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Production of biodiesel from low-quality vegetable oils with a high content of free fatty acids by acid-catalyzed transesterification

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Abstract. Research on the production and application of cheap and renewable energy sources is one of the most relevant directions in modern science. They are imposed for a number of reasons, mainly due to the limited deposits of oil, natural gas and coal, the protection of the environment and the health of people. Unfortunately, the needs for such alternative energy sources are huge, and the possibilities for obtaining them are limited. On the other hand, low-quality vegetable oils obtained as waste products or as a result of improper storage or processing, as well as oils after use represent a valuable raw material and energy source. However, this necessitates the search for ways to utilize them by turning them into better quality products. The aim of the present work is to investigate the possibility of obtaining methyl esters of fatty acids (biodiesel), from vegetable oils with high acid values, by transesterification with acid catalysts, which includes the selection of suitable catalysts and conditions for optimal process progress.

1 Introduction

Vegetable and animal fats are a natural depot for energy in nature. The energy obtained during their burning is comparable to that during the burning of oil products, due to their close physico-chemical parameters. On the other hand, growing and extracting natural fats are renewable processes. An example in this regard is the so-called biodiesel fuel (BDF, FAME), the production of which in recent years has reached enormous scales. Its main advantage is that it is an ecological product (methyl ester of higher fatty acids), which before and after use does not pollute the environment.

In addition, natural fats are consumed by other branches of industry such as the food, chemical, cosmetic and pharmaceutical industries, in the household, etc., which reduces the possibilities of using them for energy purposes. On the other hand, their increased consumption leads to an inevitable increase in their prices, which is unacceptable from the point of view of their competitiveness with mineral raw materials. For this reason, renewable energy sources are currently mostly used in areas with increased environmental risk, for example in urban transport, agriculture, parks, greenhouses, etc.

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As is known, for food and industrial purposes, high-quality vegetable oils obtained by special processing, for example refining, are used. The waste products, as well as the oils after use, are thrown away or used for animal feed. The same applies to fats with deteriorated qualities, from improper storage or processing. However, these products represent valuable sources of energy when properly processed, which necessitates expanding research into more efficient utilization of this type of raw materials. In particular, there is a need to optimize and scale up processes to convert them into low-viscosity, potential fuel materials such as biodiesel.

During long-term or short-term storage of vegetable oils, as well as under extreme conditions (temperature, humidity, mechanical effects), a gradual increase in free fatty acids is observed, as a result of accelerated β-oxidation. As a result, there is an increase in the acid values (AV) of the vegetable oils. This makes their transesterification difficult, due to the occurrence of undesirable side reactions, especially in their transesterification with an alkaline catalyst.

Refining the oils is not a solution to this problem, because with high acidity, in this process, large amounts of soaps are formed and as a consequence - losses of the oil phase.

In the Doctoral thesis of Vasil P. Kopchev [1], a solution to the problem was proposed by optimizing the conditions of the alkaline transesterification, in which the kinetic control of the synthesis was achieved, and the amounts of side products were reduced due to the limitation of side reactions. But even in this case vegetable oils with an acid value of about 9 mg KOH/g were obtained, which limits the processing of the oils due to higher acidity.

From the analysis of the transesterification methods, it can be concluded that probably the most suitable for transesterification of super-acidic vegetable oils is the process with the use of acid catalysts, since in this case both transesterification and esterification of free higher fatty acids with the corresponding alcohol. It is known that the acids most used in acid-catalyzed transesterifications are: H_2SO_4, HCl, HNO_3, $C_6H_5SO_3H$, etc., the so-called Brønsted acids. A more serious drawback of this type of preesterification, as indicated in table 2, is the oxidation of the unstable unsaturated higher fatty acids, which causes darkening of the obtained esters. This makes their use as biodiesel unacceptable. Therefore, one of the important tasks of the present work is to create "softer" acid transesterification conditions to avoid unwanted oxidation. This includes finding a suitable acid catalyst, shortening the process time and carrying out a subsequent alkaline transesterification if the results of the acid transesterification allow it. Efforts in the present work are directed in these directions, as experiments were carried out on transesterification of specially selected sunflower and rapeseed oils, with high acid value.

