Comparative study of biodiesel properties from waste oil, refined and unrefined sunflower oils: Effect of process parameters

Nebojša VASILJEVIĆ^{*},^{1,2} Vladan MIĆIĆ,¹ Mirko PETKOVIĆ,³ Milorad TOMIĆ,^{1,4} and Darja PEČAR⁵

¹Faculty of Technology Zvornik, University of East Sarajevo, Karakaj 34A, 75400 Zvornik, Bosnia and Herzegovina
 ²Faculty of Technology Novi Sad, University of Novi Sad, Cara Lazara 1, 21000 Novi Sad, Serbia
 ³Oil refinery Modrica JSC Modrica, Vojvode Stepe Stepanovića br. 49, 74480 Modriča, Bosnia and Herzegovina
 ⁴Engineering Academy of Serbia, Kneza Miloša 9/IV, 11000 Belgrade, Serbia

⁵Faculty of Chemistry and Chemical Technology, University of Maribor, Smetanova ulica 17, 2000 Maribor, Slovenia

Abstract. In this paper, the possibility of producing biodiesel using refined, unrefined and waste cooking oil, with the use of methanol in the transesterification reaction, will be examined. Potassium hydroxide was used as a catalyst in homogeneous catalysis. Various biodiesel properties were measured and compared with the ASTM D6751 and EN 14214 standards, in order to determine the quality. Biodiesel obtained from refined and unrefined sunflower oil meets the standards, because it has a low viscosity, acid number below 0.5 mg KOH/g and good properties at low temperatures, while biodiesel from waste oil showed increased moisture (> 0.08 %) and poor properties at low temperatures. The research showed that both refined and unrefined sunflower oil can serve as raw materials for biodiesel, while further research is needed for waste oils as raw materials for biodiesel production.

Keywords: biodiesel; homogeneous catalyst; refined oil; transesterification; waste cooking oil.

1. Introduction

The demand for energy is increasing, driven by the continuous growth of the population, rapid industrialization and technological development worldwide [1, 2]. As a result, fossil fuel reserves - such as oil, natural gas and coal - are becoming increasingly limited and rapidly depleted [3, 4]. On the other hand, the combustion of fossil fuels increases the emission of greenhouse gases (carbon dioxide, carbon monoxide, and sulfur and nitrogen oxides), which contribute to global warming and environmental degradation [1, 5-7]. Greenhouse gas emissions are estimated to cause 65% of global warming, with carbon dioxide accounting for approximately 65% of total emissions [7]. The transport sector, most manufacturing industries, and even electricity generation are heavily dependent on fossil fuels. Projections show that by 2030, 80% of energy will be based on fossil fuels, despite international agreements to reduce them [8, 9]. Renewable energy sources, such as wind, solar, and hydroelectric power, have the potential to reduce carbon emissions in the power sector and industry [5]. Biofuels, such as biodiesel and bioethanol, stand out as alternatives to fossil fuels in the transport sector, primarily because they can be used in existing internal combustion engines without significant modifications and because they burn cleanly [10-12].

Biodiesel is a renewable fuel produced from biomass [13]. Biodiesel production has been growing steadily, especially in the last two decades. In the European

Union, biodiesel production increased by as much as 137% between 2006 and 2016, while globally, from 2017 to 2020, production increased by about 30% [14]. Its properties largely depend on the composition of the fatty acids, which can be saturated and unsaturated [15]. Saturated biodiesel, which is rich in myristate, palmitate and stearate, has properties similar to conventional diesel. However, at low temperatures these properties deteriorate [16]. Biodiesel dominated by unsaturated oleate and linoleate have higher viscosity and higher surface tension compared to conventional diesel [17].

One of the main advantages of biodiesel is its biodegradability. In addition, the emission of greenhouse gases, such as carbon dioxide, carbon monoxide and sulfur dioxide, is quite low [10, 18, 19]. Biodiesel also has other advantages, such as a high cetane number (which allows for good flammability), optimal viscosity (which allows for good lubrication), and low toxicity, since it contains neither sulfur nor aromatic compounds [14, 20, 21]. In addition, it has a high flash point, which makes it safer for transportation and storage. It is compatible with existing diesel engines without additional technical modifications [22–24].

Comparing the emissions of biodiesel and conventional diesel, the advantage of biodiesel is clearly visible. Namely, by using 1 kg of biodiesel, CO_2 emissions can be reduced by about 3 kg. In percentage terms, the total CO_2 emissions are 65–90% lower compared to fossil diesel [8, 25]. Even fuel blends with 20% biodiesel (B20) lead to a reduction in CO_2

© 2025 Nebojša Vasiljević et al.

^{*} Corresponding author. E-mail address: nebojsa.vasiljevic@tfzv.ues.rs.ba (Nebojša Vasiljević)

emissions – a 15.66% reduction in CO_2 emissions has been recorded in city buses [8].

Various processes can be used to produce biodiesel, the most common of which are microemulsion, biomass pyrolysis, catalytic cracking and transesterification [26, 27]. However, transesterification is the most common, primarily because the resulting biodiesel is most similar to diesel fuel from fossil sources. Transesterification is a chemical reaction between triglycerides (in fats and oils) and alcohol, which produces biodiesel (alkyl ester of fatty acids) and a by-product – glycerol [19, 27]. The reaction itself takes place in several steps: triglycerides are first broken down into diglycerides, then into monoglycerides, and in each of these steps fatty acid esters are released [5, 28]. Methanol and ethanol are the most commonly used alcohols, primarily because they are available, have a low price and appropriate reactivity. Since transesterification is a reversible reaction, excess alcohol is usually added to shift the equilibrium towards biodiesel [5, 28, 29]. The efficiency of the conversion is also affected by other factors primarily the reaction time, temperature, type and concentration of the catalyst, as well as the ratio of alcohol to oil [5, 30].

Triglycerides from various sources are used as feedstock for biodiesel production - from edible and inedible vegetable oils, through waste oils, to algae and animal fats [31, 32]. The cost-effectiveness of the process depends mostly on the feedstock, the cost of which can amount to 75-85% of the total production costs [1, 33]. The use of edible oils - such as rapeseed oil, soybean oil, sunflower oil, safflower oil and peanut oil - presents a particular challenge, as they are already used as food [27, 34]. Therefore, more attention is being paid to alternatives today, among which waste oils play an important role. They are easily available and cost two to three times less than fresh vegetable oil [35-37]. An additional advantage is that their use also solves the problem of their improper disposal, which harms the environment [38].

Catalysts play a key role in transesterification, primarily because they reduce the activation energy and change the reaction pathway [28, 30]. Depending on the state of aggregation, catalysts can be homogeneous and heterogeneous. Homogeneous base catalysts, such as NaOH and KOH, are often used because they achieve high yields of biodiesel under relatively mild conditions temperature around 60 °C, ambient pressure, alcohol:oil ratio 6:1, and reaction duration around 1 h. However, their use has disadvantages. Soap formation can occur due to the presence of free fatty acids in the oil, and the catalyst itself cannot be isolated after synthesis [14, 39, 40]. On the other hand, homogeneous acid catalysts (H₂SO₄, HCl, H₃PO₄ and sulfonated acids) are more suitable if the feedstock is oil with a high content of water and free fatty acids. However, their application requires large amounts of acid, which increases costs, but also the risk of equipment corrosion [27]. Recently, heterogeneous catalysts have attracted increasing attention - among which calcined waste materials (eggshells, bones), zeolites, nanomaterials (multi-walled carbon nanotubes), as well as catalysts based on heteropolyacids stand out. Their main

advantage lies in the fact that they are easily separated after the reaction and can thus be used in subsequent cycles. However, in order to leave the same yield as with homogeneous catalysts, a longer time, somewhat higher reaction temperatures and frequent performance under pressure are required [26].

The aim of this work will be to examine the production of biodiesel from unrefined sunflower oil, refined sunflower oil and waste oil. In doing so, by changing certain process parameters (methanol/oil ratio, reaction time and catalyst concentration), it will be determined whether the obtained biodiesel has the quality to meet the criteria prescribed by the standard. In this way, a better understanding of the process and the possibility of obtaining it from different sources will be enabled.

