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Chapter

Improving the Technology of Synthesis Absolutized Bioethanol

Sergiy Kurta and Khatsevich Olga

Abstract

The article describes the technology of synthesis of absolute ethyl alcohol, as well as the types, properties and efficiency of water-withdrawing reagents and types, properties and efficiency of reagents (CaO, tetraethoxytitanium), which chemically bind water and dehydrate ethanol. The composition and properties of the absolutized ethanol were studied using the infrared spectroscopy, mass spectroscopy and gas-chromatography. The octane number of gasoline with the addition of absolutized ethanol together with the combustion activator (diethyl ether) was measured as well. It has been shown that the content of even very small amounts (up to 2%) of the combustion activator in absolutized ethanol results in the increase of the octane number and improves running abilities of gasoline.

Keywords: technology, absolutized ethanol, calcium oxide, tetraethoxytitanium, diethyl ether, octane number

1. Introduction

Some methods for obtaining absolute alcohol are well known, namely: (1) by binding water to water by subtracting substances; (2) pressure absolutization on many column rectification (distillation) plants; (3) the so-called azeotropic rectification using methods based on the phenomenon of azeotropism of three-component systems; (4) using methods based on the phenomenon of vapor diffusion through porous partitions or molecular sieves [1, 2]. Using as a desiccant, calcined calcium oxide can achieve an ethanol concentration of 99.8%, using magnesium sawdust—89.95%. With the combined use of sodium alcoholate ethanol can be absolutized to 99.5% [3].

Another way to obtain absolute ethyl alcohol is to separate the mixtures in distillation columns operating at different pressure values. The method is based on the dependence of ethanol content in the mixture on pressure. Typically, the installation consists of two columns. In the first column receive the alcohol strength of 70–95%, which comes in second column under pressure. The pressure in different methods varies from 8 kPa to 7.6 MPa. It is in the second column that absolute alcohol (99.2%) is obtained. The absolute alcohol (99.2%) is obtained in the second column. The disadvantage of these methods is their high energy consumption, because the rectification columns operate under pressure and require of the using of vapor or other high-temperature media to provide the necessary parameters [4–10]. Many industrial distillation plants that produce absolute ethanol are azeotropic using a third component, which forms an azeotrope with the components of the

mixture—alcohol and water. Analysis of the literature shows that substances such as benzene, toluene, isooctane, cyclohexane and hexane can form the third component, which is capable of forming azeotropes with ethanol and water. The concentration of alcohol, obtained by this method, is reached to 99.7% [11–21].

Others are the methods built on the application of the phenomenon of adsorption. For this purpose, the alcohol-water mixture should be converted into a vapor phase in which the water molecules are in dissociated form and can be separated by adsorbents that absorb only water molecules from the vapor mixture and can be regenerated for reuse. Such adsorbents include polymer compositions based on dioxols, silica gel, synthetic zeolites and the like. Technologically, they can be made in the form of membranes, which are ceramic tubes, the inner layer of which is covered with a thin layer of zeolite or in the form of molecular sieves. Different composition of synthetic zeolites is known, but aluminum-potassium and aluminum-sodium zeolites have become the most widely used because they have a high adsorption capacity [22–33]. Due to the high cost of synthetic zeolites, ethanol absolutization methods have been developed, using the so-called natural zeolites—clinoptilolite: $(NaK)_4CaAl_6Si_{30}O_{72} \cdot 24H_2O$ and mordenite, which are widespread in the form of ores in certain territories of Ukraine, which is an undeniable advantage of their use [34].

Due to stabilization production of the volume petroleum and decrease in its price and the ban on the use of the tetraethyl lead gasoline in recent years, many countries of the world tend to increase the usage of oxygen-containing compounds as the additions in commercial high-octane gasoline. Methyl (MA), ethyl (EA) and tert-butyl (TBA) alcohols, methyl tert-butyl ether (MTBE), having high octane numbers and low boiling points are quite widely used among the oxygen-containing compounds. The usage of these additions results in an increase of the octane number and the improvement of the oxygen coefficient and the efficiency of the fuel combustion. All types of the fuel with oxygen-generating additives reduce the release of carbon monoxide (CO) and unburnt fuel parts (C) into the atmosphere. Thus, the addition of 10–15% MTBE reduces CO content in exhaust gases by 20%. The use of alcohol-gasoline mixtures as a motor fuel is also promising. The world ethanol production has recently reached 90 million m^3 per year [35]. The main producers are the USA, Brazil and India. It should be noted that more than 80% of produced ethanol is used as a component of motor fuels (fuel ethanol). The rest is used for manufacture of the strong drinks, solvents, the ethyl ethers and esters synthesis and as a raw material for organic synthesis [36].

In many countries of the world, gasoline with 10–15% of various fuel additives is already used. In particular, a mixture of gasoline and ethanol (10–12%) is successfully used in the USA, Canada and Brazil, where its production is based on a national program. In the United States, 80% of produced ethanol is used as a fuel. In France, fuel containing ethanol (5%) is used too. Ukraine consumes around 200 million tons of fuel and energy resources annually and has a deficit of energy resources because the needs for energy consumption are covered only up to 53% by its own resources. The rest is covered by import: 75% of the required volume of natural gas and 85% of crude oil and petroleum products. Such a structure of the energy economy creates Ukraine's dependence on oil and gas exporters and is threatening its energy and national security. Motor transport occupies a leading place in the transportation of goods. The prognosis of the development of Ukraine's motor car park proves the tendency toward a steady increasing of the number of cars and fuel consumption. In 2016, the total motor car park and the park of light commercial vehicles in Ukraine consist of, according to AUTO-Consulting, 9121,000 cars, which consume 32.7 million tons of motor fuel. The alcohol industry of Ukraine fully provides internal needs of alcohol for the manufacture of alcoholic drinks, working only up to 30% of its total capacity [37].

