Full Length Article

Optimization of the production of biofuel form Jatropha oil using a recyclable anion-exchange resin

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ABSTRACT

The study of an anion-exchange resin (Amberlyst A26 (OH)) catalyzed transesterification of Jatropha (*Jatropha curcas* L.) oil was conducted to determine the effects of three variables: reaction temperature, ethanol: