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Modeling and optimization of biodiesel synthesis using TiO_2–ZnO nanocatalyst and characteristics of biodiesel made from waste sunflower oil

Mohammad Ali Zahed [a,*], Meysam Revayati [b], Nikta Shahcheraghi [c], Farhaneh Maghsoudi [d], Yasaman Tabari [e]

[a] Faculty of Biological Sciences, Kharazmi University, Tehran, Iran
[b] Department of Environmental Engineering, University of Tehran, Karaj, Iran
[c] Institute for Nanoscale Technology, University of Technology Sydney, Broadway, NSW, 2007, Australia
[d] Department of Environmental Engineering, University of Tehran, Tehran, Iran
[e] Faculty of Sciences and Advanced Technologies, Science and Culture University, Tehran, Iran

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ABSTRACT

Biodiesel as a renewable fuel is made from renewable materials such as animal fats, plant oils, and can be used in compression ignition (diesel) engines by mixing with conventional diesel. Recently, nanocatalysts are being used to generate biodiesel, as they are able to make these reactions more sufficient by having a large surface-to-volume ratio. TiO_2 and ZnO nanoparticles are categorized as metal oxide nanoparticles. Each of them has its own special characteristics. Besides, they show a level of cooperation which is discussed below.

In this paper, in addition to the surface method employed for numerical analysis, the experiments on the biodiesel production from waste sunflower oil are implemented by transesterification method using TiO_2ZnO nanocatalyst. Effective process parameters, including the reaction temperature, oil: alcohol molar ratio, catalyst percentage, and optimal conditions are determined and optimized accordingly. The highest product yield was 96.4% in the ratio of 1–6 methanol to oil, 60 °C, and 200 mg/L TiO_2–ZnO nanocatalyst. An optimization study shows that the highest biodiesel production is possible using nanocatalysts of 264 mg/L at a temperature of 66 °C.

1. Introduction

Biodiesel is an eco-friendly fuel prepared from renewable resources like straight vegetable and animal oil [1]. Biodiesel is a non-toxic alternative fuel which raises energy security and improves environmental indexes due to its zero CO_2 emission property, has attracted considerable attention in the last decade for green chemistry matters, the exhaustible nature of fossil fuel resources, environmental issues, and their economic value due to their vast applications in industrial fields [2–4]. Compared to conventional diesel, biodiesel is beneficial for the environment by reducing visible smoke, odors, engine emission of CO, NO_x, SO_x, and hydrocarbons, which will lead to a lower lifecycle of CO_2 emission. Moreover, biodiesel is secure, and it complies with all types of diesel motors, ii) preserves the permanence of diesel engines like fossil fuels, iii) is not catching fire.

Biodiesel is significantly important due to three aspects. Economically because it reduces the demand for fossil origin fuel. Environmentally, it is advantageous due to the reduction of greenhouse gas emissions. And socially, as it increases the possibilities of employment and income generation [5].

Biological sources have shown great potential for making biodiesel and supplementing other conventional sources. This is mainly due to their renewability, biodegradability, and having a better non-toxic nature compared to diesel, in terms of sulfur content, aromatic content, and flash point. Attempts have been made to produce biodiesel from both edible and non-edible oils. The main focus of edible sources has mainly been on vegetable oil seeds such as soybean, rapeseed, and sunflower [6–9].

Furthermore, other sources, such as algal lipids are developed in recent years [10,11].

Although vegetable oil is a promising alternative energy fuel for diesel engines, it presents various challenges, including lower volatility, higher viscosity, and lower efficiency under cold conditions. Thus, more studies concentrated on various vegetable oil derivatives [12].

The raw lipid could ruin the engines quickly as it rapidly accumulates the oil sludge. Therefore, viscosity of microalgae oil must be reduced in

* Corresponding author.
E-mail address: Zahed51@yahoo.com (M.A. Zahed).

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Table 1
Physical and chemical characteristics of sunflower oil.

Specific weight	0.905–0.91 mg/g
Soap index	189–194
Iodine value	110–145
Palmitic acid	30–60%
Stearic acid	13–13.3%
Oleic acid	20–40%
Saturated fatty acid	12%
Omega-3 fatty acid	3%

Table 2
Test (experimental) matrix designed by CCFD.

