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RESEARCH INTO THE PROCESS OF BIO-DIESEL FUEL PRODUCTION IN A CONTINUOUS FLOW APPARATUS WITH A VORTEX LAYER OF MAGNETIC ELEMENTS

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Abstract: The paper presents the results of experimental research into the process of bio-diesel fuel production by the methanolysis of rapeseed oil with a homogeneous alkaline catalyst in the apparatus with a vortex layer of magnetic elements. It has been established that the characteristic feature of the process of bio-diesel fuel production in the given apparatus is its high speed. The yield of reaction products is 98.7 % with reaction time of 3 s, temperature 60 °C, the molar ratio "oil – methanol" 1:6, and the amount of alkaline catalyst 0.75 % mass.

Introduction

More than fifty types of oil plants can be used to produce commodity bio-diesel fuel. As international experience has shown, bio-diesel fuel can be produced out of sunflower oil, rapeseed oil, soybean, cotton, linseed, palm, peanut and other vegetable oils [1, 2], which react with alcohols and form mixtures of higher aliphatic acids' ethers, i.e. bio-diesel fuel. The process of bio-diesel fuel synthesis is based on the reactions of transesterification of vegetable oils or esterification of fatty acids obtained through oil hydrolysis. Their generalized scheme is presented in Fig. 1.

However, among the variety of reactions of vegetable oil transesterification and fatty acids esterification, only two technologies for bio-diesel fuel production are usually implemented in industry. One is a reaction of transesterification with the use of a basic homogeneous catalyst. The other is a reaction of esterification using a homogeneous acid catalyst. In both cases methanol serves as esterification agent.

Manufacturing lines for bio-diesel fuel production with any productivity and process organization may utilize these technologies. As for the types of process organization, a periodic flow sheet is most widely implemented in industrial production of bio-diesel fuel [3]. According to it, a process of bio-diesel fuel production includes several separate stages that take place consecutively; it involves a wide range of common and cost-effective containers for various production scales.

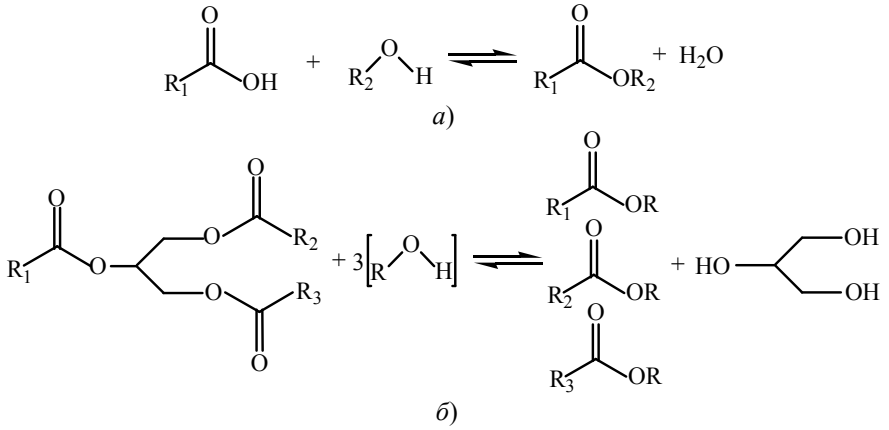

Fig. 1. General mechanism of reactions:
a – esterification in homogeneous medium; *b* – transesterification in homogeneous medium

A continuous process flow sheet implies that different stages of bio-diesel fuel production take place simultaneously and in parallel (in a flow). Key benefits of the continuous process are: decrease in the overall dimensions of installations with a given productivity due to absence of load/unload downtime; reduced energy and supplies costs; relatively simple process control automation; stable product quality. However, this type of process organization is seldom used for industrial production of bio-diesel fuel since it requires significant time for the interaction of chemical agents to ensure maximum product output.

Thus, a research into reducing reaction time as to make it possible to obtain high output of bio-fuel components in a continuous process flow seems to be very promising.

