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IMPROVED TECHNOLOGY OF BIODIESEL FUEL PRODUCTION FROM WASTE OILS

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Abstract. The process of biodiesel fuel production from waste oil is investigated. It is identified that when processing used oil, the raw material needs after-treatment, and the presence of free fatty acids in the oil leads to the appearance of an additional reaction The ways of improvement of technological scheme for biodiesel fuel manufacturing taking into account raw material characteristics are offered.

Key words: biodiesel fuel, waste oil, catalyst, technology of transesterification.

1. Introduction

The increase in the amount of waste oil from public catering facilities is a worldwide problem. Discharge of contaminated oil leads to the problems of sewage treatment and pollution of the environment. The use of oils that have been repeatedly heated can potentially cause health problems.

However, such waste has significant potential as a renewable energy source. The main purpose of all activities on solving the waste problem is to minimize their entry into waste water and landfilling with the collateral utilization of their energy potential. Waste oils are known to be used in the production of soap, thermal cracking, or the production of biofuels [1].

The basis of the biodiesel production process is the transesterification of the raw material – vegetable oils and fats. The reaction of obtaining methyl ester of fatty acid of vegetable oil is shown schematically in Fig. 1.

As a result of the reaction, ester and glycerin are formed. This reaction proceeds step by step with the production of mono- and diglycerides as intermediate products. The reaction takes place in the presence of a catalyst.

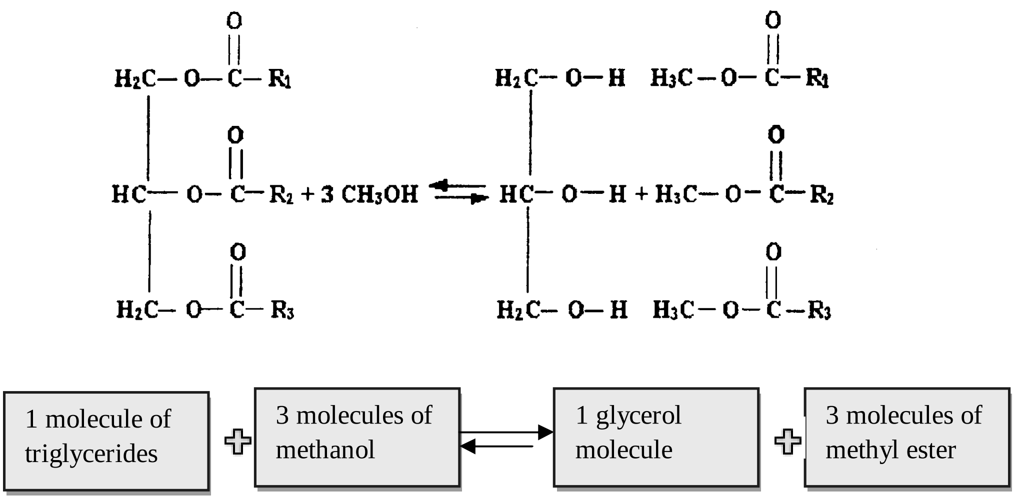

Fig. 1. Obtaining of methyl ester of fatty acid of oil: R1, R2, R3 – fatty acid residues

The resulted product of waste vegetable oil transesterification is a renewable energy resource, which significantly reduces the environmental burden and leads to the saving of non-renewable resources [2–7]. An important advantage of fuels based on vegetable oils is greater environmental friendliness both in production and in application, and in particular the fact that biodiesel fuel biologically decomposes in 21–28 days by 99 %.

When using waste vegetable oil in the production of biodiesel, the yield of methyl esters may be different from their yield when using fresh oil as raw material. Repeated heating and the presence of other substances in boiling oils can substantially change its properties. This circumstance requires carrying out additional experimental studies of the reaction of transesterification with waste vegetable oil used as raw material.

In the production of biodiesel, the following substances are used as catalysts: sulfuric acid, hydrochloric acid, sodium and potassium hydroxides. An overview of various methods of biodiesel production using different alcohols and catalysts is given in works [2, 3, 8, 9].

The use of an alkaline catalyst has advantages over the acid one due to the higher reaction rate (about 30 minutes compared with 1–8 hours for an acid catalyst). However, the yield of the final product is the same and is approximately 90 % in both cases [9]. For oils with high content of free fatty acids, preliminary treatment is recommended, which involves carrying out an esterification reaction using an acid catalyst to convert free fatty acids (FFAs) to the corresponding esters. By such approach, the high yields of the product are achieved even with high initial percentage of free fatty acids [10]. After pretreatment with the use of, for example, sodium or potassium hydroxide as a catalyst, glycerides in the oleic-ester phase are transesterified to result in the best product yield. In works [8, 9] it was shown that methoxides of sodium and potassium are more reactive than the corresponding hydroxides. But they have a higher cost, cause the formation of various by-products and require high-quality oil and water free of methanol. On the other hand, the interaction of sodium or potassium hydroxide with alcohol leads to the formation of water. Such reaction is undesirable because water can react with triglycerides, fatty acids or esters in the hydrolysis reaction with subsequent saponification [9]. Nevertheless, despite the lower reactivity, with the use of sodium hydroxide and potassium, high yield of the product can be obtained by increasing the amount of catalyst [11].

