METHODS AND FUTURE PROSPECTS OF ANIMAL FAT CONVERSION INTO BIOFUEL

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This work describes one of the promising and innovative concepts for the use of biofuel from animal fats. Diesel biofuel made from cheap raw materials can compete with traditional fuels of petroleum origin, especially in terms of non-toxicity and environmental cleanliness. Raw materials for the production of methyl and ethyl esters of fatty acids can be vegetable oils, animal and bird fat, lard, yellow fat and by-products of fish farming. The main component of oils and fats are triglycerides, which make up about 90-98% of the total mass of raw materials. In real production conditions, periodic emissions of fatty waste are not excluded, which leads to the loss of fat-retaining raw materials, which worsens the environmental situation. Therefore, the task of the poultry processing industry is to obtain food products from high-quality raw materials, as well as third-party products in order to reduce production waste. The purpose of the work is to analyze the process of processing fat-containing waste of poultry processing enterprises into biofuel and to study its potential in providing sustainable and ecologically clean energy. The research used technical chicken fat (CHF), which was heated to 75-80°C and kept at this temperature for one hour with constant stirring to remove moisture, and then filtered to separate insoluble impurities.

Keywords: animal fats, diesel biofuel, transesterification, technologies, ecology

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Introduction

A distinction is made between gaseous biofuel (biogas, hydrogen), obtained due to the decomposition of organic residues by bacteria (fermentation), and solid biofuel (wood, straw, husks). The most commercially used short-chain alcohol for the transesterification reaction is methanol due to its low price, but there are studies on the use of other alcohols, such as ethanol, propanol, and butanol (Alptekin, Canakci, 2010). Other authors have found that raw materials alone account for more than 75% of the total cost of biodiesel production, so choosing the best and cheapest raw materials is vital to ensure low production costs. Continuity of the transesterification process was also found to be another choice for minimizing production costs. Currently, biodiesel can be more efficient when used as a supplement to other energy sources. At one time, the authors Alptekin and Canakci had already conducted some research for the production of methyl esters, for the production of which inexpensive chicken fat was used. After reducing the free fatty acid level in chicken fat to less than 1%, they completed the transesterification reaction using an alkaline catalyst. Potassium hydroxide, sodium hydroxide, potassium methoxide, and sodium methoxide were used as the catalyst, and methanol was used as the alcohol for transesterification reactions. The

influence of the type of catalyst, reaction temperature and reaction time on the fuel properties of methyl ethers was investigated (Alptekin, 2011; Canakci, 1999).

Our scientific interest was the analysis, selection and determination of the most effective catalyst for reducing the level of during the esterification of chicken fat, as well as the determination of the dependence of the achievement of the optimal result on the methanol/fat molar ratio, the amount and type of acid catalyst, as well as the external conditions of the reaction (Heletukha et al., 2023).

The purpose of the work is to analyze the process of processing fat-containing waste of poultry processing enterprises into biofuel and to study its potential in providing sustainable and ecologically clean energy.

To achieve this goal, the following tasks were solved:

- study of the chemical composition of fat-containing waste generated during technological operations at poultry farms;
- collection of fat-containing waste;
- hydrogenation of extracted fat;
- research on the possibility of obtaining biofuel by transesterification of fats.

Materials and methods

In the studies, technical chicken fat was used, which was heated to 75-80°C and kept at this temperature for one hour with constant stirring to remove moisture, and then filtered to separate insoluble impurities.

The authors of the paper (Talavyrya et al., 2012) believe that the level of free fatty acids in the raw material should be reduced to 1% before using an alkaline catalyst to perform fat transesterification. Therefore, the first step in the research was the preliminary preparation of technical chicken fat. The fat used had an acid value of 5-45 mg KOH/g. Since the acid value of the fat was more than 2 mg KOH/g, it was necessary to carry out esterification of this raw material (Vis et al., 2010).

