A Case Study for the Development of Environmentally Safe Low-Lead Aviation Gasoline in Ukraine

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Abstract. The paper is devoted to the development of environmentally safe avgas compositions with low content of tetraethyl lead. Modern trends in global avgas production and consumption are shown, along with tendencies in restriction of tetraethyl lead use for anti-knock properties improvement. The main methods of avgas octane number rising are shown, among which are introduction of high-octane hydrocarbons, oxygenated compounds and anti-knock additives. The influence of individual hydrocarbons on octane number is studied. It is found that blending alkylate, isopentane, isooctane and benzene with based improves octane number by 2–4 units. Similar tendency is found for blending base gasoline with anti-knock additives. Combination of high-octane hydrocarbons and anti-knock additives has allowed to improve octane number of avgas up to 6 units. Basing on these components new compositions of avgas were developed.

Keywords: Aviation gasoline · Piston engine · Anti-knock properties · Octane number · Anti-knock additives · Ecological properties · Operation properties

1 Introduction

The reduction of the impact of aviation on the environment and increasing fuel efficiency of aircraft engines through the introduction of alternative motor fuels has become the objective. At the same time, the issue of ensuring the safe transition of aircraft equipped with piston engines to unleaded aviation gasoline (avgas) is not unsolved. Today, there is a tendency for prohibiting the use of leaded avgas [1, 2]. The world's leading organizations in the field of civil aviation develop pathways to completely replace leaded avgas with its unleaded alternative. At the same time, one of the main trends and requirements

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is environmentally safe energy-efficient development of air transport within the global strategy for sustainable development [3, 4].

Ukraine, traditionally being the country with a well-developed aviation sector, is now faced with a number of problems connected to the use of Avgas. Since 2003 in Ukraine production, import, sale, and use of gasoline, which contains tetraethyl lead (TEL), is prohibited [5, 6]. As the result, aircraft, equipped with piston engines, are fueled with unleaded automobile gasoline. This leads to early deterioration of engines, rising the number of failures – all these threaten the flight safety. Operation of these aircraft on any other fuel is a violation of technical conditions. In accordance with international standards in the field of civil aviation further operation of these aircrafts is banned, including the arrival of foreign aircraft using leaded gasoline into Ukraine [6].

Therefore, one of the urgent scientific and practical tasks is to develop new alternative environmentally safe Avgas that will have sufficient operational and environmental characteristics. Taking into account the abovementioned, the *aim of the study* is to develop the compositions of low-lead avgas for improving its anti-knock properties.

Object of the study – production of low-lead avgas with better anti-knock properties.

Subject of the study – anti-knock properties of low-lead avgas compositions.

2 Literature Overview

Avgas, is a gasoline fuel for aircraft equipped with piston engines. Such aircraft are mainly used for private needs, business aviation, flight training and harvesting, cultivation of agricultural fields, tourism, sport activities, etc. (Fig. 1) [7]. With the development of unmanned aerial vehicles (UAV) avgas is actively used to power them. Aircraft piston engines operate on the same principles as engines found in motor vehicles [8].

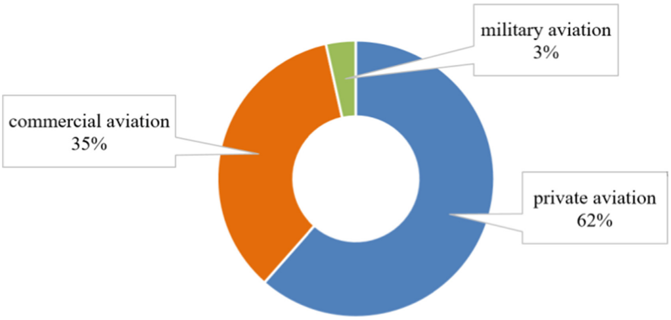

Fig. 1. Global Avgas market share, by end-users in 2020 [7].

Avgas consumption has increased due to the development of business aviation. The use of small aircraft provides high mobility, efficiency and productivity of business aviation [7, 9]. The global demand for small aircraft has grown. Various air sports are also actively developing. Modern aircraft have become cheaper, faster, more reliable, and more environmentally friendly. These encourage an increase in demand for avgas.