2. Experimental

2.1. Materials and reagents

Unrefined sunflower oil, refined sunflower oil, and waste oil were used as raw materials for obtaining biodiesel, while methanol (Centrohem, Belgrade, Serbia) was used as alcohol.

2.2. Synthesis of biodiesel

Refined and unrefined oil do not require pretreatment, while the used oil was first heated to a temperature of 105 °C to remove water remaining after using the oil (frying, deep-frying), and then hot filtered through a filter belt to remove residual solid parts of food.

For the synthesis process, a potassium methoxide solution is first prepared (slowly and carefully dissolve KOH, which acts as a catalyst, in methanol with heating), and at the same time oil is carefully poured into a flask with a ground stopper and heated to the synthesis temperature. The biodiesel synthesis temperature was 60 °C because that temperature provides optimal conditions for transesterification - it is close to the boiling point of methanol (64.7 °C) while ensuring a sufficient reaction rate. When the temperatures of the oil and the potassium methoxide solution have reached the synthesis temperature, they are combined and the synthesis time is measured from that moment. The mixing speed during the synthesis process was constant and amounted to 350 rpm. Upon completion, the mixture is transferred to a separation funnel and left overnight to separate the layers of glycerin and biodiesel. A dark, glycerine layer, remains at the bottom of the reactor, is carefully separated by decantation, and the residual, lighter biodiesel layer is used for further characterization.

2.3. Methods for biodiesel characterization

First of all, the yield of biodiesel was determined, which is calculated according to Equation 1 [41]:

$$\eta = \frac{m_B}{m_0} \cdot 100 \, [\%] \tag{1}$$

where are:

 m_B = weight of biodiesel produced, g;

 m_0 = weight of oil used, g.

The acid number - AN (in some literature the acid value - AV) was calculated by titration of sample with an alcoholic solution of KOH using phenolphthalein as

an indicator until a light pink color appeared. It is calculated according to Equation 2 [42]:

$$AN = \frac{56.1 \cdot V_t \cdot C_t}{m} \cdot 100 \ [mg \ KOH/g] \qquad (2)$$

where are:

 V_t – volume of titrant, cm³;

 C_t – concentration of titrant, mol/dm³ and

m - sample mass, g.

Water content (%) was determined by the Karl-Fischer titration method described in [43] on KF 737 Coulometer (Metrohm, Herisau, Switzerland), while viscosity at 40 °C (mm²/s) and viscosity at 100 °C (mm²/s) were determined according to ISO 3104 (the method is identical to ASTM D445) via NVB Classic Tamson (Tamson Instruments B.V., Bleiswijk, The Netherlands) [44]. Viscosity index was calculated based on viscosity at 40 °C and 100 °C, while pour point (°C), cloud point (°C), filterability (°C), and flash point (°C) were determined according to methods ISO 3016:2019, ISO 3015:2019, EN 116:2016, and ISO 2592:2017 respectively [45-48]. Filterability was determined on an A.T.P.E.M. (ISL, Houston, Texas, United States), pour point and cloud point were determined using CPP Classic (Normalab, Valliquerville, France), and flash points were determined using Cleveland Flash CLA 5 (AntonPaarGmbH, Graz, Austria).

2.4. Design of experiment

In this study, we have 4 process variables – methanol:oil ratio (two levels), catalyst concentration (three levels), time (total of nine levels) and type of sunflower oil from

which biodiesel is obtained (three different types). A one-factor-at-a-time (OFAT) method was used, where one parameter is varied while others are kept constant. The experiments are grouped into two parts: in the first part, the influence of the methanol:oil molar ratio, time and catalyst concentration on the characteristics of biodiesel obtained from refined and waste sunflower oil was investigated.

First, a preliminary analysis was performed to determine at which methanol:oil molar ratio the best biodiesel characteristics are achieved. After that, with the molar ratio at which the best biodiesel characteristics were achieved, the influence of time and catalyst concentration was investigated.

The second part of the experiments is an addition and was not foreseen in the original design of the experiment, but the goal of that part is to determine how shorter times and different catalyst concentrations affect the characteristics of biodiesel. Also, in this second part, unrefined sunflower oil was used as a raw material, thus enabling the testing of biodiesel from as many as three types of sunflower oil.

3. Results and discusion

The results obtained in the study are shown in Table 1. Three types of sunflower oil were used to obtain biodiesel (refined, unrefined, and waste oil), two levels of methanol:oil molar ratio (4.5:1 and 6:1), three different catalyst concentrations (1 - 3 wt%) and 9 different times (range from 0.5 h - 12 h).

Catalyst conc. [wt. %]	Time [h]	Methanol- to-oil ratio [mol/mol]	Biodiesel yield [%]	Pour point [°C]	Cloud point [°C]	Filterability [°C]	Flash point [°C]	
			Biodiesel from	n refined sunflo	ower oil			
	4	4.5	83.32	-3	5	-4	172	
	12	4.5	71.89	-3	5	-4	173	
2	4		95.39	-3	5	-2	185	
	8		87.02	-3	5	-4	188	
	12	6	87.51	-3	5	-2	183	
1		0	99.60	-3	7	-1	185	
2	8		87.02	-3	5	-4	188	
3			74.40	-3	7	-5	184	
Biodiesel from waste oil								
	4		93.75	12	18	10	176	
2	8		91.14	10	16	10	174	
	12	6	91.19	13	18	13	178	
1		0	93.80	13	18	12	180	
2	8		91.14	10	18	9	180	
3			75.82	12	20	12	180	
]	Biodiesel from	sunflower unre	efined oil			
	0.5		99.72	-3	26	-7	-	
	1		99.17	-3	26	-6	-	
	1.5		98.41	-3	26	-5	-	
1	2	6	97.31	-3	20	-6	-	
	3		96.60	-3	26	-4	-	
	3.5		96.59	-3	26	-4	-	
	4		95.30	-3	23	-3	-	
1			93.92	-3	8	-4	-	
2	4	4.5	77.69	-3	8	-4	-	
3			50.19	-6	22	-5	-	

Table 1. Summarized results of the study on biodiesel production from sunflower oil.

Table 1. (continued).

Catalyst	Time	Methanol-	Viscosity at	Viscosity at	Viscosity	Water	Total acid	
conc.	I Ime	to-oil ratio	40 °C	100 °C	index	content	number	
[wt. %]	լոյ	[mol/mol]	[mm ² /s]	[mm ² /s]	[-]	[%]	[mg KOH/g]	
			Biodiesel from	refined sunflow	wer oil			
	4	4.5	4.98	1.89	255	0.028	0.0564	
	12	4.3	4.33	1.74	263	0.060	0.0563	
2	4		3.98	1.63	268	0.066	0.0564	
	8		4.05	1.70	273	0.090	0.0563	
	12	6	4.09	1.68	268	0.100	0.0562	
1		0	3.95	1.67	273	0.106	0.0561	
2	8		4.05	1.7	273	0.090	0.0563	
3			4.19	1.67	263	0.137	0.0561	
Biodiesel from waste oil								
	4		5.33	1.87	241	0.190	0.1409	
2	8	6	5.23	1.87	244	0.223	0.1410	
	12		5.20	1.95	254	0.220	0.1404	
1			5.24	1.89	245	0.214	0.1409	
2	8		5.23	1.87	244	0.223	0.1410	
3			5.29	1.91	245	0.260	0.1406	
	-	B	iodiesel from s	unflower unref	ined oil			
	0.5		4.04	1.59	261	0.068	0.0298	
	1		3.86	1.59	260	0.072	0.0313	
	1.5		4.11	1.60	259	0.092	0.0305	
1	2	6	4.10	1.61	262	0.079	0.0307	
	3		4.03	1.63	269	0.088	0.0296	
	3.5		3.96	1.61	267	0.071	0.0296	
	4		3.92	1.63	272	0.095	0.0313	
1			3.84	1.60	272	0.056	0.0313	
2	4	4.5	4.34	1.72	262	0.094	0.0381	
3			4.70	1.81	257	0.147	0.0423	

 Table 2. Permissible limits of certain physical and chemical properties of biodiesel according to ASTM D6751 and EN 14214 standard.

