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Biodiesel production enhanced by ultrasound-assisted esterification and transesterification of inedible olive oil

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SUMMARY: In the first phase of this study, inedible olive oil with different initial free fatty acid concentrations (2.5, 5.0, and 10.0%) was processed through acid-catalyzed esterification. Various heating methods were used for this purpose. The ultrasound-assisted esterification and traditional magnetic stirrer-assisted esterification methods were similar to each other in terms of their effects on free fatty acid reduction. However, the ultrasound reaction time was significantly shorter than that of the traditional magnetic stirrer. In the second phase of this study, biodiesel production was carried out through the ultrasound-assisted transesterification of inedible olive oil. Independent variables were, namely, ultrasound power level (30, 90, and 150 W), methanol/oil mole ratio (3, 9, and 15), catalyst concentration (0.5, 1.0, and 1.5%), ultrasound time (15, 30, and 45 min), and reaction temperature (45, 55, and 65 °C), which affected the yield indices and physicochemical constants of the produced biodiesel. The purest biodiesel (98.95%) and the highest amount of yield (92.69%) were observed when using an ultrasound power level of 90 W, a methanol/oil mole ratio of 9, a catalyst concentration of 1.0%, an ultrasound time of 30 min, and a reaction temperature of 55 °C. Optimizing the reaction conditions of the ultrasound operation can effectively increase the biodiesel yield (92.69%), while reducing the energy consumption (4.775 kWh/kg) and shortening the reaction time (30 min), compared to the traditional magnetic stirrer (77.28%, 2.17 kWh/kg, and 120 min, respectively). Therefore, ultrasound-assisted transesterification can serve as an effective alternative because of its fast and economic operation for making biodiesel out of inedible olive oil.

KEYWORDS: *Biodiesel; Esterification; Olive oil; Transesterification; Ultrasound*

RESUMEN: ***Producción de biodiésel mejorada por esterificación y transesterificación asistida por ultrasonidos de aceite de oliva no comestible.*** En la primera fase de este estudio, el aceite de oliva no comestible tenía diferentes concentraciones iniciales de ácidos grasos libres (2,5, 5,0 y 10,0%) y se procesó mediante esterificación catalizada por ácido. Se utilizaron varios métodos de calentamiento para este propósito. La esterificación asistida por ultrasonido y los métodos tradicionales de esterificación asistida por agitador magnético fueron similares entre sí en términos de sus efectos sobre la reducción de ácidos grasos libres. Sin embargo, el tiempo de reacción usando ultrasonidos fue significativamente más corto que el de agitador magnético tradicional. En la segunda fase de este estudio, la producción de biodiesel, a partir de aceite de oliva no comestible, se llevó a cabo mediante transesterificación asistida por ultrasonidos. Las variables independientes fueron, nivel de potencia de ultrasonido (30, 90 y 150 W), relación molar metanol/aceite (3, 9 y 15), concentración de catalizador (0,5, 1,0 y 1,5%), tiempo de ultrasonido (15, 30 y 45 min) y temperatura de reacción (45, 55 y 65 °C) que afectaron al rendimiento y a las constantes fisicoquímicas del biodiesel producido. El biodiésel más puro (98,95%) y el mayor rendimiento (92,69%) se observaron cuando se utilizó un nivel de potencia de ultrasonido de 90 W, una relación molar de metanol / aceite de 9, una concentración de catalizador del 1,0%, un tiempo de ultrasonido de 30 min, y una temperatura de reacción de 55 °C. La optimización de las condiciones de reacción de la operación de ultrasonido puede aumentar efectivamente el rendimiento de biodiésel (92,69%), al tiempo que reduce la cantidad de consumo de energía (4,775 kWh/kg) y acorta el tiempo de reacción (30 min), en comparación con el agitador magnético tradicional (77,28 %, 2,17 kWh/kg y 120 min, respectivamente). Por lo tanto, la transesterificación asistida por ultrasonido puede servir como una alternativa eficaz debido a su operación rápida y económica en la producción de biodiesel a partir de aceite de oliva no comestible.

PALABRAS CLAVE: *Aceite de oliva; Biodiesel; Esterificación; Transesterificación; Ultrasonido*

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1. INTRODUCTION

In the twenty-first century, there are numerous non-fossil fuels available such as hydrogen, solar energy, wind power, etc. Among them, biodiesel (fatty acid methyl ester) is one of the most well-known fuels which can be used as an environmentally clean energy (Maneerung *et al*., 2016; Tan *et al*., 2015). The transesterification of vegetable oils is a popular method for biodiesel production (Badday *et al*., 2013).

