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# Biodiesel production from sunflower oil using electrochemical reaction as a green, low-cost and room temperature method: modeling and optimization by RSM

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## ABSTRACT

Nowadays, conversion of waste feedstocks to biodiesel production as a renewable energy source is in a high demand. Biodiesel can be attained from oils and fats by transesterification process. Traditionally, biodiesel achieves from vegetable oils and raw materials as feedstock which should be free of water. The disadvantages of the process with the presence of water are catalyst consumption, effectiveness reduction, and soap formation. In this project, a catalyst-free method was used for biodiesel fuel production by using the electrochemical method with graphite electrodes in the presence of high values of water. Response surface methodology along with central composite design was used to optimize the reaction conditions. The impact of main factors, *i.e.* voltage (5-35V), $CH_3OH$/oil molar ratio (6–18), water content (2–10%), and reaction time (1–3 h), the effect on the biodiesel production are discussed. The maximum biodiesel production yield (81%) was obtained at the optimum conditions: the voltage of 35 V, $CH_3OH$/oil molar ratio of 18, the water content of 2%, and the reaction time of 3 h. Therefore, this study investigates the electrochemical method as a reliable approach in the biodiesel production analysis due to less sensitivity to the water.

*Keywords:* Biodiesel; Transesterification; Sunflower oil; Electrolysis method; RSM

## 1. Introduction

Energy saving and cost reduction projections are of great importance in environmental issues which attracted the researchers worldwide to look for alternative energy sources [1–4]. In this context, biodiesel seems to be a suitable alternative to the diesel fuel which is also very environmentally friendly. Biodiesel is usually produced via the transesterification of vegetable oils, fats, and waste cooking oil from food industry using alcohol in the presence of acid or base catalysts [5,6].

The methodology used in the production process is an essential tool for the efficient and cost-effective production of biodiesel. The conventional catalysts which are widely used for the biodiesel production are such basic catalysts as NaOH, KOH, and $NaOCH_3$ [7–9]. The biodiesel production reaction with these catalysts is fast, and the processing conditions are moderate. However, the use of the base catalysts is associated with some limitations. The presence of water/moisture during the transesterification reaction with basic catalysts leads to a decrease in the conversion of triglycerides to biodiesel fuel and causes the hydrolysis of

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triglycerides to free fatty acids and soap formation [10].This undesirable side-reaction consumes catalysts and decreases catalyst effectiveness. The effect of water content on the transesterification of beef tallow was investigatedby by [11]; they found that during the transesterification reaction, the presence of water generates a larger adverse effect on the transesterification. In a similar work, [12] showed that the presence of water in the biodiesel production reaction is a fundamental element in the traditional catalytic transesterification of vegetable oils. According to [13], when only 5% of water is added to the reaction chamber, the conversion of triglycerides to methyl esters reduce to 6%. The major advantage of using the acid catalyst is the presence of water and the free fatty acids content in raw materials. However, compared to the alkali catalysts, the acid catalysts have not been employed widely due to disadvantages such as costly separation, slower reaction rate, high reaction temperature, high molar ratio of alcohol to oil and purification steps, high corrosion, and non-reusability (Wilson and Clark, 2000; Tashtoush et al. 2004; Ding et al. 2011).Thus, there is a need to develop efficient and cost-efficient methods of biodiesel production from vegetable and waste oil with high water content.

Two techniques have been employed to optimise a multifactorial system: The *Single variable optimisation method (*one variable at a time) and the response surface methodology (RSM) [14]. The former is typically conducted by varying a single factor while keeping all other factors fixed at a particular set of conditions. This methodology is time-consuming with no interaction effects between variables and responses [15]. In the latter technique, multi-factors are studied at a single time. This method is very valuable for optimising the multiple *factor processes*. It has been applied to optimisation and evaluation of the interactive effects of independent factors in numerous chemical and biochemical processes [16,17]. Because biodiesel production is a complicated process, the use of the one-factor-at-a-time-optimization seemed to be time-consuming, and that it could also create misleading interpretations as there would be no interaction effects between variables. Thus, the application of the RSM along with the design of experiments (DOE) seems to be a superior option. In this study, an electrochemical method with graphite electrodes is introduced for the production of biodiesel from sunflower oil and waste cooking oil at room temperature in the presence of NaCl. To analyse the process, the effects of four significant independent variables, that is, electrolysis voltage, methanol/oil molar ratios, water content, and reaction time on the biodiesel production were studied.

## 2. Materials and methods

### 2.1. Reagents and materials

All chemical materials used in this project analytical grades and used without further treatment and purification. The sunflower feedstock used in this experimental work was produced by a commercial manufacturer (Nazgul, Kermanshah, Iran).The composition of fatty acids in the sunflower oil is provided in Table 1. The waste cooking oil (WCO) samples were collected after first time cooking. Standard heptadecanoic acid methyl ester (internal standard; C17:0) and other methyl esters [palmitate (C16:0), stearate (C18:0), oleate (C18:1), and linoleate (C18:2) were purchased from Sigma. Methanol (99.0%), potassium hydroxide (KOH), and n-hexane (99.5%) were purchased from Merck.

Table 1
Composition of fatty acids in the sunflower oil

| | |
|---|---|
| Palmitic acid (saturated) | 5.6 |
| Stearic acid (saturated) | 6.4 |
| Oleic acid | 27 |
| Linoleic acid | 54.8 |
| Other acid | 6.2 |

### 2.2. Biodiesel production method

In this study, an electrolytic cell was employed to produce biodiesel. The cell provided the sufficient volume of 200 mL containing two graphite electrodes (with the diameter of 40 mm and the length of 150 mm) and a distance of 40 mm, which separated the graphite electrodes. Both carbon plate cathodes were connected to the negative pole, and the carbon anode was connected to the positive pole of the DC power supply. The electrolysis cell was filled with 50 mL of a reaction mixture containing methanol, oil, THF, water, and NaCl as a supporting electrolyte. The methanol/oil molar ratio and THF/methanol molar ratio were adjusted based on the experimental design. NaCl concentration, which was based on the oil weight, was 1wt.%. The electrolysis was done using a constant voltage method. The electrolysis voltages were adjusted in the range of 5–35 V.

