TECHNICAL UNIVERSITY OF CLUJ-NAPOCA

ACTA TECHNICA NAPOCENSIS

Series: Applied Mathematics, Mechanics, and Engineering
Vol. 69, Issue Special I, February, 2026

TRENDS IN THE USE OF NEW TYPES OF FUELS FOR THE FOUR-STROKE ENGINES

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Abstract: *Concerns over limited petroleum reserves, geopolitical instability in oil-producing countries and the effects of fossil fuel emissions over the environment have influenced the development of commercial gasoline blended with biofuels for four-stroke engines. Bioalcohols are fuels obtained from biomass and they contain C, H and O atoms in their molecules. In this paper, a comparative study was conducted between bioethanol and a blend of gasoline (90%) with bioethanol (10%), trying to understand where the quality differences come from and how bioethanol can influence te final quality of the formulated commercial product. Further, physicochemical analyses like density, viscosity, vapor pressure were performed for the products. Currently, the percentage of bioethanol added to gasoline is reconsidered for ecological reasons.*

Key words: *fuel, bioalcohols, gasoline, bioethanol, four-stroke engines.*

1. INTRODUCTION

The sustainability of fuels production refers to the ability to produce fuels, presently and in the future, without compromising the development opportunities of upcoming generations. This fundamentally requires the use of abundant or renewable raw materials and production processes that minimize environmental impact [1-3]. Bioalcohols are fuels obtained from biomass which contain C, H and O atoms in their molecules and present numerous advantages highlighted in other scientific studies [4-7]. However, bioalcohols production has also disadvantages, including: carbon emissions associated with agricultural maintenance, biomass transportation, biomass processing, as well as the transport, storage, and commercialization of fuels; food security concerns, since agricultural land is limited; deforestation for crops establishment, followed by soil erosion and loss of biodiversity, impact on groundwater and surface water resources [8,9]. The International Resources Panel has concluded that biofuels have varied impacts and, therefore, the life cycle of each biofuel must be evaluated individually.

Other disadvantages of biofuels include:¶

-hygroscopicity (the property of substances to absorb water vapor from the atmosphere) [10];

-bioethanol is miscible with water in any proportion. Gasoline and water are practically immiscible, with gasoline having a very low tolerance for water. If a small amount of water is present in bioethanol, it facilitates the dissolution of water in gasoline by forming a homogeneous ternary system of gasoline-water-ethanol;

- gasoline blended with ethanol containing excessive water can cause water sedimentation (upon cooling) and water accumulation in the fuel tank;
- a greater risk than sedimentation is the tendency of water to freeze at low ambient temperatures;
- the presence of water reduces the calorific value of the fuel, as water is non-combustible;
- bioethanol must be dried after production and stored under dry conditions. Nevertheless, fuel-biofuel blends can tolerate small amounts of water without resulting in a distinct phase.
- the calorific power (the main quality of a fuel) is lower for biofuels than for conventional fuels;

- carbon dioxide emissions in exhaust gases are, higher than those from conventional fuel (e.g., alcohol compared to diesel);
- viscosity and lubricity are, in some cases, affected when mixing biofuel with conventional fuel [11].

The production of eco-friendly fuels requires, besides to the introduction of advanced processes for converting petroleum fractions, additional operations to optimize the blending of petroleum fractions with other components [12]. Achieving the desired qualities of eco-friendly fuels involves a series of complex operations – the actual formulation – which consist of: selecting the components and blending them in the required proportions; incorporating specific additives; controlling the physico-chemical properties; monitoring and verifying the performance of the final product [13]. The components used in fuel blending can be divided into base components, correction components, and additives. Therefore, a commercial petroleum fuel is obtained by blending the following materials: base components in a proportion greater than 60%; correction components in a proportion less than 40% and additives in a proportion less than 1% [14].

