

Cleaner fuel production from waste *Phoenix dactylifera* L. kernel oil in the presence of a bimetallic catalyst: Optimization and kinetics study



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ABSTRACT

The focus of the present study is to produce biodiesel from non-edible waste *Phoenix dactylifera* L. kernel biomass feedstock in presence of a newly synthesized bimetallic heterogeneous catalyst (Mn-MgO-ZrO₂). Biodiesel production was optimized based on several process parameters such as; temperature (60–100 °C), reaction time (1–5 h), catalyst loading (1.5–7.5 wt%) and solvent to oil ratio (7.5–37.5). Furthermore, experimental plan based on selected ranges of process variables was developed by response surface methodology (RSM) towards optimizing biodiesel yield. The optimized biodiesel yield was 96.4% at process temperature of 90 °C, reaction time 4 h, catalyst loading 3 wt% and methanol to oil ratio 15. Based on the quadratic model, predicted by RSM, process temperature was rendered as the most influencing parameter among other parameters studied. Kinetic study was also performed to determine the reaction rate constants and the activation energy for the process, which was found to be 37.55 kJ/mol; with pseudo first order reaction. Moreover, the fuel properties determined for produced biodiesel showed a good agreement with the international standards of ASTM and EN.

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1. Introduction

Renewable and sustainable fuels are on high priority of developed countries and can play important role in eliminating the concerns related to fossil fuels [1,2]. Several capable renewable energy sources including solar, wind, geothermal, hydropower and biomass derived fuels are put forth to be clean energy sources [3,4]. However, the biomass is promising source from which can provide biofuel that can be stored, transported and modified. Biodiesel is one of most common and commercialized biofuel derived from biomass. Biodiesel derived from edible and non-edible biomass sources as a renewable energy source is promising alternative to fossil diesel [5]. Moreover, biodiesel is technically and economically considered to be most suitable alternative to fossil diesel due to its degradability, renewability and environment friendly [6]. Biodiesel is produced by most common way known as

transesterification of triglycerides present in oil with short chain alcohol and produces mono-alkyl ester [7]. Biodiesel production is predicted to be economical if factors such as; feedstock cost, catalysts type and process optimization has been focused.

Phoenix dactylifera L. is a tropical and subtropical tree which is mainly grown in hot arid regions of the world and Oman ranked ninth in its production [8]. *Phoenix dactylifera* L., which has large production, delivers around 62,000 metric tons of residues that are almost 23% of the total production [9]. Residue mainly from *Phoenix dactylifera* L. is their pits (kernel), which comprise almost 10–15 wt% of total which are non-edible and this much huge amount of residue of no value becomes environmental problem while best solution for this is to produce biofuel and chemicals [10,11]. Hence, *Phoenix dactylifera* L. kernel tend to be a suitable non-edible feedstock for biodiesel production.

Conventionally, biodiesel is produced in presence of homogeneous catalysts such as KOH, NaOH, NaOCH₃ and KOCH₃ which makes the reaction fast under moderate operating conditions [12,13]. Despite of this, oil to be used for biodiesel production by using these catalysts should be highly pure with low FFA content

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otherwise, it led to the soap formation, which reduces the ester yield and soap formation, avert the glycerol (by-product) separation from mono-alkylesters (biodiesel). Moreover homogenous catalysts are not recoverable from products and involve purification and separation steps which tend to increase the production cost of biodiesel and also causes corrosion and environment problems [14,15]. In order to overcome all problems related to homogeneous catalysts, heterogeneous are introduced and widely studied for biodiesel production. There are several types of heterogeneous catalysts such as basic [16–19], acidic [20], bi-functional [21,22] and enzymatic catalysts [23,24]. In addition, their easy recovery from product and reusability. Therefore, heterogeneous catalysts instead of homogeneous catalyst can help to overcome the high production cost of biodiesel.

Another factor to be considered is process optimization, this can help to reduce energy consumption and time [25,26]. Moreover, process optimization along with kinetic study for biodiesel production can help in up-scaling biodiesel production to commercial level. The process parameters, which largely effect the biodiesel production, are temperature, catalyst amount, methanol to oil ratio and time [27,28]. Moreover, optimizing the process by adopting one-variable-at-a-time technique has number of drawbacks such as; it is time consuming, increase the process expense, large number of experiments required and does not give the interactive effective of process variables on yield [18]. Thus, these all drawbacks can be overcome by using response surface methodology RSM which is a combination mathematical and statistical techniques which help optimize the process based on several changes process variables. RSM has been widely used for optimizing the biodiesel production involving several process variables. Thus, optimization along with kinetic studies for biodiesel can help to economize the process for commercialization.

In the present study, waste *Phoenix dactylifera* L. kernel biomass was utilized to produce biodiesel in presence of a new synthesized bimetallic heterogeneous catalyst (Mn-MgO-ZrO₂). Process parameters such as temperature, reaction time, catalyst loading and solvent to oil ratio were optimized using RSM. Kinetic study was also performed to determine the activation energy and reaction rate constants of the process, which helps in process upscaling. Moreover, the produced biodiesel was characterized according to international standards ASTM and EN to determine the fuel properties. Up to our knowledge, this work is the first of its kind, which has not been reported yet.

2. Experimental

2.1. Materials

Waste *Phoenix dactylifera* L. kernel biomass were obtained from local company in Muscat, Oman. The oil was extracted from the kernel by using n-hexane as solvent and soxhlet device according to AOCs official method Am 2-93. Initial characterization, yield and composition of *Phoenix dactylifera* L. kernel oil along with its comparison with conventionally used plant based oils for biodiesel production is similar as reported in a previous publication [19]. Zirconium oxide, potassium hydroxide, potassium bicarbonate, methanol and n-hexane were purchased from Sigma-Aldrich, USA. Meanwhile, magnesium nitrate hexahydrate and manganese nitrate tetrahydrate from Merck, Germany. All chemicals used were of analytical reagent grades.