Previous research has dealt with several heating methods for the transesterification of vegetable oils in order to produce biodiesel (Talebian-Kiakalaieh *et al.*, 2013). Nowadays, new heating methods such as microwave, ohmic, and ultrasound are beginning to be recognized as effective approaches for biodiesel production. Employing new heating methods can result in a reduction in reaction time, energy consumption, and the costs of biodiesel production (Ho *et al*., 2016). Ultrasound provides physical mixing as well as the activation energy required for initiating the transesterification reaction that results in temperature increase at the phase boundary of the reactants which further enhances the reaction rate (Sharma *et al.,* 2020). This effect contributes to cavitation bubbles, whereby the solution is effectively mixed, immiscible liquid layers are disrupted and mass transfer is promoted in interfacial areas (Badday *et al*., 2013). In a relevant study, Badday *et al*. (2013) showed that ultrasound-assisted transesterification (UAT) requires a maximum reaction time of 50 min in order to achieve 85% biodiesel yield from crude Jatropha oil. Traditional-assisted transesterification (TAT) entails a longer duration of reaction time (i.e. 300 min).

When olive oil is processed and produced, the presence of moisture and hydrolytic enzymes can potentially cause the free fatty acids in the olive oil to reach non-standard high amounts. This occurrence can make the olive oil inedible. Some types of inedible olive oil have high amounts of free fatty acids, meaning that high rates of loss become an inevitable part of their refining process. In fact, this makes the refining process a costly endeavor for the commercial oil industry (Kanitkar *et al.*, 2011). While biodiesel can be made out of inedible olive oil economically and valuably, the alkaline-catalyzed transesterification process turns out to be less efficient when processing olive oil samples, especially those that have substantial contents in free fatty acids. The reason for this is that soap forms between the free fatty acids and the alkaline catalyst. To complete alkaline-catalyzed transesterification, it is necessary to have free fatty acid values which are lower than 3% (Meher *et al*., 2006; Vicente *et al*., 2004). Accordingly, acid-catalyzed esterification can enable a decrease in free fatty acid content in the inedible olive oil. While acid-catalyzed esterification is regarded as a pre-treatment, biodiesel can then be made out of inedible olive oil by means of transesterification.

This study consists of two phases. In the first phase, the ultrasound-assisted esterification (UAE) of inedible olive oil is carried out with various free fatty acid concentrations in the beginning of the process. This is to be compared with traditional-assisted esterification (TAE). In the second phase, the UAT factors (i.e. ultrasound power level, methanol/oil mole ratio, catalyst concentration, reaction time, and reaction temperature) are examined which can have different effects on the purity, yield, physicochemical constants, energy consumption, and heating constants of the biodiesel which is produced from inedible olive oil. The findings are then compared to those obtained by TAT.

2. MATERIALS AND METHODS

2.1. Materials

All experimental chemicals were analytical grade and supplied from Sigma–Aldrich (St. Louis, USA) and Merck (Darmstadt, Germany). The olive oil (Molecular weight of 871.0656 g/mol, Kinematic viscosity of 36.574 ± 0.015 mm^2/s, density of 882.1854 ± 0.9636 kg/m^3, and refractive index of 1.4685 ± 0.007) was purchased from Etka Company (Rudbar, Iran). The major fatty acids in the olive oil were oleic acid (69.40 ± 2.86 %), Linoleic acid (11.09 ± 1.76 %), palmitic acid (13.98 ± 1.17 %), and stearic acid (3.38 ± 0.29 %).

2.2. Biodiesel production methods

2.2.1. Esterification procedure

According to Chai *et al*. (2014), UAE was carried out with the help of sulfuric acid (10%, w/w H_2SO_4/ free fatty acid) as the catalyst, which was dissolved in methanol (methanol/free fatty acid molar ratio

of 40). The said ingredients were mixed for 5 minutes. In conforming with the American Oil Chemists' Society (AOCS) Official Method (Ca 5a-40), the free fatty acid of olive oil is 2.36%, which can increase to 2.5, 5.0, and 10.0% by pure oleic acid (AOCS, 2000). The sulfuric acid-methanol solution was mixed with 100 g of inedible olive oil which contained high amounts of free fatty acid. The reaction lasted for 30 minutes using an ultrasonic probe (Bandelin HD 3200, Bandelin Electronics, Berlin, Germany). Distilled water was used as a temperature regulator by circulating in the jacketed vessel. A high grade titanium tip (TT13, 13 mm diameter) assisted in sonicating the substrates with an unchanging horn depth of 2 cm. Also, the hot plate mixer operated at 60 ºC, for 120 minutes, and at 600 rpm as the traditional-assisted esterification method. At the end of the reaction time, the reaction mixture was immediately cooled down to room temperature. The water-soluble components were separated from the product in a separatory funnel. Esterification yield was calculated in conformity with a method used previously by Chai *et al*. (2014).

2.2.2. Transesterification procedure

UAT was optimized including the methanol/oil mole ratio (3, 9, and 15), KOH catalyst concentration (0.5, 1.0, and 1.5 %), power level (30, 90, and 150 W), reaction time (15, 30, and, 45 min), and reaction temperature (45, 55, and 65 ºC). Each factor was optimized by considering an intermediate value (central point) of other factors.

The catalyst-methanol solution was mixed with 100 g esterified inedible olive oil. Then, the reaction took place with the help of an ultrasonic probe. A hot plate mixer operated at 60 ºC for 120 minutes and at 600 rpm as TAT.