Base components provide the essential characteristics of the final product and must meet specific requirements:

-they must be available in large quantities and at relatively low production costs;

-they should have basic properties close to those of the final product, so that the desired specifications can be achieved with the addition of small amounts of correction components and additives;

-they must exhibit high sensitivity to the supplement of small quantities of additives (i.e., the property targeted by the additive should undergo significant modification with a minimal additive dose);

-they must be chemically stable in order to maintain their properties during handling and storage;

-they should have sulfur content within the permissible limits for the final product, ensuring compliance after blending with other components;

-they must possess appropriate flow and atomization properties, consistent with the intended application of the final product [15].

Correction components are added to the finished petroleum product in order to improve specific properties such as: distillation range, cetane number, freezing point, viscosity, etc.
Additives are substances or mixtures of substances which, when added—usually in small amounts—to petroleum products, significantly enhance certain properties and may also impart new ones. With very few exceptions, modern petroleum products are no longer manufactured without the use of additives [16]. They serve to improve or correct certain qualities of petroleum products; this method is more cost-effective and simpler than reformulating the entire product, as it requires only small quantities of additives. Additives used in fuel reformulation must meet the following criteria: high effectiveness when added in small quantities; complete combustion without leaving deposits; no negative impact on other fuel properties; easy and complete solubility in the petroleum product; high chemical stability; availability through relatively simple production processes and at moderate costs [17].

2. MATERIALS AND METHODS

2.1 Analysis of gasolines obtained in different stages of refining

In this study, atmospheric distillation gasoline, hydrotreated gasoline, catalytic reforming gasoline and catalytic cracking gasoline, illustrated in figure 1, were analyzed.

Fig. 1. Gasolines from different stages of refining

Next, the four types of gasolines were characterized through the following physico-chemical analyses: density, viscosity, copper strip corrosion, STAS distillation, sulfur content and PONA analysis. Standardized methods, described below, were used to determine these properties [18-20].

Absolute density at 15 ⁰C is measured using the ASTM 1298-12 method which involves immersing a hydrometer into a cylinder filled with gasoline and allowing it to float freely, as as shown in figure 2. The apparatus consists of: a standardized hydrometer with a reading precision of 0.0005 g/cm³; a thermometer with a scale division of 0.5 °C (the scale must be graduated to allow temperature readings within the working range from -20 °C to +102 °C); and a transparent glass cylinder.

Fig.2 . Determining gasolines density with a hydrometer

The method used to determine conventional viscosity is the Engler viscometer method, according to the STAS 117-87 standard. This method involves measuring the flow time of a standard volume of product through a calibrated orifice under well-defined experimental conditions, and comparing it to the flow time of the same volume of reference substance at 20°C.

The determination of corrosive action using a copper strip was performed according to the ASTM D130-19 method. A clean and dry test tube was filled with 30 cm³ of a clear product, free from suspended particles or traces of water. The copper strip was inserted into the test tube within no more than one minute after the polishing process was completed. The test tube is sealed and maintained at 50 °C for 3 hours.

The sulfur content in petroleum products was determined according to the National Standard D2785-70, using the tubular furnace method. Approximately, 1 gram of sample is burned at a high temperature in a stream of purified air, at a controlled flow rate. The resulting sulfur dioxide is absorbed in hydrogen peroxide, where it is oxidized to sulfuric acid. The sulfuric acid is then titrated using a standard sodium hydroxide solution.

The STAS distillation of the gasoline samples was performed using the ASTM D86-20b method. The following equipment is used for the STAS distillation: a Wurtz flask containing 100 cm^3 of gasoline sample, a thermometer, a brass sheet condenser with a cooling bath and a graduated cylinder. During the distillation, the temperature is recorded every 10% volume according to the graduated cylinder, with T_1 representing the temperature at the first drop (0%). The distilled volume must not exceed 90–95%, so the final temperature is read when the distilled volume reaches 95% by volume.

The hydrocarbon class analysis of gasoline (PONA) was performed according to the ASTM 2159 method. The method combines a chemical separation scheme of hydrocarbon classes (paraffins, olefins, naphthenes, and aromatics) with a characterization technique for petroleum fractions, based on the correlation of two physically measurable properties with chemical significance.