Determination of the content of unsaponifiable substances and mineral substances (ash) was carried out by standard methods according to DSTU ISO 3596:2004. The acid number was determined according to the methodology of DSTU EN ISO 660:2019 Determination of acid number and acidity. The amount of synthesized methyl esters of fatty acids, the density of biofuel and its sulfur content were determined in accordance with DSTU EN 14214:2019 Automotive fuel. Fatty acid methyl esters (FAME) for diesel engines. Requirements and test methods.

To melt the fat, the mixture containing the fat was crushed, and water was added to it in a substrate/water ratio of 2:1. The mixture was heated to a temperature of 75-80 ºC and kept for 40 minutes.

Separation of fat from the water-protein part was carried out by centrifugation at a rotation frequency of the centrifuge rotor of 3000-3500 rpm for 20 minutes. In Figure 1 shows the dependence of fat yield on the temperature of heating.

The nature of the curve (Figure 1) shows that as the temperature rises from 55 to 80 ºC, the output of fat increases by 28%. When the temperature rises to 100 ºC, it decreases. The reason for this is, apparently, the formation of lipid-protein complexes with an excessive increase in temperature. Thus, the optimal level of heating temperature is the interval of 78-82 ºC.

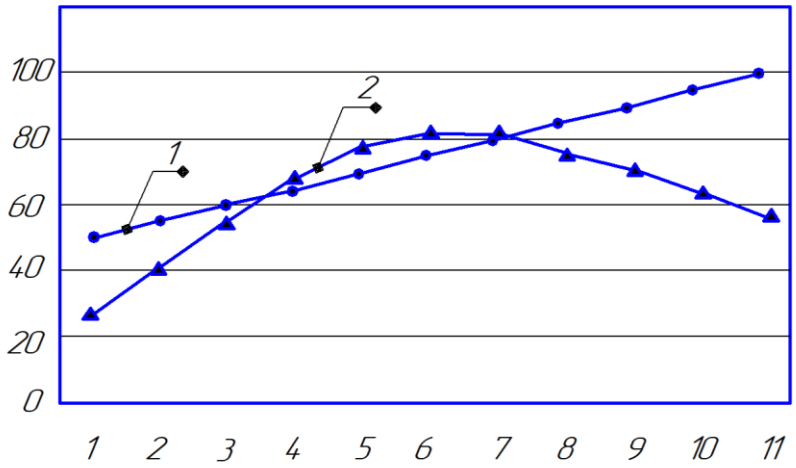

Figure 1. Dependence of fat yield on melting temperature:
1 – melting point, °C, 2 – yield of fat, %

At the specified temperature, the processes of heat denaturation of proteins are intensified, the structure of cells is destroyed, which ensures an increase in the yield of fat up to 83%.

Esterification

Methanol was used for preliminary treatment, and sulfuric (H_2SO_4), hydrochloric (HCl), and nitric (HNO_3) acids were tested as catalysts (Bello et al., 2022; Jagadale 2012). Esterification was carried out at different alcohol/fat molar ratios, concentrations of acid catalysts, and duration of the reaction. Experiments were performed with heating of the reaction mixture to 60ºC on a laboratory setup (Figure 2).