### 2.3. Analytical methods

The physical and chemical properties of the sunflower oil and biodiesel were determined using standard test methods. The FAME concentration expressed as the biodiesel purity of the product was determined by a gas chromatograph (Agilent Technologies, USA) equipped with a flame ionisation detector and a capillary column (BPX-70 great polar column, length: 50 m; internal diameter: 0.2 mm; and film thickness: 0.4 µm). Helium was exploited as the carrier gas at a flow rate of 0.7 mL/min. The temperature sequence in the oven was as follows: 5 min at 150ºC, 12ºC/min to 200ºC for 15 min, 3ºC/min to 252ºC for 7 min, and finally, 5 min at 260ºC. The temperatures of the detector and injector were 270ºC and 260ºC, respectively. The sample dissolved in n-hexane and 10 µL of the sample was injected into the column. Methyl hexanoate was employed as an analytical standard, and the FAME composition was quantified by the internal standard method. The FAME of the final product was quantified based on the retention time of each FAME standard sample and GC-Mass peaks. The most common peaks of FAME were observed at C16:0, C17:0, C18:0, C18:1 and C18:2 as depicted in Fig. 1. The following equations were used to determine the biodiesel [18].

$$W_{FAME} = \frac{\sum\left(A - A_{IS}\right)}{A_{IS}} * \left(\frac{C_{IS} * V_{IS} * M}{m}\right) \tag{1}$$

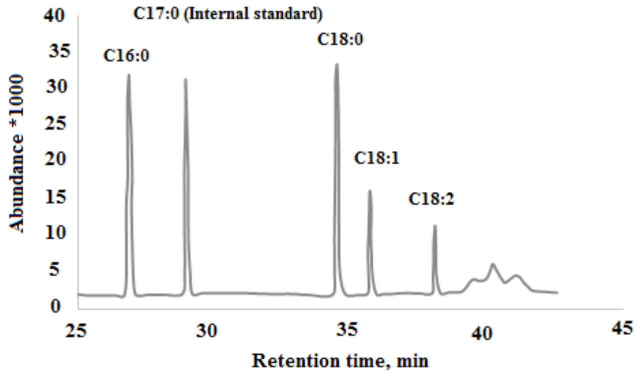

Fig. 1. A typical chromatogram of the sunflower oil.

$$Yelid = \frac{W_{FAME}}{W_{oil}} * 100 \quad (2)$$

where $W_{FAME}$ = produced methyl esters weight; $A_{IS}$ = peak area of standard; $V_{IS}$ = volume of the internal standard solution (mL); $M$ = weight of the biodiesel phase in the reaction mixture; $\sum A$ total peaks area of chromatogram; $C_{IS}$ = internal standard solution concentration (mg/mL); $m$ = weight of biodiesel for GC analysis; and $W_{Oil}$ = sunflower oil weight used in each reaction.

### 2.4. Experimental design

As a precise technique, the experimental design can be used to investigate the relationship among a set of input variables and output responses [19]. When the design of experiments (DOE)is used for optimisation of a response, it is called response surface methodology (RSM). Other conventional designs mostly used as second-order are central composite design (CCD), three-level factorial design, and Box–Behnken design (BBD) [20]. In this project, CCD was employed to derive a polynomial equation between the input variables and output responses. The CCD is an independent quadratic RSM design and can be a better alternative to the other models, because, compared to others, still provides comparable results, it also requires fewer design points. In the present study, the RSM and CCD were employed to optimise the four different operating variables statistically: (A) voltage, (B) $CH_3OH$/Oil molar ratio, (C) water content, and (D) electrolysis time, while holding biodiesel yield as the constant response variables. The experimental ranges of the input variables are shown in Table 2. Each experiment was conducted in duplicates,and the average yield of biodiesel was taken as the response variable Y. The yield of the biodiesel production was quantitatively analysed using GC-Mass. The main and interactive effects of the variables on the biodiesel production were assessed based on the central composite design plan (Table 3) and analysed by ANOVA. Analysis of variance (ANOVA) was used to examine the developed model's adequacy and the statistical significance of the regression coefficients. The experimental design consisted of 2N factorial points increased by 2N axial points and a centre point, where N is the number of variables. The four operating variables were examined at five levels, namely, (–1), (-0.5), (0), (0.5), and (+1). Consequently, 30 experiments (=$2^N$+2N+6, where N is the number of variables) were conducted with 25 tests organized in a factorial design (including 16 factorial points, 8 axial points, and 1 center point) and the remaining 5 involved the replication of the central point to get a good estimate of the experimental error. The axial points were located at (±α, 0, 0), (0, ±α, 0), and (0, 0, ±α) α is the axial point from the centre making the design rotatable. The entire design matrices of the experiments were calculated in a random sequence (the order of runs developed by DOE (Table 3) to minimise the effects of the independent factors.