2.2. Catalyst preparation characterization

The bimetallic catalyst Mn@MgO-ZrO₂ was synthesized in current research work. The base material (MgO-ZrO₂ (Mg:

Zr = 0.4)) was synthesized through conventional co-precipitation method. In start precursor solution was prepared in 150 ml of distilled water and precipitated by drop wise addition of basic solution (1 M KOH and 0.25 K₂CO₃) to maintain the pH of solution to 10 followed by continuous stirring for 120 min. The solution was allowed to stay overnight followed by filtration and thorough washing with distilled water until it was neutralized and dried for 12 h at 100 °C. The dried material is calcined in programmable furnace with heating rate of 4 °C/min at 650 °C for 4 h. Then the resultant material is impregnated with manganese nitrate tetrahydrate solution (4 wt% Mn). The resultant material is dried overnight at 100 °C and dried material is calcined at 650 °C for 4 h with heating rate of 4 °C/min. The synthesized catalyst was characterized by following techniques such as X-ray powder diffraction (XRD), Scanning electron microscope SEM, Energy dispersive X-ray spectroscopy EDS and Brunauer, Emmett and Teller BET analysis. XRD patterns were measured on PANalytical, Xpert PRO instrument, USA equipped with rotating anode and Cu K α radiation. The measurements were conducted in continuous $\theta/2\theta$ scan refraction mode. SEM image and energy dispersive X-ray spectroscopy (EDS) spectra were recorded to obtain particle morphology by SEM: JEOL JSM-7800F, Japan. The BET surface area, pore size and pore volume measurements of sample was carried out using a standard adsorption equipment (ASAP 2020, Micromeritics Instruments Inc., Norcross, GA, USA) using N₂ gas (99.995% pure).

2.3. Experimental design and statistical analysis

In general, the chemical reaction or process effectiveness is dependent on several factors. So, in order to analyze the effect of each independent variable of complex system is complicated, tough and time taking [29]. If system involves several independent variables and in order to study the effect of each on response of process/system, one can change only one at a time while all others will be constant and this way is inefficient for system in which simultaneous effect of variables has to be considered and for this design of experiments (DOE) has been used to get experimental plan [30]. Thus, to overcome all problems associated with setting the experimental plan has been overcome by using response surface methodology (RSM) in DOE, with Design-Expert software version 9.0, Stat-Ease, USA. Thus, experimental plan and statistical analysis for biodiesel synthesis from waste *Phoenix dactylifera* L. kernel oil was done by using DOE in RSM. Central composite design CCD a module in RSM was utilized to develop the complete experimental plan based on the interaction of process variables considered for methanolysis. Presently four independent variables were taken under consideration such as temperature, time, catalysts loading and methanol to oil ratio and based on their interaction, process was optimized for maximum biodiesel yield (response factor). Range and coded level of all process variables is given in Table 1. The process variables were coded into three different levels low (−1) to medium (0) and high (+1) however design is rotatable so axial points are coded as low (− α) and high (+ α). Based on these experimental plan was obtained which consist of 30 experimental runs from which 6 are repeated runs on center point while 16 on factorial points and 8 on axial points. Replication on center point was employed to evaluate the experimental and to determine the feasibility of data reproducibility. The complete experimental plan matrix is given in Table 2 where yield is taken as response factor of independent variables.

For statistical analysis, analysis of variance ANOVA was used, for the relationship between independent variables and response factor, developed based on the general form of quadratic model

Table 1Parameters along with their defined ranges for optimizing the biodiesel production from waste *Phoenix dactylifera* L. biomass oil using synthesized bimetallic catalyst.

Parameters	Units	Axial	Low	Center	High	Axial
Temperature	°C	60	70	80	90	100
Time	h	1	2	3	4	5
Catalyst	wt%	1.5	3	4.5	6	7.5
Methanol to Oil ratio	–	7.5	15	22.5	30	37.5

Table 2Experimental plan developed by using RSM for biodiesel production from waste *Phoenix dactylifera* L. biomass oil by transesterification.

Run No	Temperature (°C)	Time (min)	Catalyst Amount (wt%)	MeOH: Oil ratio	Yield
1	90	4	3	15	96.4
2	70	4	3	30	67.3
3	90	4	6	30	82.4
4	90	2	6	30	74.7
5	70	4	3	15	73.6
6	80	5	4.5	22.5	75.4
7	90	2	3	30	76.4
8	70	2	3	30	61.1
9	70	4	6	30	66.9
10	70	2	6	30	60.4
11	80	3	4.5	22.5	82.4
12	80	3	7.5	22.5	68.4
13	100	3	4.5	22.5	91.2
14	90	4	3	30	83.6
15	70	2	3	15	63.4
16	80	1	4.5	22.5	59.7
17	80	3	4.5	22.5	85.4
18	90	2	6	15	77.6
19	70	2	6	15	62.5
20	90	4	6	15	87.3
21	80	3	4.5	22.5	82.4
22	80	3	4.5	22.5	83.7
23	90	2	3	15	79.7
24	80	3	4.5	22.5	85.4
25	80	3	4.5	7.5	76.4
26	70	4	6	15	69.2
27	80	3	1.5	22.5	79.3
28	80	3	4.5	22.5	84.8
29	80	3	4.5	37.5	67.1
30	60	3	4.5	22.5	58.3

as expressed in Eq. (1). Further on optimized points are predicted based on model obtained by employing experimental values.

$$Y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ij} X_i^2 + \sum_{i>j}^k \sum_j^k \beta_{ij} X_i X_j + e \quad (1)$$

where Y is response factor (biodiesel yield) β denotes regression coefficient; x_i and x_j are coded independent variables; i for linear and j for quadratic coefficient; k is number of independent variables and e denotes to error. The predicted model was analyzed by analysis of variance ANOVA, based on p-value (probability value) obtained by Fischer's test (F-value) which should be less than 0.05 attributing the significance of predicted model with 95% confidence. ANOVA analysis determines the suitability of experimental with the predicted mathematical model by RSM [31]. Inconsistency within the experimental data can be determined by ANOVA analysis and it is referred either to random or systematic error [32]. ANOVA analysis also helps to determine that how effective each variable is to response [33]. Moreover, the coefficient of determination R^2 near to 1 and insignificant Lack of fit ensures the suitability of predicted model for the experimental data produced. 3D and contour plots interactive plots were obtained based on the predicted model, which helped to study the combined effect of two independent variables on response factor while other two independent variables were kept constant.

