



## Biodiesel Production from *Amygdalus scoparia* Using KOH/Al<sub>2</sub>O<sub>3</sub> Catalyst: Optimization by Response Surface Methodology

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### ABSTRACT

The transesterification of *Amygdalus scoparia* oil to biodiesel was performed and examined through the electrolysis method in the presence of KOH/Al<sub>2</sub>O<sub>3</sub> as a heterogeneous catalyst at room temperature. A KOH/Al<sub>2</sub>O<sub>3</sub> as solid base catalyst was prepared through the impregnation of Al<sub>2</sub>O<sub>3</sub> with KOH solution (concentration of 25g in 100 mL deionized water). The catalyst was analyzed using X-ray diffraction (XRD), scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDS). The transesterification key variables such as reaction time, methanol to oil molar ratio, and catalyst weight were optimized by applying the central composite design (CCD) approach. The maximum yield of 94% was obtained at the methanol to oil ratio of 10:1, catalyst weight of 1.6 wt/v%, voltage of 10 V, a reaction time of 2.30 h, 10 wt% acetone at room temperature (25 °C). The characterizations of *Amygdalus scoparia* oil and biodiesel were specified using a gas chromatography-mass spectrometry (GC-MS) and Fourier-transform infrared spectroscopy (FTIR) analyses.

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### INTRODUCTION

The modern industry has been mainly dependent on fossil-based fuels as the source of energy that petroleum-based fuels have played an important role in this respect. Because of some disadvantages to fossil fuels are nonrenewable and they are not suitable as the ideal option [1]. Another noticeable problem of them is the threat their emission poses for the environment and human health. The pollutant emissions such as NO<sub>x</sub>, SO<sub>x</sub>, CO, CO<sub>2</sub>, and Pb are among some of the most well-known contaminants released in the environment as a result of the processing and use of these fuels [2]. Such problems have led the people involved in the environment preservation and issues around the industry to start considering some alternative energy sources which are entirely devoid of these problems or to at least have them with a lower degree [3]. Currently, the use of low carbon energy sources and the introduction of environmentally-friendly green technology are appeared to be a viable option. One

of the commonly-used types of these alternative energy sources is biodiesel that typically has significant advantages in comparison with emission, biodegradable, and environmentally-benign furthermore, it commonly has a high flash point and cetane number that considerably reduce the consumption of fossil fuel. Biodiesel is most commonly obtained through the transesterification of triglyceride oil in present of suitable homogeneous or heterogeneous catalyst. In other words, it is a mixture of methyl esters with long-chain fatty acids produced through the transesterification process of animal fats, edible or non-edible vegetable oil and waste cooking oil [4]. Today, use of non-edible vegetable oils as feedstock for biodiesel production has attracted interest of researchers. Various oils were reported as biodiesel feedstock include *Brucea javanica* seeds oil, *Capparis spinosa* oil, *Prunus armeniaca* oil, *Firmiana platanifolia* L.f. oil, *Jatropha curcus*, and *virgin cottonseed* oil. Based on the literature, various oil seeds can be utilized for biodiesel production. At present, biodiesel production in

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Middle-East is done in the preliminary researches and on the laboratory scale [5]. It should be looking for feedstock oil that can grow in different climate conditions, be significantly available, and its seeds contain a large amount of oil [6].

Almond is one of the most common plants on earth that grows in different countries. This plant belongs to the Rosaceae family. Middle East is located in the dry and half-dry region of the world. Almond is known as one of the oldest fruit trees in Middle East that its fruits used as snacks food or applied as components in a wide diversity of food processes principally in culinary and bakery. Middle East is one of the major producers of almonds in the world that *Amygdalus scoparia* is the most significant among the wild kinds of almond cultivated in Middle East because it contains large amounts of oil (about 50% in dried seed). *Amygdalus scoparia* oil has high amounts of unsaturated fatty acids like oleic and linoleic acids [7]. There are few reports that *Amygdalus scoparia* oil has been used as a feedstock to produce biodiesel. Vares et al. [8] used *Amygdalus scoparia* as a new source for biodiesel production. They obtained the highest Fatty acid methyl ester (FAME) yield of 97.31% under optimum conditions of 1wt.% catalyst concentration, 7:1 methanol to oil molar ratio.

The homogeneous catalysts such as base ones like KOH and NaOH, or acidic ones like  $H_2SO_4$  and HCl have a low cost, and they are most capable of industrial usages. But their separation processes from products are expensive and difficult, and also they cannot be recovered after the separation for further use. On the contrary, the heterogeneous catalysts are more applicable because of their more convenient in the separation and recovering stages, more eco-friendly manner, high activity in diverse and near-ambient conditions, and particularly in solid-state. Also, these catalysts do not mix with the alcohols used in the transesterification process.

Among typical heterogeneous catalysts,  $Al_2O_3$  is widely used in the industry processes such as reforming, steam reforming, and hydrogenation due to its specific physicochemical properties like high specific area, pore size, pore-volume, and thermal stability. Also, it is utilized as a support for the catalyst with high active regions to synthesize biodiesel. Ilgen and Akin used canola oil as a primary feedstock for biodiesel production in presence of KOH/ $Al_2O_3$  catalyst. The highest yield of produced biodiesel was 89.40% [9]. Ma et al [10] synthesized KOH/ $Al_2O_3$  as a heterogeneous catalyst by the wet impregnation method for biodiesel production from *Chlorella vulgaris* microalgae. The maximum yield of biodiesel production was attained by 89.53%.