The presence of TEL is a limiting factor in the development of small aircraft [10]. TEL is an anti-knock additive that improves octane number (ON) of avgas. It reduces the tendency of the avgas to ignite suddenly and instantaneously during the combustion that leads to catastrophic failure of the engine. However, LED has negative impact on human health and environment. The largest source of TEL exposure is from the evaporative emissions associated with fuel technological processes. Lead is classified as carcinogen. It causes neurological, hematological, immune and cardiovascular effects for humans. Lead from aircraft exhausts is consumed by flora and fauna, having cumulative negative effect on animals and finally on human [11].

However, attempts to replace conventional leaded avgas with its unleaded alternatives have not satisfied the safety and operational requirements of the aircraft [8]. It is obvious that transition from leaded avgas has performance issues with possible serious consequences for the flight safety. Thus, there is a need to create an unleaded high octane avgas with required physical-chemical and operation properties to provide long-term and reliable operation of aircraft with minimal negative impact on environment.

2.1 Methods of Improvement of Anti-Knocking Properties of Avgas

There are several approaches to improve operation properties of avgas, in particular, anti-knock characteristics: addition of high-octane components; blending with oxygen-containing compounds; use of anti-knock additives [19].

Among *high-octane components* of avgas it necessary to consider isoparaffin and aromatic hydrocarbons. The most effective among them are isopentane and alkylbenzin [5, 8]. Pyrobenzene and alkylbenzene are used as aromatic high-octane components. Other high-octane hydrocarbons may be also used as components of avgas [10].

The use of *oxygen-containing compounds (oxygenates)* for improvement operation characteristics of avgas is also studied. Oxygenates are low molecular weight aliphatic alcohols and their ethers (e.g. methanol, ethanol, methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), etc.). Also oxygenates are used for expanding of feedstock for fuel production. Oxygenates naturally have high ON [5, 6].

One of the most effective method of improving octane rating of avgas is use of *anti-knock additives* [10, 11]. Depending on the type of high-octane components, its origin, and mechanism of action, they may be grouped into:

– aromatic amines;
– manganese-based anti-knock additives;
– ferrum-based anti-knock additives;
– lead-based anti-knock additives.

The principle of action of anti-knock additives is the elimination of active hydrocarbon peroxides or radicals during combustion and prevention of detonation [6, 9]. The most effective compounds are: TEL, metallocenes based on iron and manganese, alkali metal compounds and aromatic amines. Susceptibility of gasolines to the anti-knock additives depends on the group composition and anti-knock characteristics of gasoline. The lower the ON of gasoline, the greater will be the effect of the additive [8]. Additives have some disadvantages, which limits its use. Amine additives lead to accumulation of resins in fuel system and formation of deposits in the combustion chamber. Manganese additives lead to formation of metal deposits on spark plugs. Ferrum additives lead to increased fuel consumption and NO_x emissions. Concentrations of all additives in gasoline are limited and the maximum increase in ON is also limited. The dependence of the ON rise on the concentration of the additive is nonlinear [10].

2.2 Nomenclature and Specification for Avgas

Avgas grades are distinguished according to their ON. Today the number of grades of Avgas are used. *Avgas 100* is the most popular high-octane gasoline for aircraft with a high content of TEL. *Avgas 100LL* is a low lead version of Avgas 100 (LL – low lead). Specifications ASTM D910 [12] and DEF STAN 91–090 [13] determine quality requirements to these kinds of fuel. *Avgas 82UL and Avgas 87UL* – are new grades of Avgas with no TEL additive (UL – unleaded). It is a low-octane grade and may be used in engines with low compression rate. Aircraft, which are allowed to used motor gasoline are allowed to use this kind of fuel. Quality requirements are set in the specification ASTM D6227 [14]. *Avgas UL91* and *Avgas UL94* – are also unleaded Avgas modifications. Both are similar to Avgas 100LL, but absence of TEL leads to lower ON. Quality requirements to these grades are set in the specification ASTM D7547 [15].

3 Materials and Methods of the Study

Within the study a set of avgas blends with different ratios of basic components and the content of different anti-knock additives was developed and studied. The ON of avgas blends was determined in order to select the optimal composition and ratio of components. The following components were used to prepare avgas blends for testing:

- base gasoline, produced by the oil processing plant JSC “Ukrtatnafta” in Kremenchuk city, Ukraine;
- individual high-octane hydrocarbons: alkylate, isooctane, isopentane, and benzene, produced by the oil processing plant JSC “Ukrtatnafta”;
- industrially produced ethyl alcohol (96%);
- anti-knock additives: Octaburn TM 8000, Octamar FK, PLUTOcen GS 2300i, ADA-TF C8 and TEL.

