in fuel. Metal ions bound in this way cannot catalyze the oxidation reaction any longer. The most active catalysts are copper and brass [16]. By the contact of hydrocarbons with oxygen at an elevated temperature, their oxidation to organic acids, resins, and other compounds usually occurs (**Figure 7**) [17]. Antioxidants interrupt the chain reaction of the oxidation at a stage of peroxides, delaying aging changes in fuel. The mechanism of action of antioxidants consists in inhibition or interruption of the chain oxidation process by decomposition of peroxides formed in radical reactions of the process. Antioxidants can also react with free radicals to give the stable compounds breaking chain reactions [18]. Anticorrosion additives protect metal from corrosion mostly caused by the acidic products of fuel oxidation. Due to the physical adsorption or chemical reaction, metal protective layers are formed (passivation). These layers are chemically

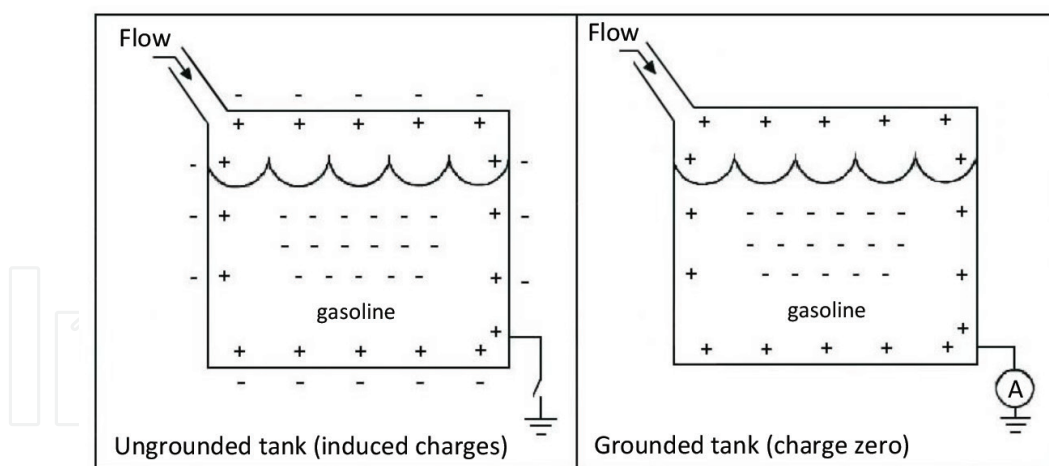


Figure 6. Fuel tank charging diagram [1, 14].

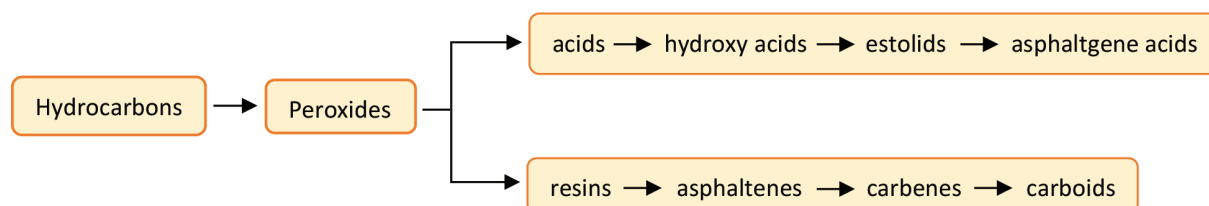


Figure 7. A scheme of hydrocarbons oxidation [17].

stable and resistant to damage caused by friction. Examples of anticorrosive compounds are the following: zinc dialkyldithiophosphates, dialkyldithiocarbamates, zinc alkylsuccinic acids and their monoesters, alkylsulfoamide acids, zinc and calcium salts, organic phosphorus compounds (phosphoric acid esters), and organic sulfur (sulfides) and amine compounds [19]. Dampness of gasoline at a temperature lower than 4°C causes the formation of ice crystals. Ice crystals are formed by the rapid evaporation of gasoline and are deposited on the surface of the shutter valve and its periphery, making it difficult for proper operation of the valve. While an engine is heated to a high temperature, ice melts, and water dripping from the surface of the aperture contributes to the restricted air flow. In order to eliminate crystallization of water, anticrystallization (anti-icing) substances are added that increase the solubility of water in fuel and reduce the temperature of crystallization of the aqueous solutions of the additive released from fuel. For this purpose, propan-2-ol, butanol, butan-2-ol, dimethylformamide (DMF) are used. Surface-active compounds are another group. They are adsorbed on the surface of ice-nucleating agents that prevent their growth and connection into deposited agglomerates [18]. The examples of components used in gasoline fuel are presented in **Table 1**.

Permanent removal of lead from gasoline was a cause of looking for other applicable substances, which are able to improve fuel properties. Therefore, refining technologies have been modernized in order to generate high-octane hydrocarbon (HC) compounds. In order to face the increasing

Group of chemicals	Chemical compound	CAS no.	Ref.
Aromatic amines	2,6-Dimethylaniline	87-62-7	[20]
	3,4-Dimethylaniline	95-64-7	[20]
	o-Toluidine	95-53-4	[20]
	o-Toluidine	95-53-4	[20]
	p-Toluidine	106-49-0	[20]
	Aniline	62-53-3	[20]
Aliphatic amines	Triethanolamine	102-71-6	[21]
	Diethanolamine	111-42-2	[21]
Phenols	2,6-Di-tert-butylphenol	128-39-2	[22]
	3,4,5-Trimethylphenol	527-54-8	[20]
	2,6-Dimethylphenol	576-26-1	[20]
	3,4-Dimethylphenol	95-65-8	[20]
	o-Cresol	95-48-7	[20]
	p-Cresol	106-44-5	[20]
Benzotriazoles	Phenol	108-95-2	[20]
	1-Methylbenzotriazole	13351-73-0	[20]
	Benzotriazole	95-14-7	[20]
Poly phenol	N,N-Disalicylidene-1,2-diaminopropane	94-91-7	[20]
Thiophenes	Benzothiophene	95-15-8	[23]
	Thiophene	110-02-1	[23]

Group of chemicals	Chemical compound	CAS no.	Ref.
Alcohols	2-Butoxy ethanol	111-76-2	[21]
	2-Ethyl 1-hexanol	104-76-7	[21]
	3-Methyl 1-butanol	123-41-3	[24]
	2-Methyl 1-butanol	137-32-6	[24]
	Isobutyl alcohol	78-83-1	[24]
	Tert-butyl alcohol	75-65-0	[1]
	2-Propanol	67-63-0	[21]
	1-Propanol	71-23-8	[24]
	Ethanol	64-17-5	[24]
	Methanol	67-56-1	[24]
	2-Methoxyethanol	109-86-4	[1]
	2-Ethoxyethanol	110-80-5	[1]
	Tetrahydrofurfuryl alcohol	97-99-4	[1]
	Tert-amyl alcohol	75-85-4	[1]
Ethers	Methyl tert-butyl ether (MTBE)	1634-04-4	[1]
	Ethyl tert-butyl ether (ETBE)	637-92-3	[1]
	Tert-amyl methyl ether (TAME)	994-05-8	[1]
	Tert-amyl ethyl ether (TAEE)	919-94-8	[25]
	Diisopropyl ether (DIPE)	108-20-3	[1]
	Tert-hexyl methyl ether (THEME)	38772-53-1	[26]
Ester	Ethyl acetate	141-78-6	[24]
Ester-acid	1,2-Bis(2-ethylhexyloxycarbonyl) ethanesulphonate potassium salt	7491-09-0	[21]
Neutral organics	1,1-Diethoxyethane	105-57-7	[24]
	2-Ethylhexyl nitrate	27247-96-7	[21]
	Tetrapropylenebutanedioic acid	27859-58-1	[21]
Undesignated	Dimethylformamide	68-12-2	[1]
	(Z)-4-Oxo-4-(tridecylamino)-2-butenic acid	84583-68-6	[21]
	Polyolefin Mannich base	–	[21]
	1-Propene, 2-methyl-homopolymer, hydroformylation products, reaction products with ammonia	68891-84-9	[21]
	Di-sec-butyl-p-phenylenediamine	101-96-2	[27]

Table 1. Examples of additives used in gasoline fuel.

demands of environmental protection, oxygen-containing compounds, organic oxygen-containing compounds started to be used. The Environmental Protection Agency (EPA) allowed the addition of detergents to all types of motor gasoline in the United States in 1995 [28]. The minimum content of MTBE in gasoline is about 11% (v/v) in the United States, while in Europe the content

is about 2.5% (v/v). In the European Union, according to Directive 2003/30/EC requirements, it is obliged to promote biofuels among the EU members and to recommend replacing conventional fuels by renewable energy sources (biofuels, etc.). The regulation initiated the reduction of greenhouse gas (GHG) emissions inter alia by allowing the use of ETBE and bioethanol. Based on the Directive 98/70/EC and the Directive 2009/30/EC, the limits of content of oxygenates are presented in **Table 2**.