Table 2
Experimental range and level of the independent variables

| Variables | Range and level | | |
|---|---|---|---|
| | –1 | 0 | 1 |
| Voltage, V | 5 | 20 | 35 |
| $CH_3OH$/Oil molar ratio | 6 | 12 | 18 |
| Water content, % | 2 | 6 | 10 |
| Electrolysis time, h | 1 | 2 | 3 |

### 2.5. Mathematical modeling

The design of experiments (DoE) and the response surface methodology (RSM) are mathematical and statistical techniques employed to decrease the number of experimental runs and evaluate the direct and crossed relations between experimental conditions and system responses. Also, this method fits empirical models to the experimental data and permits the response surfaces and counter-plots to be created for the system performance parameters of interest [16]. In this case, each response can be described by a second degree polynomial of the following type:

$$Y = \beta_0 + \beta_i X_i + \beta_j X_j + \beta_{ii} X_i^{\,2} + \beta_{jj} X_j^{\,2} + \beta_{ij} X_i X_j + \ldots \quad (3)$$

where $Y$ is the yield of the reaction (% production of bio-diesel); $\beta_o$ is the intercept term; $\beta_i$, $\beta_{ij}$ and $\beta_{ii}$ are the linear, interactive, and quadratic coefficients, respectively; and $X_i$ and $X_j$ are the independent variables (factors) under study. Analysis of variance (ANOVA) was calculated to analyse the individual linear, quadratic and interaction regression coefficient. The adequacy of the developed models and the statistical significance of the regression coefficients were tested by Design-Expert version 6.9 (State Ease, Inc.). The fitness of the polynomial equation to the responses was estimated by the coefficient of determination ($R^2$), the adjusted coefficient of determination ($R^2_{adj}$), and the predicted coefficient of determination ($R^2_{pred}$). The coefficient of determination ($R^2$) is described as the regression of the sum of squares proportion to the total sum of squares, which demonstrates the adequacy of a model. The high adjusted and predicted coefficient of determination also the model adequately fits the data [21]. The Fisher variation ratio (F-value) and the probability value (Prob > F) were employed to test the significance level of both regression model and coefficients, which demonstrated the interaction effects between each independent variable. In general, greater the F-value and

Table 3
Experimental conditions and results of central composite design

| Run | Variables | | | | Response (Biodiesel production) | |
|---|---|---|---|---|---|---|
| | Factor 1 | Factor 2 | Factor 3 | Factor 4 | Actual | Predicted |
| | A: Voltage, V | B:$CH_3OH$/Oil molar ratio | C: Water content, % | D: Electrolysis time, *h* | % | % |
| 1 | 35 | 18 | 10 | 3 | 51/7 | 50/26 |
| 2 | 35 | 12 | 6 | 2 | 45/4 | 47/19 |
| 3 | 35 | 18 | 10 | 1 | 35/4 | 35/84 |
| 4 | 20 | 12 | 6 | 2 | 43/1 | 40/49 |
| 5 | 20 | 12 | 2 | 2 | 55/5 | 51/92 |
| 6 | 5 | 18 | 10 | 1 | 23/8 | 22/44 |
| 7 | 20 | 12 | 6 | 1 | 30/6 | 34/745 |
| 8 | 20 | 12 | 10 | 2 | 28/9 | 29/06 |
| 9 | 5 | 6 | 2 | 1 | 28/7 | 29/12 |
| 10 | 20 | 6 | 6 | 2 | 29/9 | 30/93 |
| 11 | 20 | 12 | 6 | 2 | 45/2 | 40/49 |
| 12 | 5 | 6 | 10 | 3 | 22/4 | 22/87 |
| 13 | 35 | 6 | 2 | 3 | 52/4 | 51/0872 |
| 14 | 5 | 18 | 10 | 3 | 33/9 | 36/86 |
| 15 | 35 | 18 | 2 | 3 | 81/5 | 81/17 |
| 16 | 20 | 12 | 6 | 2 | 42/3 | 40/49 |
| 17 | 5 | 6 | 2 | 3 | 34/8 | 37/68 |
| 18 | 20 | 12 | 6 | 2 | 43/4 | 40/49 |
| 19 | 35 | 6 | 2 | 1 | 40/5 | 42/52 |
| 20 | 35 | 6 | 10 | 3 | 27/5 | 29/22 |
| 21 | 20 | 12 | 6 | 2 | 43/7 | 40/49 |
| 22 | 20 | 12 | 6 | 3 | 44/8 | 46/23 |
| 23 | 5 | 18 | 2 | 1 | 47/8 | 46/31 |
| 24 | 20 | 12 | 6 | 2 | 47 | 40/49 |
| 25 | 5 | 12 | 6 | 2 | 30/4 | 33/79 |
| 26 | 5 | 18 | 2 | 3 | 59/7 | 60/72 |
| 27 | 35 | 6 | 10 | 1 | 19/6 | 20/66 |
| 28 | 35 | 18 | 2 | 1 | 63/5 | 66/76 |
| 29 | 20 | 18 | 6 | 2 | 45/9 | 50/04 |
| 30 | 5 | 6 | 10 | 1 | 15/4 | 14/31 |

the smaller p-value (<0.05), more significant model can be created [22]. Furthermore, the validity of the models was determined based on the values of lack of fit. The values of lack of fit should be more than 0.05. Three-dimensional (3D) plots and their respective contour plots were obtained using the effect of the levels of two factors. Therefore, CCD results can be presented in a 3D graph with contours and could facilitate the analysis of the simultaneous interaction of the variables on the responses.

## 3. Result and discussion

### 3.1. Model fitting and statistical analysis

Thirty experimental data sets designed by DOE (Table 3) were analysed by multiple regression analysis and ANOVA. The individual linear (A, B, C, D), interaction (AB, AC, AD, BC, BD, CD) and quadratic ($A^2$, $B^2$, $C^2$, $D^2$) regression coefficient of the studied variables which were determined using Design Expert software (State Ease, Inc.) are listed in Table 4.The analyses of the variables factors were conducted by using Fisher's 'F' and Student 't' tests. The p-value was employed as a tool to check the significance of each variable and the interaction among the variables. Generally, with an increase in the magnitude of t and a decrease in the value of p, the corresponding coefficient term becomes more significant. P-values less than 0.0001 indicate that the model terms are significant, and values greater than 0.05 show that the model terms are not relevant. According to the ANOVA analysis, the positive linear effect of voltage (A), $CH_3OH$/oil ratio (B), the electrolysis time (D), and also the negative linear effect of the water content (C) were found to be signif-

