The use of propylene oxide in the composition of alcohol fuels as a way to reduce its cost

Tsygankov Dmitriy Vladimirovich

Candidate of Chemical Sciences, Associate Professor

Polozova Alena Vladimirovna

Postgraduate

T.F. Gorbachev Kuzbass State Technical University

Abstract. The main advantages and disadvantages of alcohol fuels in comparison with traditional gasolines are considered. The main problem of alcohol fuel associated with low phase stability between the hydrocarbon and alcohol parts, which requires the use of highly dehydrated alcohol, has been identified. It is proposed to use low-boiling propylene oxide ether instead of the hydrocarbon part, which significantly reduces the requirements for alcohol strength, and hence the cost of all alcohol fuel.

Keywords: ethyl alcohol, bioethanol, propylene oxide, starting fraction of alcohol fuel, phase stability.

Today, the use of alcohol fuels, mainly bioethanol, is an excellent alternative to traditional motor gasoline. The main competitive advantages of alcohol bioethanol fuels are that they significantly increase the environmental safety of road transport and, at the same time, are renewable energy resources. In addition, ethyl alcohol has a higher detonation resistance compared to even the most premium gasolines. So the octane number of alcohol is 129.5 units according to the research method, which makes it possible to increase the compression ratio of the engine to 19 units versus 10 for traditional gasoline. Under these conditions, the efficiency of an engine running on alcohol fuel becomes higher than on traditional gasoline.

The environmental friendliness of alcohol fuel is manifested in the reduction of harmful emissions with exhaust gases in terms of CO, CH and NO_x. In addition, bioethanol can significantly reduce carbon dioxide emissions into the atmosphere. The fact is that in the process of burning ethanol from plant raw materials, exactly the same amount of CO_2 is released into the atmosphere as was previously absorbed by the same plants as a result of the photosynthesis reaction [1, 2]. Of course, carbon dioxide is non-toxic to humans, but, nevertheless, it belongs to greenhouse gases and contributes to global warming on the planet. Each country that has entered the Kyoto Protocol has certain quotas for greenhouse gas emissions.

The renewability of bioethanol lies in the fact that it can be produced from almost any plant material, in contrast to oil, whose quantity on the planet is limited.

Alcohol fuel also has its drawbacks, the main of which is poor volatility compared to gasoline. This makes it difficult to start a cold engine. So with 100% alcohol, starting a cold engine becomes problematic even at temperatures below +10°C. This problem is solved by adding gasoline or low-boiling hydrocarbon fractions to alcohol, as a result, such a "starting fraction" ensures engine start at low temperatures. The most famous alcoholic composition is E85 alcohol fuel (in Russia it is labeled as Ed75-Ed85 according to GOST R 54290-2010) [3]. This alcohol fuel is subdivided into summer and winter. Summer contains 74% ethanol and 17 - 26% hydrocarbons and aliphatic ethers as a "starting fraction". Winter contains 70% ethanol and 17 - 30% hydrocarbons and simple aliphatic ethers as a "starting fraction".

The "starting fraction" solves the problem of cold starting the engine, but other problems associated with it arise. Traditionally, commercial gasoline was used for the "starting fraction", then they tried to use narrow hydrocarbon fractions, including pentane, isopentane, butane, isobutane and propane [4], to reduce the cost of the composition it was proposed to use low-quality gasolines and gasoline fractions, including by-products of oil refining and even waste. For example, low-octane fraction of direct distillation of oil or gas condensate [5], gasoline fraction of the hydrocracking process [6], coking gasoline [7] and the like. These and other hydrocarbon fractions have one common drawback - it is low phase stability, that is, under operating and storage conditions, there is a possibility of separation of the hydrocarbon part and alcohol. The presence of water in the fuel and a drop in temperature dramatically increase the likelihood of delamination. To avoid it, increased requirements are imposed on the strength of alcohol, as a rule, the moisture content in alcohol should not exceed 2%, that is, the ethanol content must be at least 98%. This degree of dehydration of alcohol requires additional costs in its production. Certain difficulties arise when refueling cars, since moisture is often present in refueling containers.

Even if we use AI-92 commercial gasoline as a "starting fraction", provided that this fraction is 30%, and 70% ethanol with an octane number of 129.5, the octane number of the finished fuel will be about 118 units according to the research method. Thus, even in the ideal case, there is an underutilization of the antiknock potential of bioethanol, which is to say about the use of non-crankcase gasolines and gasoline fractions as "starting fractions", whose octane number according to the research method rarely exceeds 70 units.

The use of cheap non-candable gasolines and gasoline fractions as "starting fractions" in some cases may be fraught with excessive sulfur and tar content.

The most important of these problems is the problem of the phase stability of bioethanol fuels. According to the authors, if it is not possible to fully stabilize the alcohol-gasoline mixture, then not only the gasoline part, but also the hydrocarbon part in general should be abandoned. Low boiling ethers can be used instead. The author proposes to use propylene oxide as such an ether [8]. Propylene oxide is a simple cyclic ether with a boiling point of 34.2°C and a density of 859 kg/m^3 at 20°C.

