

Chapter 1

Environmentally Clean Reformulated Aviation Gasoline

Olesia Kondakova and Sergii Boichenko

Production of fuel for aircraft engines is one of the priorities of world refining industry. Due to growing air traffic intensity, it is necessary to improve the fuel efficiency of aircraft and fuel quality. As soon as provision with high-quality fuel is a decisive issue of aircraft efficiency, saving and rational use of aviation fuels become of national importance.

Aviation gasoline blend components are obtained in various technological processes. The basic component in the production of gasoline is catalytic reforming at which the aromatization and isomerization of straight gasoline is the output. This increases its detonation resistance. Additional components with a high detonation resistance – alkylate, isooctane technical, pirobenzol, ethyl liquid, isopentane, and toluene – are entered into the composition of fuels (Table 1.1).

The main indicator of gasoline quality is its detonation stability. This is an ability of fuel to burn without detonation in piston engines with spark ignition; octane number has direct influence on operational and environmental performance of transport.

But today, all the known brands of aviation gasoline use tetraethyl lead as anti-knock additive in spite of its toxicity. Thus, for aviation piston engines, according to GOST 1012, aviation gasoline brands B-95/130 and B-91/115, whose oil fraction boils within 40–180 °C, are produced. Today known brands of aviation gasoline are B-92 (TY 38.401-58-47-92) and B-70 (TY 38.101913-82) with low concentration of TEL. DEF STAN 91-90 Issue 3 reflects requirements for AVGAS 100LL, AVGAS 100, and AVGAS 80. According to ASTM D 6227, new aviation gasoline 82UL, which already contains TEL, is introduced, but its testing has not yet been completed. Having analyzed these documents, we have compiled a comparative table (Table 1.2) presenting TEL content in aviation gasoline [3]. The table shows

O. Kondakova (✉) • S. Boichenko
National Aviation University, Kyiv, Ukraine
e-mail: izabellac@mail.ru

Table 1.1 Characteristics of high-octane components [19–21]

№	Indicator	TEL ^a	Isooctane	Toluene	Benzene	Piropbenzene	Isopentane	Alkylate
1	Density at 20 °C, kg/m ³	1650	691.8–692.1	865–867	878–880	850	626.2	698–715
2	Boiling temperature, °C	80	99.15–99.35	110.6	80.1	80–175	27.85	40–180
3	MON ^b	0.1% addition can increase TEL on gasoline by 10 units	100–99	102.1	111.6	88	90.3	90
4	Maximum allowable concentration of working area, mg/m ³	0.0001	300	150	5	No data	900/300	No data
5	Hazard class	1	4	3	2	No data	4	No data

^aTetra ethyl lead^bMotor octane number

Table 1.2 Content of TEL in aviation petrol [22, 23]

№	Aviation petrol brand	Regulation	Content of antiknock agents	Name of antiknock agents
1	B-95/130	GOST 1012-72	3.1 g/kg	TEL
2	B-91/115		2.5 g/kg	
3	B-92	TY 38.401-58-47-92	2.0 g/kg	
4	B-70	TY 38.101913-82	0	
5	Avgas 80	DEF STAN 91-90 Issue 3	0.14 g/l	
6	Avgas 100LL		0.56 g/l	
7	Avgas 100		0.85 g/l	
8	82UL	ASTM D6227	0	Similar to automobile gasoline but without automotive additives
9	85UL	–	0	Oxygenate-free
10	91/96	–	Almost negligible	TEL
11	91/96UL	ASTM D7547	0	Ethanol-free, antioxidant, and antistatic additives
12	100/130	–	1.12	TEL
13	G100UL	–	0	Aromatic compounds such as xylene or mesitylene
14	100SF	–	0	Mesitylene
15	115/145 (“Avgas 115”)	–	1.29	TEL

the trend to reduction of TEL concentration in aviation gasoline, but almost all brands today contain toxic TEL. Therefore, the development of new environmentally friendly aviation gasoline is an urgent modern problem that needs solution.

One solution to this problem is the introduction of aliphatic alcohols, ethanol, methanol butanol, and other oxygenates into the aviation gasoline instead of tetraethyl lead.

