Research of Isobutyl Oil as Antiknock Additive to Straight-Run Gasoline

I Y Zhukova\(^1\), A I Sobchinskiy\(^1\), I N Tyaglivaya\(^1\)

\(^1\)Department Power engineering and oil and gas industry, Don State Technical University, Gagarin's square 1, Rostov-on-Don, 344023, Russia

E-mail: inna1704@gmail.com

Abstract. The results of research of isobutyl oil (IBO) (waste of methanol production from synthesis gas) as antiknock additive to straight-run gasoline are presented. The long-term experience of using aliphatic alcohols as oxygenates is described briefly. The existing directions of application of IBO were listed. IBO contains alcohols with branched structure that have a strong detonation resistance and a calorific value comparable to hydrocarbons. A theoretical substantiation of the possibility of using IBO as additive for increases of detonation properties of gasoline is discussed. IBO as an antiknock additive to increase the octane rating of straight-run gasoline A-76 brand was investigated. It is shown that the additive of IBO allows to modernize gasoline A-76 to A-92 brand. The developed method increasing the octane number of straight run gasoline is presented.

1. Introduction

It is known that the additive of oxygenates in automobile gasolines increases their detonation resistance, as increase concentration of oxygen in the fuel support to a more complete combustion of hydrocarbons, reduces the heat of combustion of the fuel-air mixture, facilitates a faster heat removal from the combustion chamber, and as a result, the maximum combustion temperature decreases. Advantages of using oxygenates is an increase of octane rating of gasoline without increasing the content of arenes in it, reducing the toxicity of exhaust gases [1-7]. Oxygenates are aliphatic alcohols C1-C4 and dialkyl ethers, which possess anti-knock properties. Among the alcohols the main place is occupied by methanol which one can be used not only as an environmentally friendly fuel for automobile engines or as a component of motor gasoline, but also as a raw material for the synthesis of high-octane gasoline additives such as monomethylalanilne (MMA) and methyl tert-butyl ether (MTBE). Restriction of the use of this additive is the low stability of gasoline-methanol mixtures and their sensitivity to water. For their stabilization additives of propanol, isopropanol, isobutanol and other alcohols are used [8-10]. With regard to the use of ethyl alcohol as fuel - bioethanol production is currently the most dynamically developing sector of the biofuel industry [11-16]. However, the additive of ethanol to gasolines also requires the necessary stabilizing additives to the composition which allow homogenization of the gasoline-water-alcohol system. As stabilizing additives it has also been proposed to use aliphatic alcohols of a normal and branched structure [17]. Also tert-butyl and isopropyl alcohols were studied as additives to gasoline and its showed a high anti-knock efficiency [18-19].
From this point of view it is very promising to use methanol production waste from synthesis gas isobutyl oil (IBO). The fraction of IBO is isolated from 6 to 10 plates of the distillation column with the yield of approximately 2% of the amount of methanol-r raw, its composition is variable and varies within the following limits (mass%): methanol- 5-75, water- 20-95, ethanol- 0.2-0.7, propanol- 0.1, isopropanol- 0.1, isobutanol- 4-5, etc.- 2-3. IBO contains alcohols with branched structure that have a strong detonation resistance and a calorific value comparable to hydrocarbons. An additional advantage of this additive is the complete combustion of the IBO as a result of the engine operation and the absence of toxic components in summary. In Russia there is some experience with the use of IBO. Previously, pure isobutylene was mainly extracted from it, from which further isooctane and polyisobutylene, plasticizers and various aliphatic compounds have been obtained. At present methods for the preparation of para-t-butyltoluene from IBO have been developed, which is used for the synthesis of tert-butyl benzoic acids, terephthalic acids and olefinic hydrocarbons. In this method, IBO is used as an additive to pyrolysis raw materials instead of water vapor, which allows to reduce coke formation and increase the yield of aromatic hydrocarbons. In this process of obtaining anionic surfactants IBO plays the role of extractant which allows to reduce production costs. All directions of application of IBO differ from what we have studied.