Properties	ASTM D6751	EN 14214
Viscosity at 40 °C	1.9 - 6	3.5 - 5
[mm ² /s]		
Water content [%]	0.08 max	0.05 max
Total acid number	0.5 max	0.5 max
[mgKOH/g]		
Pour point [°C]	(-15) - 6	-
Cloud point [°C]	-3	12
Filterability [°C]	-	-
Flash point [°C]	93 min	120 min

To assess the quality of biodiesel, a comparison of the obtained results with the American standard (ASTM D6751) and the European standard (EN 14214) was made (Table 2) [49, 50].

Table 3 shows a preliminary analysis of the influence of the molar ratio of methanol to oil on the production of biodiesel from refined oil with the addition of 2 wt% catalyst after 4 h and 12 h.

Table 3. Preliminary analysis of the influence of the methanol:oil ratio on the properties of biodiesel.

Catalyst conc. [wt. %]	Time [h]	Methanol- to-oil ratio [mol/mol]	Biodiesel yield [%]	Pour point [°C]	Cloud point [°C]	Filterability [°C]	Flash point [°C]
	4	4.5	83.32	-3	5	-4	172
2	4	6	95.39	-3	5	-2	185
Z	12	4.5	71.89	-3	5	-4	173
	12	6	87.51	-3	5	-2	183

Table 3. (continued).

Catalyst conc. [wt. %]	Time [h]	Methano- to-oil ratio [mol/mol]	Viscosity at 40 °C [mm²/s]	Viscosity at 100 °C [mm²/s]	Viscosity index [-]	Water content [%]	Total acid number [mg KOH/g]
	4	4.5	4.98	1.89	255	0.060	0.0563
2	4	6	3.98	1.63	265	0.066	0.0559
2	10	4.5	4.33	1.74	263	0.029	0.0563
	12	6	4.09	1.68	276	0.036	0.0562

The methanol-to-oil ratio has an huge influence on the yield of biodiesel obtained from refined oil. Thus, after 4 h of synthesis, at a methanol-to-oil ratio of 4.5:1, the yield is 83.32%, while at a ratio of 6:1, the yield is 14.49% higher (95.39%). The same effect was observed after 12 h, because by changing the molar ratio from

4.5:1 to 6:1, a 21.73% higher yield was observed (from 71.89% to 87.51%). By measuring the viscosity at 40 $^{\circ}$ C and 100 °C and calculating the viscosity index, it was determined that the viscosity indices are lower at the molar ratio of methanol:oil = 4.5:1 (e.g. after 4 h, the IV is 255 at the molar ratio of methanol:oil = 4.5:1, and for the molar ratio of methanol:oil = 6:1 it is 265), which means that using such a ratio results in a less stable product [51]. The water content is practically independent of the methanol:oil ratio, because e.g. after 4 h of synthesis almost identical for both molar ratios and ranges from 0.060-0.066%. Similar to the water content, the acid number (0.56 mg KOH/g), pour point (-3 °C) and cloud point (5 °C) practically remain unchanged with a change in the mole ratio of methanol:oil. Flash point and filterability are lower at a lower methanol:oil molar ratio; thus, after 4 h of biodiesel synthesis, their values are 172 °C and -4 °C for the molar ratio methanol:oil=4.5:1, that is, 185 °C and -2 °C for the molar ratio methanol:oil=6:1.

Analyzing all the previous Responses, one can come to the conclusion that it is better to synthesize biodiesel at a methanol-to-oil ratio = 6:1, primarily because biodiesel with a higher yield and a lower viscosity index is obtained under these conditions. Therefore, in the continuation of the study, biodiesel will be synthesized only at a methanol-to-oil ratio = 6:1.

The yield of biodiesel obtained from refined and waste sunflower oil depending on time is shown in Figure 1a (catalyst conc. is 2 wt%), while the yield depending on the dose of catalyst is shown in Figure 1b (time is 8 h).



Refined oil Waste oil

Figure 1. Biodiesel yield from refined and waste sunflower oil as a function of a) synthesis time and b) catalyst concentration.

It can be seen from Figure 1a that there is a certain negative influence of time on the yield of biodiesel. First of all, looking at biodiesel obtained from refined sunflower oil, it is observed that the yield of biodiesel is the highest after 4 h (95.39%), while the yield of

biodiesel decreases with further extension of time. After 8 h, the yield dropped to 87.02%, and by further extending the time up to 12 h, a slight increase in yield is observed (87.51%). However, this small increase should be taken with caution due to possible measurement error. A similar trend is present with biodiesel obtained from waste oil. Thus, the highest yield (93.75%) is at the lowest time (4 h), and by further extending the time to 8 h, the yield decreases to 91.14% and practically remains unchanged by further extending the time to 12 h (91.19%). By comparing the yield of biodiesel obtained from refined and waste oil at a certain time, it is noticed that the yield of biodiesel obtained from waste oil is lower by 1.72% (relatively) compared to that obtained from refined oil at 4 h, while the opposite effect is observed by extending the time, so, e.g. after 8 h, the yield of biodiesel from waste oil is higher by 4.74% (relatively). According to some works, it is considered that the extension of the transesterification time leads to a decrease in the yield of the product due to the back reaction, which causes the saponification reaction and the formation of soap [52, 53].

It can be seen from Figure 1b that the amount of catalyst has a significantly greater influence on the yield of biodiesel than time. Observing the biodiesel obtained from refined oil, it is concluded that almost the maximum yield (99.6%) is achieved with the use of 1 wt% catalyst, while with a further increase in the amount of catalyst, a noticeable decrease in yield is observed. Thus, with the use of 3 wt% catalyst, a yield of only 74.4% is achieved, which represents a reduction of as much as 25.3%. Waste-oil biodiesel follows the same pattern, with the increase in the amount of catalyst from 1 wt% to 3 wt%, the yield decreases from 93.8% to 75.82%, which is a decrease of 19.17%; therefore, the yield reduction is less pronounced if waste oil is used as raw material. With the application of 1 wt% catalyst, it can be seen from Figure 1b that the yield is higher if the raw material is refined oil, while at 2 wt% and 3 wt% it is observed that the yield is higher with waste oil as raw material. The reduction in the yield is due to the addition of excess KOH catalyst which leads to more triglycerides which react with KOH to form soap [53, 54].

Viscosity values at 40 °C and 100 °C and viscosity index for synthesized biodiesels are shown in Figure 2.

The main disadvantage of vegetable oils as an alternative fuel is their high viscosity. This is reason why the transesterification process is carried out, in order to obtain biodiesel (methyl ester of fatty acids), with significantly lower viscosity [55, 56]. Transesterification converts triglycerides (highly unsaturated fatty acids that are susceptible to oxidation) into mixtures of long-chain fatty acid esters, which are more saturated [56, 57].

Viscosity at 40 °C was observed to be much higher in biodiesel originating from waste oil; for example when using 2 wt% catalyst and 4 h of synthesis, the viscosity at 40 °C is 3.98 mm²/s for that obtained from refined oil and 5.33 mm²/s for that from waste oil, which is an increase of 33.9%. Also, such high viscosity of biodiesel, which originates from waste oil, has been observed for longer periods of time. Furthermore, observing the influence of time, it was observed that the viscosity of biodiesel from refined oil increases slightly from 3.98 mm²/s to 4.09 mm²/s with the extension of time from 4 h to 12 h, while in the case of biodiesel from waste oil, a decrease in viscosity was observed from 5.33 mm²/s to 5.2 mm²/s in the same time range. The viscosity in this study matches those of other studies, *e.g.* in Naureen's study, where the viscosity was 4.719 mm²/s [58], or Zahed's study, where the viscosity was 4.6 mm²/s [59].



Figure 2. Values of viscosity and viscosity index of biodiesel from refined and waste sunflower oil as a function of a) synthesis time and b) catalyst concentration.

While biodiesel viscosity is higher than that of petroleum diesel (avg. 2.6 mm²/s [17]), it still meets the ASTM D6751 requirement of 1.9–6.0 mm²/s [49]. On the other hand, the EN14214 standard is much stricter, and prescribes that the viscosity of biodiesel at 40 °C should be in the range of 3.5-5 mm²/s [50]. According to the results of this work, biodiesel obtained from refined oil meets the requirements of this standard, while the one obtained from waste oil does not because its viscosity is greater than 5 mm²/s.