2.4. Transesterification and product analysis

Transesterification was performed in a three-neck flat bottom flask connected to reflux condenser. First, oil with continuous stirring was heated initially up to the set temperature followed by addition of desired amount of catalyst and methanol to the flask. The reaction was carried out for desired time and the reaction mixture was allowed to cool down to room temperature. The catalyst from the liquid product was centrifuged, filtered and poured into the separating funnel, to separate the biodiesel from glycerol. The product biodiesel was washed thoroughly with warm water to remove impurities completely and rotary evaporator was used to remove any small amounts of water or methanol, if still present. Furthermore, small amounts of sodium sulphate beads were added to remove the moisture completely from biodiesel. Biodiesel composition was determined by a Perkin Elmer Clarus 600 gas chromatograph mass spectrometer (GC-MS), using a DB-Wax column. Helium was used as a carrier gas with constant flow of 1.0 ml/min, with a 1 μ l sample injected with mass spectrometer set to a scan a frequency range of 40–550 amu. The initial oven temperature was set to 80 °C and held for 5 min, before being increased to 240 °C at a heating rate of 4 °C/min. Quality of the synthesized biodiesel was evaluated based on its fuel properties determined according to EU and ASTM methods. The determined fuel properties involve density (ASTM 5002), cetane number (ASTM D613), cloud point (ASTM D2500), cold filter plugging point (ASTM D6371), pour point (ASTM D97), kinematic viscosity (ASTM

D445), flash point (ASTM D93) and acid value (ASTM D664). Each test was repeated three times in order to achieve accurate data. The yield of biodiesel was calculated using Eq. (2). The reusability of catalyst was also determined. The used catalyst recovered after experiment was rinsed to eliminate all impurities with methanol, followed by drying at 100 °C for 5 h and dried material was calcined at 650 °C for 4 h in furnace before each run.

$$\text{Yield} = \frac{\text{weight of biodiesel}}{\text{weight of oil}} \times 100\% \quad (2)$$

3. Results and discussion

3.1. Catalyst characterization

Fig. 1 shows the XRD patterns for pure ZrO_2 and synthesized bimetallic catalyst Mn@MgO-ZrO_2 . It can be observed from patterns that the crystalline nature of parent material (ZrO_2) is sustained after its co-precipitation with MgO and impregnation of Mn . The presence of MgO was assured by the define peak present at 42.10° [34] and the peaks present at 17.61° and 36.22° at scale of 2θ were due to Mn [35]. Meanwhile, two definite peaks at 28.1° and 31.6° assure the monoclinic nature of ZrO_2 . Thus, based on the patterns and peaks present in them it can be concluded that crystalline nature of ZrO_2 was sustained along with the added materials (MgO and Mn).

Fig. 2 shows the SEM images of synthesized bimetallic catalyst for surface morphology and EDS plot for elemental composition. It

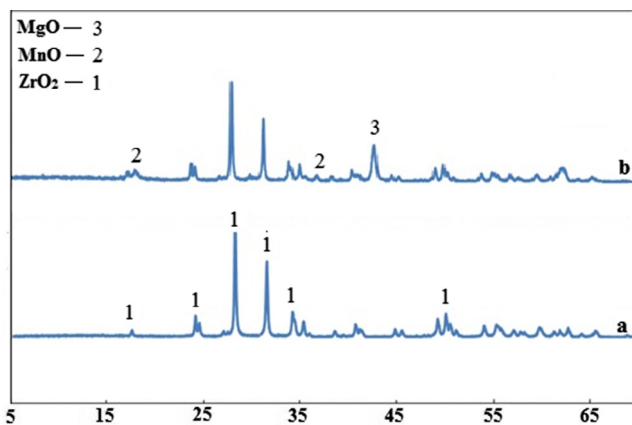


Fig. 1. XRD patterns for catalyst (a) pure ZrO_2 pattern and (b) pattern for Mn-MgO-ZrO_2 .

can be observed from the SEM image that catalyst particles possess definite crystal structure with uniform distribution of particles. Moreover, it can be observed from EDS plot that peaks for all particles (Zr , Mg & Mn) were present which assured the successful synthesis of bimetallic catalyst. Thus, based on the observation from SEM image and EDS plot it can be concluded that these are consist with the XRD results with showed crystalline nature of material along with definite peaks of each material (Zr , Mg & Mn). Moreover, the BET analysis was conducted to determine the surface area and pore size of catalyst. The specific surface area for synthesized catalyst was $45.78 \text{ m}^2/\text{g}$, pore volume $0.12 \text{ cm}^3/\text{g}$ and pore diameter 17.06 nm . It has been reported earlier that the particle size for triglyceride is 5.8 nm thus the catalyst synthesized for biodiesel production should possess pore diameter higher than the triglyceride molecule size [36]. Thus, based on results for synthesized catalyst it can be concluded that it will be suitable for biodiesel production. Hence, after catalyst characterization it was used for biodiesel synthesis from waste *Phoenix dactylifera* L. kernel oil. The biodiesel production was studied based on the experimental plan developed by RSM.