2. Methodology / experimental

To test the hypothesis of the expediency of using IBO as an antiknock additive to straight run gasoline, 3 samples of gasoline of the following productions are analyzed and modernized: Oksaray gasoline is a sample №1; Ufa gasoline is a sample №2; Neftekumsky gasoline is a sample №3.

By the motor method the octane ratings were studied, it amounted to samples №1 -74; №2 -78; №3 -78. The distillation according to Engler (fractional composition) of these samples was carried out.

Table 1.

| Fractional composition | GOST 2084-77 | Samples №1 | №2 | №3 |
|------------------------|--------------|------------|----|----|
| Initial boiling point, not lower | 35 | 40 | 39 | 35 |
| 10% of gasoline is distilled at a temperature of °C, not higher | 70 | 58 | 52 | 53 |
| 50% of gasoline is distilled at a temperature of °C, not higher | 115 | 95.5 | 84 | 96.5 |
| 90% of gasoline is distilled at a temperature of °C, not higher | 180 | 171 | 155 | 158 |
| Final boiling point, not higher | 195 | 251 | 187 | 177 |
| Residue in the flask, not more than | 1.5 | 2 | 1.3 | 1.3 |

According to obtained octane ratings and fractional composition of gasolines Ufa and Neftekumsky (samples №2 and №3) correspond to gasoline of A-76 brand, and Oksaraysky (sample №1) does not correspond to octane rating (should be ≥76) and fractional composition (by parameters: final boiling point and residue in the flask).

Modernization of straight gasoline: IBO (180 ml) is added to gasoline (840 ml), put in a thermostat for 2 hours at a temperature of 10-15 °C. Then, 20 ml of separated water (about 11-12% of the used IBO) are poured off and methanol (80ml) is added. The ratio of gasoline: IBO: methanol- 70:15:15, excluding separated water (volume ratio). The obtained samples of gasoline are analyzed in terms of TU 38.001165-97 for A-92 gasoline.
Table 2.

| №  | Significative                                      | TC 38.001165-97 | Samples | Note               |
|----|---------------------------------------------------|-----------------|---------|--------------------|
|    |                                                   | №1  | №2  | №3  |                |
| 1  | Density at 20 °C kg / m³, not more than 770       | 770 | 751 | 736 | 731 | GOST 3900-85  |
| 2  | Detonation resistance, octane rating by motor method, not less than 83 | 83  | 83  | 83  | 84  | GOST 511-2015 |
| 3  | Distillation characteristics:                    |             |        |      |      |                |
| 3.1| Initial boiling point °C, not higher             | 35  | 41  | 39  | 42  | GOST 2177-99  |
| 3.2| 10% of gasoline is distilled at a temperature of °C, not higher | 75  | 49  | 48  | 51  |                |
| 3.3| 50% of gasoline is distilled at a temperature of °C, not higher | 120 | 69  | 68  | 73  |                |
| 3.4| 90% of gasoline is distilled at a temperature of °C, not higher | 190 | 157 | 153 | 163 |                |
| 3.5| End of boiling °C, not higher                    | 215 | 186 | 184 | 211 |                |
| 3.6| Residue in the flask %, not more than             | 1,5 | 1,3 | 1,3 | 1,3 |                |
| 3.7| Residue and loss %, not more than                 | 4   | 3   | 3   | 3   |                |
| 4  | Acidity, mg KOH per 100 cm³ of gasoline, no more than 3 | 3   | 0,8 | 0,9 | 0,8 | GOST 11362-96 |
| 5  | Mechanical impurities and water                   | no  | no  | no  | no  | TC 38.001165-97 |

3. Conclusion
The resulting mixtures according to the analyzed parameters corresponded to gasoline A-92. It was experimentally established that additive IBO to low-octane gasoline significantly increases the octane rating of fuel mixture.

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