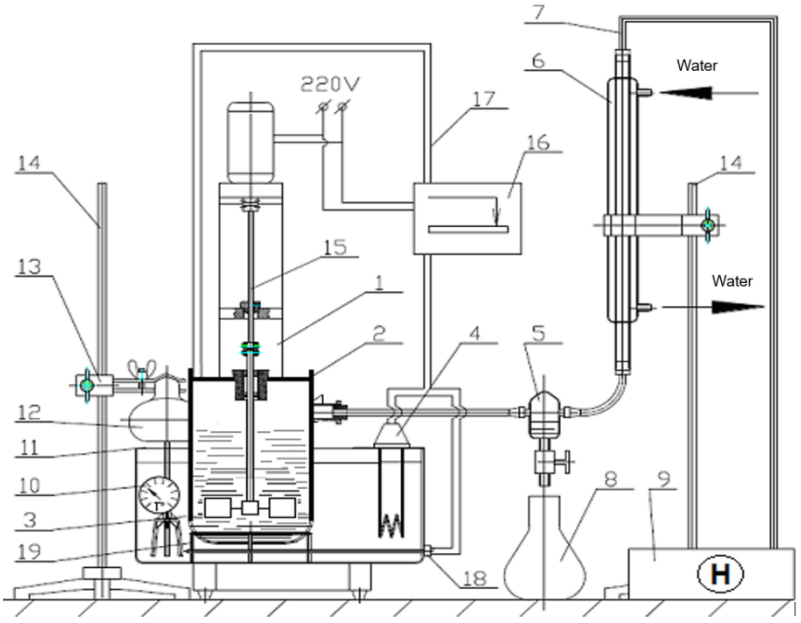

Figure 2. Laboratory setup for studying the process of obtaining diesel biofuel:
1 – tripod with engine, 2 – flask for reagents, 3 – stirrer, 4 – thermostat, 5 – condensate collection, 6 – refrigerator, 7 – pipeline, 8 – collection flask condensate, 9 – vacuum pump, 10 – thermometer, 11 – water "bath", 12 – stirrer, 13 – clamp, 14 – tripod, 15 – stirrer shaft, 16 – thermostat, 17 – cable, 18 – temperature sensor, 19 – stand

Transesterification

In the reaction, the alcohol/fat molar ratio was 6:1, the amount of the KOH catalyst was 1% by weight of the initial amount of fat. The excess of the catalyst for neutralization of the free fatty acid residue was also taken into account, which was calculated by the formula: % free fatty acids × 0.64 + 1.7% for KOH, or by the formula: % free fatty acids × 0.78 + 2.0 % for NaOH (Mushtruk et al., 2017). The transesterification process was carried out at the same laboratory facility (Figure 2). The reaction was carried out at temperatures of 25 and 60 °C, and the reaction time ranged from 1 to 4 hours. After transesterification, the glycerol layer was separated, and the resulting methyl ether was washed with warm water, filtered and dried. Samples of the obtained methyl ethers were tested in a specialized laboratory (Rosson et al., 2020).

When analyzing the results of research in works (Mushtruk et al., 2017), it is proposed to reduce the high level of free fatty acids in raw materials by conducting two or three consecutive stages of esterification. This is recommended because an increase in the amount of free fatty acids reduces the yield of esters due to the solubility of fats and esters in methanol (Hubca et al., 2008). Therefore, an attempt was made to obtain the appropriate level of free fatty acids already at the first stage, in order to ensure a high yield of ether and reduce the duration of biodiesel synthesis.

Esterification of technical chicken fat with sulfuric acid

Concentrated sulfuric acid was chosen as a reference catalyst. The esterification reaction was carried out at different molar ratios of alcohol/technical chicken fat (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 a temperature of 60°C. Initial experiments were performed with 3% and 6% catalyst at different methanol/fat molar ratios. The level of free fatty acids was reduced to 11.25% using 6% H_2SO_4 and a methanol/fat molar ratio of 30:1. It became obvious that it is necessary to increase the amount of H_2SO_4 and methanol. The following esterification conditions were as follows: methanol/fat molar ratio 20:1 and 30:1, amount of H_2SO_4 - 15%, 20% and 35%. The reaction time and temperature were not changed. The level of free fatty acids decreased with increasing amounts of H_2SO_4 and methanol compared to the previous reaction. For example, free fatty acid levels decreased to 6.26%, 2.27%, and 1.20% using 15%, 20%, and 35% H_2SO_4 with methanol at a 20:1 molar ratio to fat, respectively. For example, the main purpose of esterification of highly acidic fats is to reduce the level of free fatty acids to about 1%. When using a methanol/fat ratio of 30:1, the free fatty acid level decreased to 4.92%, 1.40%, and 1.04% in the presence of 15%, 20%, and 35% H_2SO_4, respectively.

