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BIODIESEL FROM RECYCLED MATERIALS

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ДИЗЕЛЬНЕ БІОПАЛИВО З ВТОРИННОЇ СИРОВИНИ

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Abstract. Studied the technology of biodiesel production from recycled materials processing plants with a high content of free fatty acids.

Key words: esterification, transesterification, biodiesel, methyl ester, fat.

Анотація. Досліджено технологію виробництва дизельного біопалива з вторинної сировини переробних підприємств зі значним вмістом вільних жирних кислот.

Ключові слова: естерифікації, переестерифікації, біодизель, метиловий ефір, жир.

Introduction. Increased requirements for toxic emissions of engines of automobiles, agricultural machinery and other power plants, the exhaustion of natural energy resources forced scientists and manufacturers to pay special attention to the use of an alternative fuel for diesel engines. Unlike traditional fuels based on petroleum hydrocarbon biofuels compare favorably with those of low-cost, environmentally sound, resource-saving technologies and produce comparable with conventional fuels on performance indicators. Today, for the UMP and Ukraine, countries in particular it is time to develop their own capacity for the production of biodiesel from renewable raw materials [1, 2]. The esterification process and technical of transesterification animal or vegetable oil fatty acid reacted with methyl (ethyl) alcohol in the presence of a catalyst (acid or alkali), resulting in formation of esters, and glycerin phase [3, 8].

The purpose of research. Establishing the possibility of obtaining biofuels from waste fat containing poultry processing enterprises with high acidity.

To achieve this goal the following tasks: the study of the chemical composition of the fat-containing waste produced during butchering carcasses; extracting fat from the object of study; hydrogenation of the extracted fat; investigate the possibility of producing biofuels process of transesterification of fats.

Materials and methods. In studies using chicken fat technical (CTF) which was preheated to 75-80 °C and kept at this temperature for one hour with constant stirring to remove moisture, and then filtered to separate insoluble.

The authors of [3] assume that the level of free fatty acids (FFA) in raw materials should be lowered to 1% of an alkaline catalyst before use to perform pereesterifikatsii fat. Therefore, the first step in the research was preconditioning CTF. The fat that was used had an acid number (CN) of 5-45 mg KOH/g. Since fat CN was more than 2 mg KOH/g, therefore it was necessary to feed this esterification.

Determination of water, proteins, lipids, minerals (ash) was performed by standard methods according to GOST 7636-85 [3, 5]. CN (number FFA) were determined by the method of GOST 52110 [6]. The amount of synthesized fatty acid methyl esters, biofuels density and sulfur content was determined in accordance with DSTU 6081: 2009 and EN 14214: 2003 [7].

For rendering the fat comprising fat blend was milled, water was added thereto in a ratio of substrate / water 2: 1. The mixture was heated to 75-80 °C temperature and infuse for 40 minutes.

Separation of fat from the aqueous protein was performed by centrifugation at part rotor speed of the centrifuge of 3000 revolutions / min and for 20 minutes.

The nature of the curve indicates that as the elevation of temperature from 55 to 80 ° C oil yield increases by 28%. When temperatures rise to 100 °C it decreases. The reason for this is, presumably, the formation of lipid-protein complexes at excessive temperature rise. Thus, the optimal level of rendering the temperature 80 °C. At this temperature, the processes are intensified heat denaturation of proteins is disrupted cell structure that provides an increase in fat to 83% yield.

Esterification. CTF pretreatment methanol was used and tested as catalyst sulfuric (H_2SO_4), hydrochloric acid (HCl) and nitric (HNO_3) acid [1, 5, 8]. FFA esterification was performed at different molar ratios alcohol / fat concentrations of acid catalysts and reaction. Experiments were performed by heating the reaction mixture to 60 °C in a laboratory setting (Fig. 2.)