Biodiesel is obtained through several methods such as ultrasound, reflux, microwave, and electrochemistry. The electrochemical is a practical method among them in the environmental and process applications [11]. Some processes of potentiometry, voltammetry and amperometry, detection are offered numerous advantages

of detection, selectivity, and ecological considerations. The electrolysis as an electrochemical process is a prominent and favored method on several grounds. Similar to other electrochemical processes, it can be relatively cost-effective compared with other methods, while being simple to conduct. For instance, in algae harvesting, where the minimum addition of chemicals is allowed, the electrochemical methods are a practical option that imposes low cost while allowing innovative and effective practice. Guan and Kusakabe [12] were reported biodiesel production using the electrolysis method for the first time. They synthesized biodiesel from waste cooking oil (WCO) with a high fatty acid methyl ester (>97%) and high water content (total reaction mixture > 2wt%). The catalyst used in the transesterification reaction was sodium chloride, and they achieved the optimum FAME yield of 97%. Helmi and Tahvildari [13] investigated the effects of loaded KOH concentration on clinoptilolite as the support. Their outcome showed that the biodiesel yield was 90% in the presence of 2wt% KOH/Clinoptilolite as the catalyst, 3wt% THF as the co-solvent, alcohol/oil molar ratio of 6:1, a voltage of 10 V, and reaction time of 4 h.

In the current study, biodiesel is synthesized from *Amygdalus scoparia* oil as a potential feedstock using the KOH/ $Al_2O_3$  catalyst by electrolysis method. The process optimization was performed by the response surface methodology (RSM) via central composite design (CCD) to achieve the maximum yield of biodiesel. The effects of variables such as catalyst concentration, methanol to oil molar ratio, and reaction time were also investigated. Finally, the physical properties of the biodiesel produced at the optimum conditions were characterized.

## EXPERIMENTAL

### Materials and method

Alumina ( $Al_2O_3$ ) powder, sodium sulfate (99%), n-Hexane (98%), acetone (99%), potassium hydroxide (99%), and methanol (99%) were supplied from Merck Company (Darmstadt, Germany). The fruit sample collected from Dezful in Khuzestan province, Iran (July 2019).

### Characterization technique

The following devices were used in the experiments: BATE PC21 furnace, RLABINCOM-81 stirrer (Germany), Lab Tech oven, DC Power Supply model 8303, graphite electrodes for electrolysis cell, and Fourier transform Infrared spectroscopy (FTIR, Thermo model 8700). The GC-MS analysis performed on an Agilent 5973 GC and 6890 Mass spectrometer. The samples were analyzed by X-ray Diffraction (XRD), scanning electron microscopy (SEM, philipsXL30 ESEM) to characterize the catalyst.

### Extraction of *Amygdalus scoparia* oil

*Amygdalus scoparia* seeds are manually divided into kernels and erased impurities. They dried in the shadow for a week to remove the moisture. Then, their fruit pared, and their kernels were comminuted through milling. 200 g *Amygdalus scoparia* powders were put inward filter paper. Powdered seeds and n-hexane as solvent (1:4 w/v) were put in a Soxhlet apparatus. The whole system was warmed up in a heating mantle at a constant temperature of 75 °C for 6h. Then, the oil was obtained in the flask, and the solvent was recovered by a vacuum rotary [14]. The extraction yield of oil could be measured based on Equation (1).

$$\text{Oil yield\%} = \frac{\text{Weight of produced oil}}{\text{Weight of used sample}} \times 100 \quad (1)$$

### Pre-treatment and oil characterization

Before the reaction, the oil was heated for 1h at 105 °C to remove moisture content in the oil, and then the sodium sulfate used to complete the dewatering process. The titration method was applied to measure the initial acid amount of the oil. The initial acid amount in the *Amygdalus scoparia* oil was 2.7 mg KOH/ g oil. Based on the research result, since the acid amount was less than 3mg KOH/g oil, the esterification reaction was not occurred [15].

The gas chromatography-mass spectroscopy analysis was performed to determine the fatty acid content of the *Amygdalus scoparia* oil, and its result presents in Figure 1. The nitrogen was applied as a carrier gas according to the ASTM D-1983 test method [16]. Other physical and chemical properties of the oil include density, viscosity, cetane number, flash, pour, and cloud points were measured and compared with the diesel fuel properties presented in Table 1.

### Catalyst preparation

In the current study, the alumina was impregnated with a KOH solution reported by Hajy Heidar and Tahvildari [17]. First, 25g of KOH was added to 100mL of distilled water. Then, the required amount of alumina powder was added to the solution (1:4 weight ration of Al<sub>2</sub>O<sub>3</sub> to KOH). The mixture was subsequently stirred at 25 °C for 24 h. Next, the alumina and KOH solutions were separated through filtration using a vacuum filter system. Afterward, it was dried in an oven at 90°C for 12 h. Finally, it was calcined in the furnace at 400 °C for 4 h.

