The use of Alcohols and their Compounds as Biofuel and Gasoline Blends

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Abstract
This article presents the quality requirements for bioethanol using as a biofuel or a gasoline blend. There were discussed the blends of gasoline with bioethanol. Then, there was characterized the properties of ethanol in direction its use as a biofuel. Next, there were discussed both benefits and difficulties resulting from its use. Then, for comparison there was described the possibility of using methanol and heavy alcohols as biofuels.

Keywords: Biofuels; Bioethanol; Fuel properties; Heavy alcohols; Methanol

Introduction
The limited resources of fossil fuels, their high costs and harm to the environment made it necessary to look for alternative fuels. Biofuels came opposite these problems. The Directive [1] defines biofuels as liquid or gaseous fuel for transport produced of biomass. According to the EU directive [1] a biomass is defined as the biodegradable fraction of products, waste and biological origin residues from agriculture (including plant and animal substances), forestry and related industries, including fisheries and aquaculture, and the biodegradable fraction of industrial and municipal wastes. The use of biofuels, which are renewable energy sources allows a reduction in supplying and consumption of petroleum, have ecological aspects (reduction of emissions of toxic compounds into the atmosphere, reducing the greenhouse effect, biodegradability) and allows to create new jobs in areas dealing with the location of plants producing them. European law [1] assumes that the share of biofuels in overall consumption of petrol and diesel for transport is expected to reach 10% by 2020. In addition, Member States [2] requires the introduction on the market the petrol with max. Oxygen content is 2.7% and max. Ethanol content is 5%. The Act [3] classified for bio-components used as fuel additives: bio methanol, bioethanol, an ester, biodimethylether, pure vegetable oil, liquid bio hydrocarbons, bio propane-butane, liquefied biomethane, compressed biomethane and bio hydrogen, which are produced from biomass for using to the preparation of liquid fuels and liquid biofuels. Laws [3,4] take for liquid biofuels:

1. Motor gasoline containing more than 10% by volume of biocomponents or more than 22% by volume of ethers,
2. Diesel containing more than 7% bio-components,

According to the Act [4] and the EU Directive [1] biocomponents meet the criterion of reducing greenhouse gases, if it reaches a level of at least 35% until 31 December 2016, 50% from 1 January 2017 and at least 60% from 1 January 2018, for biofuels and bio liquids produced in installations in which production started on 1 January 2017 or later. According to the Directive [1] biofuels should be used for reducing greenhouse gas emissions to at least 6% by 31 December 2020, compared to the EU average of greenhouse gas emissions throughout the life cycle per unit of energy from fossil fuels in 2010. In March of 2007, The European Council approved the implementation of a package of 3 x 20%, according to which Poland has committed itself to 2020, in relation to 2005 achieve:

1. Reduction of CO2 emissions by at least 20%,
2. Increase energy production by using the renewable sources to 20% in energy balance and increasing the share of biofuels to 10%,
3. Reduction of energy consumption by 20%.

The use of biofuels meets the applicable regulations of the European Union, which imposes emissions standards limit in new vehicles sold. Since 1993 held true EURO 1 standard (for cars and light trucks), then since 1996 EURO 2 standard (for cars), since 2000 EURO 3 standard (for all vehicles), since 2005 EURO 4 standard (for all vehicles), since 2009 EURO 5 standard (for passenger cars and light duty regulations) and from 2014 EURO 6 standard. Below in Tables 1 and 2 provides various permissible emission norms for vehicles with gasoline and diesel. The Directive [5] assumes a significant reduction in emissions of nitrogen oxides in exhaust gases connecting with introduction of Euro 6 relative to Euro 5 in vehicles with compression-ignition engines, in order to improve air quality and comply with emission limits. Achieving these limit values is necessary without having to forego the advantages of diesel engine in terms of fuel consumption, emissions of hydrocarbons and carbon monoxide. For the purposes of this study focuses on the use of alcohols as self-contained biofuels or gasoline blends. The following alcohols were taken into account:

1. Bioethanol,
2. Biomethanol,
3. Heavy alcohols (propanol, butanol, pentanol).

The biggest use has an ethyl alcohol.