Recently, ethanol production of Ukraine has decreased almost twice from 310 million liters in 1996 to 140 million liters in 2017. Today, 25% of the 80 distilleries with a total capacity of 480 million liters per year operate. To date, in Ukraine there are more than 40 licensed distilleries that can process 900,000 tons of grain per year and obtain 320 million liters of grain ethanol. The annual need of beet molasses is 1.1 million tons, from which you can get other 300 million liters of ethanol. In the structure of realization of rectified ethanol the largest part is occupied by vodka and ethanol from 81 to 94.5% in 2015. In January 2016, the manufacturer "Ukrspirt" produced more than 860,000 l of ethyl alcohol, 85,000 l of strong drinks and 756,000 l of car washers. At the same time, the company work is provided by 16 factories [38].

In recent years, the production of bioethanol has been steadily increasing. From 2000 to 2014 the amount of produced ethanol has increased by five times. The market leaders are: USA (corn), Brazil (sugar cane), Germany and France (sugar beet and grain). Governments of these countries intend to increase the bioethanol production by 70%. If 10% of bioethanol is added to gasoline, emissions of aerosol particles are reduced by 50% and carbon monoxide emissions by 30%. Therefore, there is a Directive 2009/28/EC, which requires up to 10% bioethanol in a motor fuel by 2020. Ukraine signed the Association Agreement with the European Union, so it should undertake the similar obligations. While in the EU this index is gradually approaching 5% in Ukraine, it does not exceed 1% [39].

Macroeconomic analysis has shown that adding 20% of bioethanol to gasoline leads to an annual decrease in gasoline import by $ 400 million, which will result in $ 640 million increase in Ukraine's gross domestic product (GPD). Replacing 20% of heavy distillates with biodiesel will reduce imports by $ 1 billion, which can increase Ukraine's GDP by $ 1.4 billion.

In August 2014, there were 13 enterprises operating in Ukraine that produced alcoholic fuels, 10 of which based on the state alcohol distilleries with a capacity of 23,700 tons/month. However, in August 2014 there was introduced 99 EUR tax on alternative gasoline in favor of importers and network monopolists, resulting in the fact that by the beginning of 2015 only two plants ("Haysinsky" and "Ekoeenergy") with a total capacity of 2700 tons/month worked [39]. The cost of growing rape grain in recent years ranged from 800 to 1200 UAH/t. At the same time, when the seed market price is 3000 UAH/t, the cost of production of biodiesel from the fossil is 11,000–12,000 UAH/t (about 10 UAH/l), which is 2.5 times lower than the existing prices for diesel oil from oil [40]. The dynamics of growth of bioethanol and biodiesel part in the world represented by the author [37] speaks for itself, so the production of bioethanol has exceeded 100 billion liters, and biodiesel amount reaches 30 billion liters.

It is known that for homogenization of gasoline ethanol mixtures the third component is used. This component is aromatic hydrocarbons [41], which are added to ordinary gasoline to increase the octane number. In addition, it is not profitable, because the cost of toluene is by many times higher than the cost of absolute ethanol. As for the preparation of perfect mixtures of bioethanol and biodiesel with gasoline and diesel, only absolute ethanol (99.95%) must be used, therefore the research of new methods and reagents of ethanol absolutization is an actual problem and purpose of our work, which has a practical and economic value.
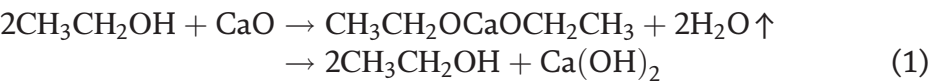
2. Experimental

The properties of known oxygen-generating additives which activate the motor fuel combustion are presented in **Table 1** [38]. The table shows reagents which do
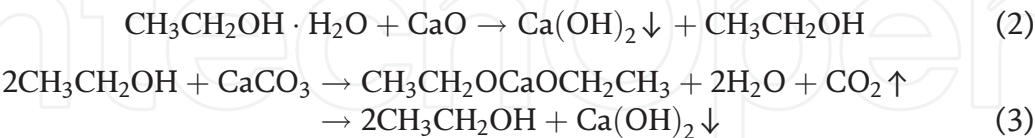
Indices	MTBE	ETBE	MTAE	DIPE	Methanol	Ethanol	*tert-*Butanol
Research octane number (RON)	112–130	120	105–115	111.6	120	106	108
Motor octane number (MON)	75–115	102	95–105	98.4	90	95	98
Octane number index (RON + MON)/2	110	111	105	105	101	100.5	103
Saturated vapor pressure, MPa (at 293 K)	0.06	0.03	0.02	0.03	0.42	0.13	0.07

Table 1.
Octane number of oxygen generating gasoline additives, which is measured by different methods.

not contain water, including ethyl alcohol and ethers, but in this work it is not described how the ethyl alcohol was absolutized, therefore in different sources it has a different octane number. Consequently, we propose our own method of ethanol absolutization with calcium oxide or tetraethoxytitanium (TET).

Researches of the method of ethanol absolutization by chemically binding water reagents such as calcium oxide and TET are conducted. Alcohols practically do not interact with alkalis, because among the reaction products there is water that decomposes formed alcoholate and a reverse reaction takes place.

$$2CH_3CH_2OH + CaO \rightarrow CH_3CH_2OCaOCH_2CH_3 + 2H_2O\uparrow$$
$$\rightarrow 2CH_3CH_2OH + Ca(OH)_2 \qquad (1)$$

Therefore, fresh prepared (1123 K, 2 h) mineral calcium carbonate, which has the following characteristics, presented in **Table 2**, was used for ethanol absolutization.

After calcination, samples of CaO were cooled in a vacuum desiccator, to reduce air access and to re-carbonize calcium oxide. Only 1 grade with minimum content of impurities was taken for work (**Table 2**).