One of the methods that allow to intensify this process is to conduct it in a vortex layer of magnetic elements. This layer can be created by means of rotating magnetic action upon ferromagnetic elements. Such devices are used to intensify a variety of processes (intensive mixing and dispersion, acoustic and electromagnetic treatment, friction, high local pressures, electrolysis) as they have an integrated effect upon the processed substances. Apparatus with a vortex layer of magnetic elements are widely used in different industries as reactors [4, 5], mixers, shredders [6], extractors, for magnetic treatments, for activation of various substances, and other purposes [7, 8]. This paper presents the results of experimental research into a possibility of bio-diesel fuel production from rapeseed oil in an apparatus with a vortex layer of magnetic elements with the use of homogeneous alkaline catalyst.

Formulating and conducting experimental research

In the experiment the following raw components have been used for the production of bio-diesel fuel in a magnetic vortex apparatus: unrefined rapeseed oil brand T, Russian State Standard specification 8988–2002, with water content 0.2 % and free fatty acids content up to 2 %; technical methanol brand B, Russian State Standard specification 2222–95; and pure potassium hydroxide with base material content of 84.5 %, Russian State Standard specification 24363–80.

The research into bio-fuel production has been conducted in the installation the diagram of which is presented in Fig. 2.

The installation includes: containers for vegetable oil *8* and methanol *9*, pumps *11*, a system of industrial pipelines with shut and control fittings *15*, and catalyst container *12*. With the help of pumps *11.1* and *11.2* a reacting mixture (vegetable oil and alkali alcoholic solution) is injected into the reactor *1*, which includes an apparatus with a vortex layer of magnetic elements and its cooling system. The reaction products

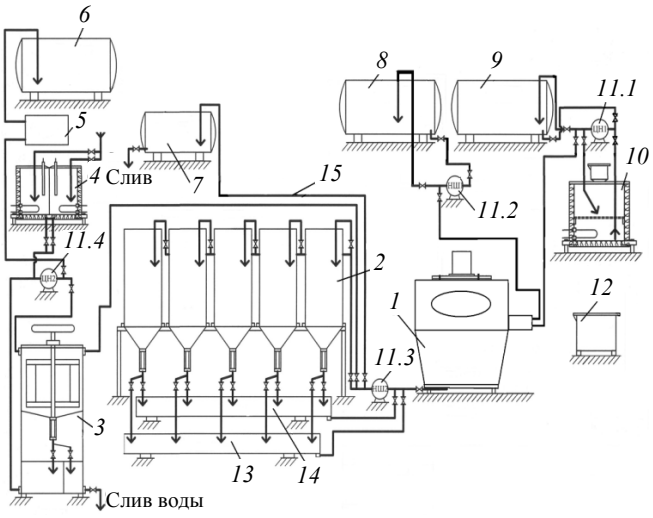

Fig. 2. Bio-diesel fuel production flowsheet:
1 – apparatus with a vortex layer of magnetic elements; *2* – separators block; *3* – purification units; *4* – rinsing agent preparation unit; *5* – centrifugal separator block; *6* – bio-diesel fuel container; *7* – crude glycerin container; *8* – container for vegetable oils; *9* – methanol container; *10* – alcoxide preparation unit; *11* – pumps; *12* – catalyst container; *13* – crude glycerin tank; *14* – crude ether tank; *15* – industrial pipeline system with fittings

are pumped over by pump *11.3* to the separators block *2*, out of which a phase containing glycerin flows into the container *7*, and methyl ethers of higher aliphatic carboxylic acids (bio-diesel fuel) – into purification and acid neutralisation units *3*. Further ether is purified in a centrifugal separators block *5* and with the help of pump *11.4* is transported into a bio-diesel fuel container *6*.