### Transesterification reaction

An electrolysis cell containing two graphite plate electrodes (20mm × 20mm) at a distance of 10mm was used. This cell contains 50mL of the reaction mixture of methanol, oil, acetone (as co-solvent), deionized water, and KOH/Al<sub>2</sub>O<sub>3</sub> as the catalyst. The methanol to oil molar ratio was set on 4:1 to 14:1. The catalyst to oil ratio was

**Table 1.** Physicochemical properties of *Amygdalus scoparia* oil

Properties	Unit	Oil	Method
Density (15°C)	Kg/m <sup>3</sup>	893	ASTM D287
Viscosity (40°C)	mm <sup>2</sup> /s	25.13	ASTM D445
Pour point	°C	-8.82	ASTM D97
Cloud point	°C	-1.841	ASTM D93
Flash point	°C	135	ADTM D93

0.66 to 2.34wt/v%. Moreover, 2wt% of deionized water was also added to the mixture. The electrolysis voltage was adjusted in 10V. The transesterification reaction was carried out at room temperature (25 °C) [18]. At the end of the reaction, the KOH/Al<sub>2</sub>O<sub>3</sub> catalyst separated by centrifuge. The reaction mixture was placed in the separating funnel, the products of the FAME and glycerol phases were separated in the top and bottom phases after a few minutes, respectively. Biodiesel was washed with the deionized water (60 °C) to remove any remaining methanol and catalyst until pH was neutralized. Finally, the FAME yield was calculated by Equation (2):

$$\text{Biodiesel yield (\%)} = \frac{\text{Weight of FAMES}}{\text{Weight of Oil}} \times 100 \quad (2)$$

### Experimental design

The response surface methodology (RSM) consists of a group of mathematical and statistical techniques that provides empirical models based on experimental data. The conditions of biodiesel production were optimized using central composite design (CCD) combined with RSM. Based on the 2<sup>K</sup>+2k+6 formula, twenty runs were designed according to the correlation that k shows the independent parameter equaled to 3 in this study. The regression analysis was carried out based on the experimental data and expressed by the empirical second-order polynomial model depicted in Equation (3).

$$Y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{i=1}^2 \sum_{j=i+1}^3 \beta_{ij} X_i X_j + \varepsilon \quad (3)$$

where Y is the predicted response (i.e., FAME yield), β<sub>0</sub> is an equation constant, β<sub>i</sub> is the linear coefficient, β<sub>ii</sub> is the quadratic coefficient, β<sub>ij</sub> is interaction coefficient made from regression programming, K shows the number of the independent variables, X<sub>i</sub> and X<sub>j</sub> are independent factors, and ε is the error [19].

The experiments were carried out by applying the CCD design to investigate the effects of independent parameters and obtain optimal conditions for biodiesel production. Table 2 shows the independent variables such as catalyst concentration (A), methanol to oil molar ratio (B), and time (C).

**Table 2.** RSM-CCD for transesterification reaction

Factors	Unit	Symbol	Low level	High level
Catalyst weight	w/v%	A	0.66	2.34
methanol to oil	molar ratio	B	4	14
Time	h	C	0.32	2.68

### Physicochemical properties of biodiesel

The physicochemical properties of produced biodiesel include viscosity (ASTM D445), density (ASTM 1298), carbon residue (ASTM D4530), cetane number (ASTM D613), and water content (ASTM D2709) measured and compared with the ASTM standard [20].

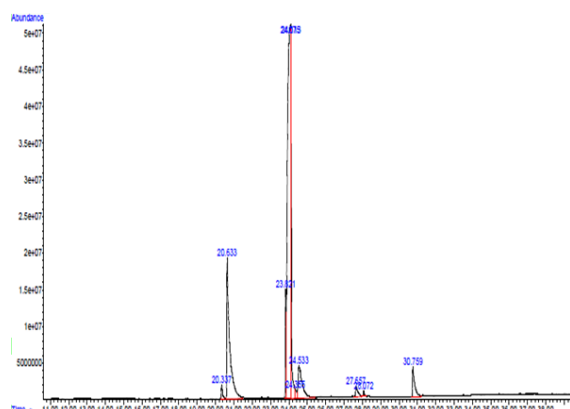
### Catalyst reusability

In order to investigate reusability of KOH/Al<sub>2</sub>O<sub>3</sub> as an alkali catalyst, end of the each experimental run, the catalyst separated by centrifuging for 10 min at 3000 rpm, and then the catalyst washed with methanol and n-hexane to remove impurities like residuals oil and glycerol, and finally dried in the oven at 60 °C for 2 h. At last reused catalyst was used to next reaction cycles under optimum reaction condition suggested by RSM-CCD method.

## RESULTS AND DISCUSSION

### GC-MS analysis of *Amygdalus scoparia* oil and characterization

From chromatogram, the fatty acid profile of *Amygdalus scoparia* oil shown in Figure 1 and Table 3. The presence of double bonds increases the degree of unsaturated fatty acid chains and leads to the autoxidation of fuels. Based on Table 3, unsaturated fatty acid (oleic acid and linoleic acid) have a higher portion of the total fatty acid profile (87.1%). Also, the color of the oil is light yellow with no smell.