It was suggested that if you take freshly calcined calcium oxide, then absolutized ethyl alcohol and alcoholates of the corresponding metals can be obtained during an irreversible reaction:

$$CH_3CH_2OH \cdot H_2O + CaO \rightarrow Ca(OH)_2\downarrow + CH_3CH_2OH \qquad (2)$$
$$2CH_3CH_2OH + CaCO_3 \rightarrow CH_3CH_2OCaOCH_2CH_3 + 2H_2O + CO_2\uparrow$$
$$\rightarrow 2CH_3CH_2OH + Ca(OH)_2\downarrow \qquad (3)$$

The component content of calcium oxide	Types of CaO obtained from mineral calcium carbonate, $CaCO_3$		
	1	2	3
Active CaO	≤90	≤80	≤70
Active MgO	≥5	≥5	≥5
$CaCO_3$ and $MgCO_3$ carbons	≥3	≥5	≥10
Impurities SiO_2 and Al_2O_3	≥1	≥10	≥15

Table 2.
Properties of calcium oxide.

The insoluble calcium hydroxide in the alcohol was filtered off, and the absolute ethyl alcohol by reactions (4) and (3) was discharged through a direct refrigerator, and the calcium hydroxide remained in the flask in the precipitate form.

Tetraethoxytitanium $(CH_3CH_2O)_4Ti$ as a dehydrator acts in different way.

$$(CH_3CH_2O)_4Ti + 4H_2O \rightarrow 4CH_3CH_2OH + Ti(OH)_4 \downarrow \qquad (4)$$

During the hydrolysis of TET the titanium tetrahydroxide, which is insoluble in alcohol, precipitates and can be filtered out; the absolutized alcohol is distilled at a special installation under vacuum, or with air dehydrators under normal conditions.

As can be seen from **Table 3** [42], ethanol has the most similar properties with gasoline according to the main indicators (boiling point and octane number). In addition, it is the cheapest and most affordable as a bioethanol—a product of natural raw materials processing, therefore, it was selected for absolutization. The ethanol concentrations were measured by the weight pycnometer method and determined by theoretical data [43]. The volume concentration of alcohol is determined by the areometers (ASP-1, ASP-2) using tabular data. Chromatography of ethanol and gasoline is carried out on by a gas–liquid chromatography, a method for determining oxygen-containing compounds in gasoline (HPCHEM\SEQUENCE \D161124A. S\METHOD\ D4815N.M) by internal standard (ISTD) based on 15 known calibrated substances, including ethanol (**Figures 2–4**). Infrared spectroscopy of ethanol samples is carried out by IR spectroscope (IS 50 FT-IR "NICOLET" Slovensko). Mass spectroscopy of the samples is carried by a mass spectroscope (MX-7304A, AO.SELMI, Sumy, Ukraine, 1 to 210 mass range). Determination of the cetane number of diesel fuel L-0.2-40 and the octane number of petrol A-80, as well as the freezing point of diesel fuel was carried out using the laboratory analyzer "Octane meter" of Shatox sx-100 k type [44]. Also, an assessment of the petrol gasoline by a motor method was carried out at the "OKKO" quality control laboratory in Galich, Ivano-Frankivsk region of Ukraine.

Parameter	Units	Methanol	Ethanol	Butanol	Gasoline
Molecular formula		CH_3OH	C_2H_5OH	C_4H_9OH	C_6H_6
Molecular weight	g/mol	32.04	46.07	74.12	78.11
Melting point	K	175	159	183	278
Boiling point	K	338	351	390	353
Density	g/cm^3	0.791	0.789	0.81	0.879
Saturated vap. pres.	kPa, 298 K	16.2	6.5–7.5	0.8	12.7
Vapor density	g/l, 298 K	1.3	1.9	2.4	3.2
Water solubility	g/100 ml	Unlimited	Unlimited	7.9 g/100 ml	1800 mg/l
Viscosity	s·Pa, 298 K	0.544	1.074	–	0.649
Henry's constant	C_{air}/C_{H_2O}, 298 K	1.087E−4	2.097E−4 to 2.571E−4	–	2.219E−1
Energy density	MJ/l	16	19.6	29.2	–
Octane number RON	–	156	132	104	82.5–98.0
Cetane number MON	–	92	89	78	95

Table 3.
Comparative physico-chemical characteristics of oxygen generating additives—gasoline combustion activators [42].

3. Results and discussion

Table 4 shows the results of the ethanol absolutization using tetraethoxy-titanium. As can be seen from the table, absolutized ethanol can be obtained with the ethanol concentration, which increases from 92.5 to 93–96 wt% (or 95.41–99.50 vol%), but does not reach 100 wt%.

Therefore, at the second stage of our research, we used a more reactive dehydrator—calcium oxide which was calcined at 1123 K; its characteristics are presented in **Table 2**. We selected a sample no. 1 with a minimum content of magnesium oxide (MgO—5%), carbonates ($CaCO_3$ + $MgCO_3$_3%) and other impurities (SiO_2 + Al_2O_3–1%). As can be seen from the results presented in **Table 4**, the CaO consumption decreases to 17 wt%, compared with 25 wt% of $(C_2H_5O)_4Ti$, and the concentration of absolutized ethanol increases to 99.5–100.0 wt %, or 99.7–100.0 vol%. In addition, the loss of alcohol decreases. After absolutization with $(C_2H_5O)_4Ti$ these losses reaches 15–25% C_2H_5OH (**Table 3**), while for CaO they decrease to 8–13% relative to the initial C_2H_5OH (**Table 4**). So we can say that calcium oxide as a chemically binding water reagent is much more effective dehydrator. As can be seen from **Figure 1**, the ethanol concentration after treatment with

Initial ethanol amount, SSU 4221:200 95 vol%, 92.5 wt %		The amount of ethanol obtained after absolutization		Ethanol yield after absolutization	The amount of Ti $(OC_2H_5)_4$		Ethanol density after absolutization	Ethanol concentration after absolutization	
V, ml	*m*, g	*V*, ml	*m*, g	wt%	*m*, g	%	g/cm³	vol%	wt%
100	82.15	85	69.07	84.08	26.65	25	0.8126	95.41	93.0
100	82.16	85.1	70.72	86.08	27.55	25.11	0.8065	95.85	93.5
100	82.10	77.59	62.1	75.14	29.15	26.20	0.8014	97.49	96.0
100	82.10	77.59	62.1	75.14	29.15	26.20	0.8014	99.50	96.0

Table 4.
Properties of ethanol after absolutization with tetraethoxytitanium.