Transesterification. In the reaction the molar ratio of alcohol/fat was 6: 1, the amount of catalyst taken KOH 1 % by weight of the starting fat. Also, the excess catalyst was taken into account for the neutralization of free fatty acids residue, which was calculated using the formula: % FFA × 0,64 + 1,7% for the KOH, or by the formula:% FFA × 0,78 + 2,0% for NaOH [4, 9]. Transesterification process conducted on the same laboratory setup (Fig. 2). The reaction was performed at 25 and 60 ° C, and the reaction time is in the range 1 ... 4 hour. After transesterification glycerol layer was separated, and the resulting methyl ester was washed with warm water, filtered and dried. Preparations of samples were tested in a specialized laboratory.

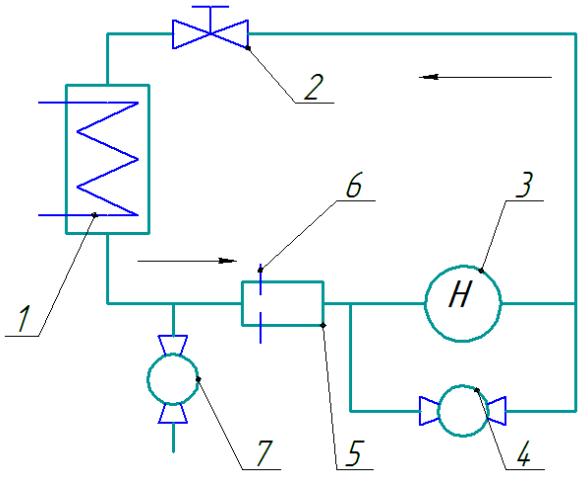

Fig. 2. Scheme laboratory cavitations' plant for biodiesel production:
1 - reactor; 2 - valve; 3 -Pump; 4 - valve; 5 - cavitator transparent body;
6 - diaphragm; 7 - tap.

Results. In [2, 3] proposed to reduce the high levels of free fatty acids in raw materials due to hold two or three successive stages of esterification. Increasing their amount decreases yield because of esters and ethers fat solubility in methanol [7]. Therefore, an attempt was made to get the proper level of free fatty acids in the first

stage, to ensure a high yield of ester and reduce the duration of the synthesis of biodiesel.

Esterification with sulfuric acid. The concentrated sulfuric acid was chosen as a reference catalyst. The reaction of esterification was performed at different molar ratios alcohol/CTF (10: 1, 15: 1, 20: 1, 25: 1, 30: 1) and amounts of H_2SO_4 catalyst (3%, 6%, 15%, 20%, 35%), depending on the level of free fatty acids, for one hour at 60 °C. Initial experiments were performed with 3% and 6% of the catalyst at different molar ratios of methanol/fat. FFA level was reduced to 11.25% with 6% H_2SO_4 and the molar ratio methanol / fat 30:1. It became apparent that the need to increase the amount of H_2SO_4 and methanol. Following esterification conditions were as follows: the molar ratio methanol / fat 20: 1 and 30: 1, the amount of H2SO4 - 15%, 20% and 35%. The time and the reaction temperature did not change. FFA levels decreased with increasing amounts of methanol and H_2SO_4 from the previous reaction. For example, decreased FFA levels to 6.26%, 2.27% and 1.20% with respectively 15%, 20% or 35% H_2SO_4 in methanol with a molar ratio of fat to 20: 1. For example, the main purpose of highly acidic esterification of fats is to reduce the FFA level of about 1%. When using the ratio of methanol / fat 30: 1 FFA level dropped to 4.92%, 1.40% and 1.04% with 15%, 20% and 35% H_2SO_4, respectively.

Esterification with hydrochloric acid. Experiments were repeated with 6%, 15% and 20% HCl and methanol at a molar ratio of fat to 20: 1 and 30: 1. Use 6% HCl was not effective. FFA level was reduced to 12.99% and 12.46% by using methanol in a ratio of 20: 1 and 30: 1, respectively. When the amount of HCl was increased to 15% and 20% FFA level decreased respectively to 5.26% and 2.83% by using methanol in a ratio of fat to 20: 1. When using the ratio of methanol / fat 30: 1 FFA level was reduced to 3.89% and 1.67% respectively in the case of 15% and 20% HCl. FFA level was lowered to 1% when using 20% HCl, the molar ratio methanol / fat 30: 1 and increasing the reaction time to 90 minutes. Kinetics of esterification with sulfuric and hydrochloric acids were very similar.