A sampling of avgas, components and additives was done using an automatic bottle dispenser, analytical scales and pipette samplers. Avgas blends were prepared by mechanical blending and stored in borosilicate glass bottles at room temperature without access to light. The volume of blends was 1000 ml. The ON was measured at the UIT-65 unit by the research method [16]. The studies were done at the Interactive Laboratory “Aviatest” of the National Aviation university.

The influence of high-octane components on the avgas ON was studied. For this the avgas blends of base gasoline with 5% (vol.) and 15% (vol.) of high-octane components were prepared. Ethanol was added to in quantity 3% (vol.) and 7% (vol.). Next, the influence of anti-knock additives on avgas ON was studied. For this the additives were added to the base gasoline in different concentrations. Finally, the anti-knock properties of avgas compositions were studied. The compositions were prepared by blending base gasoline with different amounts of high-octane components, ethanol and anti-knock-additives.

4 Results and Discussion

4.1 Study of the Influence of Individual High-Octane Components on the Octane Number of Gasoline

At the first stage the base gasoline was blended with high-octane components; the dependence of ON of base aviation gasoline on individual high-octane components was studied. Base gasoline was blended with certain components – alkylate, isooctane, isopentane, and benzene in quantities 5% (vol.) and 15% (vol.). Ethanol results was added to gasoline in quantity 3% (vol.) and 7% (vol.). Results of the research are shown at Fig. 2 (a-e). It is seen that high-octane hydrocarbons allow rising ON of gasoline on 2–4 units. Addition

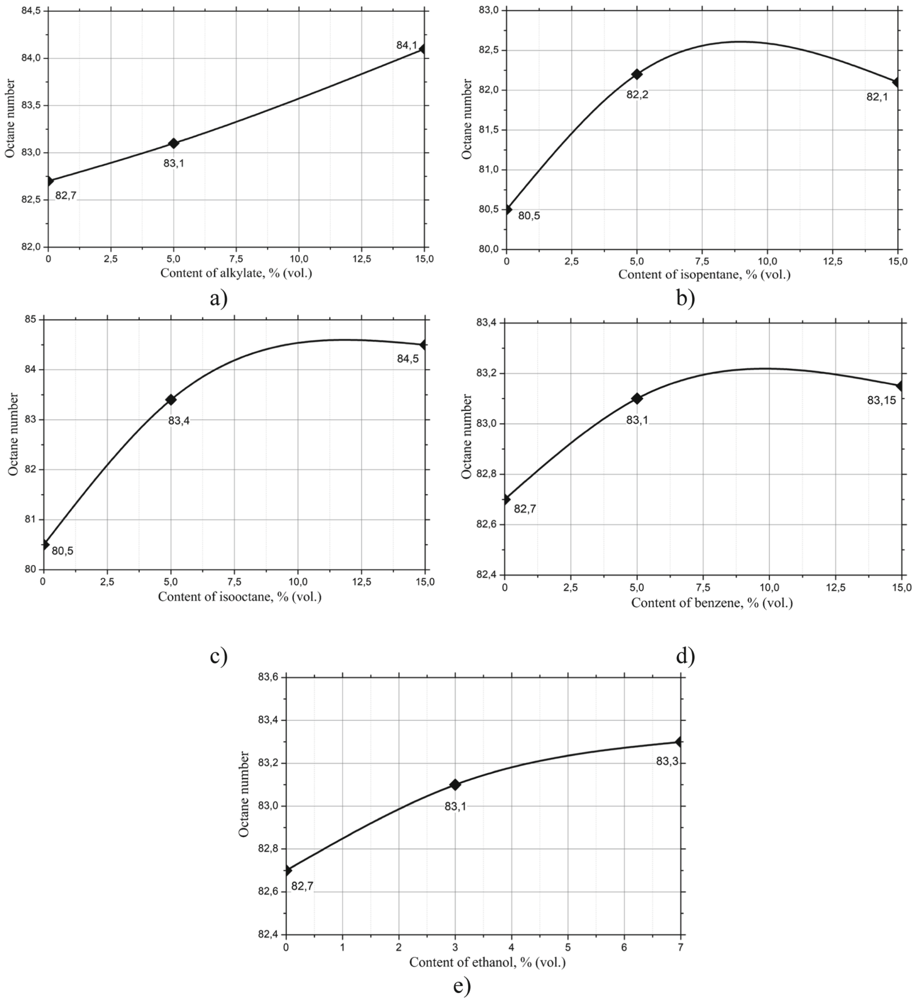

Fig. 2. Dependence of the ON of base gasoline on the content of individual high-octane components: a) – alkylate, b) – isopentane, c) – isooctane, d) – benzene, e) – ethanol.

of 5% (vol.) of components results in more intensive rise of ON. It proves theoretical data that improvement of ON may be easily reached for gasoline with low initial ON and that fact, that ON dependence on the content of high-octane components is not linear. The highest rise of ON is provided by addition of isooctane.