Run No.	Point Type	Temperature (°C)	Ratio	Catalyst (mg)
1	Fact	50	4	0
2	Fact	70	4	0
3	Fact	50	6	0
4	Fact	70	6	0
5	Fact	50	4	400
6	Fact	70	4	400
7	Fact	50	6	400
8	Fact	70	6	400
9	Axial	50	5	200
10	Axial	70	5	200
11	Axial	60	4	200
12	Axial	60	6	200
13	Axial	60	5	0
14	Axial	60	5	400
15	Center	60	5	200
16	Center	60	5	200
17	Center	60	5	200
18	Center	60	5	200
19	Center	60	5	200
20	Center	60	5	200

Table 3
Predicted and experimental results for the biodiesel production process.

Run No.	Observed	Predicted	Residual	Cook's Distance	Outlier T
1	50.6	52.0	−1.37	0.104	−0.633
2	51.4	48.2	3.16	0.550	1.589
3	55.8	54.1	1.69	0.158	0.790
4	59.6	60.2	−0.63	0.022	−0.285
5	67.1	68.7	−1.65	0.149	−0.767
6	74.7	78.7	−3.97	0.867	−2.142
7	68.0	70.9	−2.88	0.457	−1.422
8	92.3	90.7	1.65	0.150	0.768
9	86.4	82.2	4.21	0.186	1.586
10	90.0	90.2	−0.22	0.000	−0.073
11	91.1	88.8	2.31	0.017	0.700
12	94.5	95.9	−1.35	0.006	−0.405
13	56.9	59.8	−2.86	0.086	−1.016
14	90.2	83.4	6.85	0.493	3.272
15	93.1	92.3	0.78	0.001	0.218
16	90.7	92.3	−1.62	0.004	−0.459
17	93.3	92.3	0.98	0.001	0.274
18	92.2	92.3	−0.12	0.000	−0.035
19	86.9	92.3	−5.42	0.040	−1.707
20	92.8	92.3	0.48	0.000	0.133

order to produce a sustainable fuel that offers smooth engine operation [13].

There are at least four major possible ways in which mentioned oils and fats can be converted into biodiesel, namely, transesterification reaction, direct use or blending of oil, microemulsions, and pyrolysis or thermal cracking [14,15].

The most common reaction to produce biodiesel from vegetable oil and animal fats is called transesterification, which is prepared by the reaction of the triglyceride with alcohol. In this reaction, a catalyst (Acidic, alkaline, or enzyme) or Nano-catalysts mixed with vegetable oil

Table 4
Analysis of variance for the quadratic model in biodiesel production from waste sunflower oil.

Source	Sum of squares	DF	Mean square	F-Value	Prob > F	Remarks
Model	4925.86	7	703.69	53.34	<0.0001	Significant
A	160.80	1	160.80	12.19	0.0045	Significant
B	124.61	1	124.61	9.45	0.0097	Significant
C	1392.40	1	1392.40	105.54	<0.0001	Significant
A^2	119.81	1	119.81	9.08	0.0108	Significant
C^2	1380.29	1	1380.29	104.62	<0.0001	Significant
AB	48.51	1	48.51	3.68	0.0793	Significant
AC	93.16	1	93.16	7.06	0.0209	Significant
Residual	158.32	12	13.19			
Lack of Fit	128.54	7	18.36	3.08	0.1167	Not significant
Pure Error	29.78	5	5.96			
Cor Total	5084.17	19				

and animal fats to convert into esters and glycerol (Equation (1)) [16].

The catalyst is considered as a chemical compound which is capable of exerting an accelerating effect and affecting the orientation on the reaction progression, which is thermodynamically feasible. Although increasing the weight percent of the catalyst, raising the amount of produced methyl ester as well, the final cost goes up accordingly [17].