With increasing synthesis time from 4 h to 12 h, viscosity at 100 °C rises modestly for both feedstocks: from 1.63 to 1.68 mm²/s for refined-oil biodiesel and from 1.87 to 1.95 mm²/s for waste-oil biodiesel (waste-oil values remain ~14.7 % higher at 4 h). From the previous sentence, it is also noticeable that, as in the case of viscosity at 40 °C, the viscosity is higher with waste oil, by 14.72% at a time of 4 h. In accordance with the previous text, the values of the viscosity index can be guessed. Viscosity indexes for biodiesel from refined oils are in the range of 268-273, while in the case of biodiesel from waste oil, that range is in the interval of 241-254. Given that biodiesel from waste oil has a lower viscosity index, this means that the viscosity changes a lot more with temperature, that is, that this type of

biodiesel has less stability compared to the one obtained from refined oil.

By observing the amount of catalyst as a process parameter, it was noticed that there is a slight increase in viscosity at 40 °C with an increase in the amount of catalyst; in the case of biodiesel obtained from refined oil, an increase of 6.05% (from 3.95 mm²/s to 4.19 mm²/s) was observed with the increase in the amount of catalyst from 1 wt% to 3 wt%, while for biodiesel from waste oil a slight increase of only 0.95% was observed (from 5.24 mm²/s to 5.29 mm²/s). On the other hand, for viscosity at 100 °C, such an increase is even less pronounced - from 1.63 mm²/s to 1.68 mm²/s in the case of refined oil as raw material, that is, from 1.89 mm²/s to 1.91 mm²/s.

The influence of the amount of catalyst on the viscosity index is quite interesting. In the case of refined oil as a raw material, a drop in the viscosity index from 273 to 263 was observed by increasing the amount of catalyst from 1 wt% to 3 wt%, while in the case of waste oil, the viscosity index is practically unchanged and ranges from 244-245. So, biodiesel obtained from waste oil is less stable due to a lower viscosity index, but that the amount of catalyst alone has no effect on the viscosity index of such biodiesel. On the other hand, considering the drop in the viscosity index of refined oil as a raw material, we come to the conclusion that excessive amounts of catalyst create less stable biodiesel.

Figure 3 shows the effect of time and amount of catalyst on the moisture content and acid number of biodiesel obtained from refined and waste oil.



Figure 3. Water content and acid number of biodiesel from refined and waste sunflower oil as a function of a) synthesis time and b) catalyst concentration.

Biodiesel's hygroscopicity - combined with water and free fatty acids—promotes fuel-system corrosion and soap formation during transesterification, which results in a decrease in catalytic efficiency, and in yield

[61-63]. Figure 3 shows that there are significant differences in water content and acid number for the two types of biodiesel; thus observing e.g. biodiesel obtained from refined and that obtained from waste oil at 2 wt% catalyst and after 8 h, the water content and acid number for biodiesel obtained from refined oil are 0.09 % and 0.0563 mg KOH/g, respectively, and for that from waste oil are 0.223% and 0.141 mg KOH/g, respectively. So, in biodiesel obtained from waste oil, there is 147.78% more moisture, that is, 150.53% higher acid number compared to biodiesel from refined oil. Neither synthesis time (4 h-12 h) nor catalyst loading (1 wt%-3 wt%) significantly alters the acid number (narrow variation), but both parameters increase water content: by increasing the synthesis time from 4 h to 12 h, the water content in biodiesel from refined oil increased by 51.52% (from 0.066% to 0.10%), while in biodiesel from waste oil it increased by 18.42% (from 0.19% to 0.225%). Likewise, by increasing the amount of catalyst from 1 wt% to 3 wt%, the water content in biodiesel from refined oil increased by 37% (from 0.10% to 0.137%), while in biodiesel from waste oil it increased by 21.5% (from 0.214% to 0.26%).

The acid number values in this study are lower than some in other works; for example in the work of Ozorco et al., the acid number reaches values up to 0.6 mg KOH/g [64]. Also, in the study by Hossain, biodiesel from waste sunflower oil had significantly more acids and the obtained acid number was 0.44 mg KOH/g [65], while in the study conducted by Saydut et al., the acid content was in the range of 0.50–0.52 mg KOH/g for refined sunflower oil and 0.56–0.57 mg KOH/g for waste oil [66]. On the other hand, similar acid number values can be found in some works, such as in Naureen's study, where the acid number is 0.07 mgKOH/g [58], or Zahed's study (0.05 mgKOH/g) [59].

According to ASTM D6751 and EN 14214, the acid number must not exceed 0.5 mg KOH/g, which means that the synthesized biodiesel meets the required standards. According to the ASTM D6751 standard, the maximum amount of water in biodiesel is 0.08%, and according to the EN 14214 standard, this limit is even more rigorous and amounts to 0.05% [49, 50]. Therefore, biodiesel obtained from waste oil does not meet the required conditions, and as for biodiesel from refined oil, only the one synthesized using 2 wt% catalyst, molar ratio 6:1 and 4 h synthesis meets the ASTM standard. Also, by reviewing the results from the preliminary analysis, it is observed that biodiesel with a more satisfactory water content according to the ASTM standard is produced with a methanol:oil molar ratio of 4.5:1.

Table 4 shows the values for pour point, cloud point, filterability, and flash point of biodiesel obtained from refined and waste oil.

Table 4.	Values of pour point, cloud point, filterability and flash point of biodiesel obtained from refined and waste sunflower oil at
	different synthesis times and catalyst concentrations.

Variables	Raw material	Values							
Catalyst conc. [wt.%]			2		1	2	3		
Time [h]		4	8	12		8			
Doug against [9C]	Refined oil	-3	-3	-3	-3	-3	-3		
Pour point [⁺ C]	Waste oil	12	10	13	13	10	12		
Cloud agint [%C]	Refined oil	5	5	5	7	5	7		
	Waste oil	18	16	18	18	18	20		
	Refined oil	-2	-4	-2	-1	-4	-5		
Finerability [C]	Waste oil	10	10	13	12	9	12		
Flash point [°C]	Refined oil	185	188	183	185	188	184		
Flash point [C]	Waste oil	176	174	178	180	180	180		

At low temperatures, diesel engine operation can be difficult due to high viscosity, which is why it is necessary to determine fuel properties at low temperatures, such as pour point and cloud point [67]. It can be seen from Table 4 that the pour point of biodiesel obtained from refined oil is not affected by time or the amount of catalyst, that is, the pour point is always -3°C. This is in accordance with the ASTM D6751 standard, according to which the permissible limits are -15 to 6 °C [49]. In the work of Naureen et al., the pour point is -5°C, thus very similar to the value in this work [58]. In the available literature, it can be found that the average pour point of diesel fuel is 1 °C, which means that obtained biodiesel outperforms conventional diesel [67]. On the other hand, the pour point of biodiesel obtained from waste oil is in the range of 10-13 °C, thus slightly higher than the upper limit of the standard, which is why this type of fuel does not meet the legal norms regarding quality. It is noted that the lowest and therefore the most favorable values of the pour point are achieved at the central process conditions, i.e. with the addition of 2 wt% catalyst and after 8 h of synthesis. However, these values should be taken with caution due to possible measurement error.

As in the case of pour point as Response, biodiesel obtained from waste oil has a higher cloud point and flitability than that obtained from refined oil. A cloud point analysis was conducted to ascertain the temperature at which solid components, such as waxes, initiate formation in biodiesel feedstock. The cloud point for biodiesel obtained from refined oil is in range 5 - 7 °C, which is compared to some other works, such as the work of Wan Osman, in which the cloud point is 8.7 °C [68], or the work of Bello, in which the cloud point is 8.6 °C [69]. Waste-oil biodiesel shows cloud points of 16-20 °C. Limit values of the cloud point according to the ASTM D6751 standard are from (-3 °C) - 12 °C, which means that biodiesel obtained from refined oil passes the legal norm, but biodiesel from waste oil does not pass the norm.. According to the available literature, the cloud point of diesel fuel is 2 °C, which is close to the biodiesel obtained from refined oil in our study [67].

