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ORIGINAL ARTICLE

Determination of optimum parameters for esterification in high free fatty acid olive oil and ultrasound-assisted biodiesel production

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Abstract

In this study, biodiesel was produced from high free fatty acid (FFA) oil obtained from waste olives, whose food quality deteriorated by falling from the tree to the ground. The FFA value of the oil obtained from waste olives was determined as 23% by titration method. In order to produce biodiesel with high conversion efficiency, esterification process was carried out to reach at least 1% FFA value in the first stage of the study. Acid esterification experiments were designed according to Taguchi's L_{16} (4^2 2^1) orthogonal array. The amount of sulfuric acid catalyst, methanol ratio, and mixing speed were taken as the test variables for the esterification process. For the lowest FFA value, optimum test parameters were determined using the signal-to-noise (S/N) ratio. In the biodiesel production stage, ultrasound-assisted transesterification method was preferred in terms of high conversion efficiency and short reaction duration. According to the results, it was determined that the optimum reaction conditions in the esterification process were 25% by weight acid catalyst (according to the weight of the FFA in the oil), 22:1 methanol molar ratio in terms of fatty acids, and 400 rpm mixing speed. At these reaction conditions, the FFA of the oil was reduced from 23 to 0.608% in a single step. In the ultrasound-assisted process, Waste olive oil methyl ester (WOOME) conversion yield of 98.7% was achieved in a reaction time of 10 min. The fuel properties of WOOME (also called biodiesel) were determined to be within the EN 14214 standard. As a result, optimization was made to minimize the use of alcohol and catalyst in the acid esterification process. Also, time and energy savings were achieved in biodiesel production with ultrasound-assisted.

Keywords Acid esterification · Free fatty acid · Biodiesel production · Ultrasound-assisted · Taguchi

1 Introduction

Today, energy has become indispensable for the continuation of life rather than just a necessity. Factors such as the increase in the world population and the energy need of equipment that is a part of our daily life causes to an ever-increasing demand for energy. Available energy sources are insufficient to meet this increasing demand. In addition to the current need, excessive and unconscious energy consumption accelerates the increase in energy demand. Countries that want to find a solution to this situation have developed different policies over the years. First, policies were developed for the efficient use of energy. Later, it was aimed to meet the energy demand with new energy sources, and incentive policies for this purpose were started to be developed. Therefore, interest in alternative energy sources has increased all over the world. Nowadays, biomass and wastes are used as a new energy source. In this context, the use of

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biodiesel as an alternative energy in compression ignition (CI) engines is investigated.

As stated in the EASAC 2012 report, biodiesel is generally classified as first, second, third, and fourth generation according to the type of raw material from which it is produced [1–3]. While the first-generation biodiesel is obtained from edible foods, the second-generation biodiesel is produced from non-edible feedstock [4, 5]. Biodiesels obtained from microalgae and waste oils are called the third generation [6]. Finally, photobiological solar fuels and electro fuels are named as fourth generation [7]. One of the important issues in biofuel production is the possibility that the raw material used in production will cause food problems in the world. If large-scale energy agricultural production is done, it may lead to scarcity of human food resources [8–12]. Therefore, the production of 3rd generation biodiesel is important in terms of both contributing to energy needs and not causing a problem in the life cycle.

In the production of some edible oils, reasons such as the product quality of the raw material and the production method may increase the free fatty acid (FFA) value of the oil. Excessively high FFA has a negative effect on human health. The use of waste olives in olive oil production, which is one of these, increases the FFA value of the oil. It is expressed as waste olive to the olive fruit, which naturally falls to the soil and loses its edible properties. There are many factors that determine the quality of olive oil. One of the most important of these is FFA [13, 14]. The FFA values increase with the ripening of the olive fruit. In the production of biodiesel in our study, the oil obtained from this waste olive was preferred. The FFA value of this olive oil, which we use in biodiesel production, was determined to be 23.34% by titration method. This value is much above the FFA value of edible olive oil. Such oils are generally used in soap making [15]. Oils with high FFAs can be used after esterification. This is a chemical process and is esterified using an alkali or acid catalyst [16]. One of the ways to recover FFA is to esterify the oil with an acid catalyst such as sulfuric acid [17]. An increase in FFA values causes an increase in the amount of chemicals used for esterification. It is thought that the use of oils produced with excessive chemicals for cooking is not very healthy. For this reason, it would be more appropriate to choose such oils for the production of biodiesel, which is an alternative fuel.

The FFA values of the oil must be suitable for the production of biodiesel [18]. In the conventional transesterification process using alkaline catalysts for biodiesel production, the presence of FFA always creates adverse effects because of soap formation. It depletes the catalyst and reduces its catalytic activity. This situation causes a decrease in the conversion efficiency of biodiesel [19]. Researchers suggest that the FFA value of the raw material to be produced should be below 1% in order to use base catalysts in biodiesel production [20, 21]. There are many studies in the literature for this esterification process called pre-treatment. Some of the esterification methods used to reduce the high FFA values are summarized in Table 1.