The initial ethanol amount, 95 vol%, 92.5% mas.		The amount of ethanol obtained after absolutization		Ethanol yield after absolutization	The amount of CaO		Ethanol density after absolutization	Ethanol concentration after absolutization	
V, ml	*m*, g	*V*, ml	*m*, g	wt%	*m*, g	%	g/cm³	vol%	wt%
100	82.15	96	75.77	92.23	18	17.9	0.7893	100.0	100.0
100	82.16	93	73.42	89.36	17.8	17.8	0.7894	99.97	99.95
100	82.10	93	73.42	89.43	17.5	17.5	0.7895	99.93	99.89
100	82.10	90	71.69	87.32	17	17.1	0.7899	99.72	99.51

Table 5.
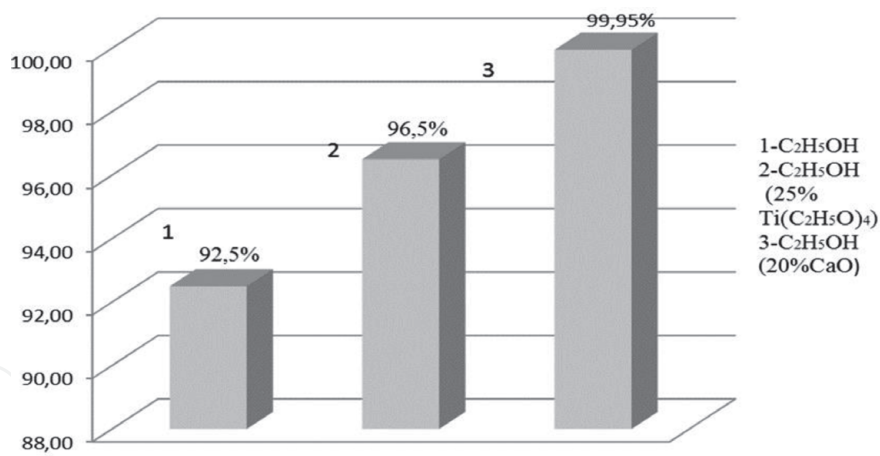*Properties of ethanol after absolutization by CaO (90%).*

Figure 1.
Dependence of the ethyl alcohol concentration after absolutization with tetraethoxytitanium (25%
$(C_2H_5O)_4Ti$) and calcium oxide (20% CaO).

calcined calcium oxide (17.5% CaO) reaches 99.95 wt%, while the absolutization with tetraethoxytitanium increases the concentration of ethanol only to 96.5 wt%.

At the same time, the non-absolutized 95% ethanol contains an admixture of MTBE (0.09531 wt %). In this case, the low-boiling impurity in the non-absolute ethanol is absent (**Figure 2**).

According to the chromatogram (**Figure 2**), the concentration of non-absolutized ethanol reaches 97.8499 vol % against 95.0%, as it was measured by the weight pycnometer method (**Tables 4** and **5**). At the same time, the concentration of ethanol absolutized with calcium oxide (**Figure 3**) is 97.5724 vol %. Taking into account 2.3432% of unidentified low-boiling impurity (T_b = 308–310 K) and 0.03433% of MTBE (according to the chromatogram in **Figure 3**), the total concentration of absolutized ethanol is 99.95 vol %, as it was determined by the pycnometric method (**Tables 4** and **5**).

Taking into account the chromatogram data in **Figure 3** and its interpretation, we determine the qualitative composition of one of the unknown components (X = 2.3432%), which appears in the chromatogram of ethyl alcohol (99.95%), absolutized with CaO for 2.8 min. At the same time, the chromatographic analysis of 99.99% ethyl alcohol absolutized by industrial method [43] (**Figure 4**), shows 100.03 vol % of ethanol. The difference of 0.03% might be a mistake of the device or an alcohol supplier analysis method.

Unfortunately, this impurity is not identified by graded chromatograms of alcohols and ethers, therefore, an IR spectral analysis of this alcohol is performed, which
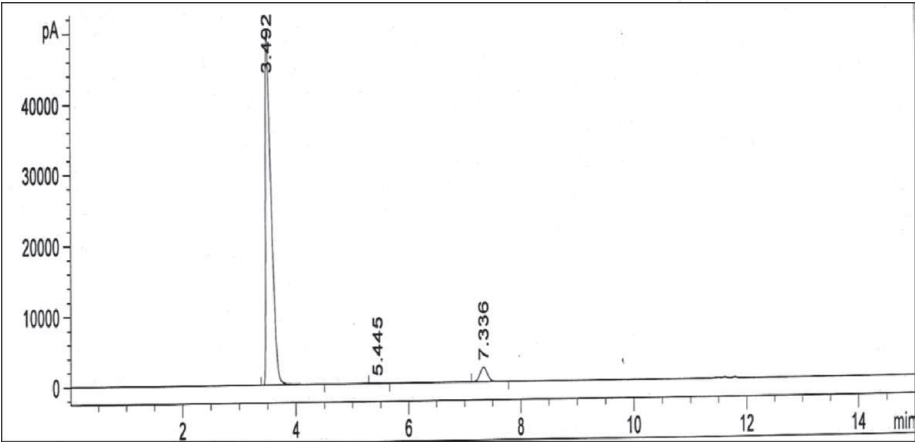