Time has no effect on the filterability of biodiesel obtained from refined oil (interval (-4) - (-2) °C), but the amount of catalyst has a negative effect on this Response because increasing the amount of catalyst decreases filterability from -1 °C to -5 °C. The filterability of biodiesel from waste oil ranges from 9 to 13°C. It should be noted that filterability values for biodiesel are not covered by any standard.

Flash point indicates the flammability of the fuel as it considers the lowest temperature at which the heated vapor and air above the fuel will ignite [70, 71]. It is an important measure because it determines safety during handling and transportation [56, 61]. From Table 4, it can be seen that there is a definite difference in the ignition point for two different types of biodiesel; for biodiesel from refined oil, the ignition point is in the range of 183 - 188 °C, while for biodiesel from waste oil it is lower, and is in the range of 174 - 180 °C. Also in the available literature are approximate flash point values [58]. In some literature, the ignition point is only 99 °C, and in such cases there is a possible problem of potential self-ignition during transport [59]. The ignition point according to the ASTM D6751 standard must be higher than 93 °C, and according to EN 14214 higher than 120 °C, which means that biodiesel obtained from both types of sunflower oil meets the norms of both standards [49, 50].

In the previous part of the work, the influence of time and amount of catalyst on the characteristics of biodiesel obtained from refined and waste sunflower oil was analyzed. According to the design of the experiment, the time test was performed at a constant central dose of the catalyst (2 wt%), however, analyzing the influence of the dose of the catalyst in the range 1-3 wt%, it was established that the addition of 1 wt% of the catalyst produced biodiesel with better characteristics. Likewise, the influence of time in the range of 4-12 h was investigated, however, the analyzes determined that the biodiesel yield decreases with the extension of time. Bearing that in mind, below, the test was performed for shorter times of 0.5 - 4 h with the addition of 1 wt% catalyst. Also, considering the insufficient results in which the molar ratio of methanol:oil = 4.5:1 was applied, this ratio was used below to test the amount of catalyst (1 - 3 wt%) on the characteristics of biodiesel (it is important to note that in these experiments the time was kept constant at 4 h, considering that this time figures in both the first part of the experiments and this, second, additional part). Finally, in the second part, unrefined sunflower oil was used as a raw material for obtaining biodiesel, because in this way it was possible to examine three different types of sunflower oil in the study.

Figure 4a shows the influence of time on the yield of biodiesel at a molar ratio of methanol to oil of 6:1 and in the presence of 1% catalyst, while Figure 4b shows the effect of the dose of catalyst on the yield of biodiesel obtained from unrefined oil at a molar ratio of methanol to oil of 4.5:1 and after 4 h of synthesis.



Figure 4. Biodiesel yield from unrefined sunflower oil as a function of a) synthesis time and b) catalyst concentration.

It can be seen from Figure 4a that the amount of methyl ester phase is extremely high and is always above 95%. The highest yield is achieved after only 30 min (99.72%), however, with further extension of time, it gradually falls and after 4 h it amounts to 95.3%. The possible reason for such a negative trend lies in the fact that in these experiments no post-treatment was performed, that is, washing and drying of the methyl ester fraction after separation from the glycerine layer. The absence of these steps could have led to the fact that residual raw materials (oil and methanol) and catalyst still exist in this fraction, which affected the incorrect estimation of the mass of the methyl ester fraction.

Figure 4b shows a pronounced effect of catalyst loading on biodiesel yield: the optimum is achieved with the addition of 1 wt% catalyst (yield is 93.92%), while a further increase in the catalyst dose leads to a drastic decrease in biodiesel yield. Thus, with the addition of 3 wt% catalyst, the yield of biodiesel is almost twice as low and amounts to only 50.19%. The possible reason for this phenomenon is that an excess of catalyst leads to the formation of a stable emulsion between biodiesel, glycerol and unconverted triglycerides. Further, the separation of phases after the reaction is difficult because of this, so part of the biodiesel remains trapped in the emulsion and is lost.

As in the first part of the experiments, there is a decrease in yield with an increase in the amount of catalyst. The most likely reason for this phenomenon is that an excessive amount of KOH leads to the reaction of KOH with triglycerides, which results in the formation of soap [53, 54].

Figure 5a shows the effect of time on the viscosity and viscosity index of biodiesel at a 6:1 methanol-to-oil molar ratio and in the presence of 1% catalyst, while Figure 5b shows the effect of the catalyst dose on the viscosity and viscosity index of biodiesel obtained from unrefined oil at a 4.5:1 methanol-to-oil molar ratio and after 4 h of synthesis.



Figure 5. Values of viscosity and viscosity index of biodiesel obtained from unrefined sunflower oil depending on a) synthesis time and b) catalyst concentration.

The viscosity at 40 °C increases with the extension of the synthesis time from 0.5 h to 1.5 h (from 4.04 mm^{2}/s to 4.11 mm^{2}/s), while further extension of the time (up to 4 h) causes a drop in viscosity to 3.92 mm²/s. The prescribed limits are 1.9-6 mm²/s according to ASTM D6751, which means that these values are within the standard limits for quality [49]. This trend of viscosity change is not observed for viscosity at 100 °C. First of all, the viscosity increases only slightly with increasing time (from 1.59 mm²/s after 0.5h to 1.64 mm²/s after 4 h). By using these two viscosities and determining the viscosity index, it is observed that the viscosity index practically does not change by extending the synthesis time from 0.5 h to 2 h (amounts 260). By further extending the synthesis time, it is noticed that the viscosity index increases, achieving a maximum value of 271 after 4 h.

As for the viscosity of biodiesel obtained from unrefined oil, it decreases with increasing amount of catalyst. Thus, with an increase in the catalyst dose from 1 wt% to 3 wt%, the viscosity at 40 °C increases from 3.84 mm²/s to 4.7 mm²/s, while the viscosity at 100 °C increases from 1.6 mm²/s to 1.81 mm²/s. Similarly, there is a change in the viscosity index with a change in the catalyst dose. Thus, the viscosity index decreases from 271 to 256 with increasing catalyst dosage from 1 wt% to 3 wt%.

The influence of time at the molar ratio methanol oil 6:1 and in the presence of 1% catalyst, and the influence of the amount of catalyst at the molar ratio methanol oil 4.5:1 and after 4 h of synthesis on the content of water and acids in biodiesel obtained from unrefined oil is shown in Figure 6.



Figure 6. Water content and acid number of biodiesel from unrefined sunflower oil as a function of a) synthesis time and b) catalyst concentration.

From Figure 6a, it can be observed that the water content in the sample increases with the extension of the synthesis time. Thus, after 30 min, it is 0.0689%, while after 1.5 h it is 0.0919%. With further extension of time, the diagram shows a slight decrease in the value of this Response, but considering that the water content after 4 h is almost identical to that at 1.5 h, we can consider this decrease to be a measurement error and can be ignored. On the other hand, the values of the acid number are almost identical in the entire range of time (0.0296 mg KOH/g - 0.0313 mg KOH/g), and therefore it is considered that time has no effect on the content of free acids in biodiesel. By observing the absolute values of the previous outputs and comparing them with the standard, it can be concluded that they are within the allowed limits (it is less than 0.5 mg KOH/g) [49].

As for the influence of the catalyst dose on the content of water and free acids in the sample, it can be seen from Figure 6b that their values increase by extending the synthesis time. Thus, with an increase in the catalyst dose from 1 wt% to 3 wt%, in the case of free acids, an increase from 0.0313 mg KOH/g to 0.0423 mg KOH/g (increase of 35.1%), and in the case of water content, this increase is even more pronounced (from 0.0558% to 0.1466%, i.e. by 162.72%). The maximum allowed amount of water is 0.08% according to ASTM D6751 [49], and according to the EN 14214 standard it is 0.05% [50], which means that there is an excess in the water content for all samples.

Table 5 shows the pour points, cloud points and filterability of biodiesel obtained from unrefined sunflower oil.

 Table 5. Values of pour point, cloud point and filterability of biodiesel from unrefined sunflower oil at different synthesis times and catalyst concentrations.