In this installation (Fig. 3) an inductor of a three-phase electric motor *1* has been used as an apparatus with a vortex layer of magnetic elements; the inductor was supplied with a cooling jacket *2*, and three coils (with equal number of loops). The axes of the coils have been shifted to form an angle of 120° and a glass tube *3* has been placed inside with minimal clearance. To prevent the escape of ferromagnetic elements from the apparatus porous insertions *5* were fitted to the connecting branches *4*. Operating and design parameters of this apparatus were kept at the following levels: the value of magnetic inductance vector was 0.13 tesla, electromagnetic field rotating velocity was 30 s^{-1}, coefficient of ferromagnetic elements filling was 0.12, dimentions of cylindric ferromagnetic elements – l = 12 mm, d = 1–1.1 mm, and reaction time was 3 s.

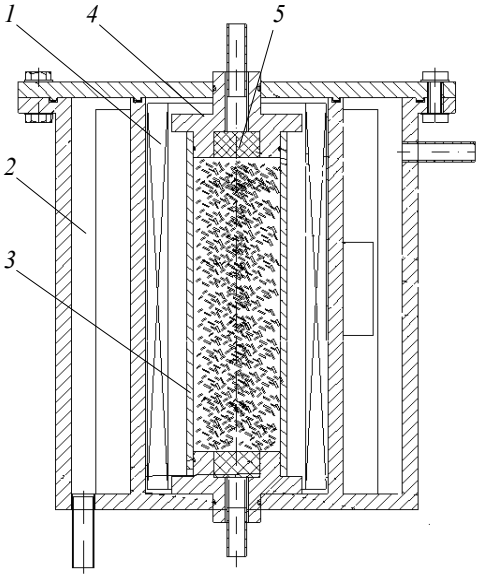

Fig. 3. Magnetic vortex apparatus with magnetic elements

The bio-diesel fuel produced with this installation has been analysed according to current European standard EN 14214:2003. Among other parameters, the output of bio-diesel fuel components (methyl ethers of higher aliphatic acids)

was determined. It has been done using the method of gas chromatography with the help of Kristall 2000M chromatographer. The chromatogrammes were processed with Chromatech Analytic software. The analysis settings were as follows: capillary quartz column ZB-5 (30 m × 0.32 mm × 0.5 μm); carrier gas – helium; detector – PID; detector temperature – 290 °C; vaporizer temperature – 280 °C; test volume – 1 μl. The density of bio-diesel fuel was measured according to EN ISO 3675, and viscosity – according to EN ISO 3104.

In the experimental research the influence of the following factors on the bio-diesel fuel output was determined – molar ratio oil : methanol, concentration of alkaline catalyst, temperature, content of free fatty acids and water in a reaction mixture.

Experimental research results and discussion

One of the most important factors that determines technological and economic parameters of bio-diesel fuel synthesis is vegetable oil : alcohol molar ratio. The 1 : 3 stoichiometric ratio of reactants makes the process setting very efficient economically (as it allows excluding the stage of methanol expulsion from ether phase). However, the output of the goal product – methyl ethers of higher aliphatic acids – only reaches 70 % when using a traditional method of synthesis (reaction time – 2 hours) [9]. According to the references, the optimal output of bio-fuel components of 93–98 % (depending on the type and quality of oil) can be reached with the ratio 1 : 6 [10]. It is inadvisable to use higher molar ratio of alcohol to oil, as it does not lead to higher output or less reaction time but, at the same time, results in larger costs of separation of unreacted alcohol and glycerin from ether phase.

In the studied method of bio-diesel fuel synthesis, the reaction mixture is exposed to electromagnetic field influence. Because of this, the energy of initial compounds increases and the energy of reaction activation subsequently decreases, which means that higher output of reaction product can be reached at a lower molar ratio “oil – methanol”. Thus, in a series of conducted experiments on synthesizing bio-diesel fuel components the molar ratio “oil – methanol” varied from 1 : 4 to 1 : 9 with the catalyst concentration 1.5 % (mass.) and synthesis temperature 60 °C. The results of experimental research are presented in Table 1.

As the data suggest, the molar ratio of oil to methanol 1 : 6 still stays optimal.