As seen in Table 1, sulfuric acid is generally preferred in the esterification process of fats with high FFAs. The amount of sulfuric acid to be used depends on the FFA of the oils

Table 1 Summary of some esterification studies in the literature

Feedstocks	FFA (%)	Catalyst type	Amount of catalyst (wt.%)	Methanol ratio (molar)	FFA after esterification (%)	Ref
Neem oil	20.3	Sulfuric acid	4.5	6:1	3.6	[22]
Silybum marianum L. seed oil	10	Sulfuric acid	6	15:1	0.68	[23]
Waste cooking oil	7.5	Glycerolysis			< 1	[24]
Waste cooking oil	11.97	Glycerolysis			< 1	[24]
Fat, oil, and grease (FOG)	> 36	Sulfuric acid	4.23	11.8:1	0.28	[25]
Fat, oil, and grease (FOG)	> 27	Sulfuric acid	3.35	15.3:1	0.61	[25]
Fat, oil, and grease (FOG)	> 92	Sulfuric acid	3.68	9.9:1	0.69	[25]
Animal waste fats	9.3	Sulfuric acid	2	6:1	1.86	[26]
Sludge palm oil	24.4	Sulfuric acid	10.54	17:1	< 1	[27]
Yellow grease	5	Sulfuric acid	10	40:1	< 1	[28]
Brown grease	> 50	Aluminum chloride hexahydrate	2	10:1	< 5	[29]
Waste lipid feedstock	84.5	Sulfuric acid	10	30:1	< 5.5	[30]
Waste cooking oil	18.35	Sulfuric acid	3.5	52:1	< 1	[31]
		Heterogeneously catalyze cement-kilndust (CKD)	2	18:1	< 1	
Sludge palm oil	52.17	The mixture solution of lipase	5	3:1	< 2	[32]
Waste cooking oil	17.2	SrO–ZnO/Al_2O_3	5	10:1	< 1	[33]

and the distribution of fatty acids. In addition, it is seen that heterogeneous catalysts are used in the esterification process. The amounts of acid catalyst expressed in Table 1 are the percentage used according to the weight of the raw oil.

Three methods are used in the conversion of vegetable and animal oils to biodiesel. These are thermal cracking (pyrolysis), microemulsification, and transesterification reaction. Transesterification reaction is the chemical reaction of oil with an alcohol so that the ester and glycerol in the triglycerides can be easily separated. In the transesterification reaction, one ester changes into another ester [4]. Transesterification is the esterification reaction of fatty acids with alcohol in the presence of a basic catalyst. The fatty acids formed by the hydrolysis of the triglycerides in the oil by the transesterification process react with the alcohol, thus forming a fatty acid ester mixture (biodiesel) and glycerine [34]. In the transesterification method, the chemical reaction can be carried out in three different ways: conventional, microwave, and ultrasound. Table 2 shows the advantages and disadvantages of these three methods.

As seen in Table 2, ultrasound- and microwave-assisted transesterification has many advantages. Because of these advantages, the ultrasound-assisted transesterification method was chosen for this laboratory-scale study. Especially low energy consumption and short reaction time are the reasons why this method is preferred by researchers.

There are very limited studies in the literature on biodiesel production from olive oil [35, 56–64]. One of the main reasons for this situation is the high cost of olive oil. In this study, it is aimed to produce biodiesel from the oil obtained from olives, which is called waste and does not have food quality, and bring it to the economy. Because Turkey has an important place in the world of olives and olive oil production it is important to evaluate these wastes olives. According to the data of the Turkish Statistical Institute, the total amount of olives harvested in 2020 was 1,316,626 t [65]. In addition, in a report prepared for olives and olive oil, it is stated that the number of olive trees bearing fruit in Turkey for 2020 is 153,168,156 [66]. It is known that under normal climatic conditions, approximately 1 kg of olives falls naturally to the ground for each tree. The amount of these olives falling to the ground may increase further with factors such as worsening climatic conditions and late harvest. According to these data, approximately 10–12% of the total amount of olives in the trees falls to the soil by natural means and turns into waste olives. The raw material used in this study was obtained from such inedible olives.

A large number of experiments are required to determine the optimum experimental conditions in the esterification process. However, this will cause a lot of workload, time, and cost loss. Therefore, optimization is required to reduce the number of experiments and achieve the most efficient results. Most researchers use optimization methods to determine the optimum conditions for the production of biodiesel and the use of the fuel in the engine [67–73].

When the literature is examined, it is seen that there are many esterification studies used to reduce FFA value. This study consists of two stages. In the first step, method optimization was performed by using Taquchi experiment design to decrease the value of high FFA olive oil by esterification. In the second stage, biodiesel was obtained by ultrasound-assisted transesterification. The novelty of this study is the conversion of oil with high FFA obtained from waste olive fruit into an alternative fuel. Moreover, it is the determination of optimum parameters in the use of sulfuric acid, which is the most widely used in esterification. With the optimization made, it is aimed to avoid the use of more chemicals than necessary. The results show that the waste olive will be transformed into a useful product with high economic value.