Since nanomaterials have unique properties for usage in various industrial fields [18], they can be used as an alternative to conventional catalysts such as KOH/NaOH, or acidity catalysts [19,20]. Methanol is the cheapest and has more physical and chemical benefits than ethanol [21,22]. The stoichiometry of the transesterification reaction consists of 3 M methanol per 1 mol of triglyceride, which produces 3 mol ester of fatty acids and 1 mol of glycerol (Eqs. (1)–(3)) [23].

$$\text{Triglyceride} + \text{R'OH} \rightleftharpoons \text{Diglyceride} + \text{RCOOR} \tag{1}$$

$$\text{Diglyceride} + \text{ROH} \rightleftharpoons \text{Monoglyceride} + \text{RCOOR} \tag{2}$$

$$\text{Monoglyceride} + \text{ROH} \rightleftharpoons \text{Glycerol} + \text{RCOOR} \tag{3}$$

A catalyst can increase the speed of a reaction in three ways: reducing the activation energy, acting as a facilitator, and increasing the reaction efficiency relative to a component when two or more products are formed. Nanocatalysts are important substances in chemical processes, energy production, and energy saving, and preventing environmental pollution [24]. The reactions of esterification and transesterification can be conducted in the absence of catalysts, but the time and energy cost involved in the completion of these reactions make them unviable [25]. Nanocatalysts are more effective than conventional catalysts as their ultra-small significantly reduces the surface area-to-volume ratio. It has been found that the size and spacing of nanoparticles has a considerable effect on catalytic activity and selectivity.

Using ZnO on TiO_2 as catalyst can lead to an increase in accessibility on methanol and triglycerides in transesterification process as they are high density materials [26,27].

The zinc oxide nanoparticles are able to increase transparency and oxygen vacancy. Besides, they possess higher affinity for polar substrate due to its hexagonal wurtzite structure and its structural, optical and magnetic properties [28].

ZnO as a catalyst, is capable to restore characteristic properties after catalysis [28,29].

TiO_2 is reported to have some additional properties compared to other conventional nanomaterials such as durability, antifungal, environmental friendly, and cheap. However there are very few literatures available on the TiO_2 based heterogeneous catalyst for biodiesel production [30].

In this research, the reaction of the exchange of esters to produce methyl ester from sunflower oil residues is studied taking into account the three main factors influencing the conversion rate of biodiesel:

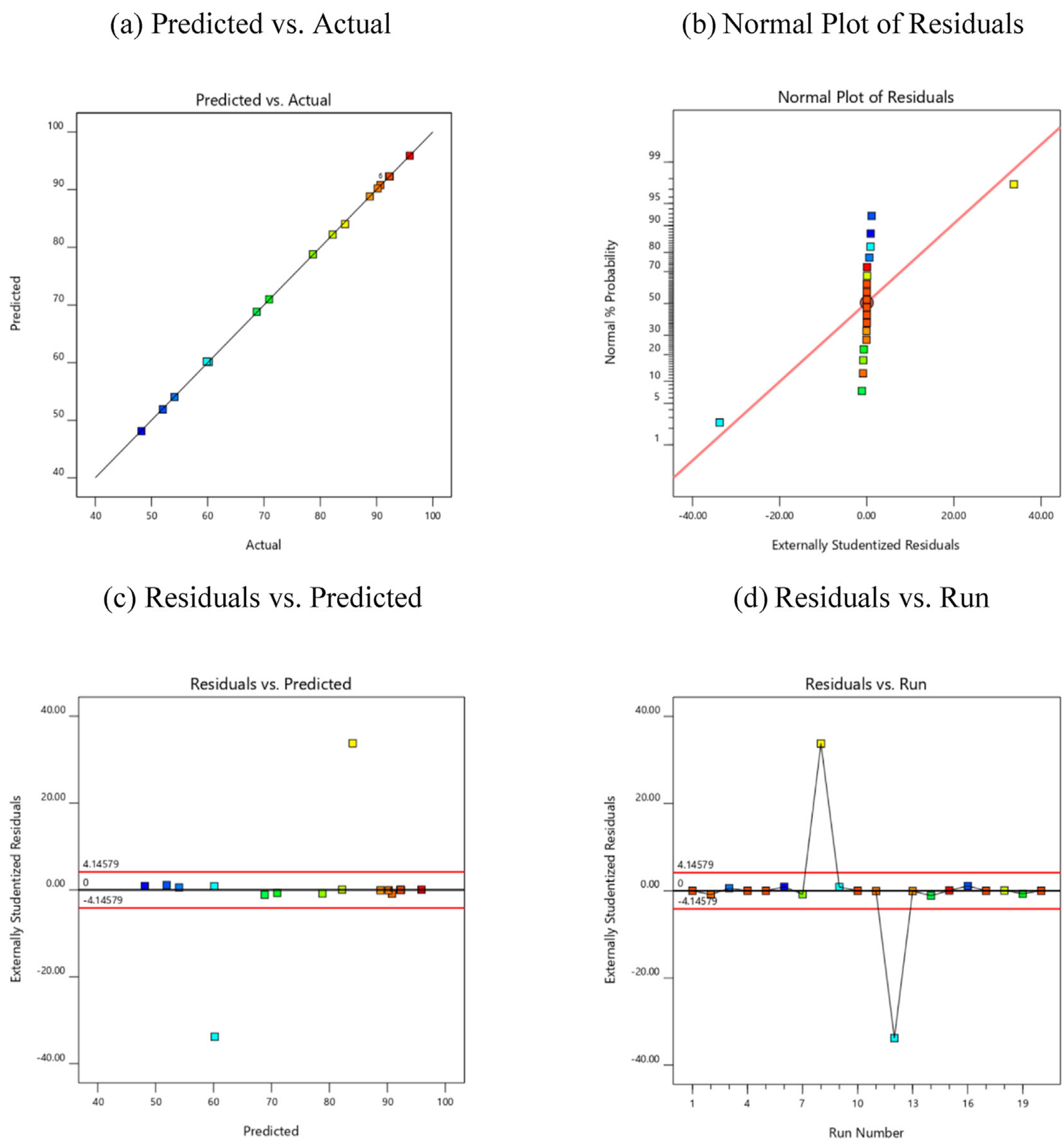

Fig. 1. The Statistical plots of the biodiesel production testing design: (a) predicted versus actual; (b) Normal plot of residual; (c) Residual versus predicted; (d) Residual versus run.

reaction temperature, catalyst content, and the amount of alcohol (methanol), Optimized [31,32].

The objective of this study is to achieve optimum conditions, a suitable combination of factors, and a biodiesel production model using the response surfing method (RSM).

Additionally, the synergistic effects among process parameters are discussed, and the accuracy of the model and the novel usage of nanocatalysts are introduced in this manuscript.

This paper discusses the outcomes of experiments designed by the RSM method using nanocatalysts through transesterification in order to increase outputs and decrease the reaction time [33–35].

2. Methods and materials

2.1. Materials

Sunflower oil was obtained from the local margarine oil industry named Naz Isfahan located in Isfahan, Iran. Crude unrefined sunflower oil is yellow in color and becomes colorless or yellowish via refining. Sunflower oil characteristics and fatty acid combinations are shown in Table 1.

2.2. Chemical and reagents

The most operational alcohol for transesterification is methanol, considering its low purchasing price and chemical properties. Therewith, separating –OH from methanol is much easier and requires less energy compared to other alcohols [36]. Methanol >99% and other chemicals used in the experiments are of an analytical reagent (AR) grade and were purchased from Merck (Darmstadt, Germany). In order to mix constituent materials, ZnO–TiO_2 is positioned together and whipped continuously in 100 until reaching a pasty mixture. First, pre samples are inflamed for an hour in 250, and later in 400 for 3 h. The exact method is carried out for nanocatalysts synthesize without titanium origin. FT-IR (Fourier Transform infrared) Perusal for all synthesized samples is accomplished in the span of 400–4000 cm-1 by FT-IR spectrometer.

2.3. Experimental design

In order to design the experiment, in the first step, the optimization of the biodiesel production process needs to be done to achieve the highest amount of production and spend the least cost [37].