Esterification with nitric acid. HNO_3 Nitric acid is poorly soluble in methanol. Therefore, it must be heated to 45 °C to obtain a mixture of alcohol-acid reagent. Use

6% HNO_3 was not effective. FFA level was reduced to 12.78% and 12.32% when using methanol to fat ratio of 20: 1 and 30: 1, respectively. When the amount of HNO3 was increased to 15% FFA level was reduced to 11.97% by using methanol in a ratio of fat to 30: 1. Therefore, the study of esterification CTF using HNO_3 were canceled as the hopeless.

Thus, the concentrated sulfuric acid catalysis gave the best results. Given that the main aim was to reduce the level of esterification of free fatty acids CTF to 1%, experimenting with its use continued. Addition of 35% concentrated sulfuric acid to the fat mass showed a total conversion of FFA, but the loss of raw material were after esterification. Therefore, the catalyst should be used as 20% sulfuric acid by increasing the molar ratio methanol / fat to 40:1, which reduces the amount of free fatty acids to below 1%.

Influence of time on a reduction of FFA levels. The studies were conducted at 60 ° C when applying the reaction durations three - 60, 70 and 80 min. FFA levels were, respectively, 0.93%, 0.80% and 0.67% after the reaction for 60, 70 and 80 minutes with 20% H_2SO_4 and the molar ratio methanol / fat 40: 1. Thus FFA level was less than 1% in all experiments. Esterification with 20% H_2SO_4 catalyst with a molar ratio methanol / fat 40:1 for 80 minutes at a temperature of 60 °C allows to stably reduce the amount of free fatty acids to less than 1%, which guarantees the high yield of biodiesel after transesterification.

Characteristics of fuel after transesterification. After esterification of free fatty acids in the fat level was 0.67%, which is sufficient for the reaction transesterification fat with methanol in the presence of alkaline catalysts. It was investigated the influence of catalyst type, reagents and reaction temperature on the properties of biodiesel.

Yield biofuel increased with increasing reaction temperature from 25 to 60 °C, but did not change significantly with increasing duration of the reaction. Minimum biodiesel yield was 71.3% (four hours of reaction at 25 °C with the catalyst NaOH), and the maximum - 88.5 % (after 60 minutes of reaction at 60 °C with a catalyst KOH.).

Typically, biodiesel density decreases with increasing reaction time and temperature. Obviously (Table 1), there is no substantial difference between the density of the fuel after transesterification carried out with potassium and sodium methylate and KOMe compared with NaOMe KOH and NaOH. Oil viscosity decreases with increasing reaction time and temperature, but there is a significant difference between the viscosity and using KOMe as compared with NaOMe KOH and NaOH.

The content of residual methanol in the fuel varies from 0.01% to 0.20%.

This indicates that the methanol content in the biomass is almost independent of the parameters transesterification reaction.

Flash point in closed crucible and is in the range 170-173 °C. fat CN after esterification was 0.67 mg KOH/g, and after transesterification fuel QP reduced to 0,22-0,3 mg KOH/g. The heat of combustion of the fuel close to 40 MJ / kg and is somewhat lower than petroleum diesel. The extent of corrosion of the copper plate is quite low, indicating a low fuel level of aggressiveness with respect to the diesel engine parts.

Conclusions

1. Sulfuric acid - the most effective catalyst for reducing the level of FFA esterification with chicken fat.

2. Reducing the level of FFA esterification with chicken fat essentially depends on the molar ratio methanol / fat, the amount and type of acid catalyst and duration of reaction.

3. Some FFA chicken fat (15-27%) can be reduced to 1% when using 20% H_2SO_4 by weight of fat and a molar ratio of methanol to fat ratio of 40:1 in the reaction at a temperature of 60 °C for 80 min.

4. The biofuel viscosity decreases with increasing reaction temperature.

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