A technology for producing biofuel components

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Abstract. The article discusses the prospects for the use of biofuels as an alternative fuel, which allows reducing the dangerous impact of exhaust gases from diesel engines on the environment. The results of the analysis of the technologies used for the production of biodiesel are presented. The expediency of using a hydrodynamic mixer as a device providing the intensity of the transesterification reaction in the production of biodiesel has been substantiated. A technological scheme of a laboratory installation for the production of biodiesel has been developed. Presented are the results of laboratory studies to determine the optimal material balance of the transesterification reaction for the production of biodiesel using a plant equipped with a hydrodynamic mixer. The main indicators of the transesterification reaction (viscosity, flash point, sediment height) were determined for a unit equipped with a hydrodynamic mixer. The optimal mass ratio of the transesterification reaction has been established, which ensures the best quality indicators of the resulting biodiesel and allows evaluating the efficiency of the hydrodynamic mixer used in the installation. Recommendations are given on the ratio of vegetable oil and methanol in the production of biodiesel. The best oil/methanol ratio in terms of biodiesel yield and quality is 7.5:1. The use of traditional fuel oil mixed with biodiesel can be seen as an effective way to reduce air pollution from vehicles and to ensure compliance with the rules of international organizations.

1. Introduction

Unstable and unpredictable oil and gas prices, environmental problems stimulate transport companies to show practical interest in the use of motor fuels from vegetable raw materials, as a partial or even complete substitute for traditional mineral fuels. The most promising direction in transport is the use of biofuels based on vegetable oils for diesel engines. Biofuel is a product obtained by mixing diesel fuel and methyl ester of vegetable oil (MEVO) or biodiesel [1, 2].

The use of biofuels reduces emissions of substances such as hydrocarbons, particulates, carbon dioxide CO₂ and carbon monoxide CO in exhaust gases, but NOₓ emissions may increase. Most studies have shown that the reduction of harmful emissions in exhaust gases due to the use of biofuels can be associated with sufficient oxygen content in the fuel. A typical relationship between the percentage of MEVO in fuel and the percentage change in emissions for four harmful emissions (carbon monoxide, NOₓ, PM and HC), based on US EPA research, is shown in Figure 1.
Considering that the use of biofuels helps to reduce the dangerous impact of exhaust gases from diesel engines on the environment, it is necessary to develop a technology for producing its component (biodiesel).

Biodiesel is obtained from vegetable oils as a result of the transesterification reaction with the addition of methyl alcohol and KOH.

The most widespread is the classical technology of biodiesel preparation (Figure 2), which is used all over the world in the extraction of fatty acids. Unfortunately, it is labor-intensive and energy-intensive, and therefore unprofitable. To obtain biodiesel, it is necessary to mix vegetable oil with methyl alcohol in special reactors and add a catalyst (usually NaOH or KOH). The mixture is heated to a temperature of 60°C, then it is settled and MEVO is formed, as well as by-products, for example, glycerol [3, 4].

The reaction of obtaining MEVO depends on the quality of the feedstock. It takes place with an excess of methyl alcohol. This excess leads to saponification of the resulting product, which must then be washed with water to remove all impurities. In particular, excess alcohol and the flash point of MEVO are reduced, from which the fuel is obtained of low quality. As a result, biodiesel has to be recovered with methane and then “dried”. This requires an additional vacuum drying unit, and, accordingly, it becomes necessary to dispose of the used water or sorbent.

To avoid the polymerization reaction, as well as other side reactions, it is necessary to maintain optimal reaction conditions: the order of feeding the reagents, temperature, concentration of NaOH or KOH in methanol and reaction time. It is also important to ensure high-quality mixing in the reactor, starting from the moment the reagents are fed into it. To obtain a homogeneous mixture, it is necessary to use special mixers, the functioning of which is based on the hydrodynamic effect on the reaction components—vegetable oil and methyl alcohol. The most preferred mixing device is an ejector-type hydrodynamic mixer. The use of hydrodynamic mixers makes it possible to more accurately maintain the stoichiometric composition with respect to methyl alcohol and the minimum volume in the reaction medium [5, 6].

Figure 1. Relationship between the content of MEVO in fuel and the content of harmful emissions
2. Materials and methods
The purpose of experimental studies was to determine the optimal ratio of methanol and vegetable oil (VO), which will provide the highest biodiesel yield and flash point, with the lowest kinematic viscosity. A general view of a laboratory plant for the production of biodiesel is shown in Figure 3.