Oxygenates include lower alcohols and ethers, which could be used as high-octane components of motor fuels. They are made of raw alternative materials, ethanol, methanol, and butanol, predominantly derived from coal, plant products, and heavy oil residues. The use of aliphatic alcohols expands resource potential for fuels production and often improves their quality. They can be primary fuel or used as additives for fuels of petroleum origin. Such fuels are characterized with better cleaning properties and better combustion and during combustion form less carbon monoxide and hydrocarbons.

The recommended concentration of oxygenates in gasoline is 3–15% (vol.). It is chosen to provide oxygen content in fuel within 2.7%. The reason is that this content of oxygenates, despite their lower value compared to petrol oil calorific value, will not have negative effects on engine power characteristics [1, 2].

In general, the use of alcohol as motor fuels and high-octane additives is known from the beginning of the last century, but their widespread industrial use began only in 80–90 years of the twentieth century.

Analysis of the existent literature [1–17] confirms that the addition of the aliphatic alcohol in fuels changes their properties.

The world centers of biofuel production in 2012 were the United States, Brazil, and the European Union. For example, in 2010, they concentrated 85% of the world production of biofuels; only the United States accounted for 48% global production of biofuels.

The most common type of biofuel – bioethanol – has 82% share in the total volume of fuel from biological raw materials produced in the world [5]. Its leading producers are the United States and Brazil.

Since today the use of aliphatic alcohols, methanol, ethanol, and butanol as additives to gasoline is widely distributed, we intend to analyze the prospects for aviation gasoline modification through the use of oxygenates and study the prospects of using alcohol as a part of aviation gasoline.

1.1 Methanol

Methanol is an alcohol with one carbon atom (CH_3OH). Methanol is one of the most promising fuels due to its high octane value [6]. As an additive to gasoline, methanol is used infrequently [3]. The most typical mixture used as motor fuel is M85 (85% methanol and 15% carbohydrates) and pure methanol M100 (100% methanol) [9]. In all cases, it allows to reduce the toxicity of engine exhaust. The use of absolute methanol is limited because of its high toxicity and corrosivity in relation to constructional materials, which reduce the life of the engine parts and quality of fuel, increasing the risk of emission of volatile organic compounds that can lead to depletion of ozone. The typical emissions of methanol combustion process include formaldehyde, while during the combustion of ethanol mainly acetaldehyde is emitted [10].

When using methanol, engine efficiency increases by 5–15% compared to gasoline. This is the high temperature of methanol vaporization, which reduces the temperature of mixture and increases the value of the fuel-air ratio and reduces the heat in the engine cylinders and exhaust gas temperature while maintaining capacity.

The most serious problems that complicate the use of methanol additive are its toxicity, poor solubility in hydrocarbons, and high water absorption. The tendency for mixture separation increases with decreasing temperature, leading to the accumulation of water and reduction of aromatic content in gasoline. To stabilize the gasoline-methanol blends, special additives, like propanol, isopropanol, isobutanol, and other alcohols, are used. The content of methanol in gasoline can be administered about 5% (vol.); in this case gasoline-methanol mixture is homogeneous [3].

Operating characteristics, energy performance, and starting quality of methanol fuel are improved after additional introduction of higher alcohols and esters. Such

fuel is called mixed alcohol fuel. Tests of one of the mixed fuel compositions have shown an increase in engine power by 4–7% and improved fuel economy (compared to pure alcohol) by 10–15%, while the content of nitrogen oxides is reduced by 25–30% compared with the work on gasoline [3].

Great interest to the use of methanol as a fuel is observed in countries with rich resources of coal and insufficient oil resources. Methanol can be produced from natural gas, coal, and biomass.

1.2 Ethanol

Ethanol is of much greater interest as an additive for fuel, because it is more soluble in hydrocarbons and less hygroscopic. Ethanol molecule consists of two carbon atoms – C_2H_5OH .

Widely known use of “gasohol” which is a mixture of gasoline with 10–20% ethanol in the United States and Brazil, with significant resources of alcohol derived from sugar cane. Sweden has introduced the state program of oil abandonment by 2020. In general, the use of ethanol as fuel is more interesting for the countries with rich plant resources, including Ukraine.

Petroleum gasoline is the largest source of man-made carcinogens. Therefore, the main environmental benefit of using ethanol as a part of mixed gasoline is the ability to exclude the use of highly toxic antiknock additive of metal and methyl tert-butyl ether (MTBE). With the addition of even 10% ethanol, gasoline is enriched with oxygen, which promotes more complete combustion and reduces emissions of carbon monoxide by 30%. Also, it decreases toxic emissions by 30% and emissions of volatile organic compounds – by more than 25. Using the mixture of gasoline and ethanol, E10, allows all the major car manufacturers to improve engine performance by adding 2–3 units of detonation resistance to fuel, prevents engine overheating, acts as antifreeze for fuel system, and does not cause contamination of the fuel injectors [10].