(Fig. 2b) and less isopentane (Fig. 2c). It correlates to that fact that isoparaffins usually have the highest ONs comparing to other types of hydrocarbons and considered to be the most effective for rising ON of gasolines. The isoparaffins have a low freezing point (below minus 60 °C), low hygroscopicity and high sensitivity to TEL [13].

Aromatics are less effective for detonation resistance improvement that is proved by the experiment (Fig. 2d).Use of aromatics has some disadvantages, mainly high freezing point, reduced sensitivity to TEL, and high hygroscopicity, which limit it content in avgas. It may be concluded that addition of 15% (vol.) of components do not result in extensive change in ON. It may be predicted that adding higher concentration of high-octane components is not effective. The use of the ethanol doesn't show any significant effect on rising of the ON of gasoline (Fig. 2e). However, it may be used for replacing some amount of crude oil components. Also it will positively affect the completeness of fuel combustion in the piston engine and quality of exhaust gases.

4.2 Study of the Influence of Anti-Knock Additives on the Octane Number of Gasoline

Next, the anti-knock additives were introduced into the base gasoline; the dependence of ON of base gasoline on anti-knock additives was studied. The additives were added in the following concentrations: Octaburn TM 8000 – 8 mg/l and 18 mg/l, Octamar FK – 22.5 mg/kg and 45 mg/kg, PLUTOcen GS 2300i – 22.5 mg/kg and 45 mg/kg, ADA-TF C8 – 1% and 3% and TEL – 0.0013 g/kg and 3.1 g/kg. Results are shown at Fig. 3 (a-e). Anti-knock additives allow rising ON of gasoline by 0.5–3 units. The highest rise of ON is provided by additive ADA-TF C8 – 3 units (Fig. 3d) and Octamar FK – 2 units (Fig. 3b). The dependence of the ON on the concentration of additives is non-liner. It is seen that the lower the ON of gasoline, the greater is the anti-knock effect of the additive. This proves the theoretical data presented in the literature overview section. It is known that different types of hydrocarbons typically have different level of susceptibility to anti-knock additives. Susceptibility decrease as the following: Paraffins → naphthenes → olefins → aromatics [6, 13]. Therefore, it is necessary to study the effect of the anti-knock additives on gasoline blended with high-octane components.

4.3 Study of the Anti-Knock Properties of Compositions of Aviation Gasolines

At the last stage the compositions of avgas were prepared and their ON was studied. Avgas compositions were prepared by blending base gasoline, high-octane components in different amounts, ethanol and anti-knock additives. The effect of TEL addition to compositions was also studied. Figure 4 presents results of the ON determination in composition with different content of high-octane components, ethanol and ADA-TF C8 additive. Similar to the previous avgas compositions, adding smaller amounts of components improve ON by 2.6 units and adding bigger compositions by 4.4. However,