Table 4

Estimated regression coefficients and corresponding to ANOVA results from the data of central composite design experiments before elimination of insignificant model terms

| Model terms | Coefficient estimate | Standard error | Sum of squares (SS) | Degree of freedom (DF) | Mean square (MS) | F-value | P-value | |
|---|---|---|---|---|---|---|---|---|
| Two factor intraction (2FI) | | | 5694/84 | 14 | 406/77 | 49/07 | < 0.0001 | Significant |
| A | 6/7 | 0/54 | 808/02 | 1 | 808/02 | 152/19 | < 0.0001 | Significant |
| B | 9/55 | 0/54 | 1643/56 | 1 | 1643/56 | 309/56 | < 0.0001 | Significant |
| C | –11/43 | 0/54 | 2352/98 | 1 | 2352/98 | 443/18 | < 0.0001 | Significant |
| D | 5/74 | 0/54 | 593/98 | 1 | 593/98 | 111/88 | < 0.0001 | Significant |
| A$^2$ | –1/35 | 1/43 | 4/77 | 1 | 4/77 | 0/90 | 0.3582 | Not significant |
| B$^2$ | –1/35 | 1/43 | 4/77 | 1 | 4/77 | 0/90 | 0.3582 | Not significant |
| C$^2$ | 2/94 | 1/43 | 22/44 | 1 | 22/44 | 4/23 | 0.0576 | Not significant |
| D$^2$ | –1/55 | 1/43 | 6/28 | 1 | 6/28 | 1/18 | 0.2939 | Not significant |
| AB | 1/76 | 0/57 | 49/70 | 1 | 49/70 | 9/36 | 0.0079 | Significant |
| AC | –1/76 | 0/57 | 49/70 | 1 | 49/70 | 9/36 | 0.0079 | Significant |
| AD | 1/187 | 0/57 | 22/56 | 1 | 22/56 | 4/25 | 0.0570 | Not significant |
| BC | –2/26 | 0/57 | 81/90 | 1 | 81/90 | 15/43 | 0.0013 | Significant |
| BD | 1/46 | 0/57 | 34/22 | 1 | 34/22 | 6/45 | 0.0227 | Significant |
| CD | –0/41 | 0/57 | 2/72 | 1 | 2/72 | 0/51 | 0.4849 | Not significant |

Table 5

Analysis of variance (ANOVA) for fit of biodiesel production efficiency from central composite design after elimination of insignificant model terms

| Model | Significant model terms | SD | *R*$^2$ | Adj. *R*$^2$ | Pred- *R*$^2$ | CV | Adeq. precision | PRESS | P value | F value | Probability for lack of fit |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Biodisel production, % 2FI model | A,B,C,D, AB, AC, BD | 3.13 | 0.96 | 0.95 | 0.94 | 7.7 | 30.06 | 369.2 | 0.0001 | 71.84 | *0.06* |

R$^2$: determination coefficient, Adj. R$^2$: adjusted R$^2$, Pred- *R*$^2$: predicted *R*$^2$, Adeq. precision: adequate precision, SD: standard deviation, CV: coefficient of variation, PRESS: predicted residual error sum of squares

icant model terms. However, the quadratic effect of the variables showed no significant effect on the response ($p>0.05$). Also, the interaction among AB, AC, BC, and BD produced significant effects on the biodiesel production (Table 4). Fitting data to the different models (linear, two-factor interaction (2FI), quadratic, and cubic) indicated that the 2FI is the most suitable for the description of the biodiesel production efficiency. The ANOVA results for the2FI model are listed in Table 5. The empirical relationship between the biodiesel production and the four test variables regarding the coded factors after the elimination of the insignificant factors is as follows:

$$\text{Biodiesel production} = +40.22+6.70A+9.56B-11.43C+5.74\quad D+1.76AB-1.76AC+1.19AD-2.26\quad BC+1.46BD \qquad (4)$$

The goodness of fit of the model was also validated by the determination coefficient (R$^2$). The ANOVA results showed that the actual, adjusted, and the predicted R$^2$ were 0.96, 0.95, and 0.94, respectively. To have a precise prediction, R$^2$pred, R$^2$ adj, and R$^2$act should not be bigger than 0.2. The high and closer values of R$^2$ show a perfect agreement between the predicted and actual data. Also, the validity of the models was determined by the values of lack of fit. The critical value for lack of fit is 0.05. The magnitude of lack of fit must be greater than 0.05 (in this case this value was 0.06).

Adequate precision (AP) is a measure of signal to noise ratio which compares the range of the predicted values to the average prediction errors. Ratios more than 4 is a sign of an adequate model discrimination which can be used to navigate the design space specified by the CCD (Torabi Merajin et al. 2014). In this study, the ratio of AP value was 30.06, which is greater than 4 and can be deemed satisfactory. Table 5 shows the effectiveness and ability of the 2FI model to predict biodiesel production at various conditions. The F-value was 71.84, and the P-value was <0.0001, which implies that the model is significant.

Other information regarding the fitting, adequacy, reliability, and the correlation between the observed and predicted data of the model performance are depicted in the