At the end of the reaction, fatty acid methyl esters were refined chemically according to a method used previously by Dehghan *et al*., 2019. Methyl margarate was added to the crude biodiesel as an internal standard (Atapour and Kariminia, 2011). The purity of biodiesel was determined using the GC/FID in conformity with the method reported by Golmakani *et al*., 2012a, 2012b. The weight of yield, purity, and final yield were determined according to methods reported by Atapour and Kariminia, 2011; Hsiao *et al*., 2010.

2.3. Physicochemical constants of biodiesel

The kinematic viscosity, refractive index and density of biodiesel were measured in conformity with the guidelines of the American Society for Testing Materials (ASTM; D445), the AOCS Cc7-25 Official Method, and the AOCS 1a-64 Official Method, respectively (AOCS, 2000; ASTM, 2013). The profile of fatty acids in the biodiesel was measured in conformity with a method used by Golmakani *et al.* (2012a) and, Golmakani *et al.* (2012b). Also, the color attributes (L*, lightness; a*, greenness-redness; b*, blueness-yellowness) of biodiesel were measured according to Habibi *et al*. (2016).

2.4. Examination of biodiesel under optimal states

An optimal state under which UAT operated efficiently was developed to a point where the purity, weight of yield and final yield of the biodiesel reached their highest values. The heating constants of the biodiesel (i.e. cloud, flash, fire, and pour points) were measured under optimal conditions in conformity with the ASTM Official Methods (D2500, D92, and D97) (ASTM, 2013). The amount of energy consumed along with the processes of alcohol separation, washing, and drying, along with the specific consumptions of energy for the production of 1 kg of biodiesel, were measured using a method reported by Motasemi and Ani (2012).

2.5. Statistical analysis

Experiments were repeated at least three times and the data were calculated as mean values of the measurements. Standard deviations are reported in the tables and figures. A general linear model (GLM) analysis from SAS (version 9.2; SAS Institute Inc. Cary, USA) was used to compare among the means.

3. RESULTS

3.1. Esterification yield

The initial free fatty acid concentration and the esterification method caused various effects on the esterification yield of inedible olive oil (Table 1). The highest esterification yield was obtained in the presence of 2.5% initial free fatty acid. By the end of the operation, this corresponded with the free fatty acid concentration being lower than 0.5%. Even

Table 1. Effect of traditional- and ultrasound-assisted esterification on the yield of high free fatty acid olive oil.

Initial free fatty acid concentration	Esterification method	Final free fatty acid concentration	Esterification yield (%)
2.5	Traditional	0.46±0.02^{c}*	81.60±0.09^{a}
2.5	Ultrasound	0.45±0.08^{c}	82.00±0.07^{a}
5	Traditional	1.00±0.00^{b}	80.00±0.02^{b}
5	Ultrasound	0.98±0.09^{b}	80.40±0.19^{b}
10	Traditional	2.05±0.04^{a}	79.50±0.50^{b}
10	Ultrasound	1.99±0.02^{a}	80.10±0.01^{b}

* Mean ± standard deviation; Number of replicates for each analysis: 3; Statistical test: ANOVA and multiple comparison of means using Duncan's multiple range test; Degree of significance: $P < 0.05$; In each column, means with different letters are significantly different.

though no significant differences were observed between the esterification yield of inedible olive oil in the presence of 5.0% free fatty acid and 10.0% free fatty acid, their esterification yields were lower than that of the sample with 2.5% free fatty acid. In spite of the fact that no significant differences were observed between the UAE and TAE methods, including their final free fatty acid concentration and esterification yield, the UAE operated at a higher speed (i.e. 4 times faster) compared to the TAE. During sonication, fluids tend to undergo rapid distortion due to the compression and rarefaction movements initiated by the sonic waves, which is followed by a cavitation effect on the reaction stream formed by the rapid creation and collapse of micro bubbles. This process significantly affects the mechanism of the reaction, thereby enhancing the reaction rate. Hence, the impact of ultrasound can increase the catalyst activity by its least contribution to the reaction. Also, it has the tendency to increase the mass transfer rate, thereby accelerating free fatty acid esterification (Yasvanthrajan *et al.,* 2020). These findings are in accordance with previous results (Trinh *et al*., 2018) in which the esterification of rubber seed oil was evaluated. The mentioned research showed that UAE and TAE methods reduced the free fatty acid concentration after being subjected to 30 and 90 min of reaction time, respectively.

3.2. Effects of UAT on biodiesel yield

3.2.1. Ultrasound power level

The power level of the ultrasound affected the yield indices of the produced biodiesel (Figure 1a). By increasing the ultrasound power level from 30 to 90 W, the final yield was enhanced from 76.10 to 92.69%. This positive effect can be attributed to broader acoustic streaming and more cavitation bubbles. The increase in the mentioned factors can cause enhancements in the dispersion and mass transferal effects of the ultrasound, while allowing the two immiscible reaction layers to be thoroughly emulsified (Joshi *et al*., 2018; Korkut and Bayramoglu, 2018). However, the final yield decreased from 92.69 to 80.62% when the ultrasound power was further increased from 90 to 150 W. In fact, high levels of power can make the tip of the horn overpopulated with bubbles, thereby resulting in bubble coalescence and acoustic decoupling. These criteria act to reduce the number of active cavitation bubbles (Korkut and Bayramoglu, 2018). The ultrasound power of 90 W proved to be high enough to obtain a purity of 98.95% and a final yield of 92.69%, under the studied conditions. These findings are in accordance with the results of Korkut and Bayramoglu (2018) who evaluated the UAT of canola oil. They reported that by raising the ultrasound power to 40 W an increase in the reaction yield by up to 99.4% was observed; whereas higher levels of ultrasound power reduced the reaction yield.