Variables		Value									
Methanol-to-oil ratio [mol/mol]		6							4.5		
Catalyst conc. [wt. %]				1				1	2	3	
Time [h]	0.5	1	1.5	2	3	3.5	4		4		
Pour point [°C]	-3	-3	-3	-3	-3	-3	-3	-3	-3	-6	
Cloud point [°C]	26	26	26	20	26	26	23	8	8	22	
Filterability [°C]	-7	-6	-5	-6	-4	-4	-3	-4	-4	-5	

The pour point remains unchanged throughout the synthesis time, and is -3 °C for any given time. This is in accordance with the ASTM standard, according to which the permissible limits are $(-15^{\circ}C) - 6^{\circ}C$. On the other hand, the cloud point and filterability values behave somewhat differently. In the first 1.5 h, the value of the cloud point remains unchanged and is 26 °C. By further extending the time, it is noticed that the cloud point value decreases (e.g. after 2 h the value is 20 °C and after 4 h the value is 23 °C). These values should be taken with caution, considering that after 3 h and 3.5 h the cloud point increased again, but it is certain that there is a trend of the cloud point decreasing after 1.5 h despite the measurement error. On the other hand, the existence of an error is not observed in filterability. The value of filterability is the lowest after 0.5 h and is -7 °C, while with further extension of time it increases and reaches -3 °C after 4 h of synthesis.

Varying catalyst concentration exerts no influence on pour point until 3 wt%, where it drops to -6 °C. The amount of catalyst has a great influence on the cloud point. Thus, at 1 wt% catalyst, the cloud point is only 8 °C, while at 3 wt% catalyst, the cloud point is at 22 °C. According to the American standard, the cloud point limits are (-3 °C) – 12 °C; therefore, only biodiesel synthesized at a molar ratio of 4.5:1 and a catalyst amount of 1-2 wt% meets the legal norm for quality according to the ASTM D6751 method. Regarding the filterability, no change was observed, as with the increase in the amount of catalyst from 1 wt% to 3 wt%, the filterability changed from -4 °C to -5 °C.

4. Conclusions

In experiments, with a methanol-oil ratio of 6:1, 1 wt% KOH and a reaction time of 0.5 to 4 h, biodiesel was obtained from refined and unrefined sunflower oil that in most parameters meets the requirements of ASTM and EN standards. The yields obtained were high, and the fuel properties — viscosity, acid number, and flash point — were within acceptable limits for commercial use. On the contrary, biodiesel from waste oil had increased water content and unfavorable characteristics at low temperatures, which indicates that a simple pretreatment (drying or washing) is necessary before transesterification itself. In further research, plan is to test improved phase separation methods, investigate the use of heterogeneous catalysts for reuse, and integrate an oil drying system to make waste oil a more reliable and economical source for biodiesel production.

Conflict of interest

Authors have no conflict of interest to declare.

References

- [1]. P. Mwenge, H. Rutto, Machine learning-based predictive modelling of biodiesel production from animal fats catalysed by a blast furnace slag geopolymer, Results in Engineering 25 (2025) 104126. Doi: 10.1016/J.RINENG.2025.104126
- [2]. S. Vellaiyan, Transforming wastewater-derived algae biodiesel with ammonium hydroxide emulsion for enhanced energy efficiency and emission reduction, Results in Engineering 24 (2024) 103332. Doi: 10.1016/J.RINENG.2024.103332
- [3]. S.I.S. Mohammad, A. Vasudevan, K.D.V. Prasad, I.R. Ali, A. Kumar, A. Kulshreshta, V.S. Mann, I.B. Sapaev, T. Kalyani, M. Sina, Evaluation of diesel engine performance and emissions using biodiesel from waste oils synthesized with Fe₃O₄– SiO₂ heterogeneous nano catalyst, Heliyon 11 (2025) e41416.

Doi: 10.1016/J.HELIYON.2024.E41416

- [4]. M. Omer, Energy, environment and sustainable development, Renewable & Sustainable Energy Reviews 12 (2008) 2265. Doi: 10.1016/j.rser.2007.05.001
- [5]. V. Okpala, K.T. Dibia, Optimized biodiesel production from palm kernel and *Jatropha curcas* oil blend using KOH-supported calcined animal bone catalyst: A response surface methodology and genetic algorithm–Bayesian hybridization, Cleaner Chemical Engineering 11 (2025) 100141. Doi: 10.1016/J.CLCE.2024.100141
- [6]. M. Li, Q. Bai, W. Du, The world is different because of you: Global warming, technological progress and economic development, Structural Change and Economic Dynamics 74 (2025) 202. Doi: 10.1016/J.STRUECO.2025.03.012
- [7]. M.S. Barbarey, M.M. El-Sayed Seleman, A.A. El Kheshen, M.F. Zawrah, Utilization of ladle furnace slag for fabrication of geopolymer: Its application as catalyst for biodiesel production, Construction and Building Materials 411 (2024) 134226. Doi: 10.1016/J.CONBUILDMAT.2023.134226
- [8]. M.A. Khan, N.A. Sheikh, K.Z. Jadoon, A. Ayub, T. W. Awotwe, R. Tariq, Utilization of locally sourced waste fats for biodiesel production: Experimental characterization and environmental life cycle assessment, Biomass and Bioenergy 194 (2025) 107692. Doi: 10.1016/J.BIOMBIOE.2025.107692
- [9]. A. Farokhnia, S.M. Jokar, P. Parvasi, A.S. Kim, A novel design for biodiesel production from methanol+mutton bone fat mixture, Biotechnology

for Biofuels and Bioproducts 15 (2022) 1. Doi: 10.1186/s13068-022-02229-4

- [10]. J. Milano, M.Y. Ong, S.K. Tiong, F. Ideris, A.S. Silitonga, A.H. Sebayang, C.H. Tan, I.M.R. Fattah, Z. Fona, N. A. Hossain, Comparative study of the production of methyl esters from non-edible oils as potential feedstocks: Process optimization and two-step biodiesel characterization, Results in Engineering 25 (2025) 104285. Doi: 10.1016/J.RINENG.2025.104285
- [11]. A. Shankar, P.R. Pentapati, R.K. Prasad, Biodiesel synthesis from cottonseed oil using homogeneous alkali catalyst and heterogeneous multi-walled carbon nanotubes: Characterization and blending studies, Egyptian Journal of Petroleum 26 (2017) 125. Doi: 10.1016/j.ejpe.2016.04.001
- [12]. B. Changmai, R. Rano, C. Vanlalveni, S.L. Rokhum, A novel *Citrus sinensis* peel ash coated magnetic nanoparticles as an easily recoverable solid catalyst for biodiesel production, Fuel 286 (2021) 119447. Doi: 10.1016/j.fuel.2020.119447
- [13]. S.T. Al-Humairi, J.G. M. Lee, A.P. Harvey, Direct and rapid production of biodiesel from algae foamate using a homogeneous base catalyst as part of an intensified process, Energy Conversion and Management: X 16 (2022) 100284. Doi: 10.1016/j.ecmx.2022.100284
- [14]. Y. Patiño, L. Faba, E. Díaz, S. Ordóñez, Biodiesel production from sewage sludge using supported heteropolyacid as heterogeneous acid catalyst, Journal of Environmental Management 365 (2024) 121643. Doi: 10.1016/J.JENVMAN.2024.121643
- [15]. V.D. Chaudhari, D. Deshmukh, Challenges in charge preparation and combustion in homogeneous charge compression ignition engines with biodiesel: A review, Energy Reports 5 (2019) 960. Doi: 10.1016/J.EGYR.2019.07.008
- [16]. S.K. Hoekman, A. Broch, C. Robbins, E. Ceniceros, M. Natarajan, Review of biodiesel composition, properties, and specifications, Renewable & Sustainable Energy Reviews 16 (2012) 143. Doi: 10.1016/j.rser.2011.07.143
- [17]. G. Knothe, K.R. Steidley, Kinematic viscosity of biodiesel fuel components and related compounds. Influence of compound structure and comparison to petrodiesel fuel components, Fuel 84 (2005) 1059. Doi: 10.1016/j.fuel.2005.01.016
- [18]. T.M. I. Mahlia, Z.A.H.S. Syazmi, M. Mofijur, A.E.P. Abas, M.R. Bilad, H.C. Ong, A.S. Silitonga, Patent landscape review on biodiesel production: Technology updates, Renewable & Sustainable Energy Reviews 118 (2020) 109526. Doi: 10.1016/j.rser.2019.109526
- [19]. M.D. Asfaw, A.T. Yadeta, B.G. Yewalie, Y.W. Negash, Production and characterization of biodiesel from *Argemone mexicana* seed oil, Results in Chemistry 13 (2025) 102055. Doi: 10.1016/J.RECHEM.2025.102055
- [20]. M. Guo, W. Jiang, C. Chen, S. Qu, J. Lu, W. Yi, J. Ding, Process optimization of biodiesel production from waste cooking oil by esterification of free fatty acids using La³⁺/ZnO–TiO₂ photocatalyst,