Organic oxygen compounds, lead	Limits in the European Union		Limits in Poland	
	Minimum	Maximum	Minimum	Maximum
Oxygen content in gasoline [%, wt.]	—	3.7	—	2.7
Methanol [%, v/v] (required stabilizer)	—	3	—	3
Ethanol [%, v/v] (stabilizer may be needed)	—	10	—	5
Isopropanol [%, v/v]	—	12	—	10
Tert-butanol [%, v/v]	—	15	—	7
Isobutanol [%, v/v]	—	15	—	10
Ethers [%, v/v] (containing five or more carbon atoms per molecule)	—	22	—	15
Other oxygen compounds [%, v/v] (other mono-alcohols and ethers with a final boiling point no higher than that 210°C)	—	15	—	10
Lead content [g/l]	—	0.005	—	0.005

Table 2. Requirements for gasoline used in vehicles equipped with spark-ignition engines [12, 13].

3. The role of detergents in gasoline fuel

During combustion processes, fuel forms deposits in the combustion chamber, valves, piston rings, parts injectors, etc. Carbon deposits accumulating on valves can be a cause of their suspension on walls of the combustion chamber and piston head. They change the conditions of heat exchange and carbon deposits in the injector worsen the quality of fuel atomization. Deposits in the grooves of the volute on a piston may lead to their immobilization. This phenomenon deteriorates the conditions of air compression, facilitates the penetration of lubricating oil into a combustion chamber, may even lead to damage to the ring. The addition of detergents soluble in fuel reduces surface tension, but mainly removes all dirt and deposits from engine elements. Their function is to maintain engine cleanliness by counteracting the formation of sludge in the above-mentioned engine elements [17].

The mechanism of action of detergents includes such physicochemical processes as solubility and the stabilizing effect. Solubility is associated with the process of micelle formation, that is, of colloidal particles electrically charged and surrounded by a layer of associated solvent molecules. One theory explaining the mechanism of action of detergents brings to such processes as peptization and neutralization. Peptization is to move the pellet into sol or colloidal state under the influence of surfactants. Dirt particles of size from 10 to 150 nm

may be subject to peptization. Larger particles are difficult to peptize. The particle size of the impurities is shown in **Figure 8**. Stages of an impact of surfactants on dirt particles are presented in **Figure 9**. Examples of detergents applied in gasoline fuel are shown in **Table 3**.

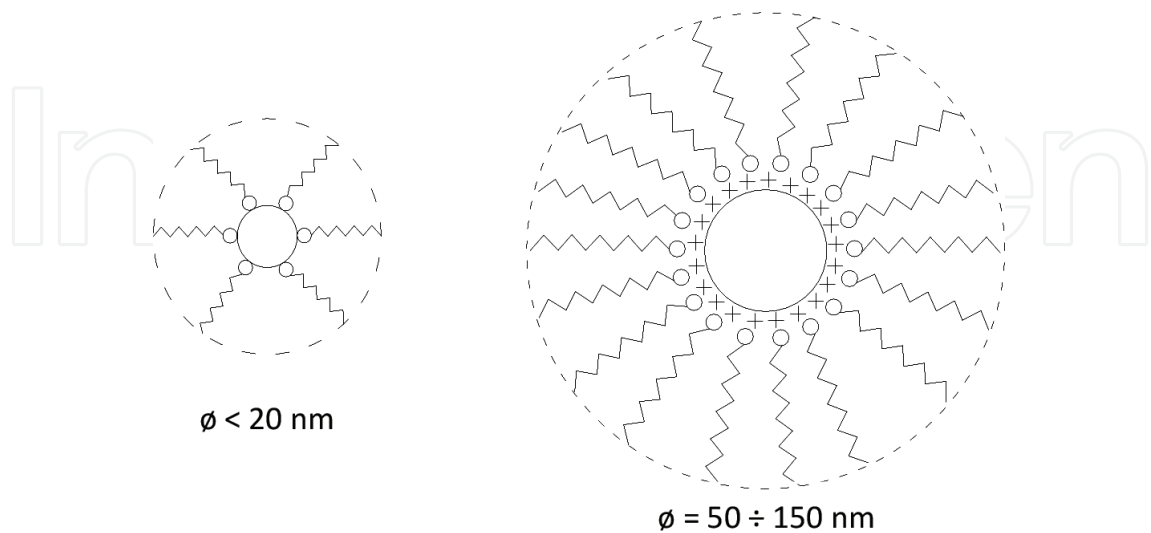


Figure 8. Schematic diagram of action of detergents [99].

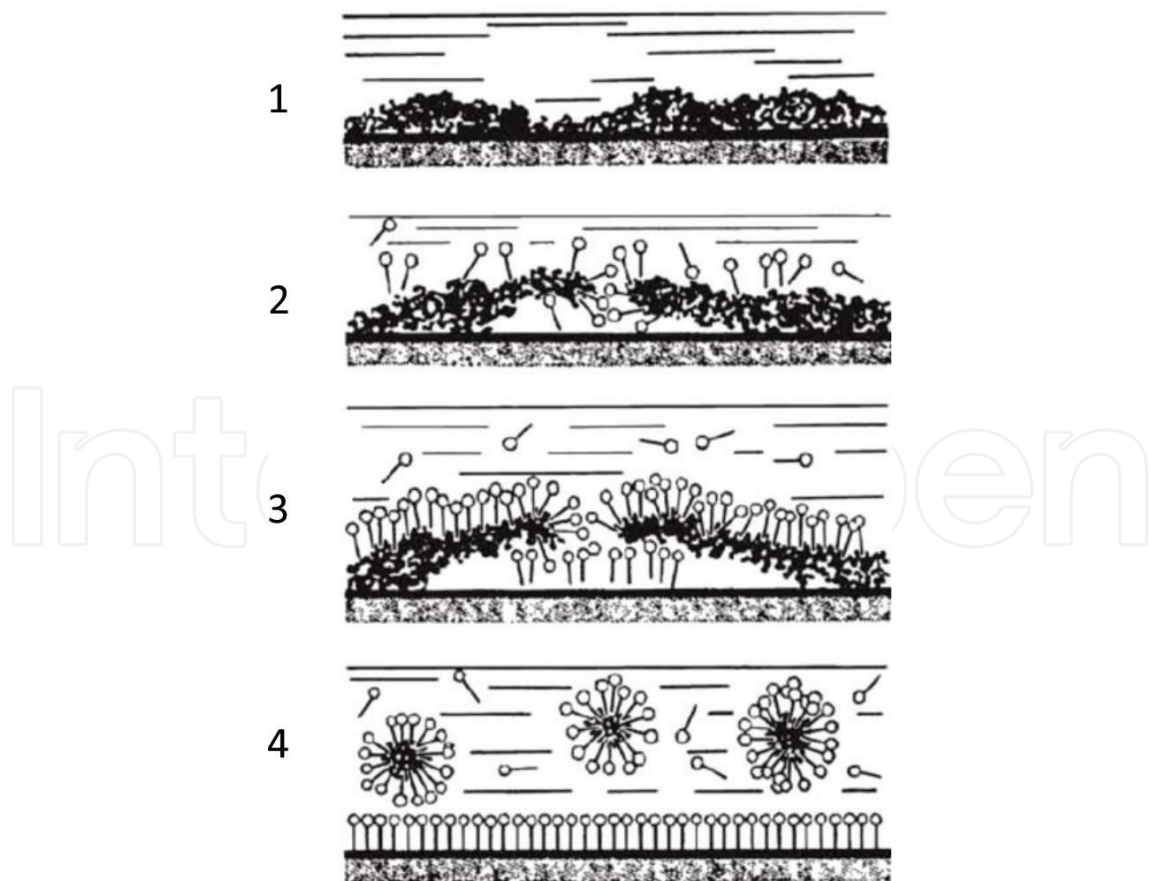


Figure 9. Steps of an influence of surfactants on dirt particles: 1, wetting and penetration; 2, adsorption; 3, emulsification and solubilization (rolling-up), dispersing; 4, emulsion [29].