2 Materials and methods

The flow chart of the method followed in this study is given in Fig. 1. Experimental study was carried out in two stages. In the first stage, the optimum parameters were determined in order to reduce the acid value to approximately 1% by the acid esterification method of olive oil,

Table 2 Advantages and disadvantages of different methods used in transesterification

Transesterification methods	Advantages	Disadvantages	Ref
Ultrasound-assisted	High conversion efficiency Low reaction time Low energy consumption Low Catalyst consumption High reaction rate	İt is industrially costly and complex High sound level	[35–46]
Microwave-assisted	Environmental method Shortens the extraction time Low reaction time High reaction rate	It is not suitable for large-scale production Expensive	[47–54]
Conventional-assisted	Cheap Large-scale production can be made	Long reaction time High energy consumption	[11, 18, 44, 53, 55]

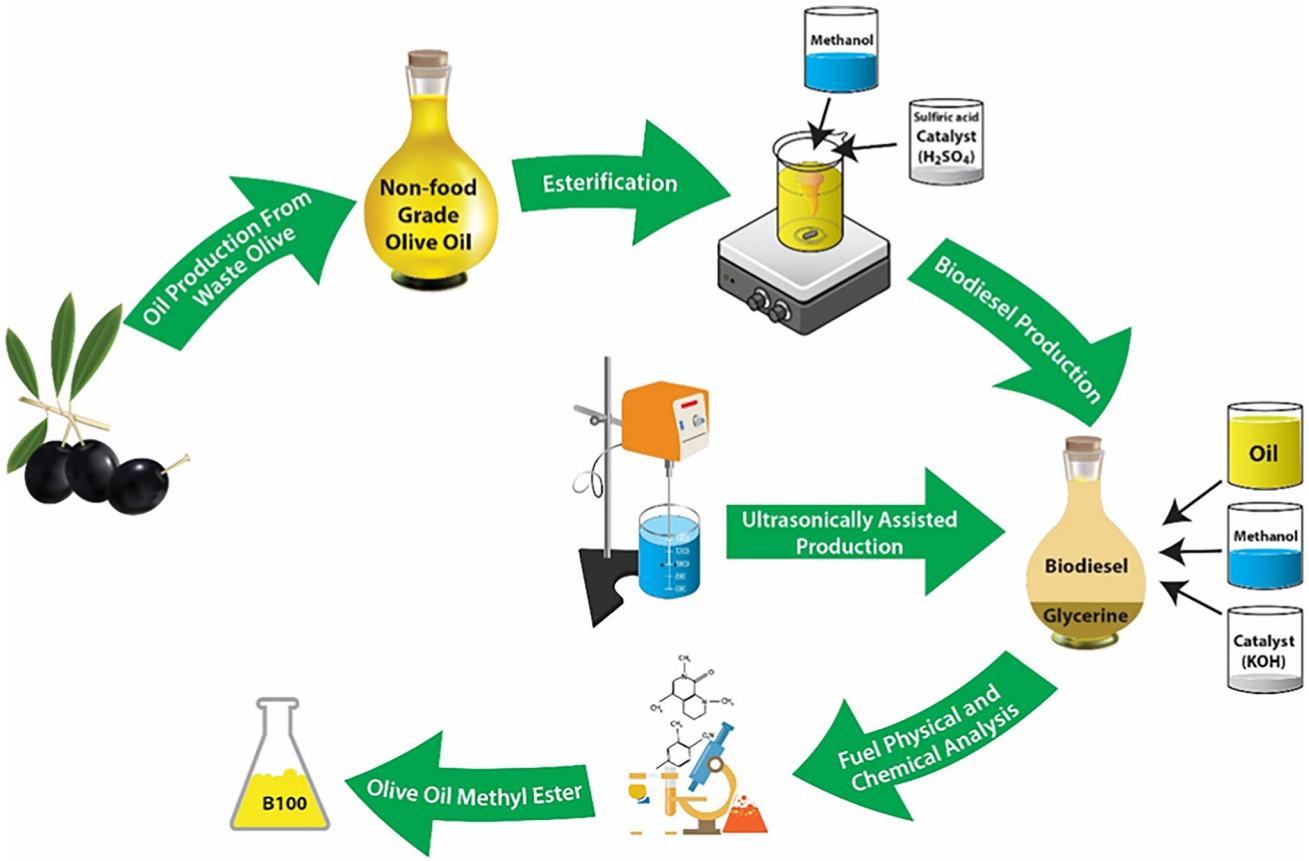

Fig. 1 The flow chart of biodiesel production from waste olives

which has high FFA. Taguchi experimental design method was used to determine the optimum parameters in acid esterification. In the second stage, biodiesel was produced by ultrasound-assisted transesterification, and some fuel properties of it were determined.

2.1 Raw material

Olive oil obtained from olives that fell to the ground naturally was used as raw material. Before any process, the olive oil was filtered and cleared of foreign substances. It was then preheated at 110 °C for half an hour to remove moisture. The acid value is a measure of the amount of FFA of the oil. It is defined as the mg of potassium hydroxide required to neutralize the fatty acids in 1 g of sample [72]. The acid value of the oil was determined by titrimetric [74, 75]. Ideally, the acid value of the oil in biodiesel production should be less than 2 mg KOH/g (roughly 1% FFA).

To ensure that the results obtained were correct, titrations were performed in triplicate. From here, both acid value (AV) and FFA content (%) can be calculated as given in Eqs. (1) and (2):

$$AV(\mathrm{mgKOH/g}) = \frac{5.64 \bullet V}{m} \tag{1}$$

$$FFA(\%) = \frac{2.82 \bullet V}{m} \tag{2}$$

where V is the volume of 0.1 molar KOH solution (ml) causing the color change, and m is the mass of the oil sample taken.