Figure 2.
Chromatogram of the initial, non-absolutized ethanol (95.0 vol%) with corresponding interpretation.
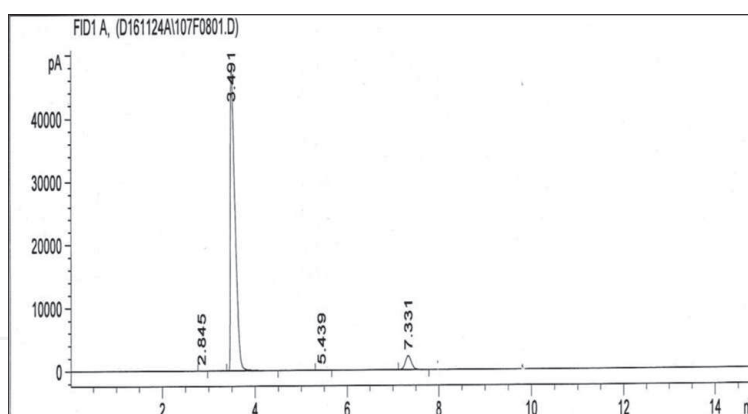
Figure 3.
Chromatogram of the ethanol (99.95 vol%), absolutized with calcium oxide with corresponding interpretation.
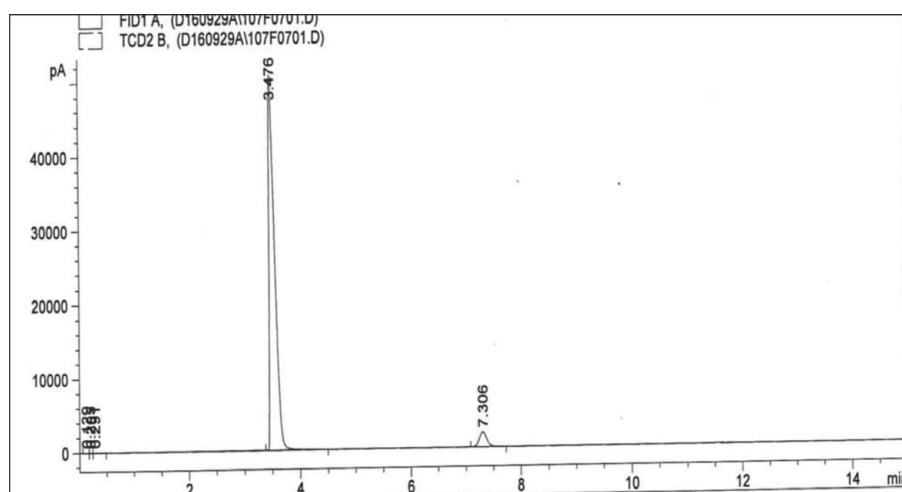

Figure 4.
Chromatogram of the ethanol (99.99 vol%), absolutized by industrial method [43] with corresponding interpretation.

is compared with the IR spectra of the original (95%) and pure absolute (100%) ethyl alcohol (**Figure 5**). As can be seen from **Figure 5**, the IR spectra of all three samples do not differ significantly from each other. Only in two absorption regions 3320–3330 and 1630–1640 cm^{-1}, there is a noticeable difference in the absorption intensity of the fluctuations of the corresponding groups, which significantly decrease from the maximum in the original non-absolutized 95% C_2H_5OH (curve 1, **Figure 5**) to a minimum in absolute 100% C_2H_5OH (curve 3, **Figure 5**).