3.2. Prediction of mathematical model

RSM based prediction for the suitable model for experimental data was considered and based on this four different kind of models were suggested as shown in Table 3. These models were evaluated based p-value test to check there significance with experimental data. It can be observed that both quadratic and linear model has p-value < 0.0001 which depicts the significance of both models as for p-value less 0.005 shows its significance with 95% of confidence level. Thus, one model has to be considered for statistical analysis, so, p-values for lack of fit for linear and quadratic models were taken under consideration, and they were 0.0015 and 0.1359 for linear and quadratic models respectively. Lack of fit shows the between residual and actual error based on replicate runs and if value is higher than 0.01 it is insignificant and insignificant lack of fit attributes that experimental data fit well with the mathematical model. So, based on lack of fit quadratic is best suitable model for present experimental data. However, adjusted and predicted R^2 are close to one only for quadratic model, which confirm its suitability for present experimental data. So, quadratic model was selected based on its fitting with experimental data for statistical analysis and predicting response variable.

3.3. Statistical analysis

The process variables, which include temperature, time, catalyst loading and methanol to oil molar ratio with respect to yield of biodiesel as a response factor, were considered for statistical analysis.

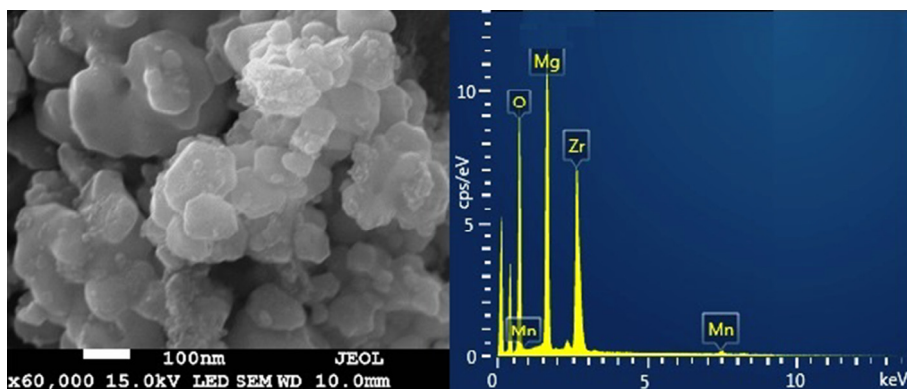


Fig. 2. SEM image and EDS plot for bimetallic catalyst Mn-MgO-ZrO_2 .

Table 3
Prediction of suitable model based on experimental data for biodiesel production.

Source	Sequential p-value	Lack of Fit p-value	Adjusted R-Squared	Predicted R-Squared	Decision
Linear	<0.0001	0.0015	0.7200	0.6975	
2F	0.9591	0.0008	0.6572	0.6512	
Quadratic	<0.0001	0.1359	0.9651	0.9078	Suggested
Cubic	0.6414	0.0442	0.9602	0.0094	Aliased

Table 4
ANOVA analysis for biodiesel production from waste *Phoenix dactylifera* L. biomass oil using synthesized bimetallic catalyst.

Source	Sum of Squares	df	Mean Square	F value	p-value Prob. > F
Model	2973.50	14	212.39	58.21	<0.0001
A	1658.34	1	1658.34	454.57	<0.0001
B	436.05	1	436.05	119.52	<0.0001
C	74.55	1	74.55	20.43	0.0004
D	128.34	1	128.34	35.18	<0.0001
AB	8.56	1	8.56	2.34	0.1465
AC	3.71	1	3.71	1.02	0.3295
AD	7.43	1	7.43	2.04	0.1742
BC	5.88	1	5.88	1.61	0.2236
BD	15.41	1	15.41	4.22	0.0577
CD	9.77	1	9.77	2.68	0.1226
A ²	111.44	1	111.44	30.54	<0.0001
B ²	399.33	1	399.33	109.54	<0.0001
C ²	137.70	1	137.70	37.74	<0.0001
D ²	209.79	1	209.79	57.50	<0.0001
Residual	54.73	15	3.65	–	–
Lack of Fit	46.37	10	4.64	2.77	0.1359
Determination coefficient (R ²)			0.9819		
Adjusted determination coefficient (Adj R ²)			0.9651		
Predicted determination coefficient (Pred R ²)			0.9078		
Adequate determination coefficient (Adeq R ²)			25.73		

As determined before that quadratic model fits well present experimental data, so based on this, significance and fitting accuracy of model as well as individual terms and there interaction was determined by analysis of variance ANOVA and are presented in Table 4. The p-value is considered to be tool for evaluating the significance of regression co-efficient and know to indicator for interaction strength for all cross product. It can be observed that F-value for model is 58.21 with the p-value of <0.0001 which shows the significance of model with 95% of confidence level. Moreover, while considering the individual process variables all of them were significant with p-value less than 0.005 which depicts that these entire process variables have significant effect on response factor. Similarly there quadratic terms A², B², C² and D² are significant despite of this linear interaction AB, AC, AD, BC, BD and CD were shown as insignificant on the response. Moreover, it can be seen that lack of fit F-value is 2.77 with p-value of 0.1359, which indicates its insignificance, which confirms the suitability of fitting of experimental data into predicted values.

Fitting of experimental data in predicted mathematical model was also confirmed from coefficient of determination R², adjusted coefficient of determination Adj. R² and predicted coefficient of determination Pred. R² whose value were 0.982, 0.965 and 0.908 respectively. Moreover, adequate determination coefficient Adeq R² that measures signal to noise ratio for predicted model it is 25.73 this should be more than 4. Hence, model is adequate for present process.