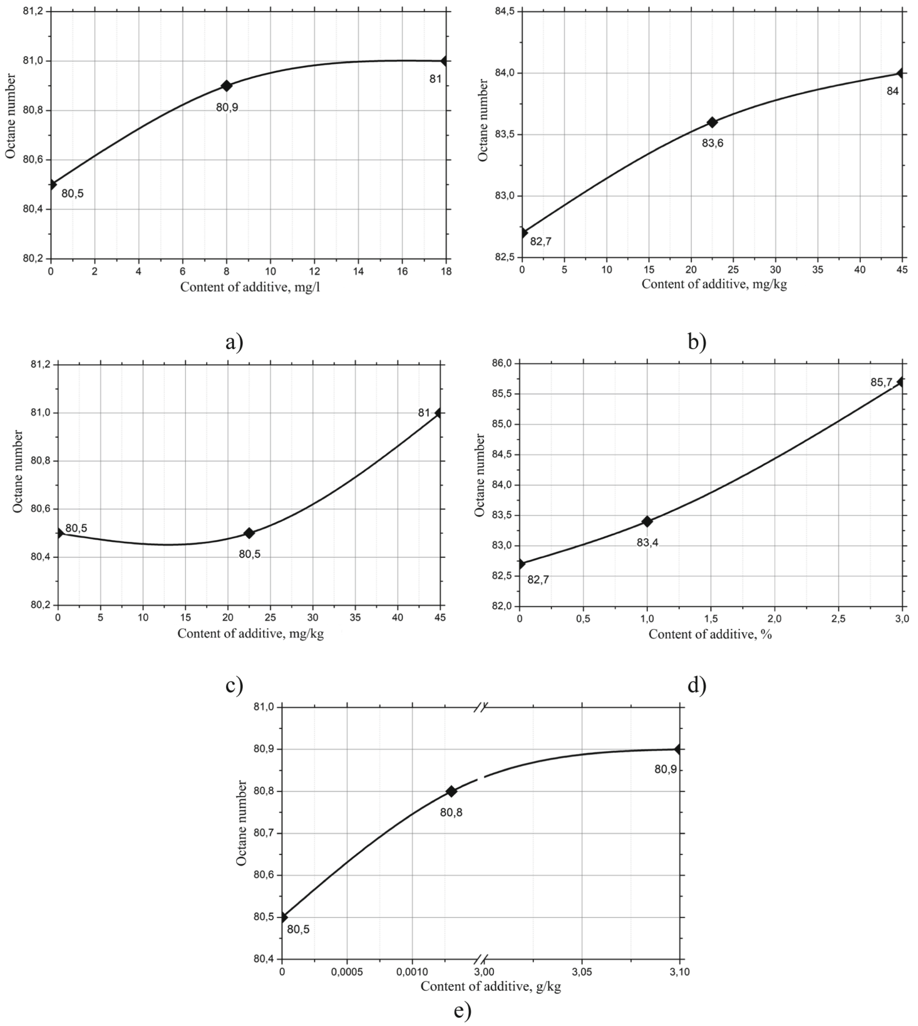

Fig. 3. Dependence of the ON of base gasoline on the content of anti-knock additives: a) – Octaburn TM 8000, b) – Octamar FK, c) – PLUTOcen GS 2300i, d) – ADA-TF C8, e) – TEL.

there is almost no effect of ADA-TF C8 additive, as the values of ON of the compositions are close to ON of compositions without anti-knock additives.

The avgas compositions containing high-octane components, ethanol and Octamar FK additive were studied (Fig. 5). Additionally, the effect of the combination of Octamar FK and TEL additives was studied.

Adding 5% of high-octane components, 3% of ethanol and low concentration of additive increases ON only by 1.6 units. Adding higher amounts of high-octane components, ethanol, and additive provide higher rise of ON (88.3). Combination of high-octane components and additive in high concentrations can be effective. Combination of TEL and Octamar FK additives doesn't result in any changes in ON.

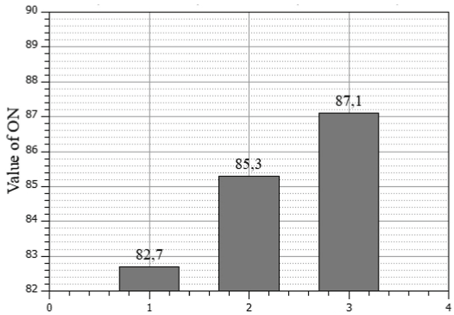

Fig. 4 ON of avgas composition with different content of high-octane component, ethanol and ADA-TF C8: 1 – base gasoline; 2 – base gasoline (77%) + alkylate (5%) + isooctane (5%) + isopentane (5%) + benzene (5%) + ethanol (3%) + ADA-TF C8 (1%); 3 – base gasoline (33%) + alkylate (15%) + isooctane (15%) + isopentane (15%) + benzene (15%) + ethanol (7%) + ADA-TF C8 (1%)

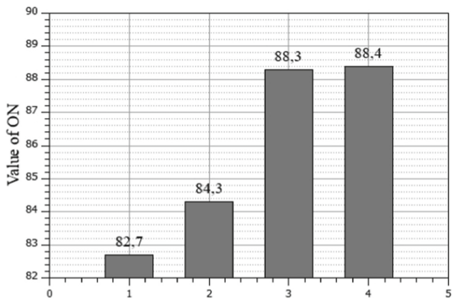

Fig. 5. ON of avgas composition with different content of high-octane component, ethanol and Octamar FK: 1 – base gasoline; 2 – base gasoline (77%) + alkylate (5%) + isooctane (5%) + isopentane (5%) + benzene (5%) + ethanol (3%) + Octamar FK (22.5 mg/kg); 3 – base gasoline (33%) + alkylate (15%) + isooctane (15%) + isopentane (15%) + benzene (15%) + ethanol (7%) + Octamar FK (45 mg/kg); 4 – base gasoline (33%) + alkylate (15%) + isooctane (15%) + isopentane (15%) + benzene (15%) + ethanol (7%) + Octamar FK (45 mg/kg) + TEL (3.1 g/kg).