First of all, the amount of water in samples of ethanol decreases from 4–5% in the initial non-absolutized alcohol (*curve* 1, **Figure 5**) to 0.1–0.05% in the absolutized with CaO ethanol (*curve* 2, **Figure 5**) and up to 0% in the absolutized 100% C_2H_5OH (*curve* 3, **Figure 5**). Therefore, the absorption intensity in the region of 3320–3330 cm^{-1}, which corresponds to the valence fluctuations of the hydroxyl groups of the H_2O molecules, decreases by 20% (according to the spectrograms in **Figure 5**). This is noticed in the transition from the non-absolutized 95% C_2H_5OH (*curve* 1, **Figure 5**) to the absolutized with CaO ethanol (*curve* 2, **Figure 5**) and to the absolute 100% ethanol (*curve* 3, **Figure 5**). In addition, in the spectrograms of the absolutized with CaO 99.95% C_2H_5OH (*curve* 1, **Figure 5**) and absolute 100% ethanol (*curve* 3, **Figure 5**) absorption disappears in the region of deformation oscillations 1630–1640 cm^{-1} of double bonds C=C or C=O [10] compared with non-absolutized 95% alcohol (*curve* 1, **Figure 5**), which can be identified as the presence of ketones, aldehydes, complex esters and ethers, and corresponds to the
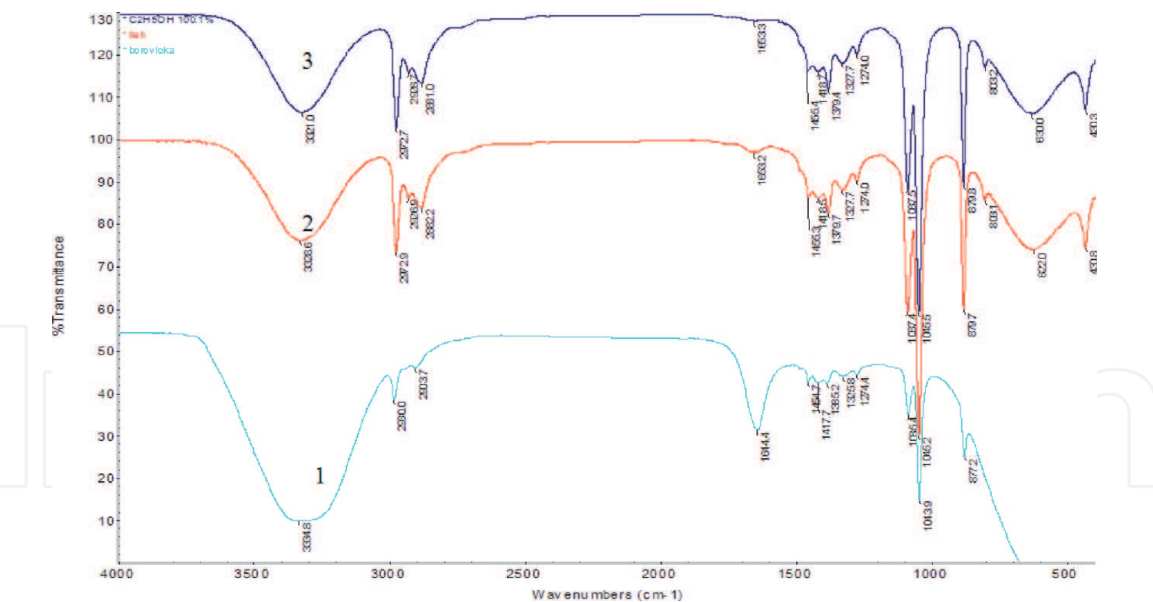
Figure 5.
Infrared spectra of different ethyl alcohols: 95.0 vol% non-absolutized C₂H₅OH (1); 99.95 vol% C₂H₅OH absolutized with CaO (2) and 100% C₂H₅OH of industrial product (3).
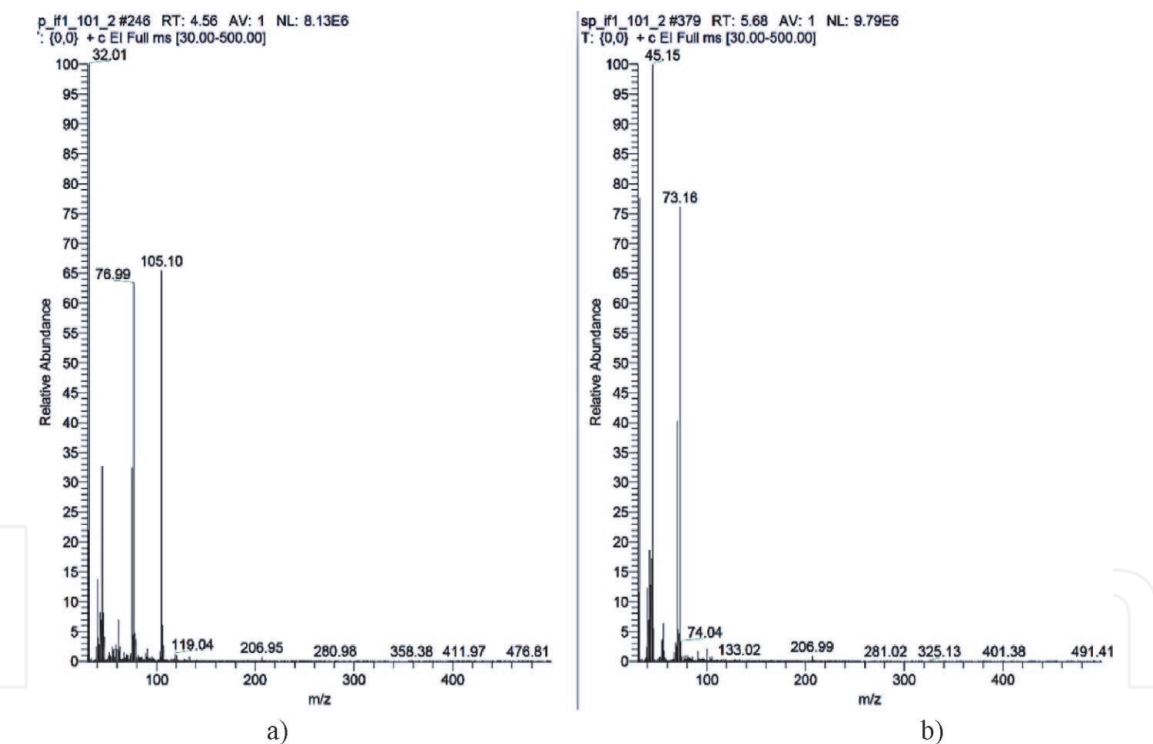

a)   b)

Figure 6.
Mass spectra of initial 95% ethanol (a) and absolutized with CaO 99.95% ethanol (b).

presence of MTBE in ethyl alcohol, which is identified in chromatograms of non-absolutized 95% and absolutized with CaO 99.95% ethyl alcohol (**Figures 2** and **3**) in the range of 0.034–0.095%.

For identification and more proper determination of the composition and structure of the impurity ($X = 2.3432\%$) in ethanol, which is identified in the chromatogram of the absolutized with CaO ethanol at 2.845 min (**Figure 5**), we carried out a mass spectrometric analysis of our samples of non-absolutized 95% and absolutized with CaO 99.95% ethanol by the mass spectroscope MX-7304A, AO.SELMI shown in **Figure 6**.