3.2.2. Methanol/oil mole ratio

As shown in Figure 1b, the methanol/oil mole ratio affected the yield indices. Rising the mole ratio from 3 to 9, significantly increased the yield indices. However, as the mole ratio increased from 9 to 15, a downward trend was recorded for the yield indices. When the methanol/oil mole ratio measured 9, the results corresponded with the highest weight of yield, purity, and final yield (93.68, 98.95, and 92.69%, respectively). Since transesterification is

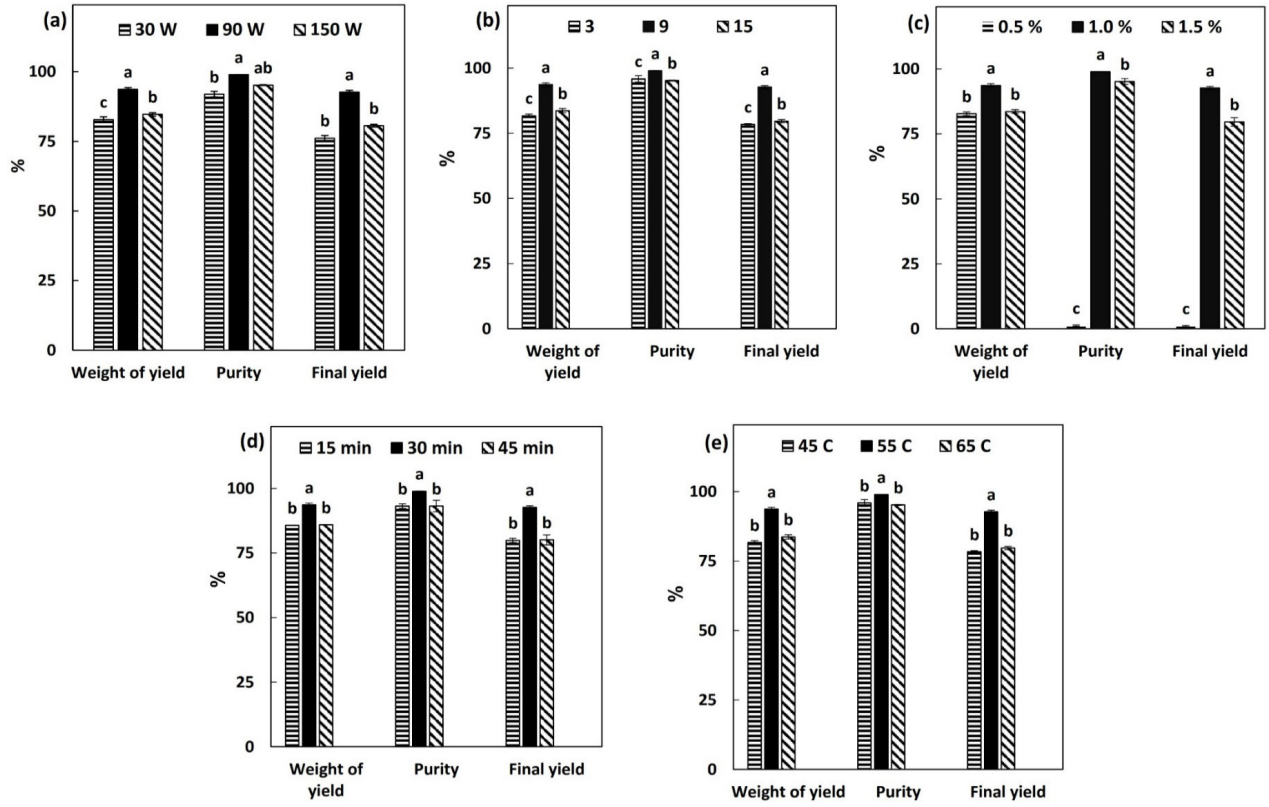

FIGURE 1. Effects of (a) microwave power level, (b) methanol/oil mole ratio, (c) catalyst concentration, (d) reaction time, and (e) reaction temperature on ultrasound-assisted transesterification of inedible olive oil. Mean ± standard deviation; Number of replicates for each analysis: 3; Statistical test: ANOVA and multiple comparison of means using Duncan's multiple range test; Degree of significance: $P < 0.05$; In each figure and for each response, means with different letters are significantly different.