With larger alcohol fraction the output of ether phase slightly increases but the viscosity increases as well, and therefore, bio-fuel contains undesirable components – unreacted tri- and diacylglycerols and glycerin. Besides, higher alcohol content in ether phase was documented (large difference in volumes in purified and unpurified ether), which increases the cost of separating unreacted methanol.

The optimal temperature range for transesterification reaction has been determined by further experiments. The reaction mixture temperature varied from 25 to 65 °C. To achieve this, vegetable oil was heated up to 50…100 °C and then mixed with alkali alcoholic solution with molar ratio “oil – methanol” 1 : 6 for 3 s in the apparatus with a vortex layer of magnetic elements. The results of conducted experiments are given in Table 2.

Table 1

Influence of molar ratio «oil – alcohol» on the characteristics of bio-diesel fuel

Molar ratio «oil – alcohol»	Output, %	Density (at 20 °C), kg/m^3	Viscosity (at 20 °C), mm^2/s
1 : 4	90.0	880	6.83
1 : 6	98.7		6.46
1 : 7	98.5		6.53
1 : 9	98.3		6.59

Table 2

Influence of synthesis temperature in the apparatus with a vortex layer of magnetic elements on the characteristics of bio-diesel fuel

Temperature, °C	Output, %	Density (at 20 °C), kg/m^3	Viscosity (at 20 °C), mm^2/s
25	90.0	881	6.62
45	92.0	880	6.60
50	98.2		6.57
55	98.4		
60	98.7		6.35
65	98.1	881	6.56

As the data show, at 60 °C synthesis temperature ether output reaches its maximum, while viscosity is minimal. A decrease in temperature by 10 °C results in only slight change in output and viscosity. Thus this temperature is also appropriate for synthesis. Further decrease in temperature leads to almost 9 % decline in output along with the increase in viscosity and even density (at 25 °C).

The concentration of a homogeneous alkaline catalyst in reaction medium is another vital process parameter of bio-diesel fuel production. Without catalysts transesterification reactions are only possible under supercritical conditions. However, in this case the cost of equipment will significantly increase the capital costs of bio-diesel fuel production. And the methanolysis reaction is impossible under atmospheric pressure. In our research potassium hydroxide has been used as main catalyst, in concentrations from 0 to 1.5 % mass. The results can be observed in Fig. 4 and Table 3.

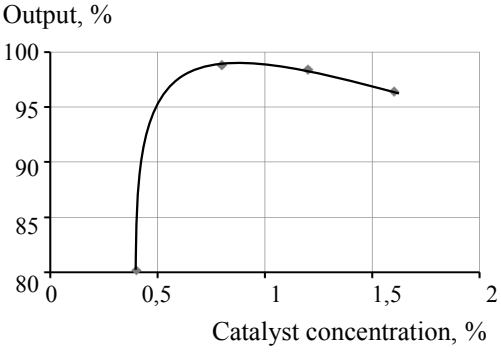

Fig. 4. Dependence between bio-diesel fuel output and catalyst concentration in reaction mixture

The studies have proven that partial methanolysis takes place even in the absence of a catalyst but the output of methyl ethers does not exceed 20 %. As the concentration of potassium hydroxide grows, ether output also starts to grow (up to 0.75 %) but then it slightly goes down. The minimal density and viscosity were also observed at alkali concentration 0.75 and 1.1 %.

Table 3

Influence of alkaline catalyst concentration on bio-diesel fuel characteristics

KOH concentration, % (mass.)	Density (at 20 °C), kg/m^3	Viscosity (at 20 °C), mm^2/s
0,0	906	29.63
0.375	884	8.08
0.75	880	6.49
1.1		6.52
1.5		6.59