For raw materials with a high content of free higher fatty acids, various Lewis acids are used as homogeneous catalysts: BF_3, $Fe_2(SO_4)_3$, $AlCl_3$, $FeCl_3$, $ZnCl_2$; as well as Brønsted acids (H_2SO_4, H_2SO_3, HCl, HNO_3, H_3PO_4, H_3PO_3, H_3PO_2, $NaHSO_4$, Na_2HPO_4, NaH_2PO_4, p-toluenesulfonic acid, etc.). In this type of processes, esterification of free higher fatty acids and transesterification of triacylglycerols (TAG) with the corresponding alkyl alcohol occur simultaneously [2÷11].

Table 1 lists some of the conditions for esterification/reesterification of various oils with acid catalysts.

The advantages and disadvantages of acid-catalyzed transesterification are listed in Table 2 [6].

Table 1. Conditions for carrying out transesterification/esterification of vegetable oils with an acid catalyst, AV – acid value.

Vegetable oil	**Acid value, mg KOH/g**	**Catalyst % (w/w)**	**Temp. ˚C**	**Mole ratio mol/mol**	**Time, h**	**Yield, % (w/w)**	**Author**
Soybean oil	201	6.53 % H2SO4	70	10:1	2	98.5	[7]
Soybean oil	201	4.83 % HCl	70	10:1	2	98.4	[7]
Soybean oil	201	8.40 % HNO3	70	10:1	2	97.4	[7]
Sunflower oil	7	5% H2SO4	60	60:1	2	AN<1	[8]
Palm oil	93% free higher fatty acids	1.834 % H2SO4	70	8:1	1	Up to 2% free fatty acids	[9]
Rapeseed oil	<1	5% AlCl3	110	24:1	18	98%	[10]
Waste frying oil	75.92	4 % H2SO4	95	20:1	10	65%	[12]
Soybean oil	<1	1% H2SO4	65	30:1	69	99%	[13]

Table 2. Advantages and disadvantages of the acid-catalyzed transesterification.

Advantages	**Disadvantages**
- It is not significantly affected by the high content of free fatty acids and water in the raw materials; -Esterification and transesterification take place simultaneously; - No soaps are formed; - It is preferred for low quality oils.	- Slow reaction rate; - Corrosion of equipment; - Many waste products from neutralization; - Impossibility of recycling the catalyst; - Low catalytic activity; - High reaction temperature; - Long reaction time; - Deterioration of the quality of the final product as a result of side reactions of destruction, oxidation and polymerization. Darkening.

2 Materials and methods

2.1 Object of the investigation

Cold-pressed unrefined rapeseed and sunflower oils were provided by certified Bulgarian producers. Methyl alcohol 99.9% was provided by Brentag Ltd.; The 85% phosphoric acid and sodium sulfate (anhydrous) were obtained from "Himtex” Ltd., Dimitrovgrad. The catalyst so-called sulfomass, which is an intermediate product in the preparation of a catalyst for furan resins with a content of 50% p-toluenesulfonic acid and a mixture of 50% H_2SO_4, sulfoglycols and water, were provided by the company "Himtex” Ltd., Dimitrovgrad. Tetraethyl titanate (TET) was provided by Merck Schuchard OHG) and p-toluenesulfonic acid monohydrate was provided by “Fluka AG SH-9470 Buchs.”

The following reagents were used to analyze the products:

- ethyl alcohol (96%) ("Himtex" Ltd., Dimitrovgrad);
- petroleum ether (Bp. 45-55°C) ("Himtex" Ltd., Dimitrovgrad);
- diethyl ether (Bp. 34-35°C) ("Himtex" Ltd., Dimitrovgrad);

- hydrochloric acid (HCl 37%) (Merck, Darmstadt, Germany);
- periodic acid (H_5JO_6, dihydrate: $HJO_4.2H_2O$) (Merck, Darmstadt, Germany).

The analyzes of the starting oils as raw materials and the obtained methyl esters were carried out according to the methods described in [14].