The use a Bioethanol as a Biofuel
Quality requirements for bioethanol
Ethyl alcohol can be used in pure form as self-contained fuel or...
in a gasoline or diesel blends. According to current EU legislation it is widely used as a 5% additive to gasoline (in accordance with the European standard for diesel fuel to DIN EN 228). The standard allows to use it also in processed form, after the esterification process, as the ethyl-tert-butyl ether (ETBE – 47% of ethanol and 53% of isobutene), in an amount not exceeding 15%. It can also be used in the form of the ethyl ester of higher fatty acids in a mixture with diesel oil and mixtures of these esters and alcohol with diesel fuel (bioxdiesel). The use of bioethanol as an additive to gasoline requires the prior dehydration, which is regulated by the relevant regulations [6,7]. Quality requirements of bioethanol used in the composition of liquid fuels are given in Table 3 [6]. The maximum water content of bioethanol used in the composition of liquid fuels are given in Table 3 [6]. The maximum water content of bioethanol used in the composition of liquid fuels are given in Table 3 [6].

### Characteristics of bioethanol as a fuel:
Bioethanol properties which affect its use as a bio-component fuel:

**Table 4:** The Octane number values for gasoline with 10% ethanol blended.

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Minimum</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power in temp. 20°C</td>
<td>%</td>
<td>99,6</td>
<td>-</td>
</tr>
<tr>
<td>Water content</td>
<td>%</td>
<td>-</td>
<td>0,1</td>
</tr>
<tr>
<td>The content of chloride ions</td>
<td>g/kg</td>
<td>-</td>
<td>0,04</td>
</tr>
<tr>
<td>Acid content expressed in acetic acid</td>
<td>%</td>
<td>-</td>
<td>0,007</td>
</tr>
<tr>
<td>The content of carbonyl compounds based on acetaldheyde</td>
<td>g/l</td>
<td>-</td>
<td>0,2</td>
</tr>
<tr>
<td>Methyl alcohol content</td>
<td>%</td>
<td>-</td>
<td>0,2</td>
</tr>
<tr>
<td>Copper content</td>
<td>mg/kg</td>
<td>-</td>
<td>0,1</td>
</tr>
<tr>
<td>Dry residue evaporation</td>
<td>g/l</td>
<td>-</td>
<td>0,02</td>
</tr>
<tr>
<td>The higher alcohols content</td>
<td>%</td>
<td>-</td>
<td>2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Gasoline base</th>
<th>Ethanol</th>
<th>Mixture 10% ethanol</th>
<th>90% gasoline base</th>
</tr>
</thead>
<tbody>
<tr>
<td>(RON + MON)/2</td>
<td>87</td>
<td>112,5</td>
<td>89,35</td>
<td></td>
</tr>
<tr>
<td>Badawcza liczba oktanowa RON</td>
<td>92</td>
<td>129</td>
<td>95,7</td>
<td></td>
</tr>
<tr>
<td>Badawcza liczba oktanowa MON</td>
<td>82</td>
<td>96</td>
<td>83</td>
<td></td>
</tr>
<tr>
<td>Czułość oktanowa (RON - MON)</td>
<td>10</td>
<td>33</td>
<td>12,7</td>
<td></td>
</tr>
</tbody>
</table>

**Octane number:** The octane number defines the resistance to the uncontrolled, spontaneous combustion of fuel for spark ignition engines, which can cause knocking combustion (detonation). As shown in Table 4 the octane number for bioethanol is 112, 5 and it is higher than for gasoline, which has a value of 87. The addition of this component into petrol results a proportional increase of the octane number the whole mixture to 89, 35 (in the case of a mixture of 10% alcohol and 90% gasoline). The high octane number allows increasing the compression ratio of the engine and provides the higher efficiency. The combustion is possible even in heavy duty engines. The Octane number values for gasoline with 10% ethanol blended are presented in Table 4 [8].

**Calorific value:** The calorific value of bioethanol is low and amount to 21, 5 MJ/dm³, which is only 52% of the calorific value of the hydrocarbon gasoline (32, 5 MJ/dm³). Therefore the addition of bioethanol lowers the energy value of gasoline-alcohol blend. While the content of alcohol in the form of ethyl tertiary butyl ether at a lesser extent (ETBE) affects to the calorific value of gasoline, which amount to 27,3 MJ/dm³ for ETBE [8].