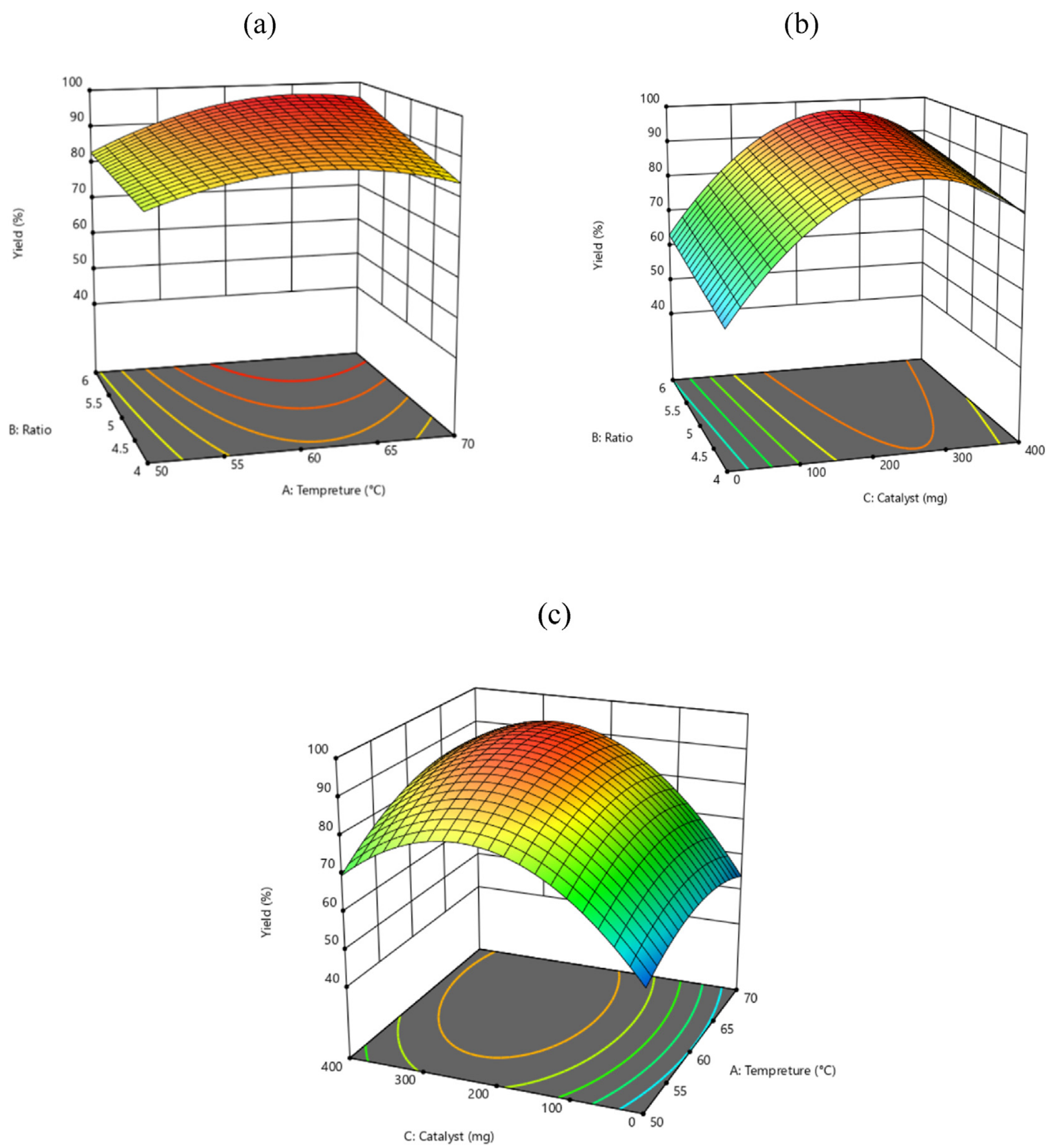

Fig. 2. (a) Three-dimensional (3D) plot between temperature and molar ratio against biofuel yield (b) three-dimensional (3D) plot between molar ratio and catalyst weight against biofuel yield(c) three-dimensional (3D) plot between temperature and catalyst weight against biofuel yield.

Table 5
Numerical optimization of the parameters for maximum biodiesel production.