SN	Examples of detergents with potential use in gasoline presented in patents and articles	Ref.
1	US 20040010966 A1, WO 2003074637. Gasoline detergents and intake valve deposit inhibitors consisting of high-molecular-weight hydrocarbyl amines in an alkoxyated alcohol carrier fluid. Gasoline detergents consist of a detergent additive, including a basic nitrogen atom that is substituted with a hydrocarbyl group, in a synthetic carrier oil component with the general structure $R-O-(A-O)_x-H$ (R = linear or branched C_{6-18} -alkyl; A = C_{3-4} -alkylene; and x = 5–35). A preferred hydrocarbyl amine is polyisobutenylamine; preferred carrier oils are mono- C_{8-15} -alkyl-terminated polyoxyalkylenes, butoxylated tridecanol. The substances are added to remove and inhibit the formation of intake valve deposits.	[30]
2	WO 200302083. Diarylamine-functionalized ethylene-alkene-alkadiene copolymers as gasoline detergents. A preferred product is the reaction product of ethylene-propylene copolymer, maleic anhydride, and N-phenyl-(p-N'-phenyl)diamine. The detergent composition can also contain a second mixture of mixed fatty acid esters, a mono- or di(hydroxyalkyl amine) and a low-molecular weight ester. The compounds can be used as gasoline antifriction detergents.	[31]
3	US 6 454 818. Gasoline detergents and octane requirement reducing agents consist of aliph. amidoamine-terminated polyoxyalkylenes of general formula $(R_4)_2N-R_3-N((C:O)R_2)-(CH_2CH(R_1)-O)_xH$, in which R_1 = C1-12-aliph.; R_2 = Me, Et, Pr, or Bu; R_3 = C1-6-alkylene; R_4 = C1-4-alkyl; and x = 5–30. To the above detergents, the gasoline can contain additional detergents, such as polyalkenyl amines, Mannich amines, alkylsuccinimides, poly(oxyalkylene)carbamates, and poly(alkenyl)-N-substituted carbamates. The compounds may be used as detergents and octane requirement reducing agents.	[32]
4	AN 2002:616810. Polyisobutylphenoxyethyl polyamines as gasoline detergents. A novel kind of detergents of polyisobutyl phenoxyethyl polyamines are synthesized using polyisobutylphenol (MW = 815,995), 1,2-dibromoethane, and polyamine with their structures identified as PIB--phenyl-- $OCH_2CH_2NHCH_2CH_2NH_2$ and PIB--phenyl-- $OCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$. The additives are utilized to inhibit deposits growth in modern gasoline engines to eliminate their adverse effects on vehicle performances in terms of drivability, power output, fuel economy, and much serious exhaust emissions.	[33]
5	US 2002066225. Mannich bases prepared from hydrogenated distilled nutshell liquid. Mannich bases functioning as deposit inhibitors and detergents in gasoline are prepared as the reaction products by reacting hydrogenated distilled cashew nut shell liquid (CNSL) with an amine having at least one active hydrogen, and an aldehyde in a CNSL-amine-aldehyde molar ratio of 1.0:1.0–1.2:1.0–1.2, at 70–175°C (preferably 90°C) for 6–12 h. Suitable amines are C_{1-20} -alkyl amines and -alkylamines (e.g., with C_{4-8} -alkyl side chains), and heterocyclic amines (e.g., morpholine, pyrrole, etc.). Suitable aldehydes are preferably aliphatic aldehydes, such as formaldehyde, acetaldehyde, and aldol (β -hydroxybutyraldehyde). The compounds may be used as gasoline detergents and deposit inhibitors.	[34]
6	A new type of adducts of polyisobutyl phenol-epoxy chloropropane-polyamine. The detergents are prepared using polyisobutylphenol, epichlorohydrin, and polyamines. The gasoline additives may inhibit deposit formation (e.g., intake valve deposits, combustion chamber deposits).	[35]
7	Poly(oxybutylene)amides. Effective compounds are amphiphilic copolymers consisting of a hydrophobic polyoxybutylene backbone and hydrophilic amide functionalities. The gasoline additives prevent automobile engine valve deposits.	[36]
8	Synthesis and <i>in situ</i> transformation of poly(oxybutylene)amides by butoxylation. A family of gasoline detergents was prepared by a two-step process: (1) preparation of amide initiators by reacting hydrophilic amines with Et acetate at high temperature; (2) consecutive butoxylation of the initiators with 1,2-epoxybutane (BO) to obtain oil-sol products. The additives improve engine performance of octane requirement.	[37]
9	Polyisobutenylsuccinimides may be used as detergents and dispersants. Reduction of forming of deposits in valve system.	[38]
10	WO 2000078898, US 6179885. Polyalkenylphenol-derived aromatic Mannich compounds may be used as diesel fuel and gasoline detergents.	[39]

SN	Examples of detergents with potential use in gasoline presented in patents and articles	Ref.
11	GB 2320719. The gasoline detergents are compounds of the formula $Z.NH(CH_2CH_2NZ)_{y,z'}$ wherein Z is N, C_{8-16} straight of branched chain alkanoyl or $RO-(CH_2CHR'O)_xOOC-Ph-CO$ with the proviso that at least one Z is $RO-(CH_2CHR'O)_xOOC-Ph-CO$ and R is C_{2-16} straight of branched chain alkyl or dodecylphenyl; R' is H, Me, or Et; x is an integer from 12 to 28; and y is an integer from 1 to 4.	[40]
12	WO 9736854, US 6053955. Polyoxyalkylene ether amino acid esters A polyalkylene glycol mono(alkylphenyl) ether $p-R_1C_6H_4(OCH_2CHR_2)_nOH$ ($R_1 = C_{4-25}$ alkyl; $R_2 = C_{1-3}$ alkyl; $n = 5-50$) is treated with $cis-HO_2CCR_3:CR_4CO_2H$ ($R_3, R_4 = H, C_{1-3}$ alkyl) or its anhydride to form a 1:1 (un)substituted maleate ester, which reacts in molar ratio $\leq (m+2):1$ with a polyamine $H_2NZ(NHZ)_mNH_2$ ($Z = C_{2-6}$ alkylene; $m = 0-6$). The additives prevent or remove combustion chamber or fuel line deposits.	[41]
13	WO 9215656. Polyalkylenepolyamines, especially polyisbutylene polyamine. The additive has a structure $R_{12}NR_2(NR_2)_xNR_{32}$ [$R_1 = H$ or polyolefin (of which ≥ 1 is a polyolefin); $R_2 = C_{1-8}$ -alkylene; $R_3 = H, C_{1-6}$ -alkyl; $x = 0-5$]. Gasoline additives for reducing valve sticking and to have detergency and deposition-inhibiting properties.	[42]
14	WO 9213047. Amine- and halogen-free gasoline detergents consisting of polypropylene glycol with hydrophobic end group.	[43]
15	GB 2247457. (Keto) diacid amides may be used as gasoline detergents being deposit inhibitors-octane requirement reducing additives.	[44]
16	US 5286265. Novel carbamates having the formula $ROC(:O)NXY$ [X and Y are independently either H, a (hetero-substituted) hydrocarbyl group, or $ZNHC(:O)OR$ (I), where Z is a divalent hydrocarbyl, a substituted hydrocarbyl, or (alkylene) $_m(NH)_n$ (alkylene) $_m$ in which $n = 0-4$, $m = 1-4$, and R is a (substituted) hydrocarbyl group, provided that if either one of X or Y is I, the other of X or Y is H]. The additives are able to remove deposits.	[45]
17	US 4729769. Reaction products of fatty acid esters and amines. Reaction products of C_{6-20} fatty acid ester with a mono- or di-(hydroxyhydrocarbyl)amine may be used as carburetor detergents.	[46]
18	US 4624682. Gasoline detergents are prepared by reacting an N-alkylalkylenediamine of formula $RNHR_1NH_2$ ($R = C_{12-18}$ alkyl, $R_1 = C_{1-3}$ alkylene) with a bicyclic keto acid derived from a catalyzed rearrangement of a C_{6-10} cyclic alken-3-yl carboxylic acid anhydride in the presence of a Bronsted acid catalyst (e.g., Nafion H-501). The aim of the compounds is removing deposits.	[47]
19	EP 186473 A2. Lubricating oil detergents and fuel (especially gasoline) deposit inhibitors-detergents are prepared by the reaction (at $100-175^\circ C \geq$) of ≥ 1 C_{10-20} fatty acids, ≥ 1 C_{12-26} -alkyl or -alkenylsuccinic acid or anhydride, and ≥ 1 polyalkylenepolyamine of formula $RNH(R_1NH)_xH$ ($R = C_{1-5}$ -hydrocarbyl, $R_1 = C_{1-5}$ -alkylene, $x = 1-9$). The compounds reduce carburetor deposits by 85% compared with the base fuel.	[48]
20	US 4508541. Vegetable oils [(esp. soybean oil, tall oil acids, or alkyl acids (esp. phenylstearic acid))] are reacted with polyamines (esp. tetraethylenepentamine) to form a product mixture for subsequent reaction with SO_2 to produce a product that has good detergent properties in fuels. The compounds can reduce deposits.	[49]
21	US 4505725. Fuel additives (detergents) obtained from borated, acid-treated mixtures of vegetable oil derived amides and esters. Reaction products of soybean oil with tetraethylenepentamine, sulfonated lubricating oil bright stock, and H_3BO_3 .	[50]
22	US 4639255. Gasoline detergents (e.g., vegetable oil-polyamine reaction products) (and optionally hydrogenated polybutenes) are mixed with C_{18-32} paraffin waxes (m. $130-160^\circ CF$) or durene, foamed, and pelleted (or encapsulated) to provide deposit-control additives which float on the gasoline and readily dissolve. The additives, present at approximately 120 lb/1000 bbl unleaded gasoline, are sol. at extreme temperatures, do not change the gasoline octane rating, and do not promote gum formation or corrosion.	[51]
23	US 4400178. Polyamine carburetor dispersants. They are prepared by the Mannich reaction of primary or secondary amines with formaldehyde and 2-nitropropane followed by reduction of the nitro group.	[52]