**Corrosivity:** The gasoline and ethanol blends have increased acidity in comparison to hydrocarbon fuels. The result is a greater affinity for metals and their alloys, and hence an increase of corrosiveness. Low water content affects the corrosive properties of ethanol. It is therefore
necessary use of the additive corrosion inhibitors for gasoline blends with ethanol, to prevent tanks and pipelines from the negative effects of their interactions [8].

Affinity for water: Alcohols, soluble in water very well (up to 600 mg/kg in temp. 20°C), in contrast to hydrocarbon fuels. This causes an increase of water content in blend of petrol and alcohol, compared to pure gasoline. During the cooling the mixture or in the case of saturation of the gasoline with alcohol, following its initial cloudiness, and then split in the gas phase (upper, poor in ethanol) and the aqueous phase (the lower, 75% ethanol). After stratification of the gasoline-alcohol blend, gas phase always has a lower octane number, which may result in the detonation combustion of the fuel in the engine. The aqueous layer is not suitable for combustion. To increase the tolerance of gasoline with alcohol blends for the water the additive of ethers or higher alcohols can be used. There are stabilizers, through which it is possible exploitation the gasoline with alcohol blends in temperatures up to -30°C in winter. The presence of water in gasoline-alcohol blends reduces their biological stability. Such fuels are more susceptible to microbial growth than hydrocarbon gasoline and require special care in the process of storage and distribution [8].

Volatility: A blend gasoline with ethanol is more volatile than gasoline without alcohol. This is due to the fact that pure ethanol has a lower vapor pressure than conventional gasoline. Ethanol was added to the gasoline in an amount of 5-10%, increases the vapor pressure of the mixture relative to the vapor pressure of gasoline base. An excessive increase in vapor pressure of the gasoline-alcohol blends can lead to vapor locks and uneven engine running during the summer. The high heat of evaporation of ethanol may result in cooling of the air-fuel mixture due to evaporation of the fuel in the intake manifold. This is an unfavorable phenomenon that may occur during start-up [8].

Types of ethanol fuel blends with gasoline used practically

There are the following ethanol fuel blends with other fuels [8]:

1. E10 constituting 10% ethanol and 90% gasoline. It can be used in the US FFV (Flexible Fuel Vehicles) adapted to supply different types of liquid fuels and their blends and for cars manufactured after 2000. The change in FFV consists of using made of alloy pistons with increased resistance to high temperatures, injectors and supply system modification. To facilitate the starting FFV are equipped with electronic controls power supplies, adapting the fuel to working conditions and ambient temperature.

2. E20, consisting of 20 vol. % of bioethanol and 80% vol. of gasoline, used mainly in Brazil for engines adapted to burn this type of fuel.

3. E85 (commonly known as ethanol fuel), which is a mixture of 70-85% ethanol and 15-30% hydrocarbon fuel. Among others it is used on a large scale in Brazil and the USA. In Europe, they work on its greater popularization, in which the Sweden has a large share. E85 can be used only in the type of FFV vehicles. In Brazil, about 80% of all sold cars sold are just this type of vehicles.

4. E95, that is biofuel for compression ignition engines (diesel engines), which is a mixture consisting of 95% vol. of bioethanol and 5% by volume of additives for improving its parameters. The fuel found applicable only in large diesel engines, used to run in properly adapted trucks and buses. This fuel is a product offered on a small scale. In Europe, E95 is used in Sweden.

5. Ethanol fuel called EtaMAX D, designed to supply diesel engines. The fuel consists of: bioethanol (90%), a chemical compound called Beriad 3540 (7%), which facilitates the auto-ignition of alcohol, EMTB (methyl tert-butyl ether) and isobutanol and corrosion inhibitors. Swedish company Scania uses this fuel to power diesel engines used in public transport buses in Stockholm.

6. E100 made of bio-ethanol of 96% by volume without admixture of gasoline, the remaining amount of 4% by volume of water, which the total isolation in the distillation process is not possible. The fuel is offered only in Brazil and Argentina. Fuel is not suitable for use in cold and transient climates due to problems with starting the engine at ambient temperatures, below 15°C.