As can be seen in the mass spectrogram of non-absolutized 95% ethyl alcohol (**Figure 6a**), radical composition of the impurity is formed by the electron action of the mass spectrometer, there can be three types of free radicals with molecular weights such as 32.01 m.u.—$C_2H_5\bullet$ = 29 m.u.; 76.99 m.u.—$(CH_3)_3O\bullet$ = 73 m.u.; 105.1 m.u.—$C(CH_3)_3OOCH_2\bullet$ = 103 m.u. They may be formed by the action of electrons of the mass spectrometer on ethyl alcohol C_2H_5OH and methyl *tret*-butyl ether $C(CH_3)_3OOCH_2$, which are identified in the chromatograms of the initial non-absolutized 95% alcohol (**Figure 2**). At the same time, for absolutized with calcium oxide 99.95% ethanol (**Figure 6b**) in the composition of the impurity radicals formed by the action of electrons of the mass spectrometer, there can be only two types of free radicals with molecular weights such as 45.15 m.u.—$C_2H_5O\bullet$ = 44 m.u. and 73.16 m.u.—$(C_2H_5)_2O\bullet$ = 74 m.u. They can be formed by the electron influence of the mass spectrometer on ethyl alcohol C_2H_5OH and diethyl ether $(C_2H_5)_2O$, which are identified in a chromatogram of the 99.95% ethanol absolutized with CaO (**Figure 3**) [44, 45].

Taking into account that we know the retention time of the impurity (X = 2.3432% at 2.845 min), which is not identified in the chromatogram of 99.95% ethanol, absolutized with CaO (**Figure 3**), therefore, we have constructed dependence the retention time of three kinds of alcohol: *i*-propanol, ethanol, methanol and diethyl ether (DEE) depending on the boiling points of this substances in the chromatogram, shown in **Figure 7**.

The analysis of the curves shows that the diethyl ether retention time at the boiling point of 307.6 K (34.6°C) is 2.85 min, which coincides with the chromatogram data (2.845 min). In this way, we confirm the assumption that during the absolutization of 95% ethanol with calcium oxide, ethyl alcohol containing 2.3432% of diethyl ether and 97.5724% C_2H_5OH can be obtained.

We checked how 2.3432% of diethyl ether influences the ethanol octane number and the gasoline octane number. Previously, the physico-chemical characteristics of some oxygen-generating additives for gasoline, shown in **Figure 8**, were analyzed. As can be seen from **Figure 8**, the density and molecular mass of diethyl ether are close to those of gasoline A-95. The boiling point of the diethyl ether 307.6 K is lower than that of gasoline. It is approaching the boiling point of the first fraction of gasoline, which is 307.6 K. These properties are especially useful for accelerated engines of gasoline cars in winter, when ignition is hampered by a lowered ambient
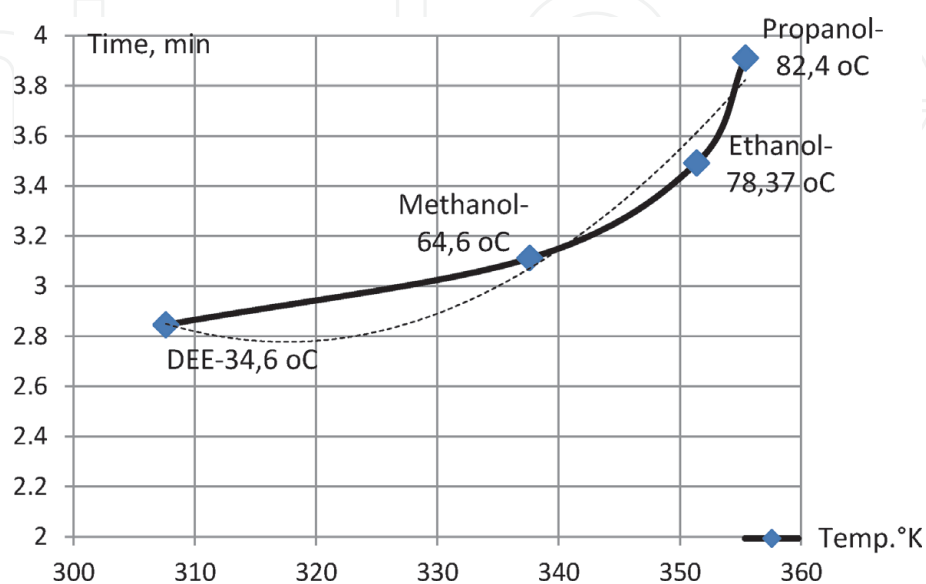

Figure 7.
*Dependence of retention time (min) of i-propanol (355.4°K), ethanol (351.37°K), methanol (337.6°K), and diethyl ether (DEE) (307.6°K), and the boiling points of these substances from the chromatogram (**Figure 3**).*
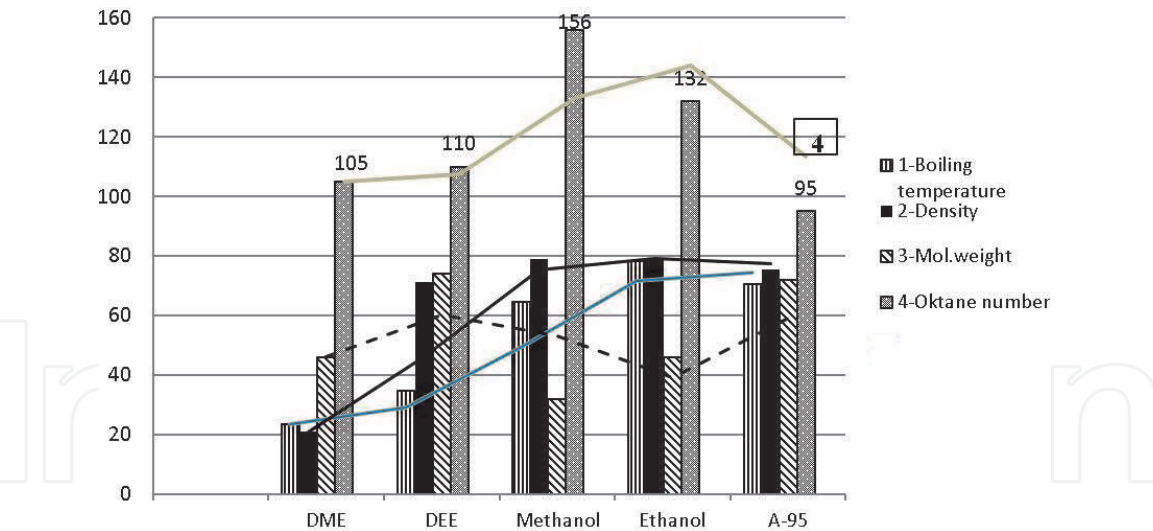
Figure 8.
Physico-chemical characteristics (1, boiling temperature °C; 2, density g/sm³ × 10; 3, molecular weight; 4, octane number) of oxygen-generating additives (DME—dimethyl ether, DEE—diethyl ether, methanol, ethanol) in comparison with the characteristics of gasoline A-95.