SN	Examples of detergents with potential use in gasoline presented in patents and articles	Ref.
24	US 4394135. Gasoline detergents prepared by reacting tetraethylenepentamine with phenylstearic acid, isostearic acid, or tall-oil fatty acids. The additives reduce engine deposits by 94–95%.	[53]
25	US 4330303. The additives (carburetor detergents) are manufactured by condensation of 1:1 (molar) amounts of ethylenediamine and acid lactones prepared by acid-catalyzed lactonization of polyisobutenylsuccinic acid or anhydride.	[54]
26	Acylation of polyamines with fatty acids in the preparation of the detergent NAIK for gasoline.	[55]
27	US 4353711. The reaction products of glycidyl ethers, whose alkoxy portion contains 6–20 atoms C, with alkylenediamines. Excellent deposit reduction resulted in various parts of the engine and in carburetor.	[56]
28	US 4292046. The additives (carburetor detergents) are manufactured by reaction of acids (naphthenic acids or dimer acids) with 2-(2-aminoethylamino)ethanol or by reaction of the resulting imidazolines with (C ₁₈₋₂₄ -alkyl)succinic anhydrides or isostearic acid.	[57]
29	US 4269606. Fuel and lubricant additives (detergents) from acid treated mixtures of vegetable oil derived amides and esters. Vegetable oils such as corn oil, peanut oil, and soya oil are treated with polyamines to give mixtures containing amides, imides, half esters, and glycerol, treated with sulfonic acids give detergent for gasoline.	[58]
30	US 4249912. Amino amides, prepared by treating EDTA or NTA with fatty amines, phenylstearylamine, or oleylamine. The amino amides are combined with dodecylbenzenesulfonic acid to obtain fuel detergents. The additives can reduce carburetor deposits.	[59]
31	US 4251233. Liquid hydrocarbon-sol. rare-earth chelates prepared from the ligand 2,2,7-trimethyl-3,5-octanedione. The additives prevent formation of or remove carbonaceous combustion-chamber deposits.	[60]
32	US 4240804. Alkyl acrylate adducts of polyamines, ether amines and ether polyamines. A mixture of an adduct (I) of 2-ethylhexyl acrylate (II) and 4-aza-8-oxaeicosylamine (III) with III. The additives cause deposit reduction.	[61]
33	US 4247300. A detergent additive imidazoline prepared by treating carboxylic acid with polyamine. The imidazoline is further combined with a sulfonic acid. The additive, prepared by treating isostearic acid with tetraethylenepentamine and the formed imidazoline with dodecylbenzenesulfonic acid, is added to gasoline. The additives can reduce deposits in an internal combustion engine.	[62]
34	SU 755830. An additive of 10–20 wt% ethylene diisopropylxanthate in a gasoline additive containing 30–40 wt% aliphatic amine and a nitrated fraction of shale oil with a boiling point at 350–370°C. The deposits were decreased on the surface of engine parts by the gasoline additives.	[63]
35	US 4204841. A primary alkylaminoalkyl-substituted asparagine and an N-(primary alkyl)alkylene diamine. An additive contains 50% N,N'-bis(3-oleylaminopropyl)asparagine and 50% N-oleyl-1,3-propanediamine. The additive has excellent deposit prevention ability in a carburetor and provides reduced corrosion.	[64]
36	US 4203730. Polyamine derivatives of oxidized olefinic substituted dicarboxylic acid compounds. The condensation of diethylenetriamine (I) with oxidized polybutenylsuccinic anhydrides (II) of different molecular weights. The detergents can reduce deposits.	[65]
37	EP 8591. Detergent additives from mixtures of vegetable oil derived amides and esters or acid treated mixtures. Vegetable oils were treated with polyethylenimine or tetraethylenepentamine and the products treated with alkylbenzenesulfonic acids or alkanesulfonic acids.	[66]
38	US 4240803. Reaction products of alkenylsuccinic anhydrides with tetraethylenepentamine or diethylenetriamine in which the alkenyl group is derived from mixed C16–28 olefins, being the bottoms from an olefin oligomerization. The succinic anhydrides were prepared by reaction of maleic anhydride with the mixed olefins at 200–210°C for 7 h and 235–240°C for 3 h. The compounds are carburetor detergents.	[67]