Advantages and disadvantages of the use of bioethanol as a fuel

Advantages of using bioethanol are as follows [9-13]:

1. Higher octane number than gasoline, which result in increasing of compression ratio,
2. Enough antiknock value to replace gasoline,
3. Wider limits of combustibility than gasoline,
4. Increased propagation velocity of the flame (about 20-30%),
5. A higher heat of evaporation, thereby evaporating the alcohol in the combustion chamber before the combustion cool engine efficiently (higher filling factor),
6. As an oxidant reduces the emission of toxic combustion products such as carbon monoxide, nitrogen Oxides, particulate matter, hydrocarbons (benzene, 1,3-butadiene),
7. Reduction of sulfur content in the exhaust gas,
8. Reduction of carbon dioxide emissions,
9. Lower toxicity,
10. It is possible to supply with poor mixtures due to the low bottom ignition limit.

The bioethanol properties, unfavorable from the point of view of its usefulness as a biofuel are following [9-11,13]:

1. Low calorific value, resulting in higher fuel consumption
2. Lower energy density
3. Corrosive effects on the lead, aluminum, iron and brass
4. Low brightness of the flame
5. Low vapor pressure and high latent heat of evaporation, which makes it difficult to start the engine at low temperatures
6. Limited miscibility with water, or stratification due to the small amounts of water, so it makes necessary to use stabilizers
7. Greater volatility
8. Causing growth of acetaldehyde emissions and growth of emission and vapor pressure [12,14]
9. The low value of the cetane index
10. Low ignition temperature
11. Acceleration of water absorption, resulting in fuel turbidity and faster corrosion devices
12. Low boiling temperature which results in a higher propensity to form vapor lock
13. Low lubricity causing decrease in the durability of injection equipment
14. Causing the destruction of some elastomers and plastics
15. Reported the existence of smaller sizes particles of particulate matter generated by the combustion than in use of gasoline (more harmful particles).

**Environmental benefits:** Ethanol is considered for the most friendly for environment fuel due to the lower emission during the combustion process, as well as the fact of obtaining it from renewable raw materials. The advantage of using bioethanol is oxygen content [15], in contrast to the gasoline. This affects the increase the octane number of fuel which is beneficial from an environmental point of view. This contributes to reducing emissions of carbon monoxide, hydrocarbons (benzene), lead, sulfur oxides, nitrogen and particulates in the exhaust and reduces greenhouse gases. The oxygen content in ethanol is at a level around 35%, which reduces the emissions of CO in the exhaust gases about 12-30%. The addition of bioethanol of about 10% to gasoline blends increases the oxygen content in the fuel and improving the combustion process, reduces emissions of carbon monoxide CO on average 20% (17-33%), NO emissions about 15% and reduces the amount of emitted HC about 10%. The use of gasoline blends with bioethanol reduces the SO₂ content of about 30% by enhancing fuel amount of emitted HC about 10%. The use of gasoline blends increases the oxygen content in the fuel and improving the combustion process, reduces emissions of carbon monoxide CO on average 20% (17-33%), NO emissions about 15% and reduces the amount of emitted HC about 10%. The use of gasoline blends with bioethanol reduces the SO₂ content of about 30% by enhancing fuel amount of emitted HC about 10%