Since ethanol is unrestrictedly soluble in water, and propylene oxide (PO) also has good solubility with water, it was assumed that phase stability in the ethanol-PO-water system would be retained even with an extremely high amount of water. The maximum amount of water in known water-fuel emulsions does not exceed, as a rule, 20% [9], therefore, for the study, we used two samples of bioethanol (ethyl alcohol № 1 with a water content of 5% by volume and ethyl alcohol № 2 with a water content 20% vol.). The characteristics of bioethanol alcohols are presented in table 1.

Table 1. – Bioethanol characteristics

№	Indicator name	Component name	
		Ethyl alcohol № 1	Ethyl alcohol № 2
1	Ethyl alcohol content,% vol.	95	80
2	Water content,% vol.	5	20
3	Density at 15 °C, kg/m^3	812.3	856.1

The main physicochemical indicator on which the phase stability of fuels depends is the cloud point; therefore, in order to assess the phase stability, the cloud points of various samples of bioethanol fuels were determined. The results are shown in table 2.

Table 2. – Bioethanol fuels research results

№	Component name		Component content% vol.				Test method
			1	2	3	4	
1.	Ethyl alcohol № 1		90	95	-	-	
2.	Ethyl alcohol № 2		-	-	90	95	
3.	Propylene oxide		10	5	10	5	
Total components			100	100	100	100	
№	Indicator name	ASTM D5798/ EN15293	Test results				
1.	Motor octane number	No lower than 85,0[1)]	100,8	101,0	101,0	102,0	Determined by calculation method
2.	Volume fraction of ethyl alcohol	No lower than 70[2)]	90	95	90	95	ASTM D 5501
3.	Volume fraction of methyl alcohol,%	No more than 0,5	absence				
4.	Mass fraction of sulfur, mg/kg, no more	No more than 10[3)]	0	0	0	0	ASTM D 5453
5.	Saturated vapor pressure, kPa	35 – 100[3)]	41.8	36.8	34	28	ASTM D 4953
6.	Boiling end, °C	No more than 215	85	82	100	100	ASTM D 86

7.	Mass concentration of resins, mg/100 cm^3						
	-not washed with solvent	No more than 20	0	2	2	0	ASTM D 381
	-washed with solvent	No more than 5	0	0	0	0	
8.	Volume fraction of water in alcohol,% vol.	No more than 2	5	5	20	20	
9.	Volume fraction of water in the composition,% vol.	No more than 1,2	4.50	4.75	18.00	19.00	
10.	Cloud point, °C	Not higher than minus 30°C	Below minus 65°C				GOST 5066
11.	Corrosion effect on a copper strip, units on a scale (3 hours at 50°C)	Class 1	Class 1				ASTM D 130
1) Requirement of GOST 32513 for motor gasoline AI-95 2) Requirement of GOST R 54290-2010 “Fuel ethanol (Ed75-Ed85) for automobile engines with positive ignition. Technical conditions". 3) The requirement of the "Technical Regulations" for motor gasoline of ecological class K5.							

As can be seen from the table, turbidity of all four bioethanol fuel samples did not occur even at a temperature of minus 65°C. According to the requirements of regulatory documents, in particular GOST R 52201 for benzanol, the cloud point should be no higher than minus 30°C. The obtained cloud point results are not only very good, they completely solve the issue of phase stability even for heavily watered ethanol.

An important point is the starting properties of the fuel. For bioethanol fuels, starting properties are determined by the efficiency of the "starting fraction", the lower its boiling point, the easier and faster the engine will start. If commercial gasoline is used as a "starting fraction", then it has a boiling point of 33 to 210°C, while PO has about 34°C. Thus, it is clear that PO has better volatility characteristics than gasoline, which means that less PO is required to achieve the same effect. To prove this, various fuels were distilled. The classic bioethanol fuel E85 (85% ethanol and 15% commercial gasoline) was used as a reference. Since the distillation temperature of 10% is responsible for starting the engine, in order to evaluate the efficiency of PO as a "starting fraction", it is necessary to compare these values for different compositions of bioethanol fuels (see table 3.).

Table 3. – Results of distillation of fuel samples

distilled fuel,%	AI-98 gasoline	85% alcohol, 15% gasoline	90% alcohol at 95% vol., 10% propylene	95% alcohol, strength 95% vol., 5%	90% alcohol with a strength of 80% and	95% alcohol at 80% vol., 5% propylene

			oxide	propylene oxide	10% propylene oxide	oxide
	distillation temperature, °C					
NR	45	62	61	70	60	70
10	53	75	72	74	72	75
20	67	78	74	76	76	77
30	79	80	76	77	77	78
40	92	86	77	77	78	79
50	106	91	77	77	79	79
60	119	93	77	77	79	80
70	130	97	77	77	80	81
80	146	101	77	77	81	84
90	176	106	77	77	85	85
	195(92%)	128(97%)	85(98%)	82(99%)	100(98%)	100(99%)
losses	6.5%	2.5%	2%	1%	2%	1%
residue	1.5%	0.5%	0%	0%	0%	0%