Energy Conversion and Management 229 (2021) 113745. Doi: 10.1016/j.enconman.2020.113745

- [21]. M.G.U. Islam, M.T. Jan, M. Farooq, A. Naeem, I.W. Khan, H.U. Khattak, Biodiesel production from wild olive oil using TPA-decorated Cr–Al acid heterogeneous catalyst, Chemical Engineering Research and Design 178 (2022) 540. Doi: 10.1016/j.cherd.2021.12.040
- [22]. H. Esmaeili, A critical review on the economic aspects and life cycle assessment of biodiesel production using heterogeneous nanocatalysts, Fuel Processing Technology 230 (2022) 107224. Doi: 10.1016/j.fuproc.2022.107224
- [23]. S. Elgharbawy, A.I. Osman, A.G.M. El Demerdash, W.A. Sadik, M.A. Kasaby, S.E. Ali, Enhancing biodiesel production efficiency with industrial waste-derived catalysts: Technoeconomic analysis of microwave and ultrasonic transesterification methods, Energy Conversion and Management 321 (2024) 118945. Doi: 10.1016/J.ENCONMAN.2024.118945
- [24]. Y. Zhang, R. Lackner, M. Zeiml, H.A. Mang, Strong discontinuity embedded approach with standard SOS formulation: Element formulation, energy-based crack-tracking strategy, and validations, Computer Methods in Applied Mechanics and Engineering 287 (2015) 335. Doi: 10.1016/j.cma.2015.02.001
- [25]. M.G. De Paola, I. Mazza, R. Paletta, C.G. Lopresto, V. Calabrò, Small-scale biodiesel production plants-An overview, Energies 14 (2021) 1901. Doi: 10.3390/en14071901
- [26]. P. Arunyanart, L. Simasatitkul, P. Juyploy, P. Kotluklan, J. Chanbumrung, S. Seeyangnok, The prediction of biodiesel production yield from transesterification of vegetable oils with machine learning, Results in Engineering 24 (2024) 103236. Doi: 10.1016/J.RINENG.2024.103236
- [27]. ? Divyachandrika, J. Hemanandh, P. Barmavatu, B. Ganesh, Enhancing Jatropha oil biodiesel by using *Citrus limetta* peels as a biocatalyst: A sustainable way to reduce emissions and enhance the efficiency of CI engine, International Journal of Thermofluids 24 (2024) 100989. Doi: 10.1016/J.IJFT.2024.100989
- [28]. S.M. Farouk, A.M. Tayeb, S.M.S. Abdel-Hamid, Osman, R.M. Recent advances in transesterification for sustainable biodiesel production, challenges, and prospects: Α comprehensive review, Environmental Science and Pollution Research International 31 (2024) 12722. Doi: 10.1007/s11356-024-32027-4
- [29]. M.R. Avhad, J.M. Marchetti, A review on recent advancement in catalytic materials for biodiesel production, Renewable & Sustainable Energy Reviews 50 (2015) 696. Doi: 10.1016/j.rser.2015.05.038
- [30]. B. Wang, S.K. Shukla, R. Wang, Enabling catalysts for biodiesel production via transesterification, Catalysts 13 (2023) 740. Doi: 10.3390/catal13040740
- [31]. H.A. Jan, A.I. Osman, I. Šurina, J. Saleh, R. Kumar, A.S. Al-Fatesh, Recycling calcium oxide

nanoparticles for sustainable biodiesel production from nonedible feedstock *Argemone Mexicana* L., Biofuels 15 (2024) 645. Doi: 10.1080/17597269.2023.2277989

- [32]. N. Supamathanon, K. Boonserm, S. Lisnund, N. Chanlek, B. Rungtaweevoranit, P. Khemthong, J. Wittayakun, N. Osakoo, Development of CaO supported on modified geopolymer catalyst for transesterification of soybean oil to biodiesel, Materials Today Communications 29 (2021) 102822. Doi: 10.1016/j.mtcomm.2021.102822
- [33]. O.A. Mawlid, H.H. Abdelhady, M.G. Abd El-Moghny, A. Hamada, F. Abdelnaby, M. Kased, S. Al-Bajouri, R.A. Elbohy, M.S. El-Deab, Clean approach for catalytic biodiesel production from waste frying oil utilizing K₂CO₃/orange peel derived hydrochar via RSM optimization, Journal of Cleaner Production 442 (2024) 140947. Doi: 10.1016/j.jclepro.2024.140947
- [34]. S.M.M. Hasnain, R.P. Sharma, R. Chatterjee, G. Kumar, S. Pandey, M.M. Khan, A.F. Deifalla, A. Zare, Investigation and impact assessment of soybean biodiesel, methyl oleate, and diesel blends on CRDI performance and emissions, Materials Science for Energy Technologies 7 (2024) 124. Doi: 10.1016/j.mset.2023.09.002
- [35]. B. Oladipo, S. Qasana, S.C. Zini, N. Menemene, T.V. Ojumu, Microwave-assisted biodiesel synthesis from waste cooking oil: Exploring the potential of carob pod-derived solid base catalyst, Fuel Processing Technology 266 (2024) 108161. Doi: 10.1016/J.FUPROC.2024.108161
- [36]. Q.H. Hassan, N.S. Mohammed Ali, H.A. Alalwan, A.H. Alminshid, M.M. Mohammed, The impact of adding nanoparticles to biodiesel fuel prepared from waste sunflower oil on the performance and emission of diesel engines, Circular Economy 4 (2025) 100138. Doi: 10.1016/J.CEC.2025.100138
- [37]. I. Tariq, M. Zubair, W. Iqbal, A. Badshah, S.M. Abbas, A. Haider, Alkaline earth metal oxides supported on WO₃@MCM-41 bifunctional catalysts for biodiesel production from corn and waste cooking oil, Hybrid Advances 10 (2025) 100477. Doi: 10.1016/J.HYBADV.2025.100477
- [38]. N. Hasan, M.V. Ratnam, Biodiesel production from waste animal fat by transesterification using H₂SO₄ and KOH catalysts: A study of physicochemical properties, International Journal of Chemical Engineering (2022) 6932320. Doi: 10.1155/2022/6932320
- [39]. N. Sangaletti-Gerhard, M. Cea, V. Risco, R. Navia, In situ biodiesel production from greasy sewage sludge using acid and enzymatic catalysts, Bioresource Technology 179 (2015) 63. Doi: 10.1016/j.biortech.2014.12.003
- [40]. X. Wu, F. Zhu, J. Qi, L. Zhao, Biodiesel production from sewage sludge by using alkali catalyst, Procedia Environmental Sciences 31 (2016) 26. Doi: 10.1016/j.proenv.2016.02.004
- [41]. G.A. Ngige, P.E. Ovuoraye, C.A. Igwegbe, E. Fetahi, J.A. Okeke, A.D. Yakubu, P.C. Onyechi, RSM optimization and yield prediction for biodiesel produced from alkali-catalytic

transesterification of pawpaw seed extract: Thermodynamics, kinetics, and multiple linear regression analysis, Digital Chemical Engineering 6 (2023) 100066. Doi: 10.1016/ j.dche.2022.100066