The density of the oil and bioadditives was measured using an ANT-2, AON-2 and ASP-2 hydrometers with a graduation value of 0.001 g/cm³, and the kinematic viscosity was measured with a VPZh-4 capillary glass viscometer.

Figure 2. Biodiesel production scheme

Figure 3. Laboratory unit for the production of biodiesel
The technological scheme of the laboratory setup is shown in Figure 4.

Figure 4. Technological scheme of the laboratory setup: 1 – pump; 2 – hydrodynamic mixer; 3 – container for oil; 4 – tank for alcohol solution; 5, 7 – taps; 6 – temperature sensor; 8 – manometer.

The calculated amount of vegetable oil preheated to a temperature of 55 °C, is poured into tank 3. The unit is switched to the “circulation” mode by turning on pump 1. Additional heating of the oil occurs due to throttling in hydraulic mixer 2. When the vegetable oil temperature reaches 60 °C, the unit is switched to the “the introduction of an alcoholic” mode, which is fed in a certain amount. Then the components are circulated for 3 minutes, and then the mixture is allowed to settle for 40 minutes. During this time, separation of the working fluid occurs as a result of the transesterification reaction. The upper layer is biodiesel, the lower layer is the glycerin-containing fraction. Further, the glycerin fraction is drained through valve 7 and disposed of.

The analysis of the data obtained involves the determination of the optimal mass ratio of oil/methanol used in the production of biodiesel (MEVO) on a plant equipped with a hydrodynamic mixer [7].

3. Determination of the optimal ratio of methanol and vegetable oil in the production of biodiesel

To obtain biodiesel in the largest amount with an increased flash point (more than 110 °C) and the lowest kinematic viscosity, it is necessary to establish the optimal material balance of the components used in the production of biodiesel taking into account the equipment used. The intensity of the transesterification reaction—the main reaction of the technological process for producing biodiesel—is regulated by the working process of the mixer. Hydrodynamic mixers are currently preferred. However, there are no recommendations for the preparation of the optimal ratio of the reaction components.

The purpose of experimental studies is to determine the optimal ratio, including the amount of methyl alcohol, catalyst (KOH) and vegetable oil, providing the highest biodiesel yield and flash point (higher than 110 °C) with the lowest kinematic viscosity.

Analysis of the data obtained assumes the determination of the optimal mass ratio PM/methanol used in the production of biodiesel (MEVO) and the efficiency of the hydrodynamic mixer used in the experimental setup.

Due to the lack of domestic standards for this type of product, the obtained biodiesel was compared for compliance with foreign national standards for biodiesel fuel: ONC1191 (Austria), DIN V 51606 (Germany), UNI 10635 (Italy), CSN656507 (Czech Republic), SS 155436 (Sweden), JournalOfficial (France).

The research results are presented in Table 1.
Table 1. Results of laboratory tests

| Oil/methanol weight ratio | Mass [kg] | Viscosity [mm²/s] at 40 °C | Flash point [°C] | Sediment height [mm] |
|--------------------------|-----------|---------------------------|------------------|----------------------|
|                          | oil       | methanol                  | KOH              |                      |
| 6 : 1                    | 9.17      | 1.506                     | 0.0917           | 4.690                | 35                    | 55.7                 |
| 7 : 1                    | 9.17      | 1.310                     | 0.0917           | 4.707                | 35                    | 57.5                 |
| 7,5 : 1                  | 9.17      | 1.220                     | 0.0917           | 5.603                | 38                    | 53.9                 |
| 8 : 1                    | 9.17      | 1.146                     | 0.0917           | 5.612                | 40                    | 85.0                 |
| 9 : 1                    | 9.17      | 1.019                     | 0.0917           | 5.648                | 42                    | 110.0                |

With the PM/methanol ratio in the range of 6:1 and 7:1, the lowest value of the kinematic viscosity of the MEVO was obtained, but the lowest value of the flash point was observed (Figure 4), which is unacceptable. The coincidence of these two facts allows concluding that there is residual methanol in the product that has not reacted. In addition, poor visual clarity of the product is noted (Figure 5). Despite the satisfactory value of such an indicator as the height of the sediment (Figure 6), it does not have a significant impact on decision making due to the poor quality of the product obtained. Therefore, with the above PM/methanol ratios, for a plant using a hydrodynamic mixer, the assigned methanol concentration is excessive.