SN	Examples of detergents with potential use in gasoline presented in patents and articles	Ref.
39	US 4191537. Fuel compositions of poly(oxyalkylene) monoether (aminoethyl)carbamates. Poly(oxypropylene) mono-Bu ether (I) carbamtes, derivs. of $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ or polyethylenepolyamines, were prepared. Also prepared were poly(oxybutylene) mono(alkylphenyl) (2-aminoethyl)carbamates and poly(oxypropylene)-poly(oxybutylene) mono-Bu ether (2-aminoethyl)carbamate. Deposit-inhibiting dispersants (carburetor and intake-valve detergents) may be used in gasoline.	[68]
40	US 4179271. Amine oxide polymers. Gasoline having detergent properties contains 0.05–0.75 wt% of a tertiary amine oxide-containing polymer(I). Gasoline was prepared by mixing Neodol 25 L methacrylate 54.5, Alfol 1620 methacrylate 16.5, Bu methacrylate 20, and 4-vinylpyridine 9 wt%, polymerizing the mixture, and oxidizing the polymer by AcOH and H_2O_2 .	[69]
41	US 4173456. Polyolefin-acylated poly(alkyleneamine) may be used as a component fuel additive to prevent deposits formation. Detergents containing triamide of tetraethylenepentamine and tall-oil fatty acids and polypropylene or polyisobutylene (the triamide 13.6, polypropylene (mol. wt. 800) 50, oxyalkylenated alkylphenol 1, corrosion inhibitor 1.1, and xylene (solvent) 34.3 wt% used at 25 lb/1000 bbl).	[70]
42	US 4132531. A detergent (to remove deposits) prepared by condensing 115 g 1-(2-aminoethyl) piperazine with 700 g polyisobutenylsuccinic acid-derived lactones (I) in 700 ml xylene.	[71]
43	US 4125382. Polyoxyalkylene ether demulsifiers. Alkylpolyamines as detergents and 5–30 ppm polyoxyalkylenes or their adducts with C_{8-18} epoxides as demulsifiers. For example, shaking 32 ml gasoline containing 500 ppm alkylpolyethylenepolyamine, 25 ppm acetal-coupled 28:72 polyethylene-polypropylene glycol (mol. wt. 2200), and 4 ppm 13:87 polyethylene-polypropylene glycol (mol. wt. 2800) and settling 2 h. The detergents can increase water tolerance.	[72]
44	US 4125383. Reaction products of a long-chain monocarboxylic acid, a polyamine, and a C_{12-18} isocyanate. For example, octadecyl isocyanate was reacted with triethylenetetramine and isostearic acid. Improved ashless gasoline detergents decrease the carburetor deposits by 70–80%.	[73]
45	US 4105417. Hydrocarbyl-substituted nitrogenous compounds (e.g., amides, carbamates, or ureas) are effective as gasoline detergents (to remove valve deposits) at a concentration of 50–1500 ppm. For example, 0.06 mol diethylenetriamine was added to 0.44 mol polyisobutenyl di-Et hydrazodicarboxylate (polyisobutenyl av. mol. wt. = 950) in 50 ml C_6H_6 to give polyisobutenyl cyclobiuret (I).	[74]
46	US 4059414. The detergents are prepared by treating long-chain monocarboxylic acids with trialkanolamines and sulfonic acids. For example, 10 lb of a detergent prepared by treating triethanolamine triisostearate (obtained by the reaction of triethanolamine and isostearic acid at 135–40°C for 6 h in the presence of $\text{p-MeC}_6\text{H}_4\text{SO}_3\text{H}$) with dodecylbenzenesulfonic acid. The detergents reduce gum deposits in an unleaded gasoline by 63%.	[75]
47	US 4054422, US 4121911. Mannich bases containing tertiary amines and fuel compositions containing said Mannich bases. Mannich condensation products have the formula $\text{RNH}(\text{CH}_2)_m[\text{NR}_1(\text{CH}_2)_{m'}]_b\text{NHR}$ ($\text{R} = \text{C}_{20-1000}$ alkylhydroxybenzyl; $m = 2$ or 3 ; $\text{R}_1 = \text{Me, Et}$; $b = 1-5$). A Mannich base was prepared by refluxing (11 h) a mixt. of 300 g of a 75 wt% solution in PhMe of polypropenylphenol (prepared. from PhOH and polypropylene of 840 mol. wt.), 14.5 g 3,3'-(methylimino)bis(propylamine) and 17 g of a 36 wt% aq. HCHO solution. The carburetor detergents can reduce gum deposits in unleaded gasoline.	[76]
48	US 4038043. Mixture of monoamine and polyamine (N,N-bis[2-hydroksy-4-(polipropylene) benzylo]methylamine with triethyltetramine with N atoms and benzyl groups). A multifunctional gasoline additive that may be used as a carburetor detergent and at the same time minimizes intake valve deposits and quick-heat intake manifold deposits.	[77]
49	US 4038044. A combination of diamine and polyamine Mannich bases. The diamine Mannich base used was based on ethylenediamine with each N atom being substituted by an alkyl- and hydroxy-substituted benzyl group in which the alkyl substituent was derived from polypropylene of 840 mol. wt. The polyamine Mannich base was based on triethylenetetramine with the terminal N atoms each being substituted with one of the alkyl- and hydroxy-substituted benzyl groups described above. The multifunctional gasoline additive may be used as a carburetor detergent and can minimize intake valve deposits and quick-heat intake manifold deposits.	[78]

SN	Examples of detergents with potential use in gasoline presented in patents and articles	Ref.
50	US 4039300. Lubricating oils containing 60 wt% aromatics (average molecular weight 350–650) and detergents. The additives inhibit deposits in the carburetor, exhaust gas recycle system, and intake valves.	[79]
51	US 4024083. Substituted phenoxy propanol diamines and amino alcohol detergent additives for fuels to remove deposits. Detergents (I; R = alkyl with mol. wt. 200–1500, R ₁ = H, C ₁₋₄ alkyl; Q C ₂₋₆ alkylene; X = NH, O; x = 0, 1; y = 1, 2, x + y ≤ 2, and z = 1–10) for gasoline, diesel fuels, and lubricating oils. A detergent was obtained by treating polyisobutenylcatechol with epichlorohydrin in the presence of BF ₃ etherate in xylene, stripping the solvent, treating the intermediate obtained with diethylenetriamine in xylene, washing with MeOH containing NaOH, and stripping off xylene.	[80]
52	Specific Mannich condensation products prepared from alkylphenols, HCHO, and an alkylene polyamine. Control of deposits on intake valves and good detergency.	[81]
53	US 3951614, US 3785789. The gasoline detergents are reaction products of hydrocarbyl amines with polyhalides, polycarboxylic acids, or organic polyisocyanates.	[82]
54	US 3944397. Mannich condensation products as carburetor detergents. A benzyl polyamine of the formula ZNH(C _n H _{2n} NR) _a (C _n H _{2n} NR) _b C _n H _{2n} NHZ (Z = alkyl- and hydroxy-substituted benzyl group wherein the alkyl group has 50–1000 C atoms and 60% of the alkyl group is para to the hydroxyl group, n = 2–3, R = H or Z, and the sum of a and b is 0–5).	[83]
55	US 3926578. Esters of 2-(alkylamino)propionic acid. For example, 62.2 g dodecylphenyl acrylate (prepared from dodecylphenol and acrylic acid) in 100 ml xylene was mixed with 54 g Armeen T (tallowamine) and heated 3 h at 120°C to give a product which, when added (7.5 lb/1000 gallons) to 100-octane gasoline. The compounds may be used as gasoline detergents and anticorrosive agents.	[84]
56	US 3923474. Alkylenediamineamides of fatty acids. A dual additive comprising RNHCH ₂ CH ₂ CH ₂ NHCOR ₁ is improved by incorporation of a second additive R ₂ OCH ₂ CH ₂ CH ₂ NHCH ₂ CH ₂ CH ₂ NHCOR ₁ in which R is a C ₁₀₋₂₀ aliphatic hydrocarbon radical, R ₁ is a C ₉₋₁₉ aliphatic hydrocarbon radical and R ₂ is C ₁₀₋₁₅ aliphatic hydrocarbon radical. These additives remain low in harmful deposits of varnish scale, which normally results from untreated fuel.	[85]
57	US 3907518. A combination of tert-alkyl primary amines, a surface-active NH ₄ carboxylate salt-ethoxylated alkylphenol ester of a trimer or dimer acid, and a hydrocarbon-sol. polyisobutylene. The compounds may be used as a carburetor deposit inhibitor.	[86]
58	GB 1378709. Polyolefin carburetor detergent. The gasoline additive, RN[C(CN):CH ₂](CH ₂) ₃ NMe ₂ (R = polyisobutenyl, mol. wt. 1300) was prepared from α,β-dibromopropionitrile by treatment with NaOH, N,N-dimethyl-1,3-propylenediamine, and polyisobutenyl chloride. The carburetor of an engine run on gasoline containing 100 ppm additive was cleaner than when the gasoline was used without additive.	[87]
59	US 3846089, US 3782912, US 3912771. Combinations of tert-alkyl primary amines, surface-active bis(alkylammonium) salts of ethoxylated alkylphenol esters of trimer acid, and dimer acid or trimer acid esters with mixtures of aliphatic and ethoxylated alkylphenols. For example, 845 g trimer acid (Emery 1834-18R), 316 g isodecyl alc., 338 g (octylphenoxy)poly(ethylene oxide), 200 ml toluene, and 1.0 g p-toluenesulfonic acid were heated to give diisodecyl (octylphenoxy) polyethylene glycol triester of trimer acid, of acid no. 1.0. Such mixed polyesters used in combination with rust inhibitors prevent rusting and pitting and provide carburetor and induction-system detergency.	[88]
60	GB 1368532. An alkylphenol, prepared by acid-catalyzed alkylation of PhOH with polybutene of average molecular weight 900–1100, with paraformaldehyde and R ₂ N(CH ₂) ₃ NH ₂ [R = Me, HO(CH ₂) ₂]. The additives clean carburetors, remove intake valve deposits, and reduce build-up of engine crankcase deposits.	[89]

Table 3. The role of chosen detergents applied in gasoline fuel: a review.

4. Experimental procedure

4.1. Materials

Basic gasoline, obtained from the petrochemical industry, was used in all experiments. The composition is shown in **Table 4**.

The following compounds were used in experiments:

- methanol (MeOH), p.a., POCH S.A., Gliwice, Poland,
- ethanol (EtOH), 96%, p.a., Sigma-Aldrich, Germany,
- propan-2-ol (isopropanol, IPA), p.a., POCH S.A., Gliwice, Poland,
- 2-methylpropanol (isobutanol, IBA), p.a., POCH S.A., Gliwice, Poland,
- butanol (BuOH), POCH S.A., p.a., Gliwice, Poland,
- methyl t-butyl ether (MTBE), 99%, p.a., Sigma-Aldrich, Germany,
- sodium bis-(2-ethylhexyl)sulfosuccinate (AOT), 99%, p.a., Sigma-Aldrich, Germany,
- Hydranal Composite 5, Sigma-Aldrich, Germany,
- deionized water.