Criteria	Goal	Lower Limit	Upper Limit
Catalyst	In range	0	400
Ratio	In range	4	6
Efficiency	Maximize	85.96	98.50

Usually, the optimization of biodiesel production process is carried out with the variation of one factor at a time and the response is a function of a single parameter which is time consuming and expensive. This technique is unable to determine the interactive effects of all the variables. Thus, the overall effects of the variables on the response cannot be predicted. To overcome these shortcomings multivariate statistical methods, such as Response Surface Methodology (RSM) are introduced [38].

Various factors affect transesterification reactions, such as the type of oil, type and amount of catalyst, type and amount of alcohol, reaction time, time, and pressure.

By careful design of experiments and using suitable mathematical models, developed for the given RSM data, it is convenient to predict the optimal process conditions with conducting minimum number of experiments thereby saving time and experimental cost [28].

The experimental plan is made using central composite design (CCD) of RSM, which is the most popular and purposive tool in optimization reaction condition [39], accomplished by design-expert 12 (State-Ease Inc, Minneapolis, USA) software.

The aim is to optimize the three following important reaction variables; 1) temperature parameter, 2) methanol to oil ratio, and 3) the amount of catalyst with the help of nanocatalyst. CCD designed 20 experiments and, in all, temperature changed in the span of 50, 60 and 70 while methanol to oil ratio changed between 4/1, 5/1 and 6/1 with these quantities of catalyst: 0, 200 and 400. From 20 experiments, 14 of them are *fact type,* 8 are *Axial,* and others are the *center type.* Experimental matrix designed by CCD has been shown in Table 2.

2.4. Biodiesel production

Edible sunflower oil is scaled 50 g, and in order to eliminate any absorbed water, 2g of $Na_2SO_4$and a magnet is added to each scaled oil in an Erlenmeyer. Afterward, the speed is regulated at 300,400 rpm, and

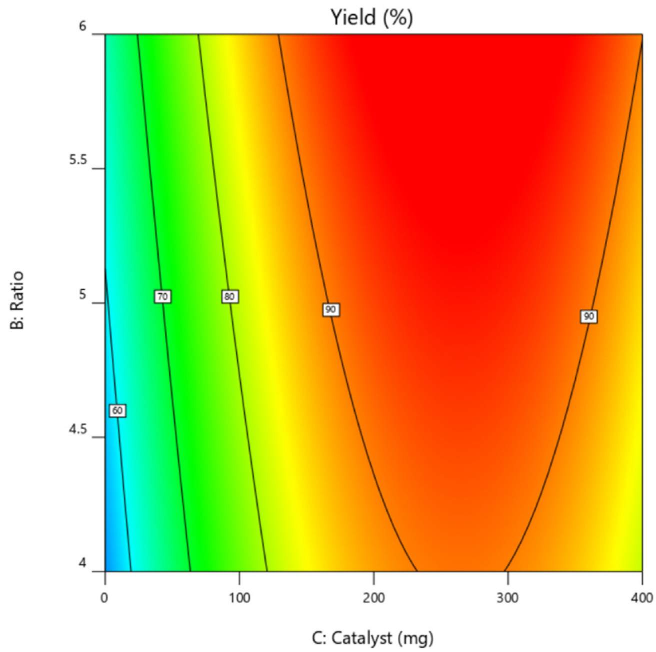

Fig. 3. Showing the synergistic effect of temperature and molar ratio in biodiesel production.

samples are heated in 60c for at least 30 min to dry. Catalysts are impregnated and during heating, the methanol is evaporated and returned to the solution through a humective, which is placed at the top. The ongoing reaction leads to the converting of ester-acids into methyl ester (glycerin), which will be separated in the next level at the bottom of the separator funnel. The purification takes almost 24 h, which directly relies on oil quality and experimental accuracy. Biodiesel characteristics were carried out using ASTM standards, which are shown in Table 7.