**Figure 1.** The result of GC-MS analysis for *Amygdalus scoparia* oil

**Table 3.** Fatty acid profile of *Amygdalus scoparia* oil by GC-MS analysis

Fatty acid profile	Molecular formula	Time (min)	By weight (%)
Oleic acid	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	24.73	62.69
Linoleic acid	C <sub>18</sub> H <sub>32</sub> O <sub>2</sub>	20.63	25.41
Palmitic acid	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	23.82	9.71
Palmitoleic acid	C <sub>16</sub> H <sub>30</sub> O <sub>2</sub>	24.53	1.19
Myristic acid	C <sub>14</sub> H <sub>28</sub> O <sub>2</sub>	27.65	1

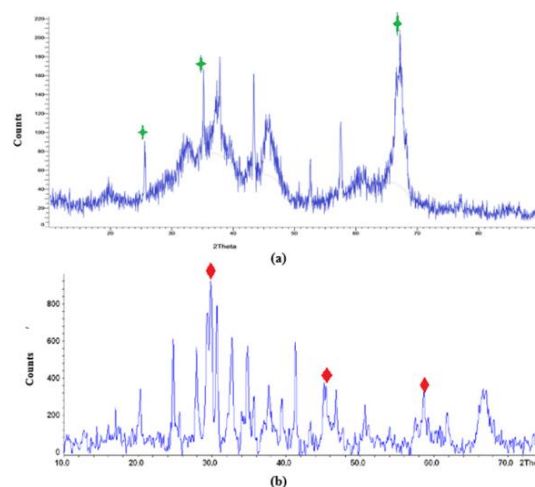
### Catalyst characterization

#### X-ray Diffraction (XRD)

The XRD analysis was conducted to determine the variation of the structure, bulk phase, and crystallinity of the raw Al<sub>2</sub>O<sub>3</sub> and KOH/Al<sub>2</sub>O<sub>3</sub> catalyst depicted in Figures 2 (a) and 2 (b), respectively. Based on the XRD pattern of the catalyst, two essential components were Al<sub>2</sub>O<sub>3</sub> and KAlO<sub>2</sub> when the calcination was done. The specific diffraction peaks of Al<sub>2</sub>O<sub>3</sub> at 2θ of 25.61°, 35.19°, and 66.61°. With the addition of KOH solution to Al<sub>2</sub>O<sub>3</sub>, the intensities of the generic diffraction peaks reduced that displays strong interaction between KOH solution and Al<sub>2</sub>O<sub>3</sub>. The diffraction peaks of KAlO<sub>2</sub> appears at 2θ of 32.73°, 47.09°, and 58.6° that was attributed to orthorhombic KAlO<sub>2</sub> types formed on the catalyst surface [21, 22]. Through calcination of KOH molecules on the Al<sub>2</sub>O<sub>3</sub> surface, they transformed into K<sub>2</sub>O. The K<sub>2</sub>O has an essential role in the transesterification of oil into fatty acid methyl esters because of its high catalyst activity.

#### Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) analyses

The comparison of the two SEM and EDX patterns of raw Al<sub>2</sub>O<sub>3</sub> as the support and KOH/Al<sub>2</sub>O<sub>3</sub> are shown in



**Figure 2.** The XRD pattern of a) raw Al<sub>2</sub>O<sub>3</sub> as support b) KOH/ Al<sub>2</sub>O<sub>3</sub> catalyst

Figures 3 (a) and (b), respectively. Figure 3 (a) shows that the SEM morphology of the raw  $\text{Al}_2\text{O}_3$  had a smooth surface and small particles on it, and only Aluminum and oxygen elements characterized by the EDX analysis. Figure 3 (b) depicts that a considerable amount of KOH is adsorbed on the  $\text{Al}_2\text{O}_3$  surface through the loading of  $\text{Al}_2\text{O}_3$  by KOH and forms a changed structure on the  $\text{Al}_2\text{O}_3$  support indicating excellent repatriation of KOH on the  $\text{Al}_2\text{O}_3$  surface. The catalyst structure, which is adsorbed KOH on the surface of  $\text{Al}_2\text{O}_3$ , is similar to raw  $\text{Al}_2\text{O}_3$  [23].

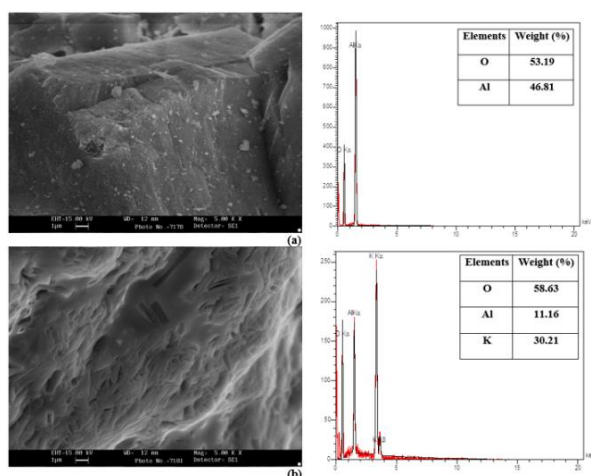
### Optimization of transesterification reaction by CCD-RSM

The obtained results of each run carried out on *Amygdalus scoparia* oil in the electrolysis method are presented in Table 4. The model of FAME yield for prediction of actual values for each run in terms of coded factors of the independent parameters is illustrated in Equation (4).

$$\text{FAME Yield} = 88.02 + 4.18A + 8.86B + 6.09C - 2.83AB - 2.71A^2 - 9.53B^2 - 5.77C^2 \quad (4)$$

The p-value of less than 0.0001 and the F-value of 51.24 shows that the model is significant at the 98% confidence level. Besides, if the lack of fit was insignificant, it shows the sufficiency of the predicted model. The analysis of variance (ANOVA) tests are conducted, and its results are represented in Table 5. The quality of the mathematical model is determined by the value of the correlation coefficient ( $R^2$ ), predicted determination coefficient (Pre- $R^2$ ), and adjusted determination coefficient (Adj- $R^2$ ) with values of 0.9788, 0.9008, and 0.9597, respectively.