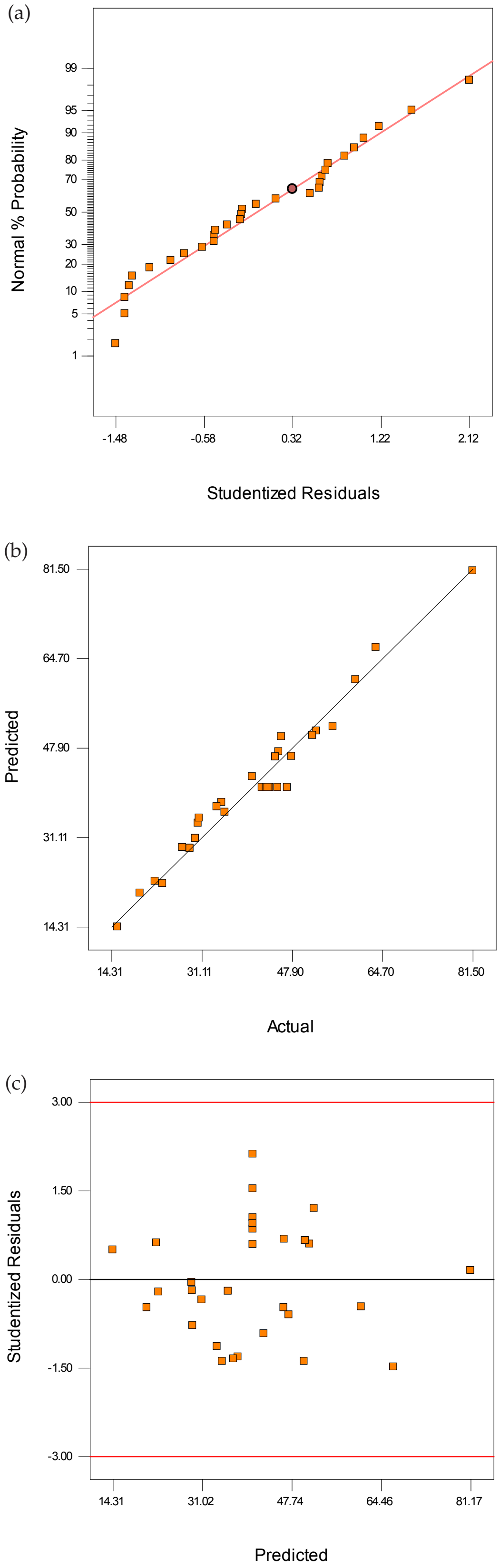

Fig. 2. (a) Normal probability plot of residual, (b) Predicted vs. actual values plot and (c) Studentized residual for biodiesel production.

diagnostic plots (Fig. 2a–c). Fig. 2a indicates the standard probability plot of the residuals for the biodiesel production, proving that the standard deviations between the actual and predicted response values follow a normal distribution [23]. As a graphical method, this plot is used to assess whether the data set is approximately normally distributed and also to identify substantive departures, if any, from normality. To be normally distributed, the data should form an almost straight line, and any departure from this straight line is a departure from normality. As indicated in this figure, the points form a nearly linear pattern, showing that the underlying errors are typically distributed as the residuals fall near to the straight line. As depicted in Fig. 2b, the predicted values of the biodiesel production efficiency obtained from the model and the actual experimental data are distributed very close to the straight line ($y = x$, $R^2 = 0.96$) which are in good agreement. The plots of the residuals against the predicted responses (Fig. 2c) check the assumption of the constant variance. The plots show that all points of the experimental runs are distributed randomly and that all values are within the ranges between –3 and 3. These findings show that the RSM proposed model is satisfactory and that the constant variance assumptions are confirmed.

### 3.2. Effect of the variables on the biodiesel production

To conduct an empirical study and a better understanding of the main consequences of the variables on biodiesel production, the three-dimensional (3D) surfaces plot was formed based on the model [Eq. (2)]. The outcome indicates that the biodiesel production is a function of 2 factors, while 2 other variables were kept at constant levels. Fig. 3 shows the 3D and counter-plots of the model for the biodiesel production percentage regarding the voltage and electrolysis time within the design space with $CH_3OH$/oil ratio of 18 and the water percentage of 2%. Fig. 3 represents that an increase in the voltage and electrolysis time at constant $CH_3OH$/oil and water percentage increases the biodiesel production yield. The highest yield of 81.56% was obtained when both variables were at the maximum point within the studied range. Among the two studied variables, voltage (B) indicated a greater effect than the electrolysis time. The figures also show that the biodiesel yields are directly influenced by the interaction of two factors at the constant values of other parameters.

The high yield of the biodiesel produced in the upper values of voltage and the electrolysis time can be attributed to the primary reactions that take place in the anodic and cathodic electrodes [24,25]. Anodic reactions are as follow:

$$2Cl^- \rightarrow Cl_2 + 2e \tag{5}$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e \tag{6}$$

The corresponding cathodic half-reaction, water reduction (Eq. (2)), is as follows:

$$2H_2O + 2e \rightarrow H_2 + 2OH^- \tag{7}$$

The above reactions show that the chlorine or oxygen molecules can be produced on the anode electrode [Eqs.

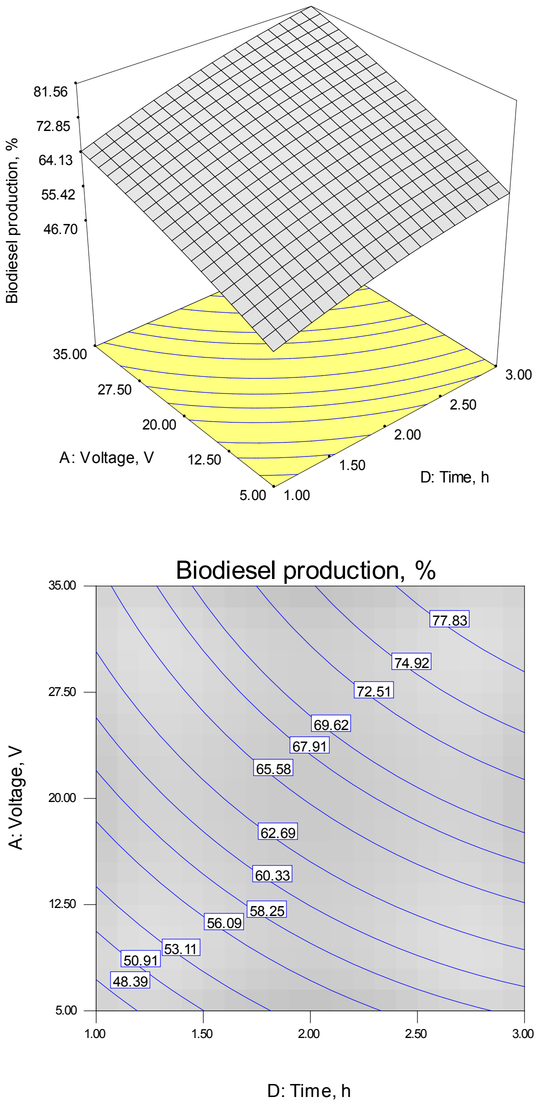

Fig. 3. Response surface and counter plots for Biodiesel production (%) with respect to Voltage and reaction time at $CH_3OH$/oil ratio of 18 and water conent of 2%.