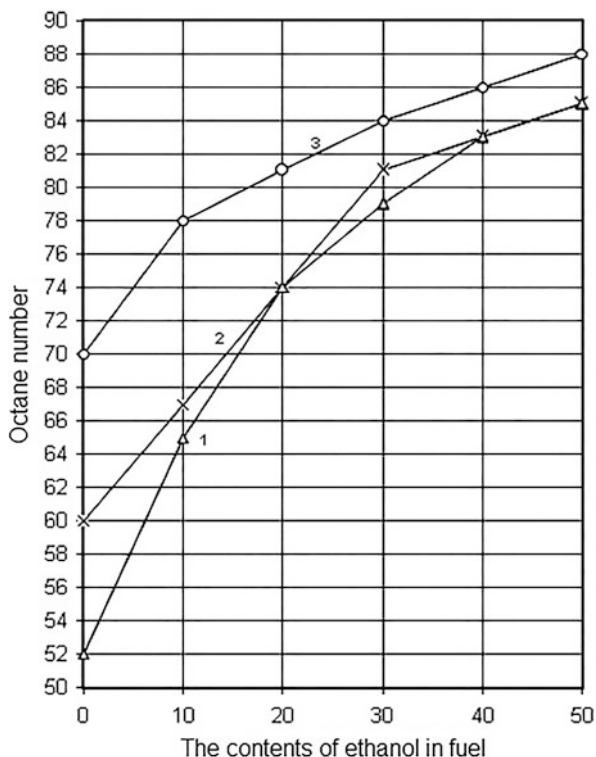
However, when using ethanol, there are a number of specific issues. Thus, bioethanol in its physical and chemical properties is significantly different from gasoline; it has higher octane number at 92 units by motor method and lower heating value (but higher corrosion activity); at the concentration of more than 12%, it may adversely affect the engine (Fig. 1.1).

The potential annual production of bioethanol from the available raw materials (molasses, corn, grain, sugar sorghum) according to the expert group “Ukrspirt” reaches 2 million tons; that will potentially replace 40% of gasoline consumed in Ukraine. The EU official documents consider Ukraine as a potential exporter of ethanol to Europe [11].

The value of efficiency of engines using alcohol gasoline in the whole range of the mixture is increased, so that the specific energy consumption per unit of power is reduced. Total fuel efficiency gradually increases with the percentage of ethanol in fuel [12].

Under real conditions, water inevitably gets into the gasoline-alcohol fuel during storage, transport, and use, which leads to phase separation. This problem does

Fig. 1.1 Ethanol affects the formation of gasoline octane number (Notes: 1 ishymbaysky gasoline; 2 B-59; 3 B-70 [5, 22])



not disappear gasoline-alcohol mixtures and when using absolute ethanol. Benzyl alcohol is proposed to be used as stabilizer [14].

Today authors [14] have developed recipes of biological motor fuel E85 (ТУ 24.6-35523958-001:2009 “motor biological fuel specifications”) that meets environmental and operational requirements to motor fuels for modern cars and takes into account raw materials of Ukraine.

1.3 Butanol

In addition to methanol and ethanol, aliphatic alcohol family includes propanol (three carbon atoms, C_3H_7OH) and butanol (four carbon atoms, C_4H_9OH) [15].

The use of butanol fuel is the next significant stage in the development of biofuels, the use of which has to meet the growing demand for environmentally friendly, renewable transport fuels [16]. Butanol is an alcohol (colorless liquid with a characteristic smell of fusel oil). The term “biobutanol fuel” is used to refer to butyl alcohol (butanol), which is produced from plant material.

Since butanol does not have corrosive properties, it can be transported through the existing infrastructure [15].