2.2 Physico-chemical characterization of bioethanol and a blend of gasoline (90%) with bioethanol (10%)

Next, a comparative study was conducted between bioethanol and a blend of gasoline (90%) with bioethanol (10%), trying to understand where the quality differences between them come from and how bioethanol can influence the final quality of the formulated commercial product [17]. Further, physico-chemical analyses were performed on both products, including: absolute density at 15 ⁰C, kinematic viscosity at 40 ⁰C, vapor pressure and others mentioned at chapter 2.1.

The kinematic viscosity at 40°C of the gasoline samples was determined according to the ASTM D445-21 E1 method. The apparatus consists of an Ubbelohde viscometer immersed in a water bath at 40°C, in which a volume of liquid flows under the action of gravity. The kinematic viscosity is calculated based on the time required for the liquid to pass through a specific section of the calibrated capillary tube.

The vapor pressure of the products was determined under the conditions specified by the STAS 121-60 Standard using the Reid apparatus.

3. RESULTS AND DISCUSSION

3.1. Dissemination of physico-chemical properties for gasolines obtained in different stages of refining

This study evaluates the physico-chemical properties, compositional characteristics, and distillation behavior of four types of gasoline derived from distinct refining processes: atmospheric distillation, hydrotreated, catalytic reforming and catalytic cracking (shown in Table 1). The analysis aims to understand how refining affects fuel quality, performance potential in the four-stroke engines and environmental impact.

Atmospheric distillation gasoline has the lowest density (730 kg/m³), hydrotreated and catalytic reforming gasolines have similar densities (736 kg/m³) an catalytic cracking gasoline exhibits the highest density (759 kg/m³), indicating a heavier composition.

So, density and viscosity increase progressively from atmospheric distillation to catalytic cracking gasoline, reflecting the higher molecular weight and complexity of cracked products. For the viscosity analysis, all the samples analyzed exhibit low viscosities, characteristic to gasoline. The values differ slightly, with the highest being recorded for the catalytic cracking gasoline (1.053°E), which may influence its behavior in four-stroke engines. A slightly higher viscosity can lead to the formation of larger fuel droplets during injection or carburation. This affects the air-fuel mixture formation, reducing the uniformity of combustion. Also, a more viscous fuel evaporates more slowly, which can negatively impact combustion, especially during cold starts. This may result in higher emissions of unburned hydrocarbons and lower combustion efficiency. Combustion may become incomplete or delayed**,** leading to reduced engine performance, such as lower power output or increased specific fuel consumption**.** Incomplete combustion can contribute to the formation of deposits on valves, pistons, and within combustion chambers**,** affecting long-term engine operation.

The determination of corrosive action using a copper strip indicates the same value for all four types of gasoline, namely 3a, which represents a pronounced color change of the strip (bright red to golden).

Atmospheric distillation gasoline contains the highest sulfur content, respectively 320 ppm. Sulfur content sharply decreases after hydroprocessing, with reforming and cracking gasolines having ultra-low sulfur content (~0.1 ppm), essential for modern emission standards.

The PONA analysis reveals that: atmospheric and hydrotreated gasolines are rich in paraffins and naphthenes, which contribute to good combustion characteristics and stability. Catalytic reforming gasoline is dominated by aromatics (83.3%), with very low paraffins and olefins, reflecting the reforming process which converts paraffins and naphthenes into aromatics to boost octane number. Catalytic cracking gasoline contains olefins (30.74%) and aromatics (34.2%), which improve octane number but reduce oxidative stability and increase gum formation potential.

Fig. 3 shows the STAS distillation curve for atmospheric distillation gasoline. This type of gasoline has a broader boiling range with a higher final boiling point (205 ºC), containing more heavy-end components.