Biodiesel production has been intensively studied over the last 20 years. Studies were conducted for both “pure” oils and fats [9, 11–14], and for cheaper raw materials such as waste oils, animal fats, and others. [5, 10–15]. At the same time, some results are controversial. Technological characteristics of processes are limited. Also, at present, there is no data on the output of the final product using waste oils and the kinetics of their transesterification.

2. Goal and tasks of the research

The goal of this research is to analyze the technological features of the process of transesterification of vegetable oils in the presence of an alkaline catalyst and to study the application of the chosen processing method for obtaining quality biofuels from waste oils.

In accordance with the goal, the following tasks are formulated:

– to obtain experimental data on the transesterification process using waste oil as raw material.

– on the basis of experimental data, determine the optimal conditions for the process;

The object of the study is the process of transesterification of waste vegetable oil with methanol using an alkaline catalyst.

The subject of the study is the technology of transesterification process of waste vegetable oil.

3. Experimental study of the process of biodiesel production

Laboratory equipment for an experimental study of the reaction of transesterification of waste vegetable oil with methanol is depicted in Fig. 2.

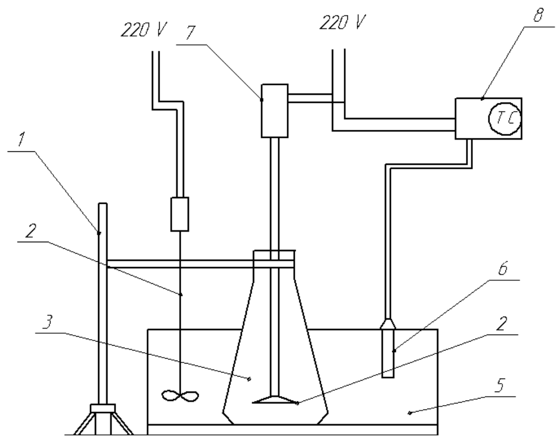

Fig. 2. Scheme of laboratory setup: 1 – stand; 2, 4 – mixing device; 3 – reaction flask; 5 – water bath; 6 – thermostat; 7 – mixer engine; 8 – thermoregulator

At the first stage of processing it is necessary to remove water from the raw material – used sunflower oil from fast food restaurants. Anhydrous sodium sulfate was used as a drying agent. Then the depleted sunflower oil was filtered to remove residues of food and other impurities from it.

To conduct the experiments on the transesterification of waste vegetable oil, a reaction mixture was prepared with the following reagents: 100 ml of used sunflower oil and 12.5 ml of methanol. Potassium hydroxide was used as a catalyst in the amount of 0.8 g. The reagents were loaded into the reaction flask 3 with stirrer 4. The flask was placed in the thermostat vessel.

The reaction begins in a two-phase system, which consists of an alkaline solution of methanol and triglycerides. During the first few minutes of mixing, the system becomes single-phase as a result of emulsification. After the formation of a significant amount of glycerol, the system becomes biphasic again.

The mixture was stirred for 1.5 hours at 25 °C. Then the mixture was left for 16 hours. As a result of this long-term upholding, two layers of liquids were formed. The upper layer is a lipophilic phase with high content of methyl esters, and the lower one is an alkaline solution of methanol in glycerol.

The upper layer of the liquid was separated. The obtained product was analyzed for the content of mono-, di-, and triglycerides and fatty acid methyl esters.

Results and discussion

The research was carried out using the following substances: used sunflower oil from fast food restaurants, methanol and potassium hydroxide as a catalyst.

The results of the study of the samples are shown in Table 1.

From the analysis of the obtained results, we can make the following conclusions:

– the temperature of the process of transesterification does not significantly affect the contctntraitions of the final product – the content of methyl esters (as can be seen from Table 1, with the increase in temperature by 2.5 times the content of methyl esters increases by 2 % only);

– an increase in the concentration of the catalyst and the reaction time increases the yield of the target product;

– the total yield of methyl esters from used oils does not exceed 65 % of the yield of the product when triglycerides from pure oil are used as a raw material.

Low yield of the target product from the used oil compared with the yield from pure oil is caused by the reaction of oligomerization of triglycerides from oil when repeatedly heated in the presence of air oxygen, which occurs in catering establishments.

From the analysis of the various factors, which influence the yield of biodiesel (the ratio of oil and alcohol, the amount of catalyst, temperature, reaction time), we can offer the following scheme of the production process (Fig. 3).