an equilibrium reaction, larger amounts of methanol can modify the reaction to make the equilibrium favorable to the formation of fatty acid methyl esters, The stoichiometric mole ratio of triacylglycerol to methanol for the occurrence of transesterification is 1:3 and, in fact, an excess amount of methanol is preferable for the completion of the reaction (Ho *et al*., 2016). At high methanol/oil mole ratios, the lower concentration of oil causes a decrease in the interaction between triacylglycerol molecules and catalytic active sites, thereby reducing the reaction kinetics and the reaction yield. Moreover, freeing the reaction mixture from unnecessary methanol requires more energy (Korkut and Bayramoglu, 2018). Ultrasound radiation rapidly generates tiny methanol droplets and, as a result, the emulsion forms easily and quickly in the oil phase. When the solution is rich in methanol, the droplets tend to become larger in the emulsion. In such circumstances, larger droplets are created as a result of the frequent encounters among small-size droplets of methanol, compared to when methanol is not abundantly present in the solution. As large droplets become more common, the transesterification reaction could then take on a slower rate (Thanh *et al*., 2010). Similarly, Yin *et al*. (2017) studied how different mole ratios of methanol to soybean oil (4-12) can affect UAT yield. They showed that the UAT yield significantly increased by rising the mole ratio from 4 to 8. Then, by rising the mole ratio from 8 to 10, the yield did not increase significantly. By its further increase to 12, the UAT yield decreased to an extent that was lower than the amount obtained when there was a mole ratio of 8.

3.2.3. Catalyst concentration

The transesterification reaction is commonly affected by the concentration of the catalyst. This factor was observed to have significant effects on the yield indices (Figure 1c). The lowest values for biodiesel purity (1.17%) and its final yield (0.97%) were recorded when the catalyst concentration was

0.5%. An insufficient catalyst concentration could not contribute adequately to the conversion of inedible olive oil to biodiesel. The yield indices of biodiesel increased as the catalyst concentration rose to 1.0% in terms of adequacy. This correlation is natural since a higher concentration of catalysts is associated with more of their active sites, and thus the conversion of reactants is better facilitated for the reaction to be pushed forward. The transesterification reaction begins with the carbonyl carbon atoms of monoacylglycerol, diacylglycerol, and triacylglycerol reacting with methoxide ions (CH_3O^-). Dissolving KOH in methanol produces CH_3O^- according to the following reaction: $OH^- + CH_3OH \rightarrow CH_3O^- + H_2O$. Since KOH is a strong alkaline, it has a large "dissociation constant" in methanol. Therefore, the concentration of CH_3O^- depends only on the concentration of the KOH catalyst. The result is that a higher concentration of KOH encourages a faster procession in the reaction (Ho *et al*., 2016; Thanh *et al*., 2010). Raising the catalyst concentration from 1.0 to 1.5% reduced the production of biodiesel. Several disadvantages usually discourage researchers from using catalysts excessively when experimenting with transesterification reactions. Large amounts of catalyst tend to increase the extent of how soluble fatty acid methyl esters can be in glycerol, thereby causing residual levels of fatty acid methyl ester after glycerol has been separated. Decreasing the fatty acid methyl ester content would reduce the purity and yield of biodiesel as well, (Thanh *et al*., 2010). Furthermore, higher concentrations of catalysts usually increase the viscosity of the reaction mixture, and this acts as a hindrance to glycerol separation (Korkut and Bayramoglu, 2018). The high concentrations of catalysts can lead to prolific levels of soap formation which then cause difficulties in the separating step of emulsification. This chain of events ultimately concludes with a lower biodiesel yield (Yin *et al*., 2017). As a consequence, the optimal amount of KOH in this study was 1.0%, as far as the relevant treatments are concerned. Similarly, Deshmane and Adewuyi (2013), produced biodiesel from soybean oil using UAT at different catalyst concentrations (0.6–1.4%). They reported that the biodiesel yield was improved by raising the catalyst concentration from 0.6 to 1%. However, further increases in the concentration amounted to almost no change or even a slight decrease in the reaction rate.

3.2.4. Reaction time

The duration of the reaction time had notable effects on the yield indices of biodiesel (Figure 1d). Prolonging the reaction time from 15 to 30 min caused an increase in the yield indices of biodiesel. At the early stages of the reaction, the provision of an insufficient contact time between the reaction mixtures led to lower levels of purity and yield. The highest values pertaining to the weight of yield, purity, and the final yield were obtained during a total reaction time of 30 min (93.68, 98.95, and 92.69%, respectively). The reversible nature of the transesterification reaction is a reason for the decrease in yield indices when reactions take longer than 30 min. This reduction could be due to the solubility of fatty acid methyl ester in the glycerol and also because of other unwanted reactions that can negatively affect the yield and purity (Badday *et al*., 2013). Similar observations were also reported (Badday *et al*., 2013) when the ultrasound method was used for transesterified crude Jatropha oil. In the mentioned research, an increase in biodiesel yield was observed when the reaction time was prolonged from 10 to 60 min, but it started to decrease if the reaction took more than 60 min.

3.2.5. Reaction temperature

The yield indices of biodiesel were affected by the temperature at which the ultrasound operated (Figure 1e). Rising the reaction temperature from 45 to 55 °C caused significant increases in biodiesel yield indices. These findings are logical to obtain because KOH has an enhanced solubility, while there is a thorough contact between the components of the reaction mixture, leading to a higher biodiesel yield (Maddikeri *et al*., 2013). However, an extra increase in the reaction temperature from 55 to 65 °C can begin to reduce the yield indices which can be attributed to the overheating of the reaction mixture. This could result in the loss of methanol and energy, along with a lower level of cavitational effects. Also, due to the lower thermal stability of fatty acid methyl esters under extreme conditions and the decomposition of the fatty acid methyl esters (especially the polyunsaturated ones) which can further produce by-products, temperatures higher than 55 °C have adverse effects on fatty acid methyl esters (Maddikeri *et al*., 2013). Therefore,

the reaction temperature of 55 °C is considered the most suitable temperature for the production of biodiesel from inedible olive oil. Similarly, Maddikeri *et al*., 2013 showed how different temperatures (i.e. 30-50 °C) affected the UAT yield of waste cooking oil. They stated that an increase in temperature from 30 to 40 °C caused an increase of 10% (from 78 to 88%) in the biodiesel yield, whereas another 10 °C increase (from 40 to 50 °C) in the reaction temperature only made a negligible improvement (from 88 to 93%) in the biodiesel yield (Maddikeri *et al*., 2013).

3.3. Biodiesel examination

Different UAT factors affected the physical constants of inedible olive oil methyl esters (Table 2). The biodiesel kinematic viscosity is one of the most important constants that can be affected by the storage condition, transportation, and the operation aimed at fatty acid methyl esters. Even though there was a high kinematic viscosity of inedible olive oil at 40 ºC (36.806 mm^2/s), the value decreased significantly after transesterification. The kinematic viscosity reached its lowest value (4.201 mm^2/s) in the presence of an optimal state of UAT operation. In conformity with the ASTM D6751 Official Method, the normal range of kinematic viscosity for biodiesel is 1.9-6 mm^2/s. Therefore, all fatty acid methyl esters fall within the standard range indicated by ASTM.

A negative correlation was observed between the kinematic viscosity and the final yield. The values pertaining to the power level, methanol mole ratio, catalyst concentration, reaction time and reaction temperature were R^2=0.65, 0.44, 0.98, 0.29, and 0.66, respectively. Being an ester, triacylglycerol consists of three fatty acids in association with glycerol. It can be converted to three fatty acid methyl esters with lower molecular weights after transes-

Table 2. Effect of ultrasound-assisted transesterification on physical constants of olive oil methyl esters.

Transesterification factor	Kinematic viscosity (mm^2/s)	Density (kg/m^3)	Refractive index	Color attribute		
				L*	a*	b*
Power level (W)						
30	5.132±0.002^{b}**	888.9797±0.9811^{b}	1.4544±0.0001^{a}	52.32±2.92^{c}	-4.27±1.59^{a}	48.11±2.15^{b}
90	4.201±0.000^{c}	892.9963±0.3292^{a}	1.4530±0.0000^{c}	57.66±5.13^{a}	-6.33±2.08^{b}	26.33±3.05^{bc}
150	5.651±0.000^{a}	886.6598±0.6398^{c}	1.4541±0.0001^{b}	48.63±3.98^{bc}	-2.31±1.11^{bc}	39.16±1.92^{a}
Methanol/oil mole ratio						
3	6.746±0.003^{a}	885.6811±0.8676^{b}	1.4669±0.0000^{a}	54.86±1.76^{c}	-4.11±1.54^{a}	52.22±6.65^{a}
9	4.201±0.000^{c}	892.9963±0.3292^{a}	1.4530±0.0000^{c}	57.66±5.13^{a}	-6.33±2.08^{b}	26.33±3.05^{b}
15	6.552±0.001^{b}	885.0180±0.6793^{c}	1.4534±0.0001^{b}	47.67±1.93^{b}	-3.22±1.35^{a}	52.45±2.61^{a}
Catalyst concentration (%)						
0.5	35.755±0.007^{a}	886.6569±0.6651^{c}	1.4664±0.0001^{a}	41.66±2.51^{c}	-1.45±0.57^{a}	51.76±1.67^{a}
1.0	4.201±0.000^{c}	892.9963±0.3292^{a}	1.4530±0.0000^{b}	57.66±5.13^{a}	-6.33±2.08^{c}	26.33±3.05^{b}
1.5	4.321±0.000^{b}	891.0325±0.2759^{b}	1.4533±0.0001^{b}	46.45±4.04^{ab}	2.54±1.64^{b}	45.74±4.26^{c}
Reaction time (min)						
15	4.252±0.001^{b}	890.0486±0.3308^{b}	1.4539±0.0001^{a}	49.33±7.23^{ab}	-4.33±1.52^{ab}	49.33±3.51^{b}
30	4.201±0.000^{c}	892.9963±0.3292^{a}	1.4530±0.0000^{c}	57.66±5.13^{a}	-6.33±2.08^{b}	26.33±3.05^{ab}
45	5.016±0.001^{a}	886.7189±0.1692^{c}	1.4535±0.0002^{b}	51.33±3.51^{b}	-3.60±2.51^{a}	50.66±4.04^{a}
Temperature (ºC)						
45	5.237±0.006^{a}	886.6705±0.3366^{b}	1.4548±0.0001^{a}	52.33±5.50^{ab}	-4.66±3.78^{b}	45.50±3.21^{b}
55	4.201±0.000^{c}	892.9963±0.3292^{a}	1.4530±0.0000^{c}	57.66±5.13^{a}	-6.33±2.08^{ab}	23.50±3.03^{ab}
65	4.556±0.004^{b}	873.7199±0.5203^{c}	1.4540±0.0001^{b}	49.66±1.52^{b}	-5.33±2.51^{a}	44.50±6.11^{a}