2.2 Acid-catalyzed transesterification of vegetable oils with high acid value

The following substances were used as catalysts for the reaction: p-toluenesulfonic acid monohydrate (p-TSA) in an amount of 5% of the mass of the oil, sulphomass - an intermediate product in the synthesis of a catalyst for furan resins, containing about 50% p-TSA and 50 % mixture of H_2SO_4, glycolsulfonates and water, 5% tetraethyl titanate [Ti(O $C_2H_5)_4$] – 0.5% of the mass of the oil. The reason for the inclusion of the latter product in the study was given by the encouraging results of the esterification of carboxylic acids with aliphatic alcohols in the presence of alkyl titanates, mainly tetrabutyl titanates [15].

The transesterification was carried out using methyl alcohol with the same molar ratio of oil/CH_3OH = 1:6 in all experiments.

The amount of vegetable oil in the reaction mixture in all experiments was 500 g. Temperature of transesterification process: 68-70°C.

In a double-necked round-bottomed flask equipped with a mechanical stirrer, a reflux condenser and a water bath to maintain a constant temperature, the estimated amount of vegetable oil is placed, which is tempered to the desired temperature. A previously prepared solution of catalyst in methyl alcohol is added to it, and the amounts of oil, alcohol and catalyst are in accordance with molar ratios between the reacting substances and the required amount of catalyst set in advance for the relevant experiment. The process of esterification and transesterification takes place under constant stirring, respecting the preset time and temperature.

After completion of the reaction, the products are transferred to a separatory funnel and left to stand for 24 h to separate them into two phases. The upper phase contains hydrophobic products (mainly the esters of higher fatty acids) and the lower phase is a mixture of glycerol, excess alcohol, catalyst and hydrophilic by-products of the reaction. Certain amounts of by-products such as mono-, di- and triglycerides, alkaline soaps and unsaponifiable products, in alkaline catalysis may also be contained in the ester phase, from which they are removed by washing. The two phases are decanted and the lower phase, which contains mainly glycerol, excess methanol, catalyst and other hydrophilic reaction products, is separated and, if necessary, analyzed for the amount of free glycerol, soaps and unreacted triglycerides.

The phase containing methyl esters passes into a conical vessel for a primary wash with water. The washing is carried out carefully, without intensive stirring, as the water is supplied dropwise on the surface of the phase. The amount of water is no more than 15 vol.% relative to the volume of the ester phase. The ester phase is then decanted from the aqueous layer, and the latter can also be analyzed for soaps and non-esterified glycerides. The resulting methyl esters are washed again with a 0.03% solution of H_3PO_4, aiming for a pH of the washings of about 3. This is followed by a third wash with water and standing for 24 hours for complete phase separation. The washed ester phase was dried over anhydrous Na_2SO_4 desiccator for 24 h, filtered and analyzed.

3 Results and discussion

In the course of the research, the changes in the acid value, viscosity and density of the obtained products were monitored. The results of the analyzes of the final products of transesterification are presented in Table 3.

Table 3. Physico-chemical characteristics of vegetable oils at different durations of transesterification with sulfomass as a catalyst.

Characteristic	Measuring units	Sunflower oil				Rapeseed oil			
		Time of transesterification				Time of transesterification			
	h	0	4	8	16	0	4	8	16
Viscosity	mm^2/s	41.93	17.61	14.66	10.14	40.76	25.82	18.79	11.19
Acid value	mg KOH/g	80.1	8.24	4.52	5.86	15.8	3.64	2.22	3.03
Density	g/cm^3	0.925	0.914	0.910	0.910	0.920	0.905	0.902	0.902
Color	Bal								

Table 4. Physico-chemical characteristics of vegetable oils at different durations of transesterification with p-TSA and tetraethyl titanate catalysts.

Characteristic	Measuring units	Type of catalyst and time							
		p-TSA				tetraethyl titanate			
	h	0	4	8	16	0	4	8	16
Viscosity	mm^2/s	40.76	12.98	8.17	6.53	40.82	-	39.64	-
Acid value	mg KOH/g	15.8	4.05	4.66	5.56	15.8	-	13.8	-
Density	g/cm^3	0.92	0.905	0.895	0.889	0.92	-	0.92	
Color	Bal								

The data from Table 3 and 4 allow to graphically express the transition from glycerides to methyl esters of higher fatty acids by changing the most sensitive parameters of the synthesis products - viscosity and acid value. The obtained dependences are presented in Fig. 1÷4.