There are certain requirements with which the raw materials for transesterification reaction with alkaline catalyst must comply. Oils must have acidity value less than 1 mg KOH/g and all materials must be water-free. When the acidity value is more than 1 mg KOH/g, more alkali in spent on the neutralization of free fatty acids. In this case soaps (salts of higher fatty acids) are formed which have no catalytic effect, more catalyst is consumed and it becomes less efficient. Because of the soap viscosity increases, gels are formed and separation of glycerin is complicated. Besides, it is not the alkali itself, but potassium methylate, formed through the interaction of alkali and alcohol, that acts as a catalyst in the methanolysis reaction

$$CH_3OH + KOH \leftrightarrow CH_3OK + H_2O.$$

This is a reverse shift reaction with the equilibrium significantly offset to the left as water has stronger acid properties than primary aliphatic alcohols and displaces alcohol from its salt (potassium methylate). Nevertheless, even small quantities of methylate formed in reaction mass are enough to catalyze the methanolysis reaction. Additional water (which might be introduced along with alcohol or oil) will shift the reaction equilibrium further to the left and will also contribute to the hydrolysis of triacylglycerols with the formation of free fatty acids. In their turn, these acids react with alkali and form soap that has the above-mentioned undesirable effects.

The paper [11] emphasizes the importance of implementing oils which are almost dry (< 0.1 %) and have low content of free fatty acids (< 0.5 %). Water content in methanol must not exceed 0.3 %, which means that concentration of methanol used in the reaction must be no lower than 99.7 %. When reactants do not meet these requirements the output of ethers significantly decreases.

A dramatic reduction of reaction time due to application of a rotating electromagnetic field with a vortex layer of magnetic elements, however, allows for the use of initial compounds of different degrees of purity. It becomes possible primarily because such short period of time (3 s) is not enough for the reactions of saponification and hydrolysis. Also, it is very likely that application of electromagnetic field leads to the increase of the speed of esterification reaction (i.e. interaction of free fatty acids with methanol when the goal products – complex methyl ethers of carboxylic acids – are formed). The results of experimental research into the influence of water and free fatty acids content on the output and properties of bio-diesel fuel components are presented in Fig. 5 and Tables 4 and 5.

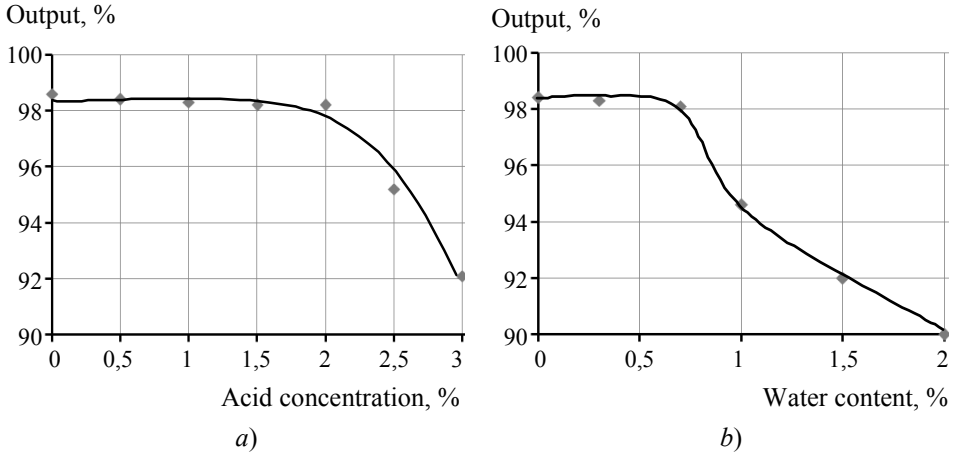

Fig. 5. Dependence of bio-diesel fuel output from the content of free fatty acids in initial oil (*a*) and from water content in initial alcohol (*b*)

Table 4

Influence of water content in alcohol on bio-diesel fuel characteristics

Water content, % (mass.)	Density (at 20 °C), kg/m^3	Viscosity (at 20 °C), mm^2/s
0,0	880	6.54
0.3		6.54
0,7		6.55
1,0		6.59
1,5		6.64
2,0		6.71

Table 5

Influence of the content of free fatty acids in vegetable oil on bio-diesel fuel characteristics

Water content, % (mass.)	Density (at 20 °C), kg/m^3	Viscosity (at 20 °C), mm^2/s
0,0	880	6.59
0.5		
1,0		6.55
2,0		6.54
3,0		

The obtained experimental data make it evident that it is possible to use a significantly wider range of initial substances in the studied conditions: alcohol with water content up to 0.7 % (mass.) and vegetable oils with the content of free fatty acids up to 2 % (mass.), including rancid and deep-fat oils. It is inadvisable to use oils with higher concentration of free fatty acids or alcohol with higher water content as the output of methanolysis reaction drops drastically in such cases.