** Mean ± standard deviation; Number of replicates for each analysis: 3; Statistical test: ANOVA and multiple comparison of means using Duncan's multiple range test; Degree of significance: $P < 0.05$; In each column and for each factor, means with different letters are significantly different.

terification (Talebian-Kiakalaieh *et al*., 2013). An increase in the final yield can be accompanied by a decrease in the molecular weight and, subsequently, a decrease in the kinematic viscosity.

Inedible olive oil showed a density of 880.1510 kg/m^3, which increased following the process of transesterification. The biodiesel increased in density and reached its highest value when there were optimal UAT conditions, resulting in the maximum final yield. Since the saturation degree of the biodiesel was not significantly affected by transesterification, triacylglycerols are not thought to cause the density value for the biodiesel and, instead, the density is defined by the molecular weight of the biodiesel (Habibi *et al*., 2016). A positive correlation was observed between the density and the final yield. The values pertaining to the power level, methanol mole ratio, catalyst concentration, reaction time and reaction temperature were R^2=0.65, 0.30, 0.97, 0.71, and 0.48, respectively. So, the highest amount of final yield (i.e. the lowest molecular weight) and the highest density were recorded under optimal states of UAT.

Inedible olive oil had a refractive index of 1.4685, which decreased because of transesterification. Optimal conditions of UAT caused the lowest value for refractive index (1.4530), thereby making the final yield increase maximally. Furthermore, a strong negative correlation existed between the refractive index and the final yield (R^2=0.86-0.99). Accordingly, a consistent feature of the physical constant is the refractive index when researchers aim to predict progress in transesterification.

Biodiesel can be evaluated qualitatively by its color, and it can be used in assessments of the transesterification process. The highest value for L* (57.66) and the lowest for a* (-6.33) and b* (26.33) were observed under optimal states of UAT. An increase in the L* value, along with a higher value for the final yield, were associated with lower a* and b* values. As the physical constants change, the transesterification yield changes significantly.

3.4. Comparison between UAT and TAT

3.4.1. Weight of yield, purity, and final yield

According to the findings, the optimal state for the operation of UAT can be described as a set of circumstances which include a power level of 90 W, a methanol/oil mole ratio of 9, a catalyst concentration of 1.0%, a reaction time of 30 min, and a reaction temperature of 55 °C. Figure 2 compares the optimum conditions of UAT and TAT. The weight of yield, purity, and final yield of UAT were higher (93.68, 98.95, and 92.69%, respectively) compared to those obtained by TAT (88.66, 87.17, and 77.28%, respectively). The cavitation and its physical effects can lead to this improved performance. Furthermore, there are related features such as the liquid micro-circulation (acoustic streaming), local turbulence and micro-emulsion formation. These features increase the interactions that are necessary for the reaction. An external, mass transfer barrier existed between the oil and the methanol phase. Since micro-emulsions joined the two phases that participated as reactants, an enormous increase was observed in the areas where the reactants collide, thereby accelerating the reaction rates. In the case of TAT, the reactants receive energy exclusively as heat, and this occurs by the mechanisms of conduction and convention. These two mechanisms do not contribute to the establishment of a sufficient contact between the reactants. Accordingly, the UAT is capable of reducing the reaction time significantly, as compared to the duration required by the TAT. The UAT can achieve higher levels of purity and more yield. These findings are in accordance with the results of Maddikeri *et al*. (2013), who produced biodiesel from waste cooking oil by using the UAT operation. A higher biodiesel yield was reported (90%) when using UAT compared to TAT (70%).

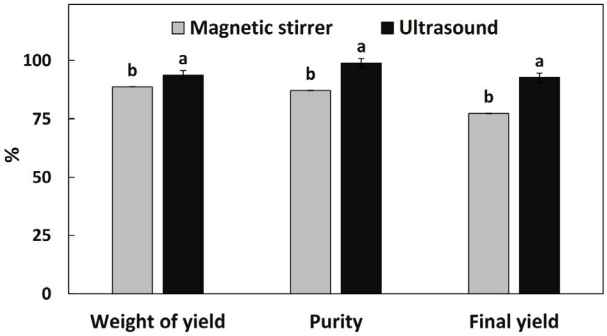

Figure 2. Effects of different transesterification methods on fatty acid methyl ester yield of inedible olive oil. Mean ± standard deviation; Number of replicates for each analysis: 3; Statistical test: ANOVA and multiple comparison of means using Duncan's multiple range test; Degree of significance: $P < 0.05$; For each response, means with different letters are significantly different.