In the test, after dissolving 5 g oil sample at 1:1 v/v ethanol-diethyl ether mixture, it was titrated with 0.1 N ethanolic KOH solution under phenolphthalein indicator. In this process, the amount of KOH solutions that turns the mixture into a permanent pink color was determined. Then, by writing the following equations, FFA and acid value (AV) in terms of oleic acid were calculated as 23% and 46 mg KOH/g.

For the acid esterification, methanol (purity of > 99.0%, Merck), and sulfuric acid (purity of > 99.0%, Merck) were

used. In the transesterification process, methanol and potassium hydroxide (KOH) were used.

2.2 Acid esterification experiments using Taguchi method

If the FFA value of the oil to be used in biodiesel conversion is high, it must first be subjected to esterification (pretreatment) process in order to prevent saponification. Many factors such as acid catalyst amount, alcohol ratio, temperature, and mixing speed are effective in acid esterification.

Taguchi is a statistical method developed by Genichi Taguchi to investigate the effect of different parameters on determining the appropriate working conditions of the process [76]. The Taguchi method, which makes statistical design using orthogonal array, also offers an opportunity to reduce the number of experiments [77, 78]. In this paper, Taguchi's L_{16} ($4^2\ 2^1$) orthogonal array is designed according to different acid catalyst amount (A), methanol ratios (B), and mixing speeds (C). The variables in the experimental design and their levels are given in Table 3.

To reduce FFA, different ratios of methanol and sulfuric acid were added to 50 g oil sample preheated at 50 °C. The resulting mixture was stirred at 300 and 400 rpm for 60 min. At the end of 60 min, the oil sample was taken to a separating funnel and kept for one day. In this study, the amount of acid catalysts and methanol was determined according to the FFA value of the oil as follows.

The molecular weight of the oil was calculated as about 280 g/mol (M_{oil}). The amount of FFA in the oil (m_{FFA}) is calculated by Eq. (3).

$$m_{FFA}(\mathrm{g}) = m(\mathrm{g}) \bullet FFA(\%) \tag{3}$$

For example, if 50 g (m) of oil is taken for an oil with an FFA value of 23%,

$$m_{FFA} = 50\mathrm{g} \bullet 0.23 = 11.5\mathrm{g}$$

The mole amount of FFA (M_{FFA}) in the oil can be calculated by Eqs. (4).

$$M_{FFA} = \frac{m_{FFA}(\mathrm{g})}{M_{oil}(\mathrm{g/mol})} \tag{4}$$

Table 3 The experiment variables and their levels

Factors code	Description	Levels			
		1	2	3	4
A	Amount of acid catalyst (w% of FFA)	20	25	30	35
B	Methanol ratio (molar)	16:1	18:1	20:1	22:1
C	Mixing speed (rpm)	300	400		

If we calculate according to the formula;

$$M_{FFA} = \frac{11.5g}{280\mathrm{g/mol}} = 0.04107\mathrm{mol}$$

For example, the amount to be used for 20% by weight acid catalyst (m_{acid}) in the experiments;

$$m_{acid}(\mathrm{g}) = m_{FFA} \bullet 0.20(\%20) = 11.5\mathrm{g} \bullet 0.20 = 2.3\mathrm{g} acidcatalyst(\text{for } 20\%)$$

The amount of methanol ($m_{methanol}$) to be used for the 20:1 molar ratio of methanol in the experiments (in Eq. (5));

$$m_{methanol} = M_{FFA} \bullet molarratioofmethanol \bullet molarweightofmethanol \tag{5}$$

Amount of methanol for 20:1 molar ratio of methanol

$$m_{methanol} = 0.04107\mathrm{mol} \bullet (20 : 1) \bullet 32.04\frac{\mathrm{g}}{\mathrm{mol}} = 26.3g$$

is calculated. Similar procedures were carried out for a total of 16 experiments to be carried out according to Taguchi's experimental design. After acid esterification, the oil was washed 2–3 times with distilled water to remove residual acid catalyst and alcohol. Also, the product was centrifuged at 5000 rpm for 10 min to ensure purity.

2.3 Optimization of acid esterification parameters

In this study, the optimization was made for the lowest FFA value of the sample obtained as a result of the experiment. Taguchi technique computes a signal-to-noise (S/N) ratio based on experimental data. This ratio defines an experiment level which gives the best performance in the reaction variables [77, 79].

S/N ratios express the logarithmic functions of the expected experimental result to provide a sound optimization [76]. There are three types of S/N ratios used in the Taguchi method and these are nominal-best, smaller-better, and larger-better [79]. In this study, the smaller-better theorem was used to evaluate the lowest FFA for S/N ratios (from Eq. (6)).

$$S/N\ ratio = -10 \bullet log\frac{1}{n}\left(\sum_{i=1}^{n} y_i^2\right) \tag{6}$$

where *S/N ratio* is signal-to-nose ratio (dB), y_i symbolizes the quality characteristic's value obtained from the tests, and "n" is the test number [80].