**Exploitation difficulties:** To adapt traditional spark ignition engine for use of pure bioethanol, due to the lower calorific value of the fuel, the regulation of ignition timing, the electronic engine control systems and the installing of a larger fuel tank is required. Due to the fact that bioethanol can corrode some of the elastomers and metals, some engine components may require a replacement. In addition, vehicles powered by E95 and E100 may have troubles with starting at low temperatures, because bioethanol weakly evaporates at this time. From the previously mentioned reasons, bioethanol usually mixes with gasoline in order to improve the ignition (E85 is a widely used blend). One of the most significant progresses in technology is the development of vehicles Flexible Fuel Vehicles – FFV, which may be powered by a wide range of mixtures of gasoline and bioethanol inclusive to E85. A motor control system in these vehicles automatically detects the type of the fuel used and adjusts the ignition properly [21]. There is no corrosion observed and even larger consumption of than which would result from the exploitation of petrol, after working up the engine to power with ethanol. In fact, in many cases even the increased service life of the engine (when it is powered by alcohol) was concluded, mainly due to the fact, that ethanol is not contaminated with engine oil as it may take place under the gasoline powered. Ethanol combustion is milder than the gasoline. Ethanol cools better the engine elements that are beneficial for candles, valves and warheads and pistons. The converter installation is not connected with any mechanical interference with the subassemblies of the car as it is on gas equipment. It is important, that after processing the car on ethanol powered there is no observed the decrease in torque, and even it was possible its increase by 3-5%. Since the installing of converter the car can drive on any proportion of gasoline and ethanol [20]. Rework the gasoline engine for ethanol supplying requires the carburetor modifications and possibly the ignition advance angle increasing. The carburetor modifying (more specifically larger - its jets) is necessary due to the fact, that for the combustion of alcohol less air is needed than for gasoline combustion (the reason for this is that the alcohol molecule consists of one atom of oxygen), because the fuel-air mixture obtained would be too weak for proper operation of the engine [22]. Alcohol may also be a fuel for diesel engine if the proper lubrication of injector nozzles will be ensured. Fuel blends with a large share of ethanol require the additives for improving the tribio logical properties of the fuel and its volatility [16]. The exceeding of the limit of the 30% bioethanol content in the fuel requires a proper adaptation of the engines, because ethanol fueled engines work defectively in temperatures below 5°C and ethanol shows corrosive effect on engine construction elements [18]. It cannot use of pure bioethanol directly as a fuel for diesel engines, but it should be injected into the air by the turbocharger of modern engines (in the evaporated form, below the 25% share in the diesel oil). This causes an increase of power and significant reduction of exhaust gas toxicity, maintaining the fuel consumption at the same level [18].

**The use of methanol as a biofuel**

Methanol has a very high calorific value, thus less heat is necessary to pick up for the cooling of the engine. However, it makes difficult to
start the engine unheated. High corrosiveness of methanol in relation to some metals causes the rapid consumption of engine components. Due to the fact, the diesel fuel and anti-corrosion components are added to methanol as the admixtures. The advantage of the use of methanol is that the water vapor and carbon dioxide are the products of its combustion, which is beneficial for the environment. Methanol is used as a engine fuel in pure form or as a gasoline blend in the form of MTBE. However, both the alcohol itself and its derivatives form with gasolines the toxic and carcinogenic compounds, therefore, its use is limited. Methanol is often considered as a fuel of the future, which can be used in new types of DMPC fuel cells, inside which it is converted into hydrogen [18]. Power of engine with gasoline and methyl alcohol effects on the external parameters of engine (maximum power, torque and general efficiency) advantageously and reduces toxic exhaust emissions. The addition of methanol causes significant differences in relation to the combustion of gasoline blends. The combustion carried out more dynamically especially in the initial phase and the combustion time is shorter. The result of the changes is greater maximum pressures, higher speed of pressure increment and of heat release. The size of the combustion parameters changes depends on the share of methanol in engine fuel. The proper use of a high antiknock resistance of methyl alcohol requires of raising the compression ratio about 1.5-2.0 units, which should contribute to increasing the overall efficiency of the engine, especially at partial loads [23].

Comparison of properties of ethanol and methanol in relation to the conventional fuels

Table 5 contains a comparison of some properties of methyl alcohol and ethyl alcohol with diesel fuel and gasoline. As the table shows, ethyl alcohol has improved properties in terms of calorific value, octane and cetane number in relation to the methyl alcohol [14].

The use of heavy alcohols

Heavy alcohols can be added to gasolines and especially to diesel fuel. However it is reported, that butanol can be used as a fuel for internal combustion engines, only with spark ignition. It has similar to gasoline energy value and evaporation heat. Butanol as a fuel or fuel additive for diesel engines has not been used so far [24]. The researches have shown that the use of butanol as a fuel is more favorable than ethanol. Butanol has a higher calorific value, which are 29.2 MJ/dm³. It has a relatively low heat of vaporization and it is less corrosive than ethanol (melting temperature -89.5°C, boiling temperature 117.2°C, flash temperature 36°C and self-ignition temperature 340°C). These properties increase its usefulness as both a gasoline additive, as well as biofuels. Currently butanol is used only as an additive to gasoline, because the engines operating only on this compound were not constructed [25]. According to literature reports, among many ethers, the heavy alcohol ethers have/l the best fuel properties (dipentyl ether (DNP) and dibutyl ether (DEE)), which the cetane number is above 90, the calorific value is 42 MJ/kg, and a flash temperature is greater than 25°C [15].