2.5. Statistical analysis

The experimental data acquired by the mentioned procedure is analyzed statistically by response surface regression method using the following quadratic polynomial equation [42]:

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n} \beta_{ii} x_i^2 + \sum_{i \neq j=1}^{n} \beta_{ij} x_i x_{ij} + \varepsilon \quad (4)$$

Where Y represents the response (biodiesel yields), and $\beta 0$, βi, βii, are an intercept, linear, quadratic and interaction constant coefficients, respectively, n is the number of independent parameters, and ε the random error.

All the adornment of the software is done by the method of specifying the range of variables.

3. Results and discussion

3.1. Mathematical modeling

The experimental measurements are analyzed mathematically by the 3-D regression model designed by CCD. This design is based on the independent variables in a frame of the regression equation, which only contains biodiesel meaningful (effective) parameters. In the experiment, biodiesel performance after eliminating the insignificant coefficients (Table 4) is as follows:

$$\text{Yield (\%)} = +92.32 + 4.01\text{ A} + 3.53\text{ B} + 11.80\text{C} - 6.12\text{ A}^2 - 20.77\text{C}^2 + 2.46\text{ AB} + 3.41\text{ AC} \quad (5)$$

All interactions have positive effects, and quadratic temperature and catalysts carry a negative coefficient. In this equation, $Y_{\text{Biodiesel}}$ represents the biodiesel yield, A the temperature variable, B the molar ratio of oil: and alcohol and C the catalyst value, respectively. AB, the combined effect of temperature and waste oil ratio on alcohol and AC, is the combined effect of temperature and amount of catalyst.

3.2. Statistical experiments results

The results of predicted and observed biodiesel production are presented in Table 3. The integrity of the mathematical design is deliberated by statistical experiments. The regression and analysis of variance (ANOVA) are used for comparison and analysis. ANOVA results of biodiesel yield are gathered in Table 4. In order to show the efficiency of the response surface methodology, the fact that all residues in each experiment are less than 3 can be magnified. For p-value, the significance level is 0.05; p-value for the liner terms A, B, and C; the quadratic terms A^2 and C^2 and the interaction terms of AB and AC are less than 0.05 and they are the significant model.

The lack of fit test is used as a support test for the adequacy of the fitted model. The lack of fit test with p-value = 0.1167 is insignificant, which shows that the model fits well with the observed data (p-value in RSM >0.05 is not significant).

The fitted model R^2 is 0.9689. The predicted R^2 of 0.8726 is in relatively reasonable agreement with the adjusted R^2 of 0.9507. The standard deviation for Equation (5) is 3.630, which indicates that the predicted value for biodiesel production yield is accurate. The mean is 78.88, and the predicted residual error sum of squares (PRESS) was 647.92. Adequate precision is 20.726. It measures signal to noise ratio, and a ratio greater than 4 is normally desirable. A low value of the coefficient of variation (CV = 4.60%) indicates an excellent precision and reliability of the model.

3.3. Diagnostic tests

The predicted output versus the experimental values for the biodiesel yield is shown in Fig. 1 a. This plot exhibits that the results of the model are extremely close to the actual data (Fig. 1a). The normal probability plot is used for comparing the data set with the normal distribution. This plot is used with the standardized residual of the linear regression model

Table 7
Physical and chemical characteristics of biodiesel fuel made from waste sunflower oil.

S-NO	Biodiesel properties	Test method	Measured values	Units
1	Viscosity at 40 °C	ASTM – D 613	4.6	mm^2/sec.
2	Cetane number	ASTM - D 613	48	–
3	Cloud point	ASTM - D 2500	1	°C
4	Acid number	ASTM - D 664	0.05	Mg KOH/g
5	Flash point (°C)	ASTM - D 93	99	°C
6	Fuel heat value	ASTM D 6751	42.5	μJ/L
7	Density at 20 °C	ASTM D 6751	0.86	g/L

Table 6
Optimized conditions by designing a biodiesel production test.