2.4 Determination of fatty acids

Fatty acid contents were determined in gas chromatography device (Thermo Scientific Trace 1310). In order to make the oil samples suitable for analysis, fatty acids were converted

into methyl esters and derivatization was made. For this, 0.25 g of the extracted oil was dissolved by adding 4 ml of heptane and 0.4 ml of 2 N KOH solution was added. This mixture was vortexed for 2 min, then centrifuged at 5000 rpm for 5 min. After centrifugation, 1.5–2 ml of heptane phase formed was transferred to glass tubes for GC/MS analysis. The samples were analyzed by Thermo Scientific ISQ LT model GC/MS gas chromatography mass spectrometry. For this analysis, Trace Gold TG-WaxMS capillary column (Thermo Scientific code: 26,088–1540) with a length of 60 m, 0.25-µm inner diameter, and 0.25-µm film thickness was used. The injection block temperature was adjusted to 240 °C and the column temperature program to increase from 100 to 240 °C. Constant flow helium gas (1 ml/min) was used as the carrier gas and a split ratio of 1:20 was applied. MS unit (ISQ LT) was used in electron ionization mode. Fatty acids were identified by comparing the standard FAME mixture of 37 components based on their arrival times.

2.5 Biodiesel production with ultrasound-assisted transesterification

Biodiesel production started with the FFA of the oil produced from non-food grade olives falling below 1%. Conventional, microwave and ultrasound-assisted methods can be used in the production of biodiesel by transesterification method. In this study, ultrasound-assisted transesterification method was preferred in biodiesel production. The FFA reduced waste olive oil will be converted to oil methyl ester in the presence of basic catalyst. The obtained biodiesel was expressed as methyl ester of waste olive oil (WOOME) in this study. In this process, methanol was preferred as alcohol and KOH (potassium hydroxide) as catalyst.

When the studies in the literature are examined, it was determined that 20% methanol and 1% KOH by weight were generally used in the transesterification process. Therefore, in this study, these values were used in the production of WOOME. Transesterification reaction was carried out with Bandelin Sonopulse HD 2200 sonicator homogenizer (Bandelin, Berlin, Germany), see in Fig. 2. Maximum power output of the device is 200 W at 20 kHz frequency. The device has a 13-mm diameter titanium flat tip probe.

The amounts of KOH and methanol to be used for a 1-l oil sample were determined. Firstly, KOH was placed in methanol and mixed for 1 min with a magnetic stirrer to obtain a homogeneous mixture. This methoxide mixture obtained was added to the oil sample. The reaction was started at the ambient temperature by adjusting the sonicator amplitude of 75% and the duty cycle of 70% of the ultrasonic homogenizer. Each experiment was performed under these settings with a reaction time of 10 min. It was observed that the reaction temperature changed in the range of 45–60 ℃ at the end of the 10-min

Fig. 2 Ultrasonic homogenizer

reaction time. The duty cycle refers to the pulse repetition in one second. The duty cycle is calculated by Eq. (7) [81]. Seventy percent duty cycle means that the device makes 0.7-s pulses in 1-s operation, while it stays off for the remaining 0.3 s.

$$Dutycycle(\%) = \frac{t_{ON}}{t_{ON} + t_{OFF}} x100 \quad (7)$$

where t_{ON} is the pulse duration (seconds) and t_{OFF} is the pulse interval (seconds). The number of pulse repetitions ($t_{ON}+t_{OFF}$) corresponds to the number of cycles during the extraction time.

After the WOOME production, the sample taken into the separating funnels was separated from the glycerine after being kept for one day. In the next step, the fuel was washed three times with distilled water. In order to separate the water from the resulting mixture, the mixture was taken back to the separating funnel and left for another 24 h. After 24 h, the water that settled to the bottom in the separating funnel was separated from the mixture. In order not to suffer the negative effects of water in the fuel, it was heated at 110 °C for 60 min and the water in it was dried. The biodiesel conversion efficiency was calculated with the following formula (Eq. (8)) [82].

$$Conversionyield(\%) = \frac{Weightofmethylester(g)}{Weightofcrudeoilused(g)} \times 100 \quad (8)$$

The conversion efficiency of biodiesel obtained at the end of all processes was calculated as 98.7%.

3 Results and discussion

3.1 Results of optimization

The experimental design determined by Taguchi's L_{16} orthogonal array and the FFA values obtained from these experiments are given in Table 4. When Table 4 is examined, it is seen that the lowest FFA value is 0.564. It was determined that this value was obtained in experimental conditions where the sulfuric acid catalyst was 20% by weight (A1), the methanol ratio was 22:1 molar ratio (B4), and the mixing speed were 400 rpm (C2). However, it is necessary to look at the S/N ratios in order to determine the variables that give the optimum result for FFA.

Table 4 Taguchi's L16 orthogonal design and experimental results

Test no	Number of levels			FFA (%)	Uncertainty
	A (amount of acid catalyst)	B (methanol ratios)	C (mixing speeds)		
1	1	1	1	2.171	±0.081
2	1	2	1	1.764	±0.068
3	1	3	2	1.416	±0.071
4	1 (20%)	4 (22:1)	2 (400 rpm)	0.564	±0.022
5	2	1	1	1.442	±0.059
6	2	2	1	1.123	±0.043
7	2	3	2	0.987	±0.037
8	2	4	2	0.620	±0.028
9	3	1	2	1.345	±0.065
10	3	2	2	1.128	±0.054
11	3	3	1	1.026	±0.046
12	3	4	1	0.976	±0.034
13	4	1	2	1.412	±0.061
14	4	2	2	1.184	±0.046
15	4	3	1	1.059	±0.039
16	4	4	1	1.015	±0.041

The effect of experimental variables on FFA was given in Fig. 3. When the graph was examined, it is seen that while the FFA value decreased until the presence of 25% acid catalyst in the reaction, it increased again after this value. It was determined that the most effective amount of acid catalyst (sulfuric acid) in terms of FFA was 25% (A2) by weight of fatty acid. It was seen that the most important factor in reducing FFA in the acid esterification process was the methanol ratio. It was found that the molar ratio of methanol has a continuous reducing effect on FFA. Similarly, it was observed that high mixing speed had a positive effect on the esterification process.