Esterification with hydrochloric acid

Experiments were repeated with 6%, 15%, and 20% HCl and methanol at molar ratios of 20:1 and 30:1 to fat. Application of 6% HCl was not effective. The level of free fatty acids decreased to 12.99% and 12.46% when using methanol in a ratio of 20:1 and 30:1, respectively. When the amount of HCl was increased to 15% and 20%, the free fatty acid level decreased to 5.26% and 2.83%, respectively, at a methanol to fat ratio of 20:1. When using a methanol/fat ratio of 30:1, the free fatty acid level decreased to 3.89% and 1.67% when using 15% and 20% HCl, respectively. The level of free fatty acids was reduced to 1% using 20% HCl, a methanol/fat molar ratio of 30:1 and increasing the reaction time to 90 min. The kinetics of esterification with

sulfuric and hydrochloric acids turned out to be very similar (Kawahara, Yoshihara, 1979).

Esterification with nitric acid

Nitric acid HNO_3 is poorly soluble in methanol. Therefore, it must be heated to 45 ºC in order to obtain a mixture of alcohol-acid reagent. Application of 6% HNO3 was not effective. The level of free fatty acids decreased to 12.78% and 12.32% when using methanol to fat ratios of 20:1 and 30:1, respectively. When the amount of HNO_3 was increased to 15%, the free fatty acid level decreased to 11.97% using a methanol to fat ratio of 30:1. Therefore, studies of esterification of technical chicken fat using HNO_3 were canceled as unpromising.

Thus, catalysis with concentrated sulfuric acid gave better results. Given that the main purpose of esterification was to reduce the level of free fatty acids in technical chicken fat to 1%, experiments with its use continued. The addition of 35% concentrated sulfuric acid to the mass of fat showed a more complete conversion of free fatty acids, but losses of raw materials after esterification were greater. Therefore, 20% sulfuric acid should be used as a catalyst, while increasing the methanol/fat molar ratio to 40:1, which ensures a decrease in the amount of free fatty acids to a level below 1%.

The influence of time regimes on the reduction of the level of free fatty acids. The studies were conducted at a temperature of 60 °C using three durations of the reaction - 60, 70 and 80 min. Free fatty acid levels were, respectively, 0.93%, 0.80% and 0.67% after reaction for 60, 70 and 80 min with 20% H2SO4 and a methanol/fat molar ratio of 40:1. Thus, the level of free fatty acids was less than 1% in all experiments. Esterification with 20% H2SO4 catalyst at a methanol/fat molar ratio of 40:1 for 80 min at a temperature of 60 °C allows for a stable reduction of the amount of free fatty acids to a level of less than 1%, which guarantees a high yield of diesel biofuel after the transesterification process.

Results and discussion

After esterification, the level of free fatty acids in the fat was 0.67%, which is a sufficient condition for transesterification of fat with methanol in the presence of alkaline catalysts. The influence of the type of catalyst, the temperature of the reagents, and the duration of the reaction on the properties of diesel biofuel was investigated. The results of the research are presented in Table 1.

Biofuel yield increased with increasing reaction temperature from 25 °C to 60 °C, but did not change significantly with increasing reaction duration. The minimum yield of diesel biofuel was 71.3% (for four hours of reaction at 25 °C with the NaOH catalyst), and the maximum was 88.5% (for 60 minutes of reaction at 60 °C with the KOH catalyst).

As a rule, the density of diesel biofuel decreases with increasing reaction time and temperature. Obviously (Table 1), there is no significant difference between the fuel density after transesterification, which is carried out with potassium and sodium methylates KOMe and NaOMe compared to KOH and NaOH. Fuel viscosity decreases with increasing reaction time and temperature, but there is a significant difference in viscosity when using KOMe and NaOMe compared to KOH and NaOH. The content of residual methanol in fuel ranges from 0.01 to 0.20%. This indicates that the methanol content in biofuel is almost independent of transesterification reaction parameters.