Conclusion

The carried out experiments allow to conclude the following:

1. The parameters of influence of the content of reaction mass components on methanolysis reaction have been defined. Thus, to obtain the maximum output of methyl ethers of higher carboxylic acids (components of bio-diesel fuel) the optimal molar ratio of oil to alcohol is 1 : 6 and optimal alkali content is 0.75 % (mass.).

2. Along with electromagnetic, acoustic and mechanical influences, thermal action is also necessary to obtain greater output of methyl ethers of higher carboxylic acids. The optimal level of thermal action has been defined – the reaction temperature must be 60 °C.

3. A dramatic reduction of reaction time allows for the use of initial compounds of different degrees of purity. In the studied conditions the decrease in goal product output has not been observed till water content in alcohol of 0.7 % (mass.) and free fatty acids content in oil of 2 % (mass).

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Исследование процесса получения биодизельного топлива в проточном аппарате с магнито-вихревым слоем ферромагнитных частиц

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Ключевые слова и фразы: биодизельное топливо; устройство непрерывного потока; этерификация; топливо; вихревой слой.

Аннотация: Представлены результаты экспериментального исследования процесса получения биодизельного топлива путем метанолиза рапсового масла в присутствии гомогенного щелочного катализатора в аппарате с магнито-вихревым слоем ферромагнитных частиц. Установлено, что процесс получения биоди-

зельного топлива в данном аппарате характеризуется высокой скоростью протекания. Выход продуктов реакции составил 98,7 % при времени реакции 3 с, температуре 60 °С, мольном отношении «масло – метанол» 1 : 6 и присутствии щелочного катализатора в количестве 0,75 % масс.

Untersuchung des Prozesses des Erhaltens des Biodieselbrennstoffes im fliessenden Apparat mit der Magnitwirbelschicht der ferromagnetischen Teilchen

Zusammenfassung: Es sind die Ergebnisse der experimentellen Untersuchung des Prozesses des Erhaltens des Biodieselbrennstoffes mittels der Methanolyse des Rüböl in Anwesenheit des homogenen alkalischen Katalysators im Apparat mit der Magnitwirbelschicht der ferromagnetischen Teilchen vorgestellt. Es ist festgestellt, dass der Prozess des Erhaltens des Biodieselbrennstoffes in diesem Apparat mit der hohen Geschwindigkeit des Ablaufes charakterisiert wird. Der Ausgang der Produkte der Reaktion hat 98,7 % bei der Zeit der Reaktion 3 Sek, bei der Temperatur von 60 °C, bei der Molarbeziehung "das Öl – das Methanol" 1: 6 und bei der Anwesenheit des alkalischen Katalysators in Höhe von 0,75 % der Massen gebildet.

Etude du processus de l'obtention du carburant biodiesel dans un appareil à écoulement avec une couche magnétique turbulente des particules ferromagnétiques

Résumé: Sont présentés les résultats de l'étude expérimentale de l'obtention du carburant biodiesel par la voie de methanolysis de l'huile de colza dans la présence du catalyseur alcalin homogène dans un appareil avec une couche magnétique turbulente des particules ferromagnétiques. Est établi que le processus de l'obtention du carburant biodiesel dans cet appareil est caractérisé par une grande vitesse de l'écoulement. Le rendement des produit de réaction est de 98,7 % avec le temps de la réaction 3 s., le température 60 °C, la relation modulaire "huile – methanol" est 1 : 6 et la présence du catalyseur alcalin dans la quantité de 0,75 % masses.

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