temperature (below 263 K). Thus, the diethyl ether presence improves the gasoline combustion efficiency, which we have checked by adding 10–95% absolutized (97.5%) alcohol containing 2.34% of diethyl ether, which is presented in **Figure 9** [46].

Octane numbers of A-80 gasoline with absolute ethanol additives (gasoline-ethanol mixture) are counted according to the authorship formula which is derived from experimental data [47]. These octane numbers are compared with the octane numbers of gasoline, in which ethanol with diethyl ether is added.

$$ONGE = [26.44—0.29(ON0)]\ln Ce + [1.32(ON0)—29.49] \qquad (5)$$

where ONGE—octane number of gasoline-ethanol mixture; ON0—octane number of initial gasoline; Ce—ethanol content [48].

Obtained data of the octane number dependence is performed in **Figure 9** (*curve* 1) and compared with the octane number of gasoline-ethanol mixtures to which
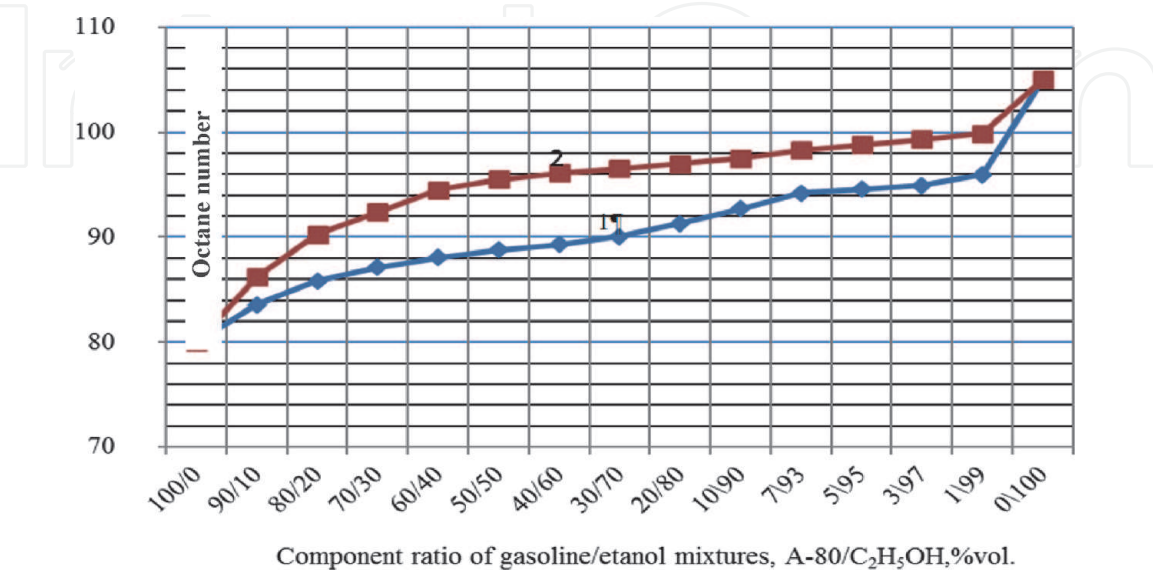

Figure 9.
Dependence of the octane number of gasoline A-80 on the amount and kind of added ethanol: theoretically calculated ON (1) of gasoline-ethanol mixtures from the formula [46] and experimentally obtained ON (2) of gasoline-ethanol mixtures with the addition of absolutized ethyl alcohol containing 2.34% of diethyl ether.

ethanol containing 2.34% of diethyl ether was added (*curve* 2). Thus, it was shown that ethyl alcohol containing diethyl ether can more effectively increase the octane number of gasoline A-80 [49], The content of 20–40% of such ethanol in gasoline A-80 increases its octane number to 91–95 U. While conventional 99.95% ethanol increases the octane number of gasoline A-80 only to 85–88 U. In the case of the maximum possible absolutized ethanol content up to 80–90% in gasoline A-80, the octane number reaches 91–93 U, and the introduction of the same amount of 99.95% ethanol containing 2.34% of diethyl ether in gasoline A-80, the octane number reaches 97–97.5 U [50].

4. Conclusions

The properties and high ability of calcium oxide and tetraethoxytitanium as dehydrators for chemical binding of water and absolutization of 96% ethyl alcohol to 99.95% have been investigated. The dependence of the properties and composition of the absolute alcohol on the dehydrator nature was shown. Infrared spectroscopy, mass spectroscopy, and gas-liquid chromatography confirmed the presence of 2–2.34% of diethyl ether in ethanol, which is absolutized by freshly prepared calcium oxide. It was determined that the octane number of gasoline A-80 with the addition of 20–90% of the absolutized ethanol containing 2.34% of the combustion activator—diethyl ether—increases gasoline octane number more significantly than with the addition of the same amount of an ordinary absolute 99.95% alcohol without diethyl ether and reaches 95–97 U, whereas the octane number of gasoline with ordinary absolute ethanol reaches only 88–95 U. We confirmed literary data that the content of even very small amounts of ethers, as combustion activators, combined with the absolute ethyl alcohol leads to an improvement in the gasoline running abilities [45].

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