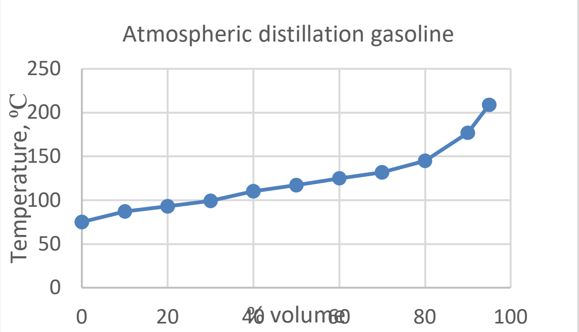

Fig.3 . STAS distillation curve of atmospheric distillation gasoline

In figure 4, the STAS distillation curve for hydrotreated gasoline is presented. Hydrotreated gasoline shows a wider boiling range with a lowest final boiling point, indicative of removal of heavier compounds and contaminants.

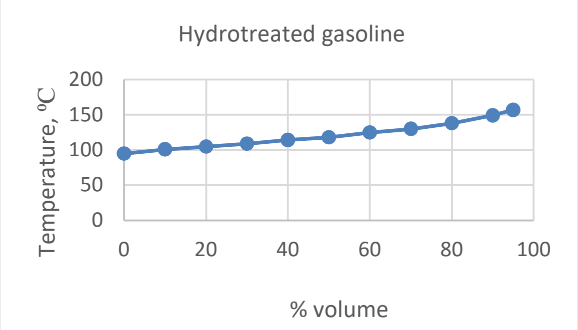

Fig.4 . STAS distillation curve of hydrotreated gasoline

Catalytic reforming gasoline exhibits an intermediate boiling profile, balancing light and heavy components, shown in figure 5.

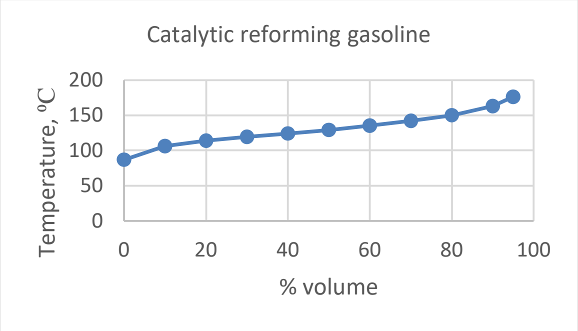

Fig.5 . STAS distillation curve of catalytic reforming gasoline

Catalytic cracking gasoline has the lowest initial boiling point and highest light fraction content (high evaporation at 100 °C), consistent with the production of lighter olefinic compounds (see fig.6).

The ASTM (STAS) distillation curve has limits that slightly depend on the season: the initial boiling point is no longer regulated but is around 40 °C; at 70 °C, between 20% and 50% of the gasoline must have evaporated (the percentage must not be too low to avoid high VOC emissions and not too high, otherwise ignition in the engine is difficult); the final boiling point is limited to 210 °C (if this value is exceeded, there may be a risk the gasoline does not burn completely in the engine, resulting in hydrocarbon and soot emissions).

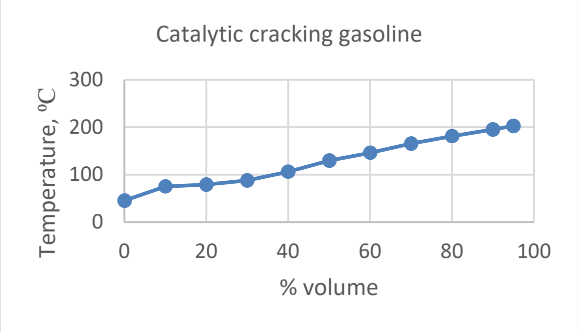

Fig.6 . STAS distillation curve of catalytic cracking

Therefore, gasoline is a light petroleum fraction with small molecules, containing between 6 and 10 carbon atoms per molecule, and boiling point ranges between 40–205 °C. Euro 5 gasoline is "reformulated," meaning modifications were made to Euro 4 gasoline by removing certain compounds and adding others so that it meets environmental requirements. The restrictions applied to the gasoline are as follows:

- the sulfur concentration must be a maximum of 10 mg/kg (ppm); therefore, the gasoline has been properly refined;
-the benzene concentration must not exceed 1%; this also ensures that the gasoline has been properly refined. Benzene is one of the toxic and carcinogenic volatile organic compounds (VOCs);
- the maximum content of olefins is 18% and aromatics 35%, which result in a gasoline that is less stable to oxidation (olefins) and burns with smoke (aromatics). This ensures that a proper gasoline formulation has been created. Additionally, the refinery is required to process higher-quality crude oil.
- the total oxygen concentration is limited to 2.7% due to corrosion concerns. Excessive temperature increase in the engine leads to the formation of nitrogen oxide (Nox) pollutants.
- The total content of alcohols and other oxygenated compounds (esters) is only limited by the requirement that total oxygen does not exceed 2.7%. These are considered volatile organic compounds that increase the concentration of VOCs in the air around storage facilities and gas stations [16].

The main components of automotive gasoline include catalytic reformate and catalytic cracked gasoline, to which various light fractions (e.g., from the HPR unit), C_5-C_6 isomerate, bioethanol, ethers (MTBE, TAME, etc.), and other additives are added. These components are blended in specific proportions to meet regulatory standards and performance requirements for automotive fuels [19].

3.2. Gasoline formulation

In most cases, bioethanol (ethyl alcohol derived from biomass) is used as the biofuel. In the gasoline delivery specification, ethanol is reported together with the content of ETBE (ethyl tert-butyl ether), which is synthetic, under the term „bio % (v/v)".

% (v/v) represents percent by volume because ETBE is synthesized from a hydrocarbon and ethanol, which may be either synthetic ethanol or bioethanol. ETBE contains 47% ethanol by volume. If the ethanol used is bioethanol (whether added directly or used in the synthesis of ETBE), the biofuel content is calculated as follows:

$$\% \left(\frac{v}{v}\right) bio = \% \left(\frac{v}{v}\right) Ethanol + 0{,}47\% \left(\frac{v}{v}\right) ETBE \qquad (1)$$

The delivery specification does not indicate a minimum biofuel content, as would be expected based on European directives [21]. Instead, only the percentage resulting from the above calculation is reported. Outside Europe, where the biofuel content is not restricted by the oxygen limit (maximum allowed is 2,7% w/w), gasohol with 10% or 15% ethanol is commonly used in the United States, and even 100% alcohol is used in Brazil. Engines running on bioethanol require only minor modifications to achieve maximum efficiency. However, due to the widespread use of bioethanol, parts of the Amazon rainforest have been cleared to make way for agricultural exploitation. Currently, the proportion of bioethanol added to gasoline is being reconsidered for environmental reasons. In present, the maximum content of bioethanol in Romania is 8%.

Further, a comparative study was conducted between bioethanol and a blend of gasoline (90%) with bioethanol (10%). The physicochemical characteristics of bioethanol are shown in Table 2.

Table 2.

Physico-chemical properties of bioethanol

Physico-chemical characteristic	Unit of measurement	Value
Absolute density at 15 ºC	kg/m^3	787
Kinematic viscosity	mm^2/s	1,2
Vapor pressure	kPa	17,2

Ethers added to gasoline are oxygen-containing compounds with branched molecules which increase the high octane numbers. Among the ethers currently used as fuel additives, we mention especially ETBE. There are also other chemical compounds known as "octane boosters": manganese compounds, nitrogen compounds and lead compounds. The emissions from the combustion of these compounds are toxic and they have been banned in the European Union. Other ethers, such as isooctane, ferrocene and iron pentacarbonyl are accepted. Ethers are added in small concentrations, up to a maximum of 3%, due to their high cost and to avoid exceeding the allowable oxygen content (2,7%), as oxygen is also present in alcohols. Pure alcohols are not used alone as fuels to prevent surpassing the permissible oxygen consumption. In Table 3 are presented the physicochemical characteristics of a blend of gasoline (90%) with bioethanol (10%).

Table 3.