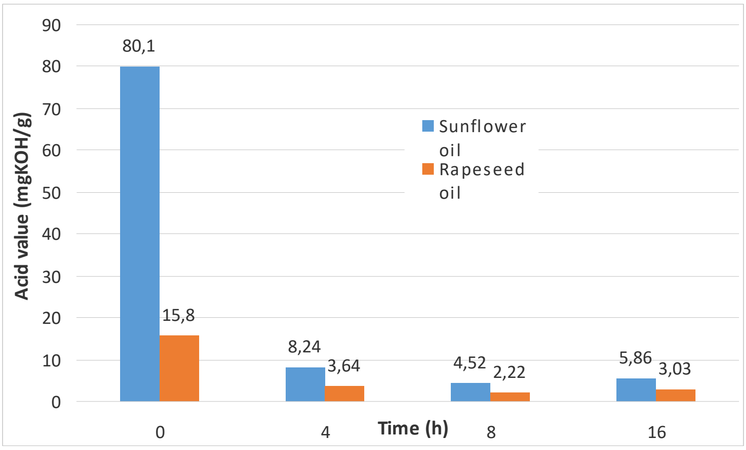

Fig. 1. Dependence of the acid value on the time for transesterification of the rapeseed oil and sunflower oil using sulfomass as a catalyst.

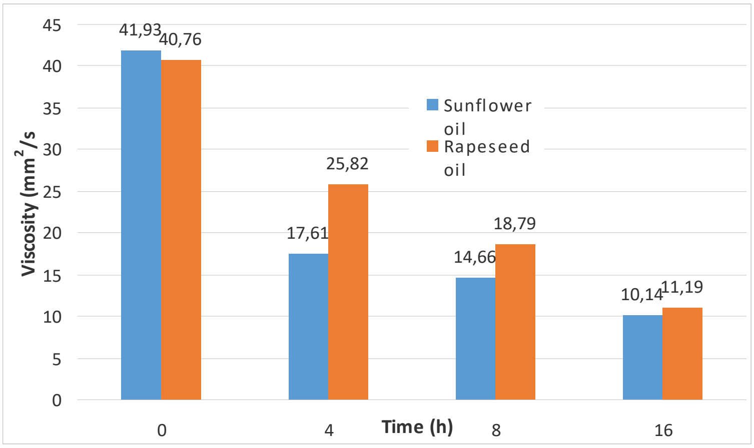

Fig. 2. Dependence of the viscosity on the time for transesterification of the rapeseed oil and sunflower oil using sulfomass as a catalyst.

The data from fig. 1 and 2 show a tendency towards a sharp decrease in the acid value (AV) and the viscosity of the oil phase already in the first 4h of the transesterification process. This especially applies to sunflower oil, in which, in addition to transesterification, its parallel reaction - esterification of higher fatty acids with methyl alcohol - probably takes place intensively. An increase in the duration of the process does not lead to a proportional decrease in the acid values, but on the contrary, to their albeit insignificant increase, which can be explained by the occurrence of side hydrolysis reactions of the methyl esters already formed in the first 4 h. Quite expectedly, the viscosity of the products drops sharply after the first 4h and decreases smoothly during the rest of the transesterification time.

Analogous results were achieved using the p-TSA catalyst.

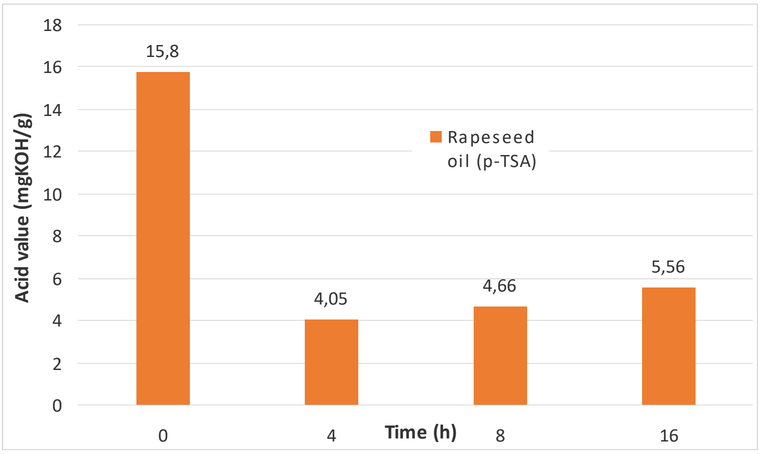

Fig. 3. Dependence of acid value (AV) of the rapeseed oil on the time of transesterification using p-TSA as a catalyst