The model predicted by RSM based on experimental data in terms of coded factors is given as shown below in Eq. (3).

$$\begin{aligned}
 \text{Yield} = & 84.10 + 8.31A + 4.26B - 1.76C - 2.31D + 0.73AB \\
 & - 0.48AC - 0.68AD - 0.61BC - 0.98BD + 0.78CD \\
 & - 2.02A^2 - 3.82B^2 - 2.24C^2 - 2.77D^2 \quad (3)
 \end{aligned}$$

In order to confirm the significance of experimental data a plot was developed for actual value versus predicted values by model

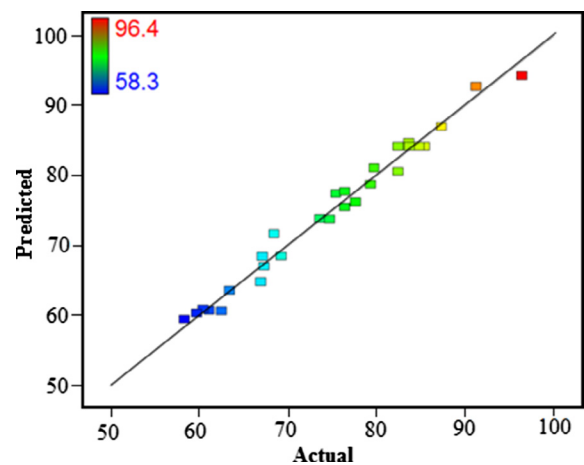


Fig. 3. Plot between the actual yield calculated based on experimental data and predicted yield calculated based on predicted quadratic model.

as shown in Fig. 3. It can be seen that the straight line has been drawn in normal plot of actual versus predicted values, which gave the good agreement between both values. So based on the plot it can be assured the accuracy and validity of model predicted by RSM for experimental data.

3.4. Parametric effect of process variables

Methanolysis was affected by several process parameters, which include process temperature, time, catalyst loading and methanol to oil molar ratio. In order to determine the optimized conditions for methanolysis interactive effect of process variables on yield of biodiesel has been taken in account. Fig. 4 shows plots for interactive effect of process variables on yield based on the 3D

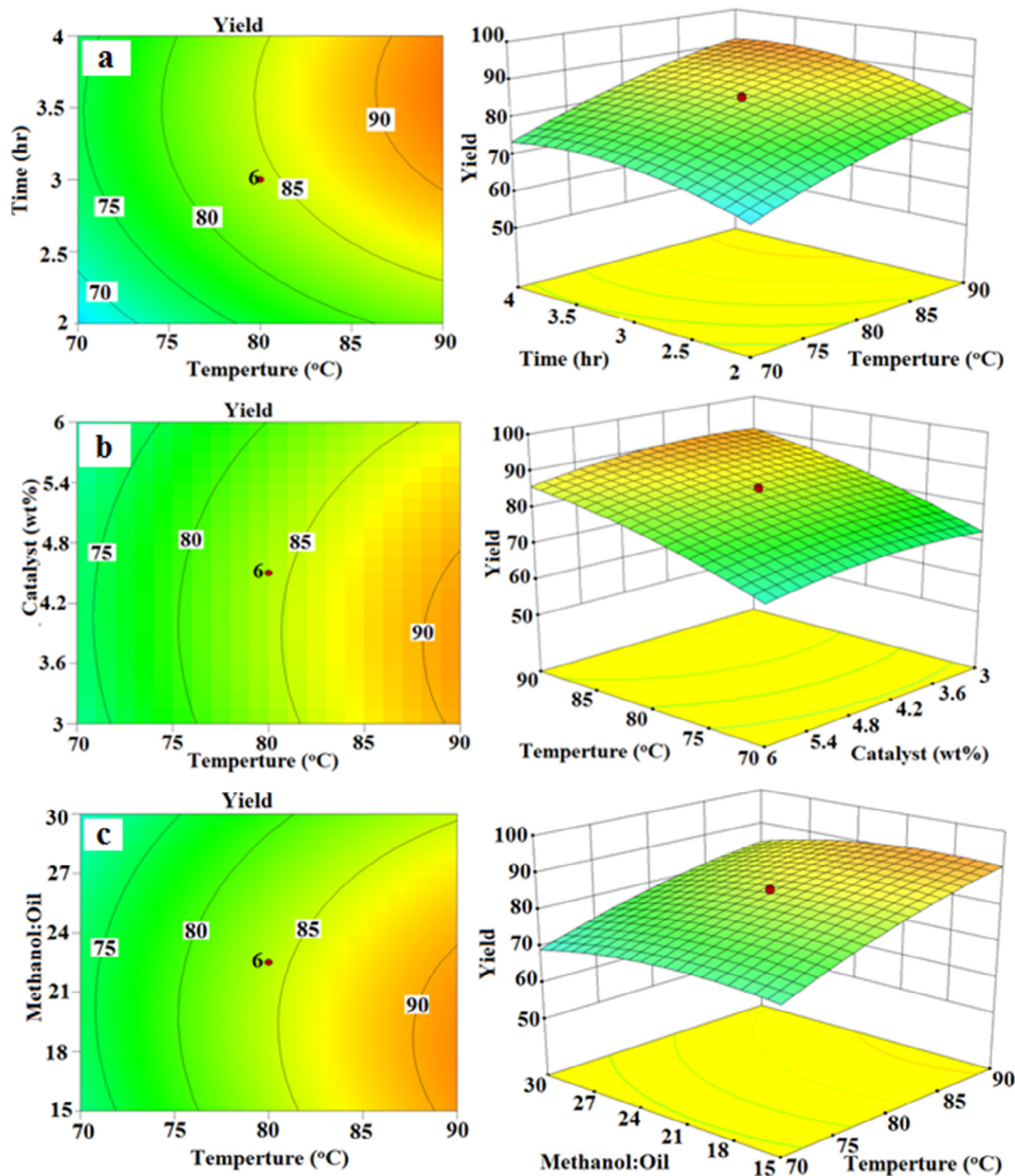


Fig. 4. Parametric effect for biodiesel production from waste *Phoenix dactylifera* L. biomass (a) interactive effect of temperature and time on biodiesel yield; (b) interactive effect of catalyst loading and temperature on biodiesel yield and (c) interactive effect of temperature and methanol to oil ratio on biodiesel yield.