3.4.2. Physicochemical constants of biodiesel

No considerable differences were observed between the profiles of fatty acids when using the UAT and TAT. Accordingly, different transesterification methods had no selectivity on the transesterification of different fatty acids (i.e. with various saturation degrees and chain length). Nonetheless, the UAT created a biodiesel that showed higher values for density and L* value, but lower values for a* value, b* value, kinematic viscosity, and refractive index. These differences can be due to the higher amount of final yield obtained by transesterification when using the UAT compared to the TAT. The UAT produced a biodiesel that showed higher levels of purity than those produced by TAT. Accordingly, the application of UAT can yield a biodiesel which exhibits a higher brightness value (L* value), and thus the purification steps can be reduced.

As shown in Table 3, no significant differences were observed between the UAT and TAT, including their flash point, fire point, and cloud point. In conformity with the ASTM D6751 Official Method, the flash point, cloud point, and pour point of biodiesel must be at least 130 °C, -3 to 12 °C, and -15 to 10 °C, respectively. In this research, the biodiesel became a product that fell into the standard ASTM range. In conformity with the findings of the pour point, the

Table 3. Effects of traditional- and ultrasound-assisted transesterification on energy consumption and physicochemical constants of inedible olive oil methyl esters.

Constant	Transesterification method	
	Traditional	Ultrasound
Physical constants		
Kinematic viscosity (mm^2/s)	5.385±0.000[a]**	4.201±0.000[b]
Density (kg/m^3)	886.9347±0.0135[b]	892.9963±0.3292[a]
Refractive index	1.4553±0.0004[a]	1.4530±0.0000[b]
L*	58.13±0.85[b]	57.66±5.13[a]
a*	-8.43±0.43[a]	-6.33±2.08[b]
b*	46.40±1.14[a]	23.50±3.03[b]
Heating constants (ºC)		
Flash point	180.5±3.5[a]	181.5±2.1[a]
Fire point	190.5±4.9[a]	193.5±0.6[a]
Cloud point	3.0±1.4[a]	4.0±0.0[a]
Pour point	-3.0±1.4[a]	-8.0±0.0[b]
Fatty acid profile (%)		
Palmitic acid	15.66±0.60**	16.47±0.12
Palmitoleic acid	1.42±0.03	0.95±0.12
Stearic acid	1.39±0.40	2.30±2.60
Oleic acid	71.07±0.08	71.36±2.60
Linoleic acid	9.95±0.14	8.73±1.30
α-Linolenic acid	0.51±0.16	0.19±0.00
Energy consumption		
Transesterification reaction (kWh)	0.227	0.045
Separation of alcohol (kWh)	0.063	0.063
Separation of catalyst (kWh)	0.008	0.008
Drying (kWh)	0.071	0.071
Total energy consumption (kWh)	0.369	0.217
Specific energy consumption (kWh/kg)	4.775	2.17

** Mean ± standard deviation; Number of replicates for each analysis: 3; Statistical test: ANOVA and multiple comparison of means using Duncan's multiple range test; Degree of significance: $P < 0.05$; In each row, means with different letters are significantly different.

biodiesel that had been produced by UAT eventually showed less viscosity which allowed it to be pumped at more efficient rates.

3.4.3. Energy consumption

Table 3 shows energy consumptions by UAT and TAT during the transesterification step and further through all of the steps of biodiesel purification. The percentages of energy consumption during the transesterification step were 20.74 and 61.52% for UAT and TAT, respectively. The amount of energy that was consumed during the transesterification step in TAT was 0.227 kWh, which is at least five-fold compared to that of the UAT (0.045 kWh). However, during their purification steps, the energy consumptions for both UAT and TAT were equal. TAT requires 4.775 kWh/kg to produce 1 kg biodiesel. This amount was at least 2 times higher than that required by the UAT (2.170 kWh/kg). It can be concluded that UAT can significantly increase the final yield, shorten the reaction time and reduce the energy consumption (Motasemi and Ani, 2012). The main production costs of biodiesel strongly depend on energy consumption during the transesterification step in addition to the cost of feedstock. Processing inedible olive oil by UAT has many advantages for biodiesel production. These advantages are primarily a lower energy consumption and a lower feedstock cost.

4. CONCLUSION

A comprehensive purpose of this research involved finding descriptions of how the ultrasound method can affect the esterification and transesterification of inedible olive oil compared to the traditional hot plate mixer method. No significant differences were observed between the yield obtained by UAE and TAE, but the duration of the reaction time required by UAE was significantly 4 times shorter than that of TAE.

Processing inedible olive oil by UAT showed an optimal performance, compared to that of the TAT method. The conditions in which UAT can operate optimally are an ultrasound power level of 90 W, a methanol/oil mole ratio of 9, a catalyst concentration of 1.0%, a reaction time of 30 min, and a reaction temperature of 55 °C. The UAT can significantly increase the weight of yield, purity, and final yield of the produced biodiesel (93.68, 98.95, and 92.69%, respectively) compared to TAT (88.66, 87.17, and 77.28%, respectively).

The UAT can operate within 4 times shorter amount of time and can consume lower amounts of energy compared to the TAT method. Therefore, the UAT evidently has advantages as a method for producing biodiesel by processing inedible olive oil which would be otherwise considered as a waste if it is not used in this regard and as such.

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