In S/N ratio graphics, the highest S/N ratio gives the optimum levels for operating parameters [78]. In Fig. 4, the S/N ratios of the experimental variables are given. Optimal levels obtained from S/N ratios are marked on the graphics into a red box. The ratios with the highest S/N ratio indicate optimum values that contribute to obtain the lowest FFA in the acid esterification process.

When Fig. 4 was examined, it was determined that the optimum esterification reaction conditions, which gave the lowest FFA value, were A2, B4, and C2 experiments. In other words, the experimental conditions where the amount of sulfuric acid is 25% by weight of fatty acid, the methanol ratio is 22:1, and the mixing speed is 400 rpm are the optimum conditions for the lowest FFA value.

Esterification was performed in triplicate under optimum reaction conditions, and the FFA value of each sample was measured by titration. As a result of esterification in the optimum reaction parameters, the mean FFA value of the waste olive oil was determined to be 0.608%. When Taguchi's S/N and mean value analyses were examined, it was determined that the most important effect for the lowest FFA in acid esterification was the methanol ratio, followed by the amount of sulfuric acid and the mixing speed, respectively.

When similar studies in the literature are examined, it is seen that two-stage esterification was performed in some studies [83]. In some studies, using a one-step acid esterification process, it was observed that the FFA was reduced

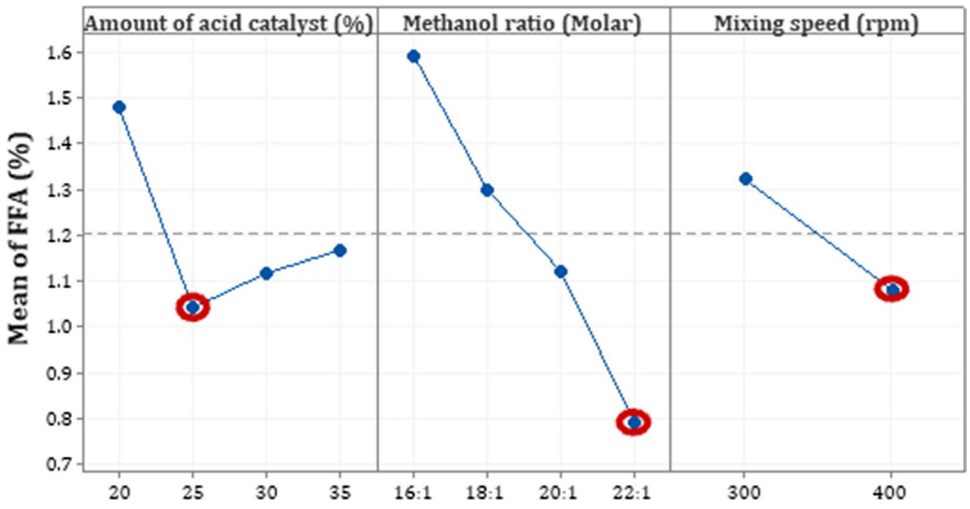

Fig. 3 The main effects plot for FFA means

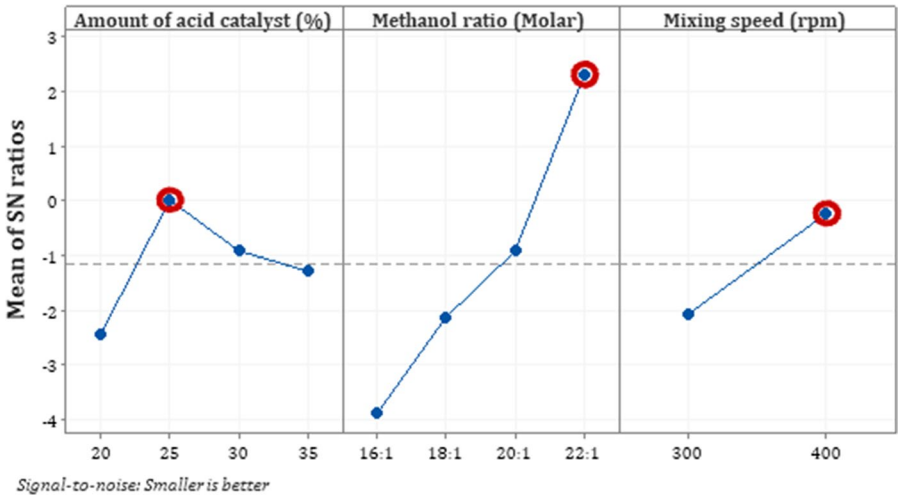

Fig. 4 The main effects plot for mean of SN ratios

below 1%. However, it was determined that methanol and acid catalyst were used at high rates during these processes [27, 31]. In this study, waste olive oil with an FFA of 23% was reduced to less than 1% by a one-step acid esterification. It was observed that the ratio of methanol used in acid esterification remained relatively low compared to the literature [23, 28]. Moreover, since the acid catalyst used was determined by the amount of fatty acids, less acid was used compared to many studies [84, 85]. Finally, waste olive oil with reduced FFA value was converted to methyl ester with ultrasound-assisted transesterification.