Butanol provides cleaner energy for duty cycle than ethanol or methanol and about 10% more than gasoline. Currently derived from corn, butanol attracted increasing attention of experts for its use as a fuel, in connection with the introduction of new highly efficient butanol fuel production technologies. It is possible that in the next 10–15 years, ethanol will lose its priority. The success is due to a number of advantages of butanol over ethanol, including:

- Butanol contains 25% more energy than ethanol: 110,000 BTU per gallon of butanol to 84,000 BTU per gallon of ethanol. Gasoline also contains about 115,000 BTU per gallon.
- Butanol is much less aggressive substance than ethanol, so it can be transported through the existing fuel pipelines, while ethanol must be transported by rail or water transport.
- Butanol can be mixed with gasoline.
- Butanol can completely replace gasoline, while ethanol can only be used as an additive to gasoline with the maximum content in the mixture not more than 85% and only after significant alterations in engine structure. Currently, the mixture of 10% ethanol is dominant in the world.
- Modified butanol has higher energy output than ethanol.
- Burning butanol produces no sulfur or nitrogen oxides, which gives significant advantage in terms of ecology.

Butanol fuel improves fuel efficiency and increases vehicle mileage per unit of fuel consumed [15]. Biobutanol fuel is produced from the same raw material – corn, sugar beets, sorghum, cassava, sugarcane, cornstalks and other biomass, and ethanol – but it can replace gasoline in equal measure.

Biobutanol fuel provides significant environmental advantages over petroleum-based fuel, including lower levels of greenhouse gas emissions. Biobutanol fuel will also reduce the emission of carbon dioxide into the atmosphere [15].

Today, biobutanol fuel can be added to gasoline in concentrations of up to 10% in Europe and 11.5% in the United States without engine modifications. In the future, there is potential to increase the maximum use of biobutanol fuel in gasoline to 16% by volume.

Biobutanol fuel, despite the presence of water, is less prone to separation than ethanol/gasoline, so it allows distribution through the existing infrastructure, not requiring modifications to facilities for mixing, storage, or refueling.

According to [17], the relative cost ceiling of biobutanol fuel is 0.73 of the cost of MTBE and 0.8 of the cost of bioethanol. Values are benchmarks in assessing the competitiveness of high-biobutanol fuel and as a component of motor gasoline.

The main advantages of biobutanol fuel include larger combustion heat than that of ethanol; therefore, it can be used in higher concentrations in gasoline. Obtaining biobutanol fuel from non-plant materials is an efficient way of recycling wastes of agriculture and timber industry.

Butanol is safer in exploitation, because it evaporates six times less intensively than ethanol and it is 13.5 times less volatile than gasoline. Vapor pressure of butanol by Reid is 2.3 kPa, gasoline is 31 kPa, and ethanol is 14 kPa. It makes butanol safer when used as an oxygenate and does not require any changes in the proportions

of mixture for winter and summer. Now it is used as an oxygenate in the states of Arizona, California, and others.

Butanol can replace gasoline as a fuel better than ethanol due to its physical properties, economy, security, and the fact that its use does not require modernization of motor vehicles. Until recently, no one knew of butanol as an alternative fuel, and its production has never been considered economically feasible [15].

Analysis of the existing literature leads to the conclusion that the addition of aliphatic alcohol affects the properties of traditional fuels [3–15]. We have compared the physical and chemical properties of different components of aviation gasoline.

According to Table 1.3, we see that the heat of combustion of ethanol, methanol, and butanol is significantly lower than the heat of combustion of aviation gasoline, causing increase in fuel consumption when using these alcohols. However, the oxygen content in the composition of oxygenates results in a higher completeness of combustion, so the difference in combustion heat is not so noticeable.

The main advantages of alcohols include their high-efficiency workflow and high detonation resistance (octane number between 99 and 111). The value of alcohol efficiency in the engines is over that for gasoline in the whole range of mixtures, so that the specific energy consumption per unit of power is reduced [16, 17]. Ignition limits of gasoline-ethanol mixture are broader than for pure gasoline [18].

The use of alcohol reduces emissions of products of incomplete combustion, reduces the formation of soot but at the same time increases emissions of aldehydes (as a product of incomplete oxidation of alcohols), and may also increase emissions of nitrogen oxides. This problem can be eliminated by adding water (5%) or 0.8% aniline to alcohol, heating inlet air to the engine [18]. The development and implementation of catalytic converters of exhaust gases can provide oxidation of aldehydes, acids, and other products of incomplete combustion of fuel alcohol to water and carbon dioxide [16].