Equation (4) has been applied to examine the result of experimental parameters on FAME yield and also investigate the regression model quality that is the main section of the data analysis method because if results are



**Figure 3.** SEM and EDX analysis of (a) raw  $\text{Al}_2\text{O}_3$  support (b) SEM micrographs of KOH/ $\text{Al}_2\text{O}_3$

**Table 4.** CCD-RSM of independent variable of transesterification reaction

Run	A:catalyst weight	B:methanol to oil	C:Time	FAME Yield
	w/v%	molar ratio	h	%
1	1.5	14	2	78.23
2	0.66	9	2	72.77
3	2	6	1	61.51
4	1.5	9	2	89.48
5	1.5	9	3.68	85.12
6	1	6	1	46.94
7	1.5	9	2	87.62
8	1	12	3	77.36
9	2.34	9	2	89.85
10	1	12	1	74.74
11	1.5	9	2	83.35
12	2	6	3	75.16
13	1.5	9	2	86.53
14	2	12	1	73.64
15	1.5	4	2	46.78
16	2	12	3	85.59
17	1.5	9	2	91.44
18	1.5	9	0.32	60.22
19	1	6	3	59.98
20	1.5	9	2	89.36

poor or misleading, the model is not proper. Therefore, diagnostic plots are studied in Figure 4. Figure 4 (a) illustrates the normal probability plot indicating the difference between actual and predicted values of FAME yield. The vicinity of all points to a straight line demonstrates an acceptable agreement between the values. The RSM analysis can predict the actual values well. When the plot is s-shaped, the residuals do not follow the normal distribution because a wrong model was chosen, and an additional variation in the response residuals is essential. The actual and predicted values of FAME yield are indicated in Figure 4(b). The actual values of response are achieved from each run in Table 4, and the predicted values are calculated by Equation (3). From Figure 4(b), the values of Adj- $R^2$  and Predicted- $R^2$  were measured 0.9788 and 0.997, respectively. Furthermore, the adjusted- $R^2$  value is high enough to demonstrate the significance of the model [24]. The outlier t plot for all experimental runs are illustrated in Figure 4(c) for the transesterification reaction that describes the exact value of the residuals for each run. Also, any run with a large residual could be easily

**Table 5.** ANOVA for quadratic biodiesel model

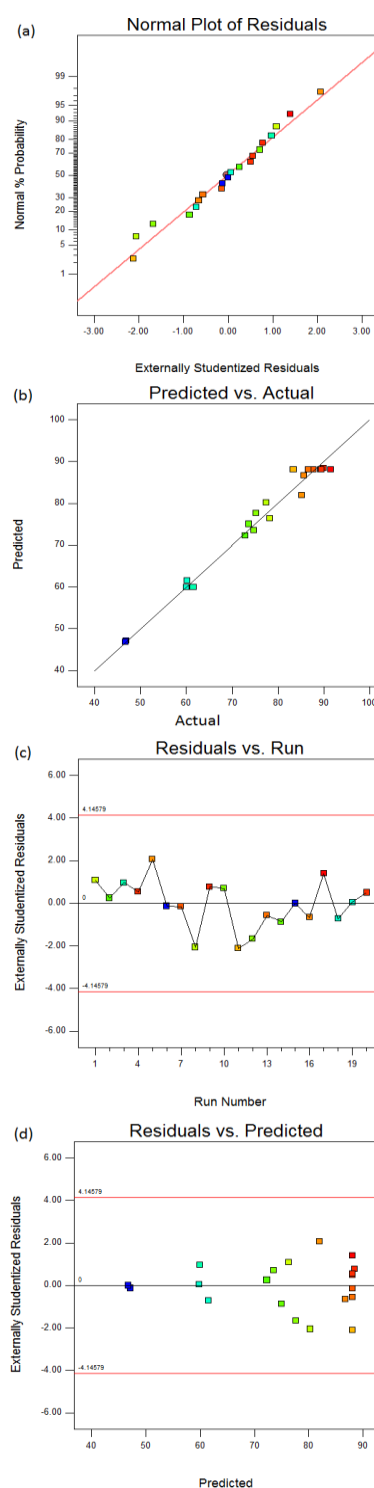
Source	Sum of Squares	df	Mean Square	F-Value	p-value
Model	3624.97	9	402.77	51.24	< 0.0001
A-catalyst weight	315.14	1	315.14	40.09	0.0011
B-methanol to oil	1065.07	1	1065.07	135.50	< 0.0001
C-Time	506.00	1	506.00	64.38	< 0.0001
AB	63.96	1	63.96	8.14	0.0172
AC	12.35	1	12.35	1.57	0.2385
BC	18.36	1	18.36	2.34	0.1574
A <sup>2</sup>	105.39	1	105.39	13.41	0.0044
B <sup>2</sup>	1271.46	1	1271.46	161.76	< 0.0001
C <sup>2</sup>	478.40	1	478.40	60.86	< 0.0001
Residual	78.60	10	7.86		
Lack of Fit	38.81	5	7.76	0.98	0.5106
Pure Error	39.79	5	7.96		
Cor Total	3703.57	19			
R-squared	0.9788	AdjR-squared	0.9597		
Mean	75.78	PredR-squared	0.9008		
C.V%	3.70	Adeq precision	21.018		

identified. Generally, a threshold of standard deviation is used to describe an outlier. This plot exhibits the range of actual to predicted values. All of the standard residuals lie well within the  $\pm 4.16$  interval [24]. If the actual data are beyond this interval, it shows an operator error in the actual data or an error possibility in the model [25]. Based on Figure 4(d), there was no actual data outside the interval that elucidates a good estimation between the model and response surface. The residuals of the predicted FAME yield plot are illustrated in Figure 6(d). In this plot, the scatter of the data should be random, indicating that the changes in the primary observation are not related to the values of the response [26].