(5) and (6)] and, on the other hand, the hydroxyl ions and hydrogen [Eq. (7)] can be formed on the cathode. Biodiesel production (the transesterification of triglycerides with methanol) needs an active species, i.e., methoxide ion ($CH_3O^-$), which can be produced when methanol reacts with a hydroxyl ion ($OH^-$) [Eq. (8)]. When methoxide ions are formed, these ions attack the carbonyl moiety in the glyceride molecules as a strong nucleophilic. In consequence, the biodiesel can be produced using the electrolysis method.

$$CH_3OH+OH^- \rightarrow CH_3O^- +H_2O \quad (8)$$

$$CH_3O^- + \text{triglyceride} \rightarrow \text{biodiesel} + \text{glycerol} \quad (9)$$

A higher voltage applied to the electrodes causes the cathode electrode to have more power to generate reduction reaction and, as a result, the anode will have more power for oxidation process. The Higher potential difference between the anode and cathode electrodes causes the electrolytic cell to oxidise or decrease the more complicated compounds. Thus, a higher voltage might make unstable molecules break down and react with other molecules. In this project, the applied voltage varied from 5 to 35 V, and the resultant graph is depicted in Fig. 3. The rate of the hydroxyl ions production is gradually increased when the applied voltage increases; this can be attributed to the issue that the uniform charge density of the surface of the cylindrical electrode is also increased. As a result, the hydroxide ions created on the cathode electrode surface might immediately react with the nearby methanol, and hence the oil transesterification reaction may occur in the methanol phase [24]. Moreover, an increase in the electrolysis voltage caused an increase in the biodiesel yield (Fig. 3). The effect of the electrolysis time was investigated in the range 1–3 h. Reaction time is one of the critical parameters of the transesterification process. As depicted in Figs. 3–5, increasing the time from 1 to 3 h led to an increase in the biodiesel production. Based on Faraday's law,an increase in the electrolysis time enhances the production of hydroxide ions on the surface of the cathode electrode. Consequently, the rate of the methoxy ions formation and the esterification reaction in the reaction cell was increased, and followed by enhancing the yield of the biodiesel production. The maximum observed biodiesel production was 81.56% at the voltage of 35 V, $CH_3OH$/oil ratio of 18, water percentage of 2%, and the reaction time of 3 h. Meanwhile, the minimum predicted biodiesel production yield (33.86) was obtained at the voltage of 5 V, $CH_3OH$/oil ratio of 6, the water percentage of 10%, and the reaction time of 1 h. The biodiesel production is increasing with time and higher voltage because the prolongation of time leads to an increase in the conversion, and an increase in energy favours the complete conversion of biodiesel. Therefore, the interaction between these two variables showed a significant positive effect on the FAME content.

Along with voltage and the reaction time, the methanol to oil molar ratio is also one of the factors that significantly affect the transesterification process [21]. The effects of changing $CH_3OH$/oil ratio and the reaction time on the biodiesel production are shown in Fig. 4. The biodiesel production yield is increased by an increase in $CH_3OH$/oil ratio from 50.79% at $CH_3OH$/oil ratio of 6 till it reaches 81.56% at $CH_3OH$/oil ratio of 18 with the reaction time of 3 h. This can be attributed to the fact that excess methanol increases the transesterification reaction and enhances the biodiesel yield. Thus, an optimal methanol to oil molar ratio can shift the reaction equilibrium to the forward direction and helps maximum yield to be achieved. Stoichiometrically, one mole of triglyceride needs 3 moles of alcohol in the transesterification reaction. The higher molar ratio is required to drive the reaction towards the desired product of higher yield and conversion, which is due to the reversible nature of transesterification reaction [1].

Fig. 4 shows the percentage yield of biodiesel was directly proportional to the methanol to oil molar ratio. Therefore, excessive alcohol is required to shift the equilibrium,to higher yields of biodiesel, and enhance the contact between the oil and alcohol. However, when the ratio of oil to alcohol is too high, it could have adverse effects on the

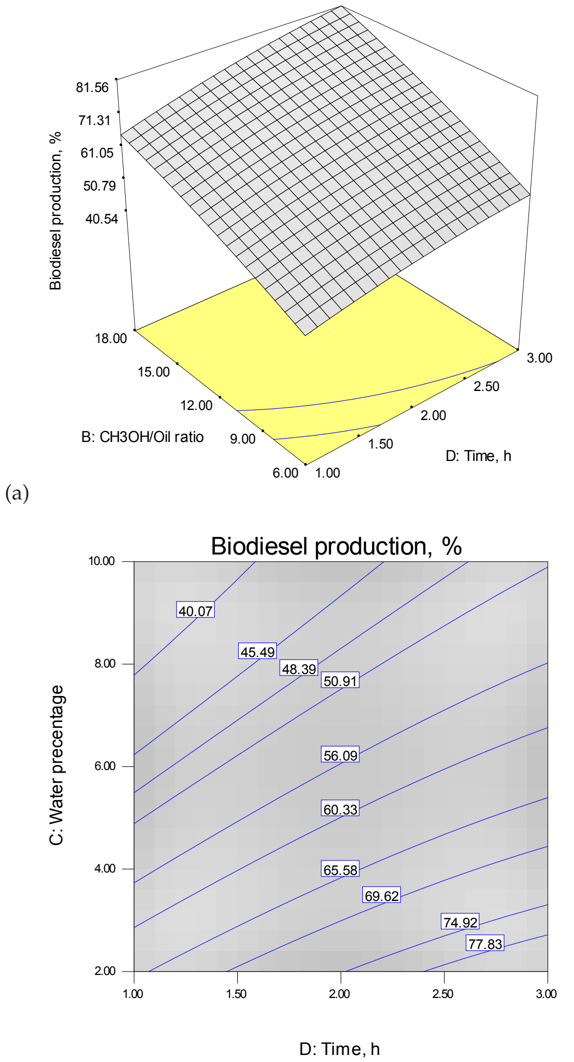

Fig. 4. Response surface and counter plots for Biodiesel production (%) with respect to (a) $CH_3OH$/oil ratio and reaction time at voltage of 35 V and water content of 2%.