Temperature (°C)	Ratio	Catalyst (mg)	Observed	Predicted	Error (%)	StD* Production
66	6	267	96.4	99.8	3.4	2.4

*Standard deviation.

to validate the adequacy of the model, which shows that insignificant errors are actually normally distributed in a straight line. Residual is the difference between the observed and predicted values. In other words, the plot of residuals versus predicted response illustrates a structureless plot suggesting that the model is appropriate and that the model does not show any violation of the independence or constant variance assumption [39]. This analysis was investigated by using the normal probability plot of residuals (Fig. 1b), the plot of the residuals versus predicted values (Fig. 1c), and the residuals versus run values (Fig. 1d). Therefore, based on the observed results, the regression model of the second order is quite correct. Furthermore, in this model, there is no violation of the independence or constant variance assumption in all runs.

3.4. Effects and interaction of parameters

The three-dimensional (3D) response surface plots are significantly efficient as the interplay and relevance of two independent parameters on biodiesel efficiency has been determined by them. In relation to other indicators, their value has been considered constant and zero. A response surface plot in Fig. 2 a describes the change of biodiesel yield with varying ratios and temperatures. Although the highest biodiesel yield is obtained in the temperature span of 55–65 and the ratio of 5, (whereby) higher ratio has a negative effect on yields and are only cause to using more materials.

In Fig. 2 b the interaction between temperature and nanocatalyst values shows that biodiesel yield increases with the increase in nanocatalyst concentration directly at the beginning, while any additional catalyst thereafter raises the experiment. Fig. 2 c shows that when nanocatalyst concentration is 200 mg, and the ratio is 5, the experiment is carried out with the highest yield.

3.5. Optimization of the TransesterificationProcess parameters

Through the response surface technique, the optimum conditions were determined and indicated by Table 5 and Fig. 3.

As shown in Fig. 3, the highest theoretical yield is obtained in the upper cycle of the graph. Accordingly, the upper cycles are the most suitable spots to adjust the most economical and efficient condition of the experiment. Optimum conditions found by Design-Expert for biodiesel production are tabulated in Table 6.

The experiment is carried out at the temperature of 66 °C, and a ratio of 1/6 with 267 mg nanocatalyst obtained the highest yield of 96/4% with a StD of 2.4, which is in good agreement with our result.

3.6. Specification of product biodiesel

The purity and the quality of biodiesel fuel can be directly influenced by the quality, and the type of the oilseed, and the process used to convert the feedstock to this renewable non-toxic diesel. Table 7 presents the physicochemical properties of the biodiesel produced from sunflower oil via transesterification using nanocatalyst.

As documented, the biodiesel produced in this research can be used in diesel vehicles as a supplement, or alternative to diesel, to save on fossil fuels, and to prevent air pollution.

[40] increased the specific surface of the catalytic activity of biodiesel by preparing nano-sized CaO–based catalysts and utilizing them in biodiesel production to improve it [40]. [41] used Snail shell CaO nanocatalyst for transesterification in order to enhance the construction of biodiesel from dairy scum and Hydnocarpus wightiana oil [42]. [41] used the pyrolysis of waste cork for the transesterification of waste cooking oil with the purpose of preparing a heterogeneous catalyst [41]. [43] reduced the cost of biodiesel production by consuming KOH/Clinoptilolite as a heterogeneous catalyst in the microreactor as an innovative reactor to speed up this procedure and producing biodiesel with the transesterification of waste cooking oil and methanol [43]. [44] used a new bio-oil extracted from Chlorella vulgaris micro algae in constructing biodiesel, enhancing the nano-biocatalyst efficiency as a result of lipase grafting with long-chain molecules [44].

4. Conclusion

In summary, in this work, biodiesel was recognized as an interesting alternative to petro diesel due to availability, low cost of production, renewability, and biodegradability. The production of biodiesel from sunflower oil residue was investigated by the transesterification method. Effective factors were optimized to achieve the highest conversion rate of the production of biodiesel by transesterification method including methanol: oil molar ratio of 1:6, the reaction temperature of 66 °C, and the amount of TiO_2–ZnO nanocatalyst 264 mg/L that resulted in the highest efficiency of 96.4%. The biodiesel thermal value is lower than diesel, but the density of biodiesel is higher than diesel. Furthermore, some chemical and physical properties of biodiesel were specified and compared with diesel fuel. The results were satisfactory, and a comparison between these two fuels suggested that biodiesel can be an appropriate alternative for diesel.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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