#### The effect of independent parameters on fame yield

The interaction effects between the independent parameters of catalyst weight (A), methanol to oil molar ratio (B), and reaction time (C) is showed in Figure 5. In this case, the effect of two parameters on the FAME yield is investigated, and the third parameters are considered constant [27].

Figure 5 (a) illustrates the effects of methanol to oil molar ratio and catalyst weight on the FAME yield when the time is constant. The FAME yield is enhanced from



**Figure 4.** (a) Normal probability of residuals plot (b) the predicted response and the studentized residuals plot (c) the outlier t plot (d) the actual and predicted plot

72.77% to 92.77% when the catalyst weight and methanol to oil ratio are increased from 0.66 to 1.79w/v. % and 4:1 to 9.76:1, respectively. Because of the low catalyst concentration, there are insufficient active sites for the

reaction, but the active site increased as the catalyst concentration increases [28]. As the catalyst concentration increased to 2.34w/v%, the FAME yield hardly decreased. Therefore, the suitable catalyst concentration selected 1.76w/v.%

Figure 5(b) shows the effect of catalyst weight and reaction time while methanol to oil fixed. At a low reaction time of 0.32 h and catalyst weight 0.66 w/v. %, the FAME yield was 60.22%. When the time of transesterification reaction increased to 2.4 h and catalyst weight enhanced to 1.79 w/v% the FAME yield was 92.77%. But the FAME yield was reduced when the reaction time increased to 2.4h due to reversible transesterification reaction at a long time [29].

The transesterification reaction of *Amygdalus scoparia* oil carried out in a constant catalyst concentration of 1.79 w/v% and reaction time of 2.4 h with different molar ratios of methanol to oil. Figure 5(c) indicated the interaction effects of methanol to oil molar ratio and reaction time on FAME yield. It can be seen that the FAME yield increased from 46.87% to 92.77% as the methanol to oil enhanced from 4:1 to 9.76:1. As the methanol amount increases, the concentrations of the catalyst and reactant were decreased. Moreover, it is difficult to recover the solvent at the higher ratios of methanol to oil. The optimum methanol to oil molar ratio was chosen 9.76:1, and the excess methanol was recovered by the vacuum rotary.

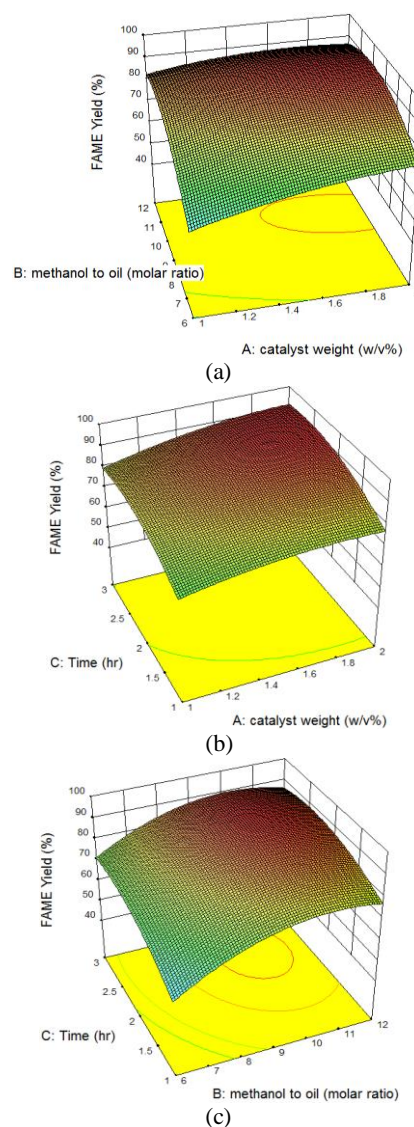
### Optimization of transesterification process

The RSM numerical optimization analysis was applied to achieve the optimal transesterification reaction conditions by considering the standard error (StdErr) that happened in the model. The upper and lower ranges of all factors are presented in Table 6. The predicted optimum reaction conditions for producing biodiesel from *Amygdalus scoparia* oil were predicted as catalyst weight 1.79w/v%, methanol to oil ratio of 9.76:1, and reaction time is 2.4 h. The maximum predicted FAME yield was 92.77% at these conditions. The biodiesel production from *Amygdalus scoparia* oil using KOH/Al<sub>2</sub>O<sub>3</sub> was performed three times under optimum conditions, and the average values were reported in the present study. The mean value of the obtained FAME yield was 94% given in Table 5. Table 6 depicts a comparison of optimum reaction condition and FAME yield using KOH/Al<sub>2</sub>O<sub>3</sub> with previous literatures. As it can be seen, the KOH/Al<sub>2</sub>O<sub>3</sub> as a basic catalyst has a high catalyst activity that produces biodiesel with a efficiency of 94% in a short period of time (2.30 h).