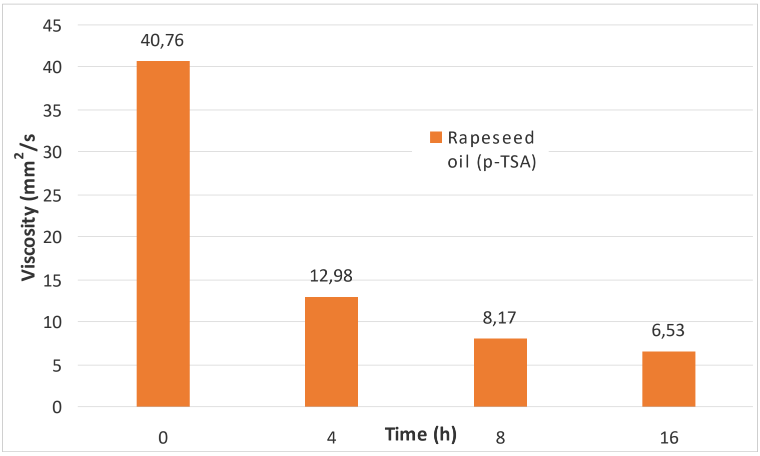

Fig. 4. Dependence of viscosity of the rapeseed oil on the time of transesterification with p-TSA used as a catalyst

The data from figure 1 and 2 on the one hand and from figure 3 and 4 on the other hand show a higher activity of p-TSA, compared to the sulfomass catalyst in the transesterification of rapeseed oil. It is likely that this trend is also observed in other vegetable oils. When p-TSA is used, however, an increased degree of darkening of the methyl esters is observed, especially with longer transesterification (Table 4), which is undesirable in view of their use as biodiesel. At the same time, the results of transesterification with tetraethyl titanate catalyst show unsatisfactory efficiency of this catalyst in the specific case (Table 4).

In general, the results of the studies carried out confirm the disadvantages of acid catalysis, mentioned above, regarding the low rate of transesterification, weak catalytic activity, darkening, due to side reactions of oxidation, destruction and polymerization. None of the products obtained in the experiments has the necessary parameters to allow its direct use as biodiesel. At the same time, the sharp reduction of the acid value at the relatively short time of transesterification, the resistance to clouding (catalyst sulphomass), allow applying additional (alkaline) transesterification, i.e. the so-called mixed transesterification to obtain methyl esters with the required qualities. In connection with this, the studies of the next stage of the development, experiments were carried out on alkaline transesterification of the products of the acid transesterification, of vegetable oils with high acid values.

4 Conclusion

The obtained results allow to make the following conclusions:

1. The carried out research expands the raw material base for the production of methyl and other alkyl esters by incorporating degraded vegetable oils, in particular very high acidity oils (with high acid value)
2. It has been established that in order to carry out sufficiently deep transesterification of oils with high acid value, it is necessary to carry out a two-stage transesterification - first stage with an acid catalyst, and second stage - with an alkaline catalyst.
3. In order to obtain methyl esters of fatty acids (FAME) with the necessary qualities, it is mandatory to use a "softer" acting acid catalyst as well as to shorten the time of the first stage of the preesterification as much as possible, in order to avoid darkening of the obtained methyl esters and oil phase losses.

4. Fatty acid methyl esters obtained from oils with high acidity are not inferior in terms of their characteristics to those obtained from standard oils, and are suitable for use as biodiesel fuel in internal combustion engines. Their use would contribute to reducing the price of biodiesel fuel and expanding the assortment of raw materials for its production.

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