As can be seen from the table, the distillation temperature of 10% for the classic bioethanol fuel was 75°C, and the same temperature values for the samples containing PO instead of gasoline did not exceed 75°C. This means that 5% PO in bioethanol fuel can easily replace 15% of commercial gasoline in terms of starting characteristics. To obtain a more complete picture of the starting properties of the fuel, along with the fractional composition, it is also necessary to take into account the saturated vapor pressure (see table 2). As can be seen from the table, those samples of bioethanol fuel, where the moisture content of 5% in terms of saturated vapor pressure, fits well into the GOST indicators, which means that PO really has good starting properties and is three times more efficient than commercial gasolines. Those samples of bioethanol fuel, where the amount of moisture of 20% does not quite reach the standard values in terms of saturated vapor pressure, but one must understand that 20% is an outrageous amount of water and not every water-fuel emulsion contains it in such an amount. If the goal of using such a watered fuel is set, it can be easily achieved by slightly increasing the PO concentration in the bioethanol fuel.

The fact that PO in the "starting fraction" requires three times less gasoline or gasoline fractions is a very important competitive advantage. First, the smaller the "starting fraction", the larger the ethanol portion, which means that alcohol will be able to more fully realize its antiknock qualities. Secondly, the octane number of PO should be approximately at the level of isopropanol, according to the research method it is 119.1, which is much higher than AI-92 gasoline, not to mention straight-run fractions, whose octane number is not higher than 70 units. Even if the octane number of PO was 92 units, it would still be more profitable to use it than AI-92, since PO is needed three times less, which means that when mixed with ethanol, the octane number drawdown is less. Thirdly, these are economic indicators, if the volume of the "starting fraction" is less, then its final price will be lower. Yes, the PO price today is 150 thousand rubles per ton, which significantly exceeds not only cheap straight-run fractions, but also commercial gasoline, but since its volume is three times lower, the total cost will be comparable to AI-92 gasoline, the price of which is about 50 thousand rubles per ton. In addition, the use of PO as a "starting fraction" completely solves the problem associated with the sulfur content in the fuel and significantly reduces tar.

However, the main advantage of using PO as a "start-up fraction" is the ability to use water-cut alcohol. Thus, the first stage in obtaining commercial alcohols is to obtain "raw alcohol", in which the moisture content is about 12%, and then for classic fuel ethanol the moisture content is brought to 2 - 3%, which significantly increases the cost of alcohol. PO allows you to use not only alcohol with a strength of 95%, but even raw alcohol, the strength of which is 88%, which has a very significant effect on the cost of alcohol.

References

1. Tsygankov D. V. Alcohol fuel as the fuel of the future / D. V. Tsygankov, D. S. Konovalov // Collection of materials of the XI All-Russian, scientific-practical conference of young scientists with international participation "Young Russia", April 16-19. 2019, Kemerovo [Electronic resource] / FSBEI HE "Kuzbass state tech. un-ty n.a. T. F. Gorbachev"; editorial board: S. G. Kostyuk (editor-in-chief) [et al.]. – Kemerovo, 2019.

2. Konovalov D.S.Alcohol as a promising fuel / D. S. Konovalov, D. V. Tsygankov // Synthesis of science and society in solving global problems of our time: Collection of articles following the results of the All-Russian scientific and practical conference (Perm, April 30, 2019). – Sterlitamak: AMI, 2019. - P. 116-119.

3. GOST R 54290-2010 "Fuel ethanol (Ed75-Ed85) for automobile engines with positive ignition. Technical conditions".

4. Oerlikon Maschf, Method of regulating electrical power plants to a constant power factor. Great Britain patent GB 243326 - 1926-07-22

5. Alternative automotive fuel. Pat. 2549179 RF. IPC S10L1/18/M.A. Ershov, T.A. Klimova, S.P. Evdokushin, Open Joint Stock Company All-Russian Research Institute for Oil Refining, JSC "ARSRI OP" Appl. 30.01.2014. Publ. 20.04.2015, Bull. № 11

6. Alternative automotive fuel and the method for its production. Pat. 260554 RF. IPC S10L1/182/M.A. Ershov, E.V. Grigorieva, I.F. Khabibullin, V.E. Emelyanov. Joint Stock Company "All-Russian Research Institute for Oil Refining" (JSC "ARSRI OP") Appl. 25.12.2015. Publ. 10.01.2017, Bull. № 1

7. Ershov M.A.Test results of E30 bioethanol fuel on a full-size injection engine in comparison with standard gasolines / M. A. Ershov, I. F. Khabibullin, E. V. Grigorieva, V. E. Lazarev, E. A. Lazarev // Chemistry and technology of fuels and oils. – 2017. - №3, P.3-10.
8. Alternative automotive fuel and the method for its production. Pat. 2723546 RF. IPC S10L1/02/D.V. Tsygankov, A.M. Miroshnikov, A.V. Polozova, D.S. Konovalov. Appl. 08.10.2019. Publ. 16.06.2020 Bull. № 17.
9. Fuel-water emulsion. Pat. 2367683 RF. IPC S10L1/32/Yu.V. Vorobiev, V.B. Teteryukov. Appl. 23.10.2006 Publ. 20.09.2009 Bull. № 26.