### FTIR analysis for *Amygdalus scoparia* oil and biodiesel

Fourier Transform Infrared (FTIR) spectroscopy was conducted to analyze the *Amygdalus scoparia* oil shown in Figure 6(a). The important difference in the FTIR spectrum of oil and biodiesel in the regions of 1377.73-

1464.15cm<sup>-1</sup> and 1162.21-1196.38cm<sup>-1</sup>. These peaks are seen in the biodiesel spectrum but not in the oil. The peaks at 1162.09cm<sup>-1</sup> and also in the range of 1377.73-1464.15 cm<sup>-1</sup> are related to the oil which they are not detected in the biodiesel FTIR spectrum [30]. The stretching vibrations at the 1743.59-1655.12 cm<sup>-1</sup> range are related to three carbonyls (C=O) functional groups of TG, and the C-O ester stretching vibration has some peaks at 1377.73-1162.09cm<sup>-1</sup> region. As well as, the specific peak appeared in the wavenumbers of 1464.15cm<sup>-1</sup> and 1377.73cm<sup>-1</sup> are associated with the bending vibration of the alkyl C-H groups linked to strong oxygen adsorption. The bending vibration of the alkyl C-H has a peak at 2927.26cm<sup>-1</sup> wavenumber [31]. Also, the peak at 3472.31cm<sup>-1</sup> represents -OH groups.



**Figure 5.** surface plots for interaction effects of (a) catalyst concentration and methanol to oil molar ratio, (b) catalyst concentration and reaction time, and (c) reaction time and alcohol/oil molar ratio

**Table 5.** Comparison between actual values and model optimized

Process parameters	Model optimized value	Experimental optimized value
FAME yield (%)	92.77	94
Catalyst weight (w/v%)	1.79	1.6
Methanol to oil molar ratio	9.76:1	10:1
time (h)	2.4	2.30

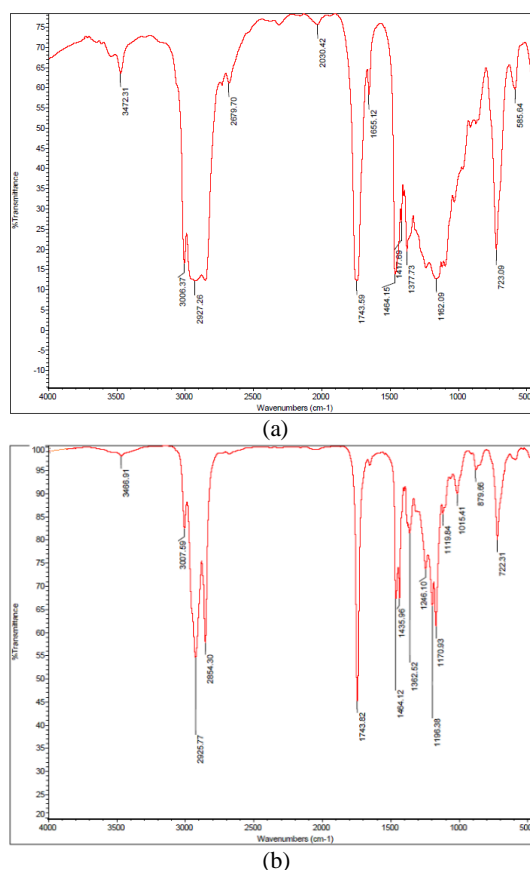
**Table 6.** Comparison of reaction condition and FAME yield for this study and previous letritures

Catalyst	Yield (%)	Time (h)	Catalyst weight	Methanol to oil molar ratio	Ref
KOH/Al <sub>2</sub> O <sub>3</sub>	94	2.30	1.6	10:1	Present study
NaOH	95.5	4	1	9:1	[25]
Na <sub>3</sub> PO <sub>4</sub>	98	1	1.25	8:1	[19]
H <sub>2</sub> SO <sub>4</sub>	97.32	1.30	2	6:1	[2]
KOH/meta Kaolin	96	1.20	3.5	17.5:1	[32]
KOH	90	0.5	1	6:1	[33]
NaOH-HZSM5		12	8	9:1	[34]
KOH	78.9	1	2	6:1	[35]
Mixed Clay-Eggshell	70.7	3	3	12:1	[36]
Coconut Waste	90	6	5	12.5:1	[37]

Based on the biodiesel FTIR spectra peaks in Figure 6(b), the peaks in the 1170.93-1196.38cm<sup>-1</sup> and 1362.52-1464.12cm<sup>-1</sup> ranges are related to the ester O-C bending vibration and C-H asymmetric bending, respectively. These peaks confirmed that the oil is converted to biodiesel, whereas they are not identified in the oil spectrum. The stretching vibration of the carbonyl group of triglyceride, diglyceride, and monoglyceride are indicated at a wavenumber of 1743.82cm<sup>-1</sup>. The stretching vibration of C-O ester groups has two peaks at the wavenumbers of 1196.38 and 1015.41cm<sup>-1</sup> [38]. Also, the OH alcohol and water indicated the peaks in the 3466.91cm<sup>-1</sup> region. These lower peaks show a higher quality for the produced biodiesel.