and 2D contour plots. The red point in each plot either for 3D surface plot or 2D contour plot depicts the center point of process variables and it has six repeated experimental runs on it just to minimize the error to get better scaling up data. Fig. 4a shows the combined effect of temperature and time on the yield while other two parameters were kept constant. It can be observed that by increasing the temperature (70–90 °C) yield of biodiesel increases indicating that miscibility of reactants increased and allowing more conversion of reactants to biodiesel. As methanolysis is endothermic reaction so it is favored at high temperature [37]. However, similar observation was done for time, as it can be yield of biodiesel increases by increasing time along with temperature. Despite of this it was observed that by increasing temperature and time yield of biodiesel increases but up to certain extent and after it there was small decrement observed (axial point 100 °C and 5 h). This decrement might due to excess increment in temperature, which causes the excess vaporization of methanol in the

system and tends to less availability of it for methanolysis. Moreover, in general observation it can be seen that even in less time if temperature is increased the yield of biodiesel is increased but for time if at low temperature the reaction time is increased the yield is not that much significantly affected like temperature.

Fig. 4b shows the interactive effect of temperature and catalysts loading while other two parameters were kept constant. Similar to process temperature catalyst loading plays important role in the methanolysis as it depends on the presence of active sites of catalyst. However, it can be observed that along with temperature there was slight increase in the yield by increasing the catalyst loading (1.5–3 wt%) but further increasing the catalyst amount the yield decreased as mentioned also in Table 2. Certain amount of active sites are necessary for effective methanolysis if the catalyst amount is further increased their occurs the problem in mixing between reactants and interaction with active sites of solid catalyst and due to this limitation in mixing occurs and mass transfer resis-

tance between liquid–solid causes the yield of biodiesel to decrease at same operating conditions [18,38,39]. It has been reported earlier that increasing catalyst amount beyond certain limit cause the reversible reaction to occurs and also products from methanolysis get adsorbed on catalysts and thus tending to decrease the yield of biodiesel [40].

Fig. 4c shows the interactive 3D surface plot and 2D contour plot for temperature and methanol to oil molar ratio with their effect on yield of biodiesel. It is shown that temperature has positive effect on biodiesel yield however, when methanol to oil ratio increases yield of biodiesel decreases in range defined. Methanol to oil ratio is one of the important process parameter as it constitutes one of reactants amount as 2 mol methanol are required to one mole of triglyceride to produce biodiesel. As the reaction is reversible, so adequate amount of methanol is required in order to keep reaction on right side and based on this observation methanol is normally provided in excess amount to avoid reversibility of reaction. It has been reported earlier that excess methanol may tend to dilute oil up to large extent and moreover at higher methanol to oil ratio separation of glycerol layer become difficult and which tends to decrease the biodiesel yield [9].

3.5. Optimization

Biodiesel yield was optimized to find out the optimum combination of independent process variables on which maximum oil can be converted to biodiesel. Numerical optimization, a program in Design Expert 9 software was applied in which specific range for response factor as well as for independent variables has to be set. The specific range for independent variables (temperature, time, methanol to oil molar ratio and catalyst loading) was set between low and high levels while in terms of factors mentioned such as -1 and $+1$ respectively. The response factor (biodiesel yield) with maximum value was ultimate objective for which the lowest achieved value and maximum achievable was set. Software interpolates the data by numerical optimization technique within the range for response factor with maximum achievable value on optimum set of conditions within the defined range of independent variables. The optimum set of operational conditions obtained is temperature $90\text{ }^{\circ}\text{C}$, time 4 h, catalysts loading 3 wt% and methanol to oil molar ratio 15. Therefore, the yield of oil extracted at optimum conditions was 96.4 wt%. In order to validate the accuracy of quadratic model triplicate runs were conducted on the optimum conditions and yield of biodiesel was found to be 96.4 ± 0.3 wt%.

3.6. Determination of kinetic parameters

Biodiesel production through transesterification follows the mechanism as shown in Fig. 5. Generally, three molecules of alcohol are required to convert the one molecule of triglyceride to form methyl ester. As shown in Fig. 5 it can be seen that transesterification involves three steps to form biodiesel. However, it has been assumed that this consists of single step and intermediate reactions of di, mono-glyceride is ignored and due to excess availability of methanol, the reaction moves in forward direction only.

Thus, for the biodiesel production from *Phoenix Dactylifera* kernels in the presence of synthesized heterogeneous catalyst through

transesterification is also assumed to occur in single step elementary reaction. Kinetic calculations have been applied for triglyceride as methanol is in excess amount and is readily available in reaction mixture throughout the reaction time. The rate law based on the assumption that reaction is elementary reaction can be written as shown in Eq. (4):

$$\text{Rate} = -r_b = -\frac{d[\text{TG}]}{dt} = k[\text{TG}] \cdot [\text{MeOH}]^3 \quad (4)$$

where k is rate constant; $[\text{TG}]$ and $[\text{MeOH}]$ are concentrations of triglyceride and methanol in reaction vessel. Based on the stoichiometric calculation and rate law the order of reaction is four but due to excess availability of methanol in system its concentration does not limit the reaction and it was considered constant through the reaction. Thus in order to tackle this kind of system the reaction is considered to be pseudo first order reaction. So based on this assumption rate become as shown in Eq. (5):

$$\text{Rate} = -r_b = -\frac{d[\text{TG}]}{dt} = k'[\text{TG}] \quad (5)$$

where $k' = k[\text{MeOH}]^3$ is considered to rate constant after assuming that methanol concentration throughout reaction is constant so equation can be written as Eq. (6):

$$\text{Rate} = -r_b = -\frac{d[\text{TG}]}{[\text{TG}]} = k' dt \quad (6)$$

Integrating Eq. (6) by considering $[\text{TG}]_o$ initial concentration at time = 0 and $[\text{TG}]_t$ final concentration after the time interval when time = t yield to Eq. (7).

$$\int_{[\text{TG}]_o}^{[\text{TG}]_t} \frac{-d[\text{TG}]}{[\text{TG}]} = \int_0^t k' dt \quad (7)$$

Integrating Eq. (7) yield to:

$$-\ln\left(\frac{[\text{TG}]_t}{[\text{TG}]_o}\right) = k't \quad (8)$$

Conversion of triglyceride or formation of methyl ester can be expressed as shown in Eq. (9)

$$X = \frac{[\text{TG}]_o - [\text{TG}]_t}{[\text{TG}]_o} \quad (9)$$

Eq. (8) can be written as follow taking into account Eq. (9).

$$-\ln(1 - X) = k't \quad (10)$$

Thus, based on the nature of plots obtained in Fig. 6 for each temperature, which linear and value of coefficient of determination is more than 0.9 for each, which confirmed the assumption took, that reaction is pseudo first order reaction. From plot, the results obtained shows that rate constants for each temperature were 0.0062, 0.0093 and 0.0128 (min^{-1}) for 70, 80 and $90\text{ }^{\circ}\text{C}$ respectively. Similar kind of results have been reported earlier by Sivakumar et al. who reported the biodiesel production through transesterification and rate of reaction was pseudo first order [41].

Arrhenius equation is used for calculating activation energy, which gives the relationship between reaction rate constant, activation energy and temperature as shown in following Eq. (11):

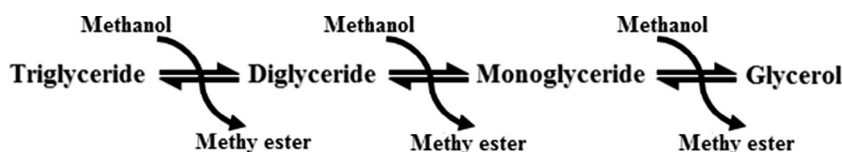


Fig. 5. Reaction scheme in which biodiesel formed from triglycerides present in waste *Phoenix dactylifera* L. biomass oil.

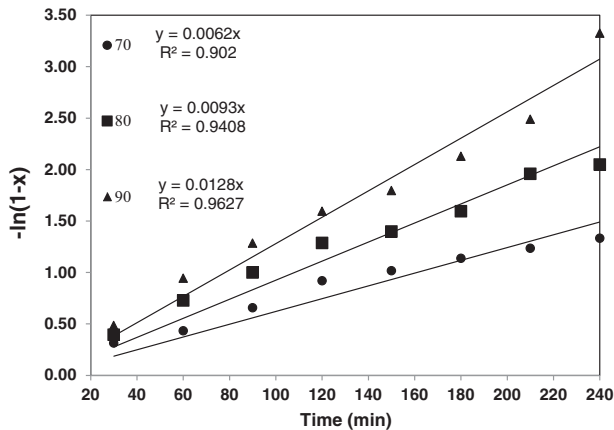


Fig. 6. Plot for determining the rate constant (k) at different temperatures for biodiesel produced by transesterification in presence of synthesized bimetallic catalyst.

$$k = Ae^{-\frac{E_A}{RT}} \quad (11)$$

where k is rate constant, A is pre-exponential factor or frequency factor, E_A is activation energy, R is gas law constant and T represents temperature. The equation can be modified by taking natural log of both sides and can be written as Eq. (12):

$$\ln k = \ln A + \frac{-E_A}{RT} \quad (12)$$

Equation can be written as Eq. (13):

$$\ln k = \ln A + \frac{-E_A}{R} \left(\frac{1}{T} \right) \quad (13)$$

A plot can be drawn based on the equation as shown in Fig. 7. Activation energy was calculated based on the linear equation obtained from plot. The activation obtained was 37.55 kJ/mol. While after comparing the results, the activation energy obtained for current process was in good agreement with previously reported results in literature as shown in Table 5. Thus, it can be concluded that in the current process, the activation energy is quite low and process can be up-scaled efficiently.

3.7. Quality analysis of biodiesel and catalyst reusability

Table 6 shows the fuel properties of produced biodiesel. It can be observed that biodiesel gave prospect regarding its fuel

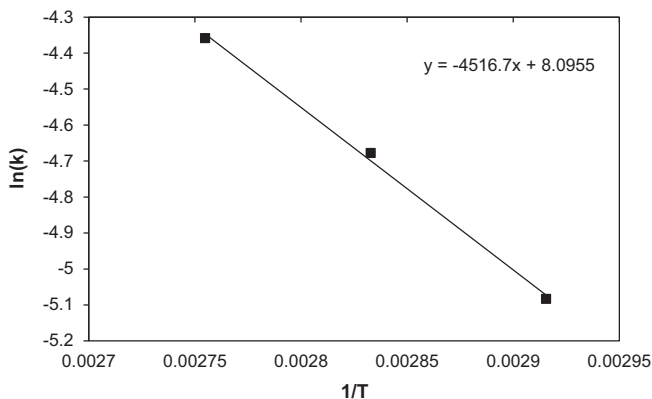


Fig. 7. Plot for modified form of Arrhenius model for determining the activation energy and frequency factor for biodiesel produced by transesterification in presence of synthesized bimetallic catalyst.

Table 5

Activation energy calculated by using different catalysts for biodiesel production.