4.2. Advantages and disadvantages of the use of sodium bis-(2-ethylhexyl)sulfosuccinate (AOT)

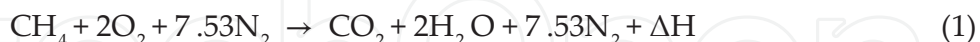
Sodium bis-(2-ethylhexyl)sulfosuccinate (AOT) is an anionic surfactant with a sulfone group directly connected to a hydrophobic group ($C_{20}H_{37}NaO_7S$, molecular weight 444.56 g/mol, CAS Number 577-11-7). Water solubility in hydrocarbon fraction can be increased with an addition of AOT due to the formation of ternary microemulsion system consisting of water, the organic phase, and AOT. Microemulsions can form different types of structures as discontinuous spherical water droplets, interconnected channels of water, and so on. Their size can be controlled by the water content (w_o), that is, the molar ratio of water to AOT ($w_o = [H_2O]/[AOT]$). Microemulsions may be created as “oil-in-water” (o/w) or “water-in-oil” (w/o) depending on the nature of the solvent. Due to high interfacial activity and good hydrophilic properties, the surfactant AOT is able to form reversed micelles in the hydrocarbon phase, which absorbs large amounts of water. Reverse micelles occur in the situation when $w_o = [H_2O]/[AOT] < 10-15$. AOT can be hydrolyzed in the presence of an acid or a base, which results in formation of 2-ethylhexyl alcohol and sulfosuccinate anion (**Figure 10**) [90].

The surfactant AOT contains seven oxygen atoms in its structure, which presence has a positive effect. The compound contained in fuel introduces additional oxygen into the system, which plays an important role in combustion processes. Air-fuel ratio is of great importance and essential measure for antipollution and performance reasons. Air-fuel ratio is the amount of air needed to burn fuel in the engine and in other words, it is mass ratio of air to fuel present in the combustion chamber. Combustion efficiency depends on the right amount of air,

Number of carbon atoms	The components of basic gasoline [%, v/v]						Total
	n-Alkanes	Iso-alkanes	Olefins	Naphthenes	Aromatics	Oxygenates	
C1	—	—	—	—	—	—	0.000
C2	—	—	—	—	—	—	0.000
C3	0.055	—	—	—	—	—	0.055
C4	1.204	2.633	4.820	—	—	—	8.658
C5	3.218	10.137	3.869	0.56	—	—	17.783
C6	0.764	12.351	1.427	1.781	0.484	—	16.806
C7	1.308	4.695	0.949	1.913	6.590	—	15.454
C8	0.655	6.887	0.142	2.381	7.833	—	17.897
C9	0.286	1.665	0.011	0.847	11.612	—	14.421
C10	0.125	0.841	0.074	0.093	5.495	—	6.629
C11	0.047	0.680	—	0.042	0.215	—	0.984
C12	0.045	0.071	—	0.035	0.747	—	0.898
C13	0.058	—	—	—	—	—	0.058
C14	0.004	—	—	—	—	—	0.004
Total	7.768	39.960	11.292	7.652	32.975	0.000	99.647
Total heavies							0.034
Total unknown compounds							0.320
Grand total							100.000

Table 4. The components of basic gasoline used for the research [1].

which is reflected on the engine power. Air contains about 21% oxygen, 79% nitrogen, and smaller amounts of other elements. When fuel burns in the presence of O₂ and N₂, it is converted to carbon dioxide, water, nitrogen, and heat according to Eq. (1):



The exhaust gases from internal combustion engines mainly consist of the products of complete combustion, small amounts of the oxidation products of sulfur and nitrogen, and components derived from the fuel and various lubricants. The composition of gases is shown in **Table 5** [91].

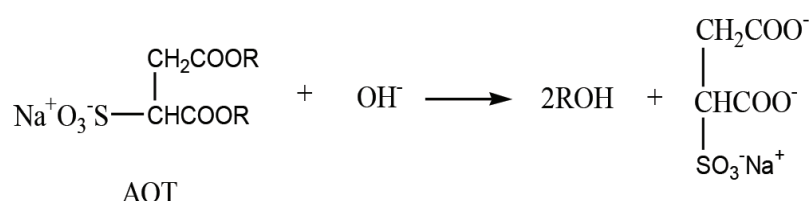


Figure 10. Alkaline hydrolysis of AOT (R—ethylhexyl group) [90].

Major components (>1%)	Minor components (<1%)
Water, H ₂ O (c)	Oxides of sulfur, SO ₂ , SO ₃ (c)
Carbon dioxide, CO ₂ (c)	Oxides of nitrogen, NO, NO ₂ (c)
Nitrogen, N ₂ (c)	Aldehydes, C _n H _m CHO (c)
Oxygen, O ₂ (c)	Organic acids, C _n H _m COOH (c)
Carbon monoxide, CO (a)	Alcohols, C _n H _m OH (c)
Hydrogen, H ₂ (a)	Hydrocarbons C _n H _m (c)
	Carbon monoxide, CO (b)
	Hydrogen, H ₂ (b)
	Smoke (c)

(a) Spark-ignition engine, (b) diesel engine, (c) both engines.

Table 5. Components of internal combustion engine exhaust gases [91].

The disadvantage of the surfactant AOT is the presence of one sulfur atom in its structure. There is a tendency to eliminate sulfur from fuel composition in order to reduce its content in emitted gases after combustion processes in engines. In the air, SO₂ is present in the largest quantities, but other sulfur oxides (SO_x) are found in the atmosphere at much lower concentrations. SO₂ influences human health when it is breathed in, at concentrations above 1000 µg/m³, measured as a 10-min average. The gas irritates the nose, throat, and airways to cause wheezing, coughing, shortness of breath, and a tight feeling around the chest. The large amounts of SO_x in the atmosphere can harm all types of plants by damaging foliage and decreasing growth. Sulfur oxides are responsible for contributing to acid, which can harm sensitive ecosystems. Therefore, the concentration of sulfur oxides in air is constantly monitored in order to react appropriately in the case of a high concentration.

4.3. Apparatus and procedures

Samples of basic gasoline (25 ml) containing 3% (v/v) of a hydrophilic additive were mechanically shaken with 1% of deionized water for 2 h at 4000 revolutions per minute and left to phase separation for 24 h. The content of water in saturated gasoline samples was determined using the Karl Fischer method. The potentiometer 702 SM Titrino (Metrohm, Switzerland) was used for titration using Hydranal Composite 5 (Sigma-Aldrich, Germany). The basic gasoline was modified with the anionic surfactant AOT at various concentrations and hydrophilic additives. After saturation with deionized water, the content of water was determined.

Electrolytic conductivity of modified gasoline samples was determined using pH/conductivity meter CPC-551. The K12 tensiometer with a platinum ring (Krüss, Germany) was used to measure the interfacial tension (water/gasoline). After preparation of the systems (15 ml of water and 9 ml of modified gasoline) for measurements, interfacial tension was measured using the Du Noüy ring method at room temperature. All experiments mentioned above were made in triplicate for each method.

5. Results and discussion

5.1. The influence of biocomponents on water solubility in gasoline

The composition of gasoline, type, and concentration of hydrophilic oxygen-containing additives (i.e., alcohols, ethers), amphiphiles (i.e., surfactants), and other functional components affect the solubility of water in the fuel. Preliminary studies demonstrated that the content of water in basic gasoline saturated with 1% of deionized water was about 0.01% (v/v). The solubility of water in basic gasoline modified with the anionic surfactant AOT and chosen hydrophilic alcohols and ether (3%, v/v) is shown in **Figure 13**. The addition of AOT causes significant changes and depends considerably on its concentration. The multifunctional surfactant increases the solubility of water up to about 1%. The sudden increase is observed at very low AOT concentration equal to 6.25×10^{-4} mol/l. This phenomenon can be explained by the fact that the surfactant AOT initiates structural changes and it is able to increase the solubility of water in the fuel through the formation of reverse micelles. The relative standard deviation of the measurements is presented in **Table 6**.