### Biodiesel characterization

The physical properties of biodiesel are very important to check that biodiesel is a viable option as a source of energy in the modern world or not. Some of the key

**Figure 6.** FTIR spectroscopy of a) *Amygdalus scoparia* oil, b) biodiesel

factors to be considered are viscosity (40 °C), cloud point, pour point, density (15°C), flash point, and cetane number determined in Table 7. These properties of the product were compared against the ASTM D-6751. The viscosity and density are the important considerations, particularly in low temperatures, refer to the fluidity of a liquid/fuel, fuel infusion, and combustion accurately. If the flash point stood at above in ASTM standard scales, it is safe for storage and transportation as a fuel. The cetane number is the index of combustion quality and the essential factor for the grounds of eco-preservation and public health that indicates the lag period of the fuel combustion in engines. A higher cetane number causes a shorter delay period in the engine [39]. The pour and cloud points are not universally set, and they are rather determined locally based on ambient climatic conditions such as the average temperature. The optimized biodiesel was within the standard range for the physicochemical properties.

### Catalyst reusability

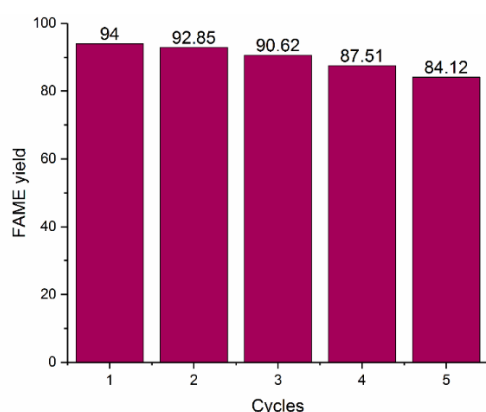
One of the advantages of using the homogenous catalysts is their low price. Nonetheless, the heterogeneous catalyst recovery reduced the process costs [40]. The catalyst recovery was performed at the optimum conditions of



**Table 7.** Physicochemical properties of optimized biodiesel

Index	Unit	ASTM standard	Biodiesel
Cetane number	-	Max 47	43.2
Flash point	°C	Min 130	145
Pour point	°C	-15 to 10	-5
Cloud point	°C	-3 to 12	-2
Viscosity (40°C)	mm <sup>2</sup> /s	1.9-6	4
Density (15°C)	g/cm <sup>3</sup>	0.881	725

1.6wt/v% catalyst weight, methanol to oil molar ratio of 10:1, and a reaction time of 2.3h. The KOH/Al<sub>2</sub>O<sub>3</sub> catalyst was separated and then washed, and finally dried. recycled catalyst was used for transesterification. Figure 7 illustrates the reusability result after the 5th cycle that indicates the reuse of the KOH/Al<sub>2</sub>O<sub>3</sub> as the catalyst. The FAME yield significantly decreased after 4th times recycle, and its value was 84.12% in the 5th cycle. A significant decrease is observed in the yield due to formations of K<sup>+</sup> and CH<sub>3</sub>O<sup>-</sup> caused by the leaching reaction [41].

**Figure 7.** Reusability test of KOH/Al<sub>2</sub>O<sub>3</sub> catalyst for transesterification reaction

## CONCLUSION

The electrolysis can serve as an appropriate method for the production of biodiesel obtained from high-water-content oils. The quantity and quality of the yield can be controlled through manipulating factors such as methanol molar ratio, catalyst weight, and reaction time. By considering these factors in the current study, the highest yield was achieved at 10:1 methanol to oil molar ratio, 1.6 wt/v% catalyst, the reaction time of 2.3 h at room temperature, 10wt% acetone as a co-solvent, a voltage of 10V, and a stirrer speed of 100 rpm. The FAME yield of 84.12% was obtained after the 5th cycle of KOH/Al<sub>2</sub>O<sub>3</sub>. The physicochemical properties of optimum biodiesel are in the ASTM standard range.

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Persian Abstract

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چکیده

ترانس-استریفیکاسیون روغن بادام کوهی تلخ به بیودیزل طی فرآیند الکترولیز با استفاده از الکتروگرافیت در حضور کاتالیست  $\text{KOH}/\text{Al}_2\text{O}_3$  در دمای اتاق انجام شد. کاتالیست ناهمگن  $\text{KOH}/\text{Al}_2\text{O}_3$  با استفاده از روش اشباع-سازی  $\text{Al}_2\text{O}_3$  در محلول  $\text{KOH}$  با غلظت ۲۵ گرم در ۱۰۰ میلی لیتر آب دیونیزه آماده شد. خواص کاتالیست با استفاده از آنالیزهای XRD، SEM و EDX بررسی شد. فاکتورهای اصلی واکنش ترانس-استریفیکاسیون مانند زمان واکنش، نسبت الکل به روغن و درصد وزنی کاتالیست با استفاده از روش طراحی مرکب (CCD) بهینه-سازی شدند. بالاترین بازده واکنش ۹۴٪ شد در شرایط بهینه نسبت ۱۰:۱ امتانول به روغن، درصد وزنی کاتالیست ۱/۶ wt/v%، ولتاژ ۱۰ V، و مدت زمان ۲/۳۰ h، ۱۰ wt% استون و در دمای محیط (۲۵ °C). خواص روغن بادام کوهی تلخ و بیودیزل با استفاده از آنالیز کروماتوگرافی گازی-طیف سنجی جرمی (GC-Mass) و طیف سنجی مادون قرمز (FTIR) بررسی شد.

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