Next, the avgas compositions containing high-octane components, ethanol and Octaburn TM 8000 additive were studied (Fig. 6). The effect of the combination of Octaburn TM 8000 and TEL additives was also studied. Adding 5% of high-octane components, 3% of ethanol and low concentration of additive increases ON by 2.5 units. But, adding higher amounts of high-octane components, ethanol, and additive provide significant increase of ON – by 5.9 units. The combination of high-octane components and anti-knock additive in high concentrations showed its effectiveness. The cumulative action of high-octane hydrocarbons and Octaburn TM 8000 additive is seen. Combination of TEL and Octaburn TM 8000 additives doesn't result in significant change in ON. Therefore, the use of TEL is not effective.

Basing on the results it may be concluded that combination of high-octane hydrocarbons, ethanol and some anti-knock additives allows obtaining avgas compositions

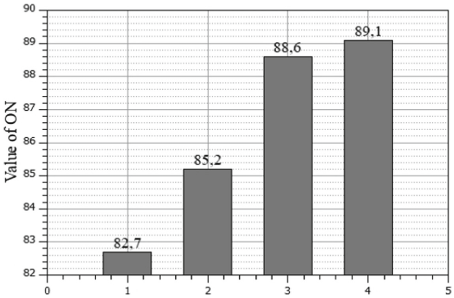

Fig. 6. ON of avgas composition with different content of high-octane component, ethanol and Octamar FK: 1 – base gasoline; 2 – base gasoline (77%) + alkylate (5%) + isooctane (5%) + isopentane (5%) + benzene (5%) + ethanol (3%) + Octaburn TM 8000 (8 mg/kg); 3 – base gasoline (33%) + alkylate (15%) + isooctane (15%) + isopentane (15%) + benzene (15%) + ethanol (7%) + Octaburn TM 8000 (18 mg/kg); 4 – base gasoline (33%) + alkylate (15%) + isooctane (15%) + isopentane (15%) + benzene (15%) + ethanol (7%) + Octaburn TM 8000 (18 mg/kg) + TEL (3.1 g/kg)

with sufficient anti-knock properties. The use of high-octane components provides balanced composition and properties of avgas. Using alkylate provides proper fractional composition, saturated vapor pressure and rise of ON. Isooctane and isopentane provide sufficient fractional composition and freezing point of avgas. Aromatics balance its fractional composition. Ethanol positively affects the combustion process and reduce amounts of unburned hydrocarbons in exhausts. Octaburn TM 8000 and Octamar FK additives in combination with high-octane hydrocarbons increase the ON of avgas by about 5 units compared to base gasoline. They do not contain TEL, so are not toxic.

5 Conclusions

The influence of high-octane hydrocarbons on ON of gasoline was studied. It was found that blending alkylate, isopentane, isooctane, and benzene may improve ON of gasoline by 2–4 units. Addition of ethanol doesn't have a significant effect on ON rise. The influence of anti-knock additives on ON of gasoline was studied. The ON of base gasoline was improved by 0.5–4 units. ON dependence on the concentration of additives is non-linear and it is easier to rise the ON of fuel with initially lower ON.

The new compositions of avgas were developed and ON number was studied. The compositions were produced from base gasoline fraction, alkylate, isopentane, isooctane, and benzene, ethanol and different anti-knock additives. Combination of high-octane hydrocarbons and anti-knock additives has cumulative effect and improves ON of compositions up to 6 units. Octaburn TM 8000 and Octamar FK additives have shown the greatest effect. Both additives do not contain TEL and considered non-toxic.

At the same time results create the basis for further research aimed at the development and implementation of new environmentally safe avgas. The next researches will be devoted to studies of physical–chemical properties of new Avgas, operation properties, bench tests on model piston engines, and assessment of its emission characteristics.

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