The experimental data shown in **Figure 13** demonstrate the dependence that the solubility of water in gasoline increases with the growing number of carbon atoms in the alcohol molecule. The greatest values of water content are observed in the case of an addition of AOT and mixtures of AOT and MTBE in a range of concentrations from 10^{-5} to 10^{-3} mol/l. Samples of fuel containing AOT and MTBE were very cloudy, which can be probably the result of reverse micelles formation. The hydrophilic part of the surfactant AOT creates the micelle cores, which are filled with deionized water and thus, a quick rise of solubility of water is noticed. The association phenomena are dependent on a type of hydrophilic components, which are able to act as cosurfactants, which is shown in the schematic diagram in **Figures 11** and **12**. The components present in reverse micelles lead to an increase in micelle's size and water solubility, and they promote the change of structure with formation of microemulsion.

Figure 13 shows the higher surfactant AOT concentration, the higher amount of water in the modified fuel. In the presence of MTBE, the content of water is higher compared to samples including various alcohols (3%, v/v). At first, it may be explained that hydrophilic components enhance polarity of gasoline mixture and cause an increase in the solubility of water. Larger amounts of the additives may not act as cosurfactants and furthermore they can delay association of surfactant AOT into reverse micelles with water pools. Second, alcohols methanol and ethanol contain short hydrocarbon chains, therefore due to their low molecular weights they cannot join the micelles. As a result of that, water solubility in gasoline consequently achieves low level and the situation is improved only by an increase in the concentration of

Molar concentration AOT [mol/l]	2.25×10^{-2}	1.13×10^{-2}	5.63×10^{-3}	1.88×10^{-3}	6.25×10^{-4}	2.09×10^{-4}	6.95×10^{-5}
Relative standard deviation for AOT (RSD)	±0.048	±0.051	±0.049	±0.086	±0.154	±0.161	±0.225

Table 6. Relative standard deviation values for content of water measurements. Source: own research.

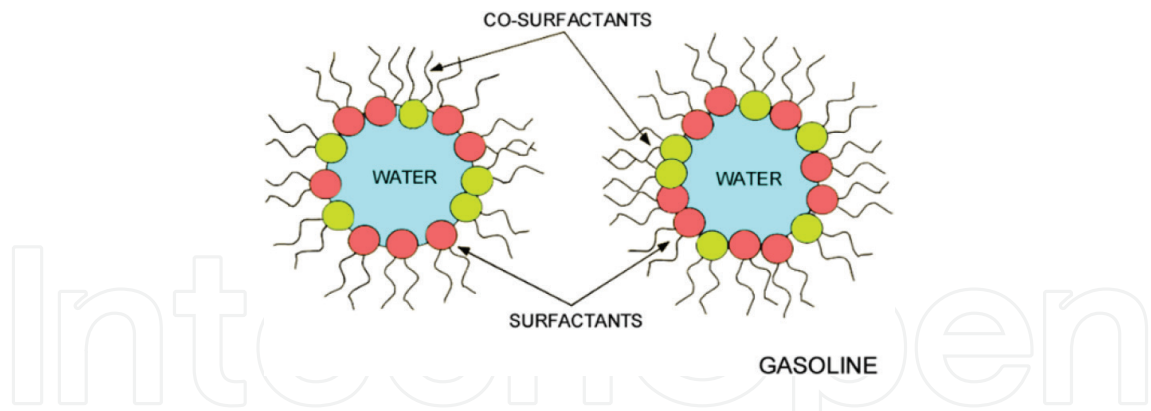


Figure 11. Reverse micelles formed in gasoline modified with hydrophilic additives and surfactants [1].

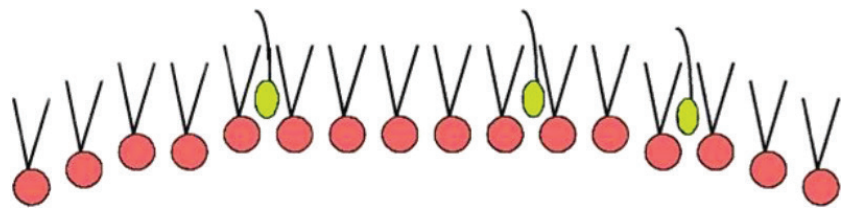


Figure 12. A scheme of solubilization site for alcohols [1].

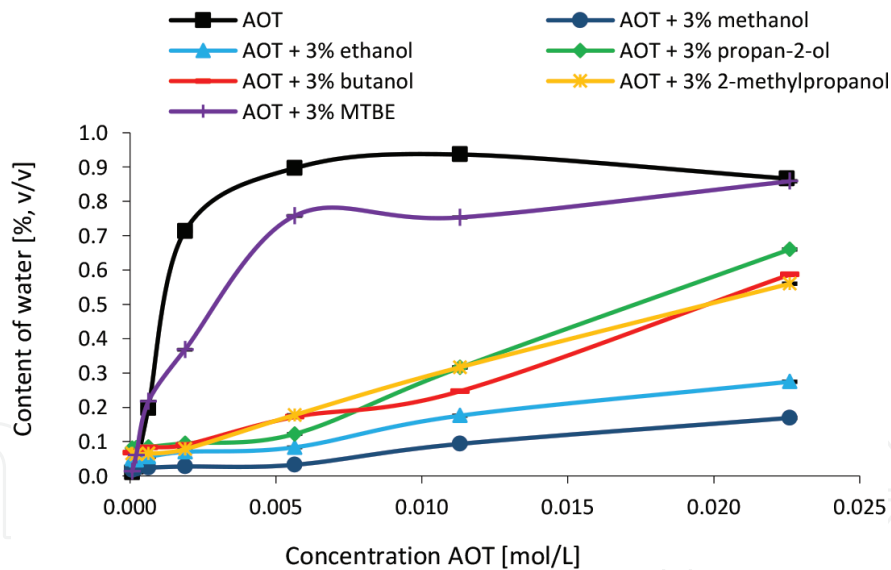


Figure 13. Solubility of water in gasoline containing hydrophilic additives (3%, v/v) and AOT.

surfactant AOT. The ether MTBE has a higher molecular weight and a branched hydrocarbon chain; therefore, in the presence of a small amount of AOT it is possible to enhance the water content significantly. In comparison to methanol and ethanol, such alcohols as propan-2-ol (IPA), 2-methylpropanol (IBA), and butanol (BuOH) have ability to be highly included in micelles, because of their higher molecular weights and amphiphilic properties. Solubility of water caused by the tested alcohols is low and very similar to basic gasoline. Only an addition of MTBE significantly improves water solubility (Figure 13). The impact of the additives changes in the following order: AOT > AOT/MTBE > AOT/IPA < AOT/IBA > AOT/BuOH >

AOT/EtOH > AOT/MeOH. Similar results were obtained in the case of an addition of AOT, MTBE, and the alcohols in the amount of 2% (v/v) in our previous studies [1].

5.2. Conducting properties improvement of modified gasoline

Initial studies demonstrated that electrolytic conductivity of basic gasoline and basic gasoline previously saturated with an addition of deionized water (1%, v/v) was 0 $\mu\text{S}/\text{cm}$. **Figure 14** shows the presence of only AOT caused a sudden and fast increase in electrolytic conductivity even at a concentration of 2×10^{-4} mol/l. The relative standard deviation of measurements is shown in **Table 7**. Yet, the conductivity achieved the value 0.16 $\mu\text{S}/\text{cm}$ and next remained on a constant level above the concentration of 1.88×10^{-3} mol/l. The highest values were obtained after modification with MTBE (3%, v/v). While the conductivity achieved the level of 0.19 $\mu\text{S}/\text{cm}$, it did not change with the increasing concentration of AOT. The lowest values were observed in the case of an addition of 3% MeOH (0–0.02 $\mu\text{S}/\text{cm}$) and EtOH (0–0.05 $\mu\text{S}/\text{cm}$). Nonetheless, higher branched alcohols (IPA, IBA, and BuOH) with a higher molecular weight significantly caused an increase in conductivity. The anionic surfactant AOT in the presence of MTBE and water generated the highest values due to the formation of reverse micelles. It is reported in the literature that electrolytic conductivity is very sensitive to the microemulsion system structure [92]. The occurrence of conductivity percolation is revealed due to an increase in the droplet size, interactions and the exchange rate of substances between droplets. The percolation threshold coincides with the formation of the first clusters of droplets [93]. The change of electrolytic conductivity demonstrates the alteration of the reverse micellar microstructure and after that the percolation