3.2 Distribution of fatty acids

The fatty acid distributions of raw oil, acid esterified oil, and oil methyl ester (WOOME) determined by gas chromatography are given in Table 5. The table is arranged to group saturated and unsaturated fatty acids.

The carbon numbers of the fatty acids shown in Table 5 express the number of carbons forming the compound and the bond shape. For example, palmitoleic acid (C16: 1) indicates that there are 16 carbons and 1 double bond. Double bonded acids are expressed as unsaturated fatty acids. Accordingly, it was seen that the ratio of unsaturated fatty acids of raw oil (FFA of 23%) is around 66.5% in total. The saturated fatty acid content was found to be 32%. After acid esterification, the unsaturated fatty acids of the oil were 67.5%, while the saturated fatty acids were 28.5%. According to the results, it was determined that the ratio of saturated fatty acids decreased with acid esterification. The saturated ester ratio in the fatty acid methyl ester called WOOME is 28%. The unsaturated ester content was also determined as 64%. Unsaturated esters have a lower mass heating value than saturated esters while having a higher volume heating value due to their higher density [86]. The oleic acid ester content is an important value that determines the kinematic viscosity. The high oleic acid content of the oil causes an

Table 5 Distribution of fatty acids

General name of fatty acid		Carbon number	Relative wt.%		
			High FFA (23%)	Low FFA (< 1%)	WOOME
Unsaturated fatty acids	Palmitoleic acid	C16:1	2.98 ± 0.055	0.71 ± 0.01	0.70 ± 0.02
	Linoleic acid	C18:2n6c	10.01 ± 0.04	17.57 ± 0.12	14.70 ± 0.2
	Elaidic acid	C18:1n9t	4.36 ± 0.01	2.45 ± 0.15	2.10 ± 0.3
	Oleic acid	C18:1n9c	45.5 ± 0.02	41.27 ± 0.14	39.65 ± 0.15
	Heptadecenoic acid	C17:1	0.83 ± 0.06	1.37 ± 0.01	1.34 ± 0.01
	Alpha linolenic acid	C18:3n3	2.41 ± 0.02	3.56 ± 0.015	3.52 ± 0.04
	Eicosenoic acid	C20:1	1.31 ± 0.035	2.09 ± 0.045	2.00 ± 0.1
Saturated fatty acids	Palmitic acid	C16:0	17.61 ± 0.025	23.08 ± 0.3	22.82 ± 0.16
	Stearic acid	C18:0	9.09 ± 0.03	1.14 ± 0.2	1.98 ± 0.2
	Behenic acid	C22:0	0.59 ± 0.07	1.07 ± 0.06	1.08 ± 0.17
	Heptadecanoic acid	C17:0	0.42 ± 0.05	0.58 ± 0.03	0.53 ± 0.1
	Arachidic acid	C20:0	1.76 ± 0.04	2.51 ± 0.01	2.51 ± 0.05
	Tricosanoic acid	C23:0	3.35 ± 0.08	0.04 ± 0.01	0.03 ± 0.01
Sum of unsaturated fatty acids (%)			66.5	67.5	64
Sum of saturated fatty acids (%)			32	28.5	28

increasing trend in kinematic viscosity [87]. When Table 5 is examined, it is observed that oleic acid content decreases with acid esterification and transesterification processes.

As a result, when the fuel properties were examined, it was observed that the kinematic viscosity value of WOOME was within the limits. The presence of saturated fatty acids linked to glycerol has a detrimental effect on the cloud point and cold-filter plugging point (CFPP) of biodiesel due to its very low solubility in methyl esters [88].

Increasing the length of the hydrocarbon chain in the oil raises the viscosity, while the viscosity decreases with increasing unsaturation. Low viscosity value has a positive effect on combustion as it will reduce the flow resistance in the engine fuel system [89]. When Table 5 was examined, it was determined that the total amount of unsaturated fatty acids decreased with acid esterification and transesterification processes. When the fuel properties are examined, it is seen that the kinematic viscosity of the obtained biodiesel is within acceptable limits.

3.3 Features of biodiesel

The oil obtained from waste olive, whose FFA value was reduced below 1% after acid esterification carried out with the conditions determined in the optimization, was converted into WOOME by ultrasound-assisted transesterification. The kinematic viscosity, density, water content, flash point, and iodine number of the obtained WOOME were examined in an accredited laboratory affiliated to the Ministry of Agriculture of the Republic of Turkey. In addition, the cetane number and cold-filter plugging point properties of WOOME were determined by using equations derived from fatty acids in the literature.

The cetane number (CN) was calculated with the following Eq. (9) [90, 91].

$$CN = 61.1 + 0.88 \bullet x_1 + 0.133 \bullet x_2 + 0.152 \bullet x_3 - 0.101 \bullet x_4 - 0.039 \bullet x_5 - 0.247 \bullet x_6 - 0.395 \bullet x_7 \quad (9)$$

where x_1, x_2,x_3,x_4,x_5,x_6, and x_7 denote the weight percent values (wt.%) of myristic, palmitic, stearic, palmitoleic, oleic, linoleic, and linolenic acid esters in the fatty acid esters of WOOME, respectively.