The main disadvantage of gasoline-alcohol fuels is their phase instability under even small amounts of water and, consequently, limited mutual solubility of the components. Introduction of special additives for corresponding modification and stabilization to alcohols cannot overcome the emerging challenges. To ensure the stability of the alcohol-containing gasoline during production, storage and use it is necessary: remove water; use stabilizing additives or cosolvents, homogenizing system gasoline-water-alcohol. We recommend adding alcohol to gasoline directly before refueling [1].

The following stabilizers are offered for gasoline-alcohol mixtures: aliphatic alcohols C3–C12 with normal and branched structure, phenols, alkylacetate, ethers and esters and their organometallic derivatives, ketones, amines, surfactants and glycols and their ethers, aldehydes, ketals, acetals, alkylcarbonates, carboxylic acids, and mixtures of these compounds.

Among aliphatic alcohols, the most researched and effective is ethyl alcohol. Its high antiknock quality is known to have widespread use in internal combustion engines with forced (spark) ignition [18]. Equally efficient performance is typical for methanol, but its high toxicity and aggressiveness are significant obstacles for its application.

Table 1.3 Characteristics of physicochemical properties of alcohols and aviation gasoline [7]

Characteristics	Avgas 100 LL	B91/115	82 UL	Methanol	Ethanol	Butanol
Density at 20 °C, kg/m ³	Report	Does not normalize		792	789.3	810
Boiling point, °C	75–170	40–180	–	64.5	78.4	117.5
Freezing point, °C	Minus 58	Minus 60	Minus 58	Minus 98	Minus 114.1	Minus 90.2
Weight fraction oxygen, %	–	–	–	50	34.7	21.6
The heat of evaporation, kJ/kg	Not specified			1115	839.3	591.2
The heat of combustion, kJ/kg	43,500	42,947	40,800	24,000	26,945	35,520
Vapor pressure, kPa	38–49	29.3–47.9	–	–	17	8.4
Solubility in water	Insoluble			Unlimited		7.9
Octane number	Not determined 99.5	Not determined 91	Not determined 82	111 94	108 92	99,6 94
Research method						
Motor method						
Kinematic viscosity at temperature 20 °C	Not determined			–	1.52 cSt	3.64 cSt
TEL	0.56 g/l	2.5 g/kg	0	–	–	–
Limit content in gasoline by EN 228:2000	–	–	–	3%	5%	7–10%

Today growing interest is paid to butyl alcohol as an antiknock additive. Its advantage is that it can be transported through the existing fuel supply system and manufactured at plants producing ethanol with minor changes in technology. Butanol is less poisonous; its maximum allowable concentration is 10 mg/cm^3 , while ethanol is 5 mg/cm^3 and methanol – 1 mg/cm^3 .

Foreign countries are more active in terms of producing aviation fuel; today they have patented a wide range of alternative fuels for aviation. Specifically, the patent US 7559961 B2 presents alternative aviation petrol composite forming hydrocarbon mixture of alcohols. According to US 0011765 A1, the regulated brand includes ingredients extracted from biomass, but they should be distinguished from pure chemicals. In addition, this patent states that the water content in the fuel should not exceed 2%. If the water content is higher, it will grade fuel as unacceptable. Also, amines are used, which are quite expensive chemical components, production of which in Ukraine is not yet organized. The patent US 7553404 B2 mixtures include 60% traditional gasoline, butane, isopentane, and cyclohexane. Overall, 93% are mixed composite fuel. But all of them are expensive and therefore cannot be used for economic reasons [6].

Having analyzed the existing studies, we have formed an integrated comparative characteristic of physical, chemical, and environmental properties of alcohols (Table 1.4).

Table 1.4 Comparative physicochemical and environmental properties of alcohols

Alcohols	Properties
Methanol	Highest octane number (156 units)
	Improvement in fuel economy by 10–15%
	Engine efficiency increases by 5–15%
	High toxicity and aggressiveness on construction materials
	Content in the exhaust gases of nitrogen oxides is reduced by 25–30%
Ethanol	Octane number (132 units) is significantly higher than gasoline (82.5–98 units)
	Separation in the presence of water
	Requires modification of the engine with increasing content
	Low heat of combustion
	Is less toxic
	A couple of the less flammable
	Significantly higher electrical conductivity
Butanol	Octane number (104 units)
	Energy intensity close to the energy intensity of gasoline
	The mixture does not separate in the presence of water
	Does not require engine modifications
	Has no corrosive properties
	Low vapor pressure of butanol fuel should not lead to the emergence of high levels of emissions of volatile organic compounds

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