With PM/methanol ratios between 8:1 and 9:1, the viscosity has a maximum value (Figure 5). It does not exceed the maximum permissible values for biodiesel fuels according to CSN656507 (Czech Republic), but approaches the maximum permissible values of regulatory documents in other countries and does not comply with DIN V 51606 (Germany), which today imposes the most stringent requirements for biodiesel fuel.

The flash point, with PM/methanol ratios between 8:1 and 9:1, reaches the maximum value from the entire series of experiments (Figure 5), which favorably affects the quality of the biodiesel obtained. The quality can be indirectly judged by the appearance of biodiesel (Figure 7).

Figure 5. Dependence of viscosity and flash point on the content of methyl alcohol

However, the sediment formed in these experiments, and especially its consistency and amount (Figure 7), indicate that it was not possible to avoid the polymerization reaction and other side reactions, since the optimal conditions for the transesterification reaction were violated and part of the oil did not react. The height of the sediment after settling is inversely proportional to the practical yield of the finished product, therefore, with the PM/methanol ratio of 9:1, the biodiesel yield is the smallest for this installation (Figures 7 and 8).
Figure 6. The transparency of the MEVO depending on the different oil/methanol weight ratio.

Figure 7. Sediment height after settling at different oil/methanol weight ratios

Figure 8. Dependence of the height of the sediment on the content of methyl alcohol
The oil/methanol ratio of 7.5:1 demonstrated the best kinematic viscosity and flash point (Figure 5). Also, in the experiment with this ratio, the lowest value of the sediment height was revealed; therefore, the practical yield of biodiesel at a ratio of 7.5:1 is the maximum of the entire series of experiments. At the specified ratio, the product has a satisfactory appearance and transparency. Moreover, the ratio 7.5:1 is the maximum permissible value, which follows from Figure 7.

As a result of the experimental studies, it was found that for a setup with a hydrodynamic mixer, the optimal oil/methanol ratio is 7.5:1.

4. Conclusion
As a result of the research carried out, a technology for producing bioadditives (MEVO) for diesel fuel was presented. The main indicators of the transesterification reaction for a plant equipped with a hydrodynamic mixer have been determined. The best oil/methanol ratio in terms of biodiesel yield and quality is 7.5:1. The use of traditional fuel oil mixed with dietary supplements can be seen as an effective way to reduce air pollution from vehicles.

References
[1] Kesieme U, Pazouki K, Murphy A and Chrysanthou A 2019 Biofuel as alternative shipping fuel: technology, environmental and economic assessment Sustainable Energy Fuels 3 899-909. DOI: 10.1039/C8SE00466H
[2] Tamandzha I and Shuytasov N N 2010 Prospects and grounds for the application of a biodiesel in marine power plants Bulletin of Astrakhan State Technical University Series: Marine Engineering and Technologies 1 158-166 (In Russ)
[3] Lin C-Y 2013 Strategies for promoting biodiesel use in marine vessels Marine Policy 40 84–90. DOI: 10.1016/j.marpol.2013.01.003
[4] Gromakov A V and Fil’ A V 2019 Prospects of biofuels as fuel for marine diesels Operation of sea transport 4(93) 53-59. DOI: 10.34046/aumsuomt93/10 (In Russ)
[5] Bogdanovich V P, Gromakov A V and Byrko S I 2010 Vegetable oil - the raw material for motor fuel. Rural machine operator 11 30 (In Russ)
[6] Byrko S I 2011 Existing biodiesel production technologies and technical means Innovative technologies and technical means for field cultivation in the south of Russia: Collection of scientific works of NCRMEA RAAS, ed V I Pakhomov (Zernograd: NCRIMEA RAAS) pp 136-142 (In Russ)
[7] Byrko S I 2012 Improvement of the technology of obtaining bioadditives to diesel fuel Agroengineering science in the field of AIC: innovations, achievements: Collection of scientific works of NCRIMEA RAAS, eds V I Pakhomov, V B Rykov, A I Bur’yanov, N M Bespamyatnova et al (Zernograd: NCRIMEA RAAS) pp 34-38 (In Russ)