Table 1. Properties of diesel biofuel from technical chicken fat*

1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*	*13*
g	25	1	886	1	170	0.04	4	40	0.03	0.30	5.4	80
g	25	2	885	1	171	0.11	3	40	0.03	0.29	5.2	82
g	25	4	884	1	172	0.13	3	40	0.03	0.25	5.1	85
g	60	1	885	1	171	0.01	2	40	0.03	0.25	5.1	88
g	60	2	884	1	171	0.01	2	40	0.04	0.24	5.0	87
f	25	1	885	1	170	0.12	3	40	0.02	0.30	5.4	73
f	25	2	885	1	172	0.06	2	40	0.03	0.29	5.3	72
f	25	4	884	1	172	0.03	2	40	0.02	0.24	5.2	71
f	60	1	885	1	171	0.20	2	40	0.02	0.28	5.2	79
f	60	2	884	1	172	0.08	2	40	0.01	0.24	5.1	78
j	25	1	891	1	170	0.02	4	40	НП	0.30	6.7	85
j	25	2	890	1	172	0.01	3	40	0.02	0.27	6.3	83
j	25	4	888	1	172	0.01	3	40	0.01	0.25	5.8	82
j	60	1	887	1	171	0.01	3	40	0.01	0.29	5.6	89
j	60	2	886	1	172	0.01	3	40	0.01	0.26	5.6	85
j	60	4	886	1	172	0.01	3	40	0.01	0.24	5.6	86
s	25	1	891	1	171	0.03	4	39	НП	0.30	6.8	76
s	25	2	890	1	171	0.12	3	40	0.02	0.28	6.2	79
s	25	4	888	1	172	0.05	3	40	0.04	0.25	5.9	80
s	60	1	886	1	171	0.20	2	40	0.02	0.26	5.4	86
s	60	2	886	1	173	0.12	2	40	0.01	0.25	5.5	85

*1 – catalyst (g - KOH, f - NaOH, j - KOMe, s - NaOMe), 2 – reaction temperature (°C), 3 – reaction time (hour), 4 – density (15 °C, kg/m^3), 5 – corrosion of a copper plate (degree of corrosion), 6 – flash point in a closed crucible (°C), 7 – methanol content (%), 8 – solidification temperature (°C), 9 – heat of combustion (mJ/kg), 10 – free glycerol (%), 11 – acid value (mgKOH/g), 12 – viscosity (40 °C, mm^2/s), 13 – yield of diesel biofuel (%), NP – not checked.

Taking into account the obtained data, a decrease in the viscosity of biofuel is observed with an increase in the reaction temperature. We can state that the density, flash point, methanol content, solidification temperature, heat of combustion, acid number and corrosion on the copper plate of diesel biofuel do not significantly depend on the parameters of the transesterification reaction.

The flash point in a closed crucible is stable and is in the range of 170-173 °C. The acid number of the fat after esterification was 0.67 mg KOH/g, and after transesterification the acid number of the fuel decreased to 0.22–0.3 mg KOH/g. The heat of combustion of the fuel is close to 40 mJ/kg and is somewhat lower than that of petroleum diesel fuel, which is inherent in diesel biofuel. The degree of corrosion of the copper plate is consistently low, indicating a low level of aggressiveness of the fuel in relation to diesel engine parts.

Conclusions

1. Sulfuric acid is one of the most effective catalysts for reducing the level of free fatty acids during the esterification of chicken fat.

2. The decrease in the level of free fatty acids during the esterification of chicken fat depends significantly on the molar ratio of methanol/fat, the amount and type of acid catalyst, as well as the duration of the reaction.

3. The initial level of free fatty acids in chicken fat (15–27%) can be reduced to 1% by using 20% H_2SO_4 by weight of fat and methanol in a molar ratio to fat of 40:1 in a reaction at a temperature of 60 °C for 80 min (Sukhenko et al., 2014).

Conflict of interest

The authors state no conflict of interest.

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