- [42]. W. Bajwa, A. Ikram, M.A.I. Malik, L. Razzaq, A.R. Khan, A. Latif, F. Hussain, A. Qazi, Optimization of biodiesel yield from waste cooking oil and sesame oil using RSM and ANN techniques, Heliyon 10 (2024) e34804. Doi: 10.1016/J.HELIYON.2024.E34804
- [43]. P. Rivera-Quintero, G. S. Patience, N. A. Patience, D. C. Boffito, X. Banquy, D. Schieppati, Experimental methods in chemical engineering: Karl Fischer titration, The Canadian Journal of Chemical Engineering 102 (2024) 2980-2997. Doi: 10.1002/cjce.25295
- [44]. ASTM D445-06, Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity), Manual on Hydrocarbon Analysis, 6th Edition (2018)
- [45]. ISO 3016:2019 Petroleum and related products from natural or synthetic sources — Determination of pour point, International Organization for Standardization, 3rd Edition (2019)
- [46]. ISO 3015:2019 Petroleum and related products from natural or synthetic sources — Determination of cloud point, International Organization for Standardization, 3rd Edition (2019)
- [47]. EN 116:2016 Diesel and domestic heating fuels Determination of cold filter plugging point Stepwise cooling bath method, (2016)
- [48]. ISO 2592:2017 Petroleum and related products Determination of flash and fire points — Cleveland open cup method, International Organization for Standardization, 3rd Edition (2017)
- [49]. ASTM D6751-15c, Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels, ASTM International (2010)
- [50]. J.A. Melero, G. Vicente, G. Morales, M. Paniagua, J. Bustamante, Oxygenated compounds derived from glycerol for biodiesel formulation: Influence on EN 14214 quality parameters, Fuel 89 (2010) 2011–2018. Doi: 10.1016/j.fuel.2010.03.042
- [51]. Y. Wang, X. Liang, Y. Wang, H. Yu, Effects of viscosity index improver on morphology and graphitization degree of diesel particulate matter, Energy Procedia 105 (2017) 4236. Doi: 10.1016/j.egypro.2017.03.910
- [52]. F. Ma, L.D. Clements, M.A. Hanna, The effects of catalyst, free fatty acids, and water on transesterification of beef tallow, Transactions of the American Society of Agricultural Engineers 41 (1998) 1261. Doi: 10.13031/2013.17292
- [53]. J. K. Efavi, D. Kanbogtah, V. Apalangya, E. Nyankson, E.K. Tiburu, D. Dodoo-Arhin, B. Onwona-Agyeman, A. Yaya, The effect of NaOH catalyst concentration and extraction time on the yield and properties of *Citrullus vulgaris* seed oil as a potential biodiesel feedstock, South African

Journal of Chemical Engineering 25 (2018) 98. Doi: 10.1016/j.sajce.2018.03.002

- [54]. B. Freedman, E.H. Pryde, T.L. Mounts, Variables affecting the yields of fatty esters from transesterified vegetable oils, Journal of the American Oil Chemists' Society 61 (1984) 1638. Doi: 10.1007/BF02541649
- [55]. M.F. Elkady, A. Zaatout, O. Balbaa, Production of biodiesel from waste vegetable oil via KM micromixer, Journal of Chemistry (2015) 630168. Doi: 10.1155/2015/630168
- [56]. I. Simbi, U.O. Aigbe, O. Oyekola, O.A. Osibote, Optimization of biodiesel produced from waste sunflower cooking oil over bi-functional catalyst, Results in Engineering 13 (2022) 100374. Doi: 10.1016/j.rineng.2022.100374
- [57]. S. Jain, M.P. Sharma, Thermal stability of biodiesel and its blends: A review, Renewable & Sustainable Energy Reviews 15 (2011) 438. Doi: 10.1016/j.rser.2010.08.022
- [58]. R. Naureen, M. Tariq, I. Yusoff, A.J.K. Chowdhury, M.A. Ashraf, Synthesis, spectroscopic and chromatographic studies of sunflower oil biodiesel using optimized base catalyzed methanolysis, Saudi Journal of Biological Sciences 22 (2014) 332. Doi: 10.1016/j.sjbs.2014.11.017
- [59]. M.A. Zahed, M. Revayati, N. Shahcheraghi, F. Maghsoudi, Y. Tabari, Modeling and optimization of biodiesel synthesis using TiO₂–ZnO nanocatalyst and characteristics of biodiesel made from waste sunflower oil, Current Research in Green and Sustainable Chemistry 4 (2021) 100223. Doi: 10.1016/j.crgsc.2021.100223
- [60]. M. M. Roy, W. Wang, J. Bujold, Biodiesel production and comparison of emissions of a diesel engine fueled by biodiesel-diesel and canola oildiesel blends at high idling operations, Applied Energy 106 (2013) 198. Doi: 10.1016/j.apenergy.2013.01.057
- [61]. J. Yang, C. Caldwell, K. Corscadden, Q.S. He, J. Li, An evaluation of biodiesel production from *Camelina sativa* grown in Nova Scotia, Industrial Crops and Products 81 (2016) 162. Doi: 10.1016/j.indcrop.2015.11.073
- [62]. A. Mukhtar, S. Saqib, H. Lin, M.U. Hassan Shah, S. Ullah, M. Younas, S. Rezakazemi, M. Ibrahim, A. Mahmood, S. Asif, A. Bokhari, Current status and challenges in the heterogeneous catalysis for biodiesel production, Renewable & Sustainable Energy Reviews 157 (2022) 112012. Doi: 10.1016/j.rser.2021.112012

- [63]. B. Thangaraj, P.R. Solomon, B. Muniyandi, S. Ranganathan, L. Lin, Catalysis in biodiesel production – A review, Clean Energy 2 (2019) 2. Doi: 10.1093/ce/zky020
- [64]. D. Avila Orozco, N. Kovachev, M.Á. Aguirre Pastor, C.E. Domini, B.S. Fernández Band, A.C. Hernández, Analysis of metals and phosphorus in biodiesel B100 from different feedstock using a Flow Blurring® multinebulizer in inductively coupled plasma–optical emission spectrometry, Analytica Chimica Acta 827 (2014) 15–24. Doi: 10.1016/j.aca.2014.04.016
- [65]. B.M.S. Hossain, A.N. Boyce, Biodiesel production from waste sunflower cooking oil as an environmental recycling process and renewable energy, Bulgarian Journal of Agricultural Science 15 (2009) 312.
- [66]. A. Saydut, A.B. Kafadar, Y. Tonbul, C. Kaya, F. Aydin, C. Hamamci, Comparison of the biodiesel quality produced from refined sunflower (*Helianthus annuus* L.) oil and waste cooking oil, Energy Exploration & Exploitation 28 (2010) 499. Doi: 10.1260/0144-5987.28.6.499
- [67]. K. Ayetor, A. Sunnu, J. Parbey, Effect of biodiesel production parameters on viscosity and yield of methyl esters: Jatropha curcas, *Elaeis guineensis* and *Cocos nucifera*, Alexandria Engineering Journal 54 (2015) 1285. Doi: 10.1016/j.aej.2015.09.011
- [68]. W.N.A. Wan Osman, J. Khoo Lee Min, S. Samsuri, Exploring the thermal properties of biodiesel after purification via solvent-aided crystallization, Results in Engineering 22 (2024) 102343. Doi: 10.1016/J.RINENG.2024.102343
- [69]. U. Bello, N.A. Amran, M.S. Hazwan Ruslan, E.H. Yáñez, U. Suparmaniam, H. Adamu, S.I. Abba, U.I. Tafida, A.A. Mahmoud, Enhancing oxidative stability of biodiesel using fruit peel waste extracts blend: Comparison of predictive modelling via RSM and ANN techniques, Results in Engineering 21 (2024) 101853. Doi: 10.1016/j.rineng.2024.101853
- [70]. H. Ishida, A. Iwama, Some critical discussions on flash and fire points of liquid fuels, Fire Safety Science 1 (1986) 217. Doi: 10.3801/iafss.fss.1-217
- [71]. M.H. Al-Abdullah, G.T. Kalghatgi, H. Babiker, Flash points and volatility characteristics of gasoline/diesel blends, Fuel 153 (2015) 67. Doi: 10.1016/j.fuel.2015.02.070

Received: 30.05.2025 Received in revised form: 20.06.2025 Accepted: 24.06.2025