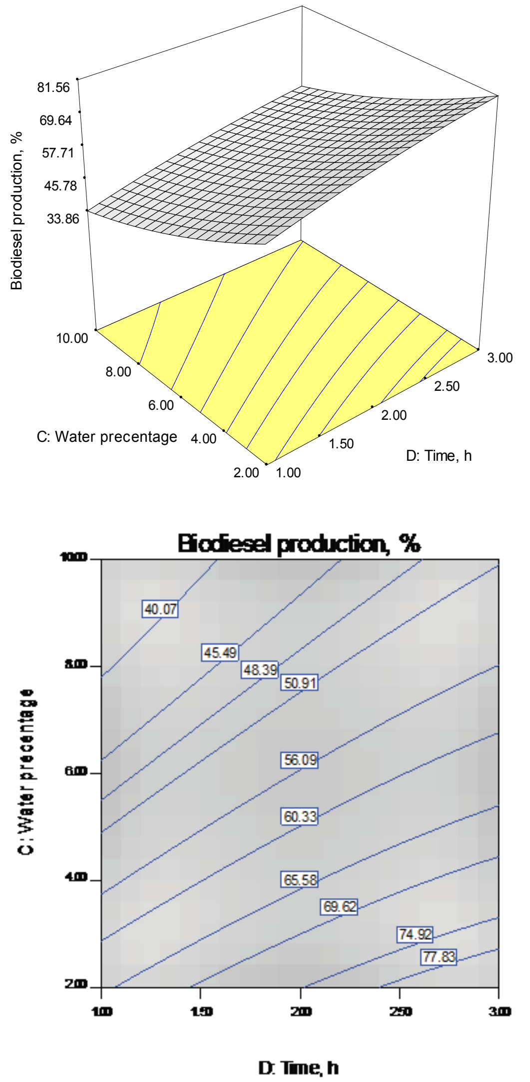

Fig. 5. Response surface and counter plots for Biodiesel production (%) with respect to water content and reaction time at voltage of 35 V and $CH_3OH$/oil ratio of 18.

biodiesel yield. The related literature indicates that adding a large quantity of alcohol can make methanol slow down the separation of the esters and glycerol phases, which influences the final biodiesel yield [6,23].

Water content has a significant role in the methods of the traditional biodiesel production (acid- and alkaline-catalyzed methods) [24]. In these methods, the water content in the reaction always generates adverse effects because the presence of water increases the hydrolysis of alkyl esters to FFAs and soap formation, consumes catalyst, and decreases the catalyst effectiveness [24]. Thus, vegetable oils/fats and alcohol used as raw materials for the transesterification should be water-free or less than 0.1% [11]. These problems may prevent the most efficient use of waste vegetable oils and crude oils, as they contain water. In this work, to study the effect of water on the reaction system, the experiments were carried out with a greater amount of water (2–10%) in the reaction mixture. The effect of the water content and reaction time on the biodiesel production is presented in Fig. 5. This figure indicates that an increase in the water content of 2% to 10% decreases the biodiesel production. Fig.5 shows that as 2wt.% of water was added to the electrolysis cell, the biodiesel production yield reached to 81.57% in 3 h. However, the biodiesel production yield reached to 51%, when the water content increased to 10 wt.% (in the same condition) which shows that extra water might have a negative impact on the transesterification reaction. However, water plays a significant role in the electric charge transfer between the electrodes. Furthermore, the presence of water in the reaction cell can more easily separate the product, because of glycerol, a coproduct of transesterification is more soluble in water than in methanol. In fact, the presence of a certain amount of water can increase the methyl esters formation. This finding suggests that in the electrolysis approach, crude vegetable oil, as well as its wastes containing water (less than 2%), can be readily employed for biodiesel fuel production in a simple preparation and that the electrolysis method is more water-tolerant than the conventional one with the use of an alkaline catalyst. The minimum predicted biodiesel yield (15%) was obtained at a voltage of 5 V, $CH_3OH$/oil ratio of 18, the water content of 10%, and the reaction time of 1 h.

### *3.3. Fuel properties of biodiesel*

To assess the quality of the biodiesel produced from sunflower oil, the physicochemical properties of the obtained biodiesel such as density, kinematic viscosity, flash point, cloud point, acid value, ash content, and heating value were evaluated and compared with the ASTM standards. Table 6 provides the various physiochemical properties of the produced biodiesel compared with the ASTM standards. The table shows that the characteristics of the prepared biodiesel are within the appropriate range of ASTM D6751.

### *3.4. Optimisation and confirmation*

The optimisation process aimed to achieve the maximum value for the biodiesel production yield. The optimisation process was performed by the numerical optimisation defined in the Design Expert software. Table 7 shows that the optimal conditions were specified by maximising the desirability of the response.