Physico-chemical properties of a blend of gasoline (90%) with bioethanol (10%)

Physico-chemical characteristic	Unit of measurement	Value
Absolute density at 15 ºC	kg/m^3	765
Kinematic viscosity	mm^2/s	0,74
Vapor pressure	kPa	57

The blend's density is slightly lower than pure bioethanol; this is because gasoline typically has a lower density (around 720–780 kg/m^3), so when mixed, it reduces the overall density of the blend. Lower density can affect fuel atomization and combustion characteristics.

The blend has significantly lower viscosity than pure bioethanol. Gasoline has very low viscosity, so mixing it with bioethanol increases in a small proportion the viscosity. Lower viscosity generally improves fuel flow and spray characteristics in the engine but can also affect lubrication properties in fuel systems.

The vapor pressure of the blend is much higher than that of pure bioethanol. Gasoline typically has a higher vapor pressure (around 50–70 kPa), so the blend's vapor pressure increases considerably. Higher vapor pressure means the fuel evaporates more easily, which can improve cold starting but may increase evaporative emissions.

In the gasoline reformulation process, additives for various other purposes are also taken into consideration: antioxidants (to increase oxidation stability); detergents (to clean deposits in the engine); dyes dissolved in solvents (to color different types of gasoline).

For racing cars, certain additives are permitted that enhance engine performance but are also pollutants (methanol, acetone, nitrous oxide, nitromethane). The reformulation and additive processes take place at the refinery, which is the only entity that guarantees the quality of gasoline from all points of view.

4. CONCLUSIONS

Bioethanol as a biofuel offers environmental benefits but also presents challenges such as hygroscopicity, water miscibility and lower calorific value compared to conventional gasoline.

In Romania, the total content of alcohols and other oxygenated compounds (ETBE) is only limited to the requirement that total oxygen does not exceed 2.7%.

The physicochemical properties of gasoline vary significantly depending on the refining stage, affecting engine performance, fuel stability and emissions.

Blending gasoline (90%) with bioethanol (10%) modifies key fuel properties—reducing density and viscosity but increasing vapor pressure—which can influence combustion efficiency and evaporative emissions.

Fuel formulation requires careful selection and blending of base components, correction components and additives to meet performance, stability and environmental requirements.

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Table 1.

Physico-chemical characteristics of gasolines obtained in different stages of refining

Physico-chemical characteristic	**Unit of measurement**	**Atmospheric distillation gasoline**	**Hydrotreated gasoline**	**Catalytic reforming gasoline**	**Catalytic cracking gasoline**
Absolute density at 15 ºC	kg/m³	730	736	736	759
Conventional viscosity	°E	0,967	1,01	1,019	1,053
Corrosive action using a copper strip	-	3a	3a	3a	3a
Conținut de sulf	ppm	320	5	0,1	0,1
P	%w	51	50	11,5	24,04
O		4,6	2	0,2	30,74
N		26,33	30	5	11,02
A		18,07	18	83,3	34,2
STAS distillation					
Initial	°C	75	95	87	45
E70	%	0	0	0	9,5
E100	%	30	9,5	8,5	38
E150	%	81	92	80	63
E180	%	93	100	97	79,5
Final	°C	205	157	176	203

Tendințe de utilizare a noilor tipuri de combustibili pentru motoarele în patru timpi

Incertitudinile legate de sursele finite de țiței, controlul extracției acestuia de către țările instabile din punct de vedere politic și impactul emisiilor combustibililor fosili au influențat formularea benzinelor comerciale cu biocombustibili pentru motoarele în patru timpi. Bioalcoolii sunt combustibili obținuți din biomasă și conțin atomi de C, H și O în moleculele lor. În această lucrare, a fost realizat un studiu comparativ între bioetanol și un amestec de benzină (90%) cu bioetanol (10%), încercând să se înțeleagă de unde provin diferențele de calitate dintre ele și cum poate influența bioetanolul calitatea finală a produsului comercial formulat. În plus, au fost efectuate analize fizico-chimice precum densitatea, viscozitatea, presiunea de vapori pentru produse. În prezent, procentul de bioetanol adăugat la benzină este reconsiderat din motive ecologice.

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