Catalysts	Activation energy (kJ/mol)	Reference
Mn-(MgO-ZrO ₂)	37.55	Present work
KOH	92.70	[42]
CaO	79.00	[43]
TPA/Nb ₂ O ₅	34.40	[44]

Table 6

Fuel properties of produced biodiesel from waste *Phoenix dactylifera* L. biomass oil using synthesized bimetallic catalyst.

Property	EN 14214	ASTM 6751	PDOB ^c
Cetane number	51 min	47 min	60.31
Cloud point (°C)	-a	-	3.9
Pour point (°C)	-a	-b	-1.4
Cold Filter Plugging Point (°C)	-a	-b	-0.62
Flash point (°C)	120 min	93 min	141
Calorific Value (MJ/kg)	-b	-b	43.24
Viscosity (mm ² s ⁻¹) at 40 °C	3.5–5.0	1.9–6.0	4.24
Density (kg m ⁻³) at 25 °C	860–900	-	881
Acid Value (mg KOH/g)	0.50 max	0.80 max	0.32
Free Glycerin (%)	0.020 max	0.020 max	0.014
Total Glycerin (%)	0.250 max	0.240 max	0.190
Sulphur content	10 mg/kg max	15 mg/kg max	0.001

^a Not specified. EN 14214 uses time- and location-dependent values for the cold filter plugging point (CFPP) instead.

^b Not specified.

^c *Phoenix dactylifera* L. oil biodiesel.

properties that fulfils the international standards ASTM and EN. The cetane number for biodiesel is important factor to be determined as it effects the engine performance directly as it can be seen in Table produced biodiesel has cetane (60.31) higher than minimum limit defined by standards (ASTM & EN). Meanwhile, the low temperature properties; cloud point, pour point and cold filter plugging point were measured to 3.7 °C, -1.6 °C and -0.62 °C respectively. Low temperature properties for biodiesel gave its possibility for colder regions. These properties are very dependent on biodiesel composition. Biodiesel containing more saturated compounds leads to poor low temperature properties. Due to this, biodiesel with high amount of saturated esters are not preferred for colder regions. Flash point is the temperature at which liquid fuel catches flame. The flash point for biodiesel synthesized is 141 °C which satisfies the standards. It is the minimum temperature by which fuel vapors can ignite in open atmosphere and it is important property related to fuel's storage and transportation. Therefore, biodiesel with better flash point can help in storage and for its transportation. Calorific value confirms the energy produced after fuel combustion and helps to estimate engine thermal efficiency. The calorific value for synthesized biodiesel was 43.24 MJ/kg. Kinematic viscosity is important to be determined for sake of engine efficiency as high viscous fuel can causes engine deposits and which reduces atomization required for ignition. Thus, low viscous fuels are preferred and the kinetic viscosity for produced biodiesel at 40 °C was 4.24 mm²/s, which satisfies the standard limits defined by ASTM and EN. The density was measured to be 881 kg/m³, which found to be within the standard limits defined by EN14214. Normally biodiesel is denser than the petroleum diesel due to the presence of unsaturated compounds. Acid value was measured according to the standard method of ASTM D664 and was found to be 0.12 mg KOH/g which indicates that produced biodiesel quite less acidic and it is less than the minimum limits defined by ASTM and EN standards. High acidity of biodiesel is referred to the formation of free fatty acids by natural degradation of products due long storage time. So, based on the determined properties synthesized biodiesel satisfy the international standards

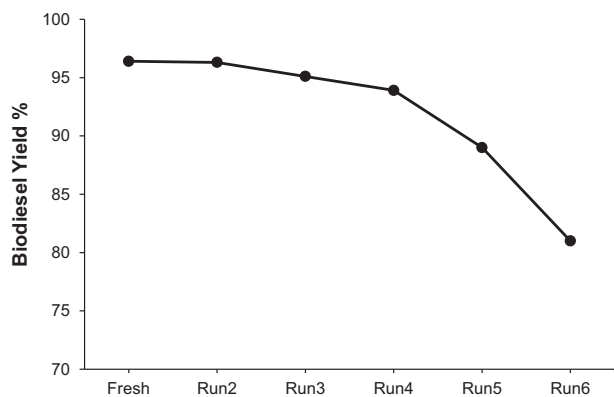


Fig. 8. Reusability of catalyst used for biodiesel production from waste *Phoenix dactylifera* L. kernel oil.

ASTM and EN. The catalyst was also evaluated to check its reusability and it was reused up-to six experimental runs as shown in Fig. 8. It can be observed from the trend for biodiesel yield in the plot that catalyst is highly active till fifth run and there was a significant decrement in yield of biodiesel in sixth time usage. Thus, this can be attributed to the fact it might be due to some reactants deposition on catalyst surface which allow less availability of active sites to upcoming reactants [10,45]. However, based on trend obtained it can be concluded that catalysts is highly active and reusable.

4. Conclusions

The four-factor, RSM based CCD experimental design was conducted for studying the transesterification of waste *Phoenix dactylifera* L. biomass oil. Thus, the selected ranges for operating variables satisfied the expected outcome for optimized biodiesel yield 96.4%. The quadratic model predicted based on experimental data was significant. The biodiesel yield calculated by using predicted model was in good agreement with actual biodiesel yield obtained from experiments. Moreover, with co-efficient of determination R^2 value was 0.98 which is close enough to 1 predicted the good fitting of experimental with model data with insignificant lack-of-fit 0.139. Hence, these RSM based results revealed the authenticity of data calculated based on predicted quadratic and can be used for up scaling. Moreover, pseudo first order reaction was assumed for kinetic calculations latter on based on the trend shown by plot shown between time and $-\ln(1-x)$ confirmed this assumption by giving straight line. The activation energy, for current process was 37.55 kJ/mol, this also confirmed the assumption of considering the reaction to be of pseudo first order. In conclusion, current process provides all possible means for economical production of biodiesel by considering non-edible waste *Phoenix dactylifera* L. kernel biomass

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