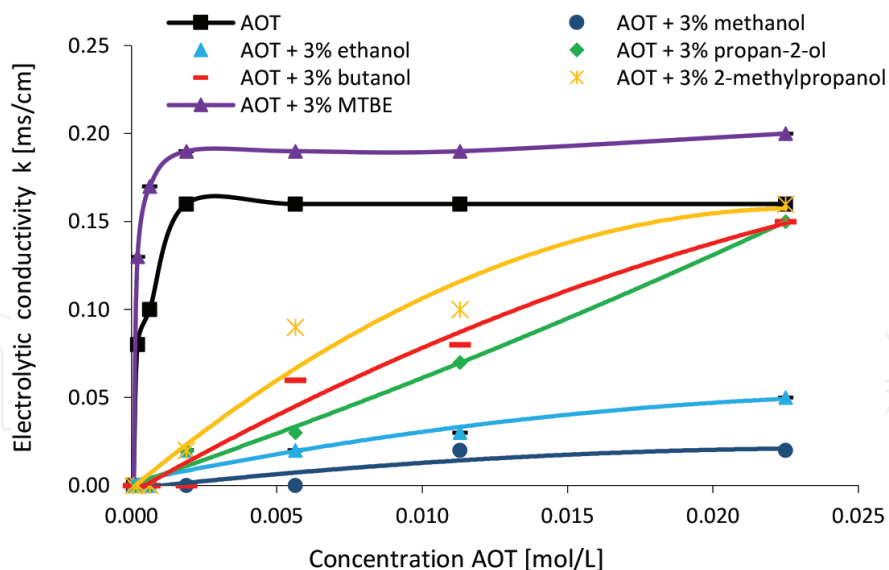


Figure 14. Conductivity of gasoline containing hydrophilic additives (3%, v/v) and AOT.

Molar concentration AOT [mol/l]	2.25×10^{-2}	1.13×10^{-2}	5.63×10^{-3}	1.88×10^{-3}	6.26×10^{-4}	2.09×10^{-4}	6.95×10^{-5}
Relative standard deviation for AOT (RSD)	± 0.084	± 0.178	± 0.180	± 0.567	± 0.221	± 0.178	± 0.189

Table 7. Relative standard deviation values for electrolytic conductivity measurements. Source: own research.

transition occurs. It is reported that conductivity is firmly related to droplet diameter, however, a temperature, the presence of external entity, or the composition of the microemulsion system also have an influence on the conducting properties of reverse micelles. Microemulsion is able to transport charges and affects the changes in the electrolytic conductivity [1].

5.3. The effects of additives on interfacial tension

In preliminary studies, it was indicated that interfacial tension at the interface of basic gasoline/deionized water was 27.16 mN/m. The basic gasoline saturated with 1% of deionized water demonstrated the value equal to 25.12 mN/m. **Figure 15** shows the influence of various additives on interfacial tension at the gasoline/water interface. At the abscissae of **Figure 15**, a common logarithm (log to base 10) of the molar concentration c [mol/l] of the surfactant AOT was used to present the interfacial tension isotherms in a clearer way. The relative standard deviation of measurements is shown in **Table 8**. The decrease in interfacial tension depends

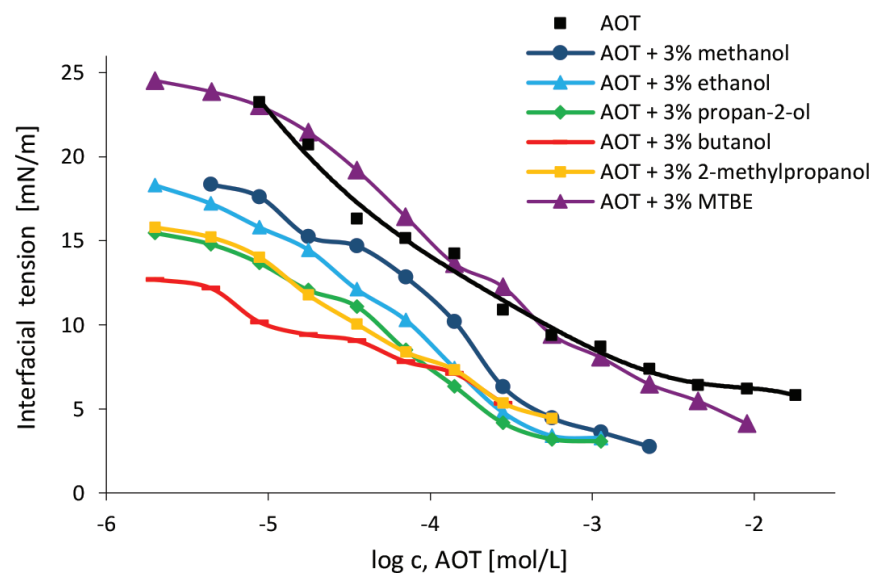


Figure 15. Interfacial tension isotherms at the modified gasoline/water interface.

Molar concentration AOT [mol/l]	1.49×10^{-2}	7.43×10^{-3}	3.72×10^{-3}	1.86×10^{-3}	9.29×10^{-4}	4.65×10^{-4}
Relative standard deviation for AOT (RSD)	0.011	0.008	0.026	0.028	0.031	0.018
Molar concentration AOT [mol/l]	2.32×10^{-4}	1.16×10^{-4}	5.81×10^{-5}	2.9×10^{-5}	1.45×10^{-5}	7.26×10^{-6}
Relative standard deviation for AOT (RSD)	0.032	0.037	0.023	0.041	0.015	0.016

Table 8. Relative standard deviation values for interfacial tension measurements. Source: own research.

on concentration of the surfactant AOT and the type of an additive. Interfacial tension isotherms of gasoline samples with AOT (23.2–5.8 mN/m) and with AOT and 3% MTBE (24.5–4.12 mN/m) have a similar course. Alcohols BuOH (12.7–5.3 mN/m), IPA (15.5–3.0 mN/m), and IBA (15.8–4.4 mN/m) showed the greatest surface activity. The effect of examined gasoline additives can be presented in the following order: AOT/BuOH > AOT/IPA > AOT/IBA > AOT/EtOH > AOT/MeOH > AOT/MTBE > AOT.

6. Conclusions

The multifunctional anionic surfactant AOT causes an increase in the solubility of water and electrolytic conductivity in gasoline. The obtained properties are the result of the association phenomenon of the surfactant and formation of reverse micelles comprising water pools in the hydrophilic micelle cores. Alcohols containing higher number of carbon atoms in their molecule lead to an increase in the solubility of water. Yet, the compounds may reduce the positive effect of the surfactant AOT on water solubility in gasoline. The results showed that some examined additives may act as cosurfactants.

Alcohols with highly branched hydrocarbon chains (isopropanol, isobutanol, and butanol) essentially increase the electrolytic conductivity. Modification of gasoline with the surfactant AOT and ether MTBE indicated the highest increase in electrolytic conductivity because of the formation of reverse micelles, which are able to transport charges.

The effect of the addition of AOT is the decrease in the interfacial tension at the water/gasoline interface. The decrease depends on the surfactant concentration and type of hydrophilic additives. The lowest values were observed in the presence of butanol, isopropanol, and isobutanol. The examined components have an influence on the interfacial tension, electrolytic conductivity, and the solubility of water in the same order: butanol > 2-methylpropanol > propan-2-ol > ethanol > methanol > MTBE. The research results demonstrated strong relationship between the length of the hydrocarbon chain, the molecular weight of hydrophilic components, and the tested properties of gasoline.

The conducted studies are innovative and can significantly contribute to an increase in knowledge and research of new water-in-gasoline emulsion (WiGE) fuel. The fuel with the addition of hydrophilic oxygen components in the presence of small amounts of surfactants and water may have unique properties. Oxygen compounds have a lot of useful properties, including antiknock properties, enhancing octane number, and they can be produced from renewable agricultural raw materials. Gasoline as an emulsion may have a beneficial effect on the combustion process, and the result is the almost complete combustion of hydrocarbons to the low toxic gases and the absence of carbon black among combustion products. The presence of water in gasoline reduces fuel consumption, increases engine power, decreases the temperature of its work, thus reducing emissions of volatile organic compounds, NO_x, SO₂, CO, and particulate matter. The use of water in fuel can be a unique chance for development of global economy in terms of energy production. The research may contribute to the commercialization of new environmentally friendly fuel that may provide an alternative source of energy for spark-ignition engines in the future.

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