The CFPP was calculated numerically with the Eq. (10) [92].

$$CFPP = -13.688 + 0.518 \bullet C16:0 + 0.778 \bullet C18:0 + 3.066 \bullet C20:0 \quad (10)$$

In this equation, C16:0, C18:0, and C20:0 represent the weight percent values of palmitic, stearic, and eicosanoic acid esters in WOOME, respectively.

The characteristics of WOOME determined by analysis and numerical calculations are presented in Table 6. It was observed that the results obtained were in accordance with EN 14,214 standards.

Density of fuel is one of the most important features affecting performance, combustion, and engine emissions in diesel engines. It also affects combustion, injection pressure, injection characteristics, ignition delay, and engine emissions. Many performance parameters such as cetane number and heating value are related with the density [93, 94]. The density of WOOME was found to comply with EN 14,214 standards. Kinematic viscosity

Table 6 Some fuel features of WOOME

Property	Units	EN 14214	WOOME
Density (at 15 °C)	kg m^{-3}	860–900	879.6
Kinematic viscosity (at 40 °C)	mm^2 s^{-1}	3.5–5.0	4.852
Water content	ppm	max. 500	431.3
Iodine value	g I.100 g^{-1}	max. 120	81.47
Flash point	°C	min. 101	190
Cetane number*	-	min. 51	57.9
Cold-filter plugging point	°C	-	7.38

*Numerically calculated fuel properties

is the most important feature that determines atomization in fuel injection. Higher viscosity of fuels is the cause of poor vaporization [95]. As a result of the analyses made, it was seen that the kinematic viscosity value of WOOME was in accordance with the EN 14,214 standards. The water content of biodiesel is higher than diesel [96]. The high water content of the fuel showed that it reduced NO_x formation [97, 98].

In the EN 14,214 biodiesel standard, the iodine value is limited to a maximum of 120. The iodine value of WOOME corresponds to the unsaturation measure of waste olive oil given in Table 5. The iodine value is a parameter used to determine the degree of unsaturation in a vegetable or animal oil [99].

Flash point is an important property for fuel transportation and storage. Flash point is defined as the lowest temperature at which the vapor and air mixture on the liquid fuel flashes when it comes into contact with a fire source under certain conditions[100, 101]. Vegetable oils using methanol in the production of biodiesel have a higher flash point than diesel due to their low volatility [102]. WOOME's flash point is well above the standard. This feature of WOOME creates an advantage over diesel fuel in storage and transportation.

The cetane number (CN) is a number that indicates the auto-ignition property of the fuel. Since biodiesel is largely composed of long-chain hydrocarbon groups, it typically has a higher CN than diesel [103]. The higher the CN, the better the ignition quality of the fuel [104]. According to EN 14,214 standards, the CN must be at least 51. The CN of WOOME is well above the standards. This feature of WOOME is expected to improve the combustion performance of the fuel.

The cold-filter plugging point (CFPP) refers to the temperature at which plugging begins in the filter due to crystallization of the fuel [102]. CFPP is a parameter that directly affects the operation of the engine in winter and cold weather. High CFPP can cause clogging in the fuel system and injector. The lower CFPP value of biodiesel is proportional to the level of unsaturation [105]. Although there is no standard for CFPP in the EU and the US, the CFPP value for biodiesel is expected to be low.

4 Conclusions

The results obtained from this study, which aims to produce high-efficiency biodiesel in the shortest time with the least chemicals from oils with high FFAs, are as follows.

- Acid esterification reaction parameters were optimized in order to reduce the value of raw oil with high FFA below 1%. The tests were carried out according to Taguchi's L_{16} experimental design, and the results were optimized using the S/N ratios. According to the results, 25% by weight sulfuric acid catalyst (based on FFA), 22:1 (mol to mol) methanol and 400 rpm stirring speed were determined as optimum reaction parameters. The raw oil with FFA of 23% (as oleic acid) was reduced to 0.608% under these optimum reaction conditions.
- In the ultrasound-assisted transesterification process, which is preferred in biodiesel production, 98.7% conversion efficiency was achieved in the reaction carried out with 20% methanol and 1% KOH to the oil sample. At this time, the ultrasonic homogenizer was set to 75% sonicator amplitude and 70% duty cycle, and a reaction time of 10 min was achieved. The reaction process, which was between 45 and 60 min with conventional heating, was realized in 10 min with this method. With ultrasound-assisted transesterification, both time and energy are saved. These advantages can contribute to reducing costs, which is one of the biggest problems in the production of biofuels.
- In the use of catalysts, unlike most studies in the literature, the amount of catalysts was calculated based on the weight of the FFA in the oil instead of the amount of oil used. With this method, reaction deterioration that can be caused by the use of missing catalysts can be prevented. Likewise, the increase in the sulfur content of the fuel can be limited by preventing the use of excess catalysts.
- The produced biodiesel (WOOME) was found to comply with EN 14,214 standards. As a result, the esterification process was carried out successfully in one step with 16 times less experiments. In addition, biodiesel conforming to standards was obtained with a high yield in a short time. Taguchi and ultrasound-assisted transesterification methods can be used in fuel production stages.

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