Summary

Currently, bioethanol is the most widely used biofuel. On balance, as a fuel, it constitutes as about 2/3 of global production. In Brazil, it is used for this purpose in more than 95%, in the US in more than 60%, and in the European Union in 5%. The largest share in the production of ethanol has Brazil and the United States (together 65% of production), Asia - 18% and Europe - 15%. Bioethanol is well suited for use as fuel in petrol engines. It is characterized by clean combustion process, which results in lower emissions of particulate matter, hydrocarbons and carbon monoxide. The biggest benefit of using ethanol is the potential for reducing of CO₂ emissions. Its use is justified by the fact that the energy using for the process is less than the energy obtaining from the combustion. The cars with traditional gasoline engines can use fuel with a maximum ethanol blended reaching 10%, without the need to adapt engine. While the use of pure alcohol requires construction and regulatory changes. Regulation the ignition, the engine electronic control systems and installing larger fuel tank is necessary. Due to the fact that the bioethanol may corrode, some the elastomers and metals and some engine elements may require a replacement. One of the most significant progresses in technology is the development of Flexible Fuel Vehicles (FFV) in which the engine control system automatically detects the type of the fuel used and adjusts the ignition respectively. After working up the engine to power of ethanol, it was not observed the corrosion or even larger using than what would result from the exploitation of gasoline. The use of methanol and its derivatives as an additive for gasoline is limited, due to the fact that forms with gasoline toxic and carcinogenic compounds. In addition, ethanol has improved properties in terms of calorific value, octane and cetane number in relation to the methyl alcohol. Other alcohols, such as butanol are used only as an additive to gasoline because it was not constructed engines operating only on these compounds.

References


<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Methanol</th>
<th>Ethanol</th>
<th>Gasoline</th>
<th>Diesel oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>kg/m³</td>
<td>791</td>
<td>789</td>
<td>740</td>
<td>840</td>
</tr>
<tr>
<td>Kinematic viscosity</td>
<td>cSt</td>
<td>0,8</td>
<td>0,9</td>
<td>0,6</td>
<td>4,0</td>
</tr>
<tr>
<td>Calorific value of the fuel</td>
<td>MJ/dm³</td>
<td>15,6</td>
<td>21,3</td>
<td>32,5</td>
<td>35,7</td>
</tr>
<tr>
<td>Calorific value of the blend</td>
<td>kJ/m³</td>
<td>3175</td>
<td>3650</td>
<td>3439</td>
<td>3475</td>
</tr>
<tr>
<td>Stoichiometric constant</td>
<td>kg/kg</td>
<td>6,4</td>
<td>9,4</td>
<td>14,9</td>
<td>14,6</td>
</tr>
<tr>
<td>Octane number MON RON</td>
<td>-</td>
<td>92</td>
<td>95</td>
<td>84</td>
<td>-</td>
</tr>
<tr>
<td>Cetane number</td>
<td>-</td>
<td>110</td>
<td>-</td>
<td>92</td>
<td>-</td>
</tr>
<tr>
<td>Content of C</td>
<td>kgC/kg fuel</td>
<td>0,375</td>
<td>0,521739</td>
<td>0,864865</td>
<td>0,870</td>
</tr>
<tr>
<td>Content of H</td>
<td>kgH/kg fuel</td>
<td>0,125</td>
<td>0,130435</td>
<td>0,135135</td>
<td>0,125</td>
</tr>
<tr>
<td>Content of O</td>
<td>kgO/kg fuel</td>
<td>0,5</td>
<td>0,341782</td>
<td>0,005</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 5: Properties of alcohols compared to diesel fuel and gasoline.
amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC.