Table 1

Content of methyl esters of fatty acids after transesterification of used oils

Experiment number	Temperature, °C	Reaction time, min	Concentration of the catalyst, mass %	Content of methyl esters, %
1	20	30	0.6	42.1
2	20	60	0.6	44.8.
3	45	30	0.6	42.2
4	45	60	0.6	44.8
5	20	30	0.8	45.6
6	20	60	0.8	48.4
7	45	30	0.8	45.8
8	45	60	0.8	48.5

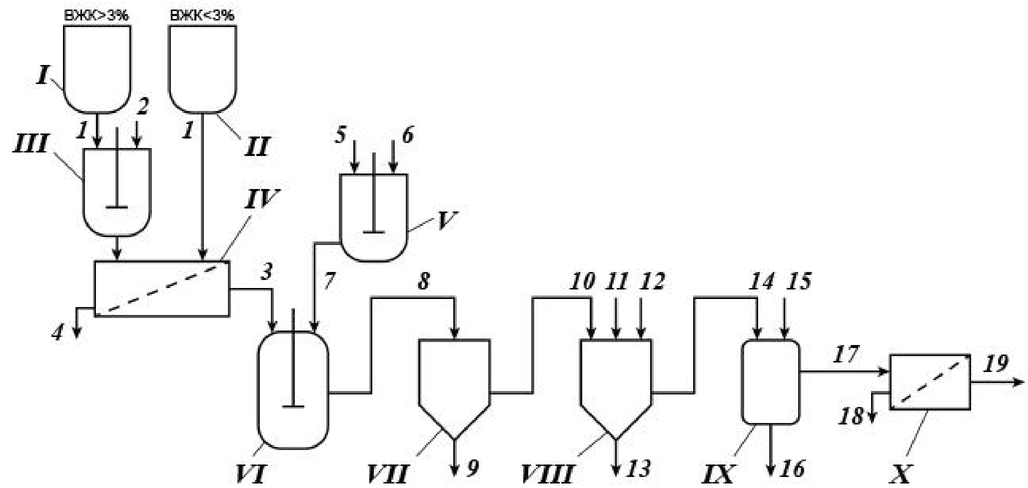

Fig. 3. The proposed scheme of biodiesel production
I, II – oil container; III – mixing container; IV– oil filter; V – mixing container; VI – transesterification reactor; VII – settling tank, VIII – separator; IX – container for biodiesel washing; X – filter;
1 – oil; 2 – acid catalyst; 3 – oil after filtration; 4 – impurities; 5 – methanol; 6 – potassium hydroxide; 7 – methoxide; 8 – reaction products; 9– impurities; 10 – a mixture of biodiesel, methanol and glycerol; 11 – hot water; 12 citric acid (0.4 %); 13 – glycerine; 14 – biodiesel with impurities; 15 – water for washing; 16 – water after washing; 17 – biodiesel with impurities; 18 – impurities; 19 – biodiesel for distillation

This scheme takes into account the need of filtration of used oil from mechanical impurities and the possibility of raw materials processing with wide range content of fatty acids. For oils with high content of free fatty acids, a preliminary treatment is recommended, which includes carrying out the esterification reaction using an acid catalyst to convert free fatty acids (FFAs) to the corresponding esters. The product should undergo further distillation to ensure the conformity with the norms of the National Standard DSTU 6081: 2009 ("Motor fuel: Methyl esters of fatty acids from oils and fats for diesel engines – Technical requirements" dated January 20, 2009) because of the presence of oligomers with high boiling points which are not methyl esters of fatty acids. The distillation residue with high calorific value can be used as heating oil.

Conclusions

The analysis of technological characteristics of transesterification of sunflower oil using methanol in the presence of potassium hydroxide enabled the identification of the sequence of technological processes for the production of biodiesel.

Experimental studies of transesterification process of used vegetable oil with methanol in the presence of alkaline catalyst have shown that the temperature of the process of transesterification does not significantly affect the yield of the final product. This circumstance will allow carrying out the transesterification without additional heating.

It is shown that an increase in the concentration of the catalyst and the reaction time increases the yield of the target product. Thus, the costs of a slight increase of the amount of the catalyst for the reaction will be offset by a significant increase in the yield of the target product.

The total yield of methyl esters from the used oils compared with the yield of the product when using the triglycerides from pure oil as a starting material is determined. It will allow the correct calculation and adjustment of the technological scheme for the production of biodiesel from used oils.

Based on the analysis of the experimental results, correction of the technological scheme for the production of biodiesel is proposed, which will provide a sufficiently high yield of the final product. It was established that when processing used oil, the raw material needs after-treatment, and the presence of free fatty acids in the oil leads to the appearance of an additional reaction, which should be taken into account when making calculations.

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