Table 6
Physicochemical properties of sunflower biodiesel

| | Unit | Biodiesel standard (ASTM 6751) | Sunflower biodisel |
|---|---|---|---|
| Density @15°C | g/cm³ | 870–900 | 883 |
| Kinematic viscosity, 40°C | mm²/sec | 1.9–6.0 | 4.7 |
| Flash point | °C | ≥130 | 147 |
| Cloud point | °C | –3–12 | 4 |
| Acid value | Mg KOH/g | ≤0.8 | 0.3 |
| Ash content | % mass | ≤0.05 | 0.04 |
| Heating value | MJ/kg | ≥35 | 37 |

The optimal conditions by the numerical RSM method were obtained at the voltage of 34.83 V, the $CH_3OH$/oil ratio of 17.99, and 2% of the water content. Also, the reaction time and desirability was observed in 3 h and 0.99, respectively (Table 7).

The biodiesel production yield predicted by design was 81.03%. To confirm the predicted results, a new experiment was conducted at the specified optimal conditions (Table 8). The validation results indicated that the experimental value (76.7%) is in good agreement with the value predicted by CCD (81.03%) (Table 6). The errors between the predicted and actual values were 5.34%.

### *3.5. Waste cooking oil as feedstock*

The biggest problem in the biodiesel commercialization is high cost. Previous research shows that the high cost of biodiesel is mainly due to the cost of virgin vegetable oil. The Energy and cost analyses of biodiesel production from waste cooking oil was investigated by [26]. The cost analysis was obtained from waste cooking oil with approximately 60% portion of the cost, and 30% human labour which is placed in second order. According to their results, total cost and total income were 1.2 and 2.5 $\$ L^{-1}$ for biodiesel production, respectively. The total costs for biodiesel production were 1.201 $\$ L^{-1}$ while the gross production value was found to be 2.499 $\$ L^{-1}$. About 99% of the total expenditure was related to the variable costs, whereas 1% was fixed expenditures. Based on these results, the gross return, net return, benefit to cost ratio, productivity from biodiesel production were calculated as 1.302 $\$ L^{-1}$, 1.298 $\$ L^{-1}$, 2.081 and 0.946 kg $\$^{-1}$, respectively.

Thus, the limited availability and the raw material cost of vegetable oil feedstock are always determining factors for biodiesel production. Recently, much attention has been directed at exploring different methods to reduce the cost of biodiesel, mostly concentrating on minimising the raw material cost. Instead of virgin oil, waste cooking oil is used for the production of biodiesel which is an effective way

Table 7
Numerical optimization for central composite design

| Number | A: Voltage, V | B: $CH_3OH$/Oil molar ratio | C: Water content, % | D: Electrolysis time, h | Biodiesel production% | Desirability | |
|---|---|---|---|---|---|---|---|
| Optimized Phenol removal calculated from central composite design | | | | | | | |
| 1 | 34.83 | 17.99 | 2.00 | 3.00 | 81.03 | 0/99 | Selected |
| 2 | 34.50 | 17.95 | 2.00 | 3.00 | 80.71 | 0/98 | |
| 3 | 33.77 | 18.00 | 2.00 | 2.82 | 79.06 | 0/96 | |
| 4 | 35.00 | 17.07 | 2.00 | 3.00 | 78.84 | 0/95 | |
| 5 | 35.00 | 17.99 | 2.00 | 2.59 | 78.20 | 0/95 | |
| 6 | 35.00 | 16.56 | 2.01 | 3.00 | 77.51 | 0/93 | |
| 7 | 35.00 | 17.93 | 2.00 | 2.27 | 75.72 | 0/91 | |
| 8 | 35.00 | 18.00 | 2.00 | 2.10 | 74.71 | 0/89 | |
| 9 | 35.00 | 18.00 | 2.00 | 1.39 | 69.58 | 0/81 | |
| 10 | 35.00 | 17.98 | 2.01 | 1.15 | 67.74 | 0/79 | |

Table 8

Confirmation between optimized biodiesel production calculated from mathematical design and experimental study

| Optimized biodiesel production calculated from central composite design (predicted value) | | | | |
|---|---|---|---|---|
| A: Voltage, V | B: $CH_3OH$/Oil molar ratio | C: Water content, % | D: Electrolysis time, h | Biodisel production, % |
| 34.83 | 17.99 | 2.00 | 3.00 | 81.03 |
| Confirmation study of optimized biodiesel production (experimental value) | | | | |
| 34.8 | 18 | 2 | 3 | 76.7 |
| $Error(\%) = \frac{Actual\ value - predicted\ value}{Actual\ value}$ | | | | 5.34% |

to decrease the raw material cost, as it is estimated to be about half the price of virgin oil. Additionally, using waste cooking oil as the raw material can also help protect the environment and solve the problem of waste oil disposal. Thus, in this project, the ability of the electrolysis method in the biodiesel production using waste cooking oil under the optimal condition obtained by RSM (the voltage of 35 V, $CH_3OH$/oil ratio of 18, the water content of 2%, and the reaction time of 3 h) were investigated. Waste cooking oil sample used in this study was collected from Kermanshah University of medical science restaurant and was filtered to remove the inorganic residues. The characteristics of the WCO samples are the density of 0.925 g/cm$^3$, an acid number of 2.5 mg KOH/g, the flash point of 261°C, and the cloud point of 18°C. The biodiesel production efficiency from this sample was about 67%.

## 4. Conclusion

In this study, using the electrolysis method and optimised by RSM-based CCD, out the transesterification of sunflower oil containing relatively high content of water was carried out. Based on the surface methodology experiments, the maximum biodiesel production obtained from sunflower oil was 81.03%, yielded by the following optimal values of the variables: the voltage of 35V, $CH_3OH$/ oil ratio of 18, the reaction time of 3 h, and the water content of 2%. Moreover, the biodiesel production yield for WCO in the optimal condition was found to be about 67%. The quality of the produced biodiesel was in the range of ASTM standards. Among the transesterification parameters, the effects of voltage, $CH_3OH$/ oil ratio, and the reaction time showed a significant impact on the biodiesel production yield, while the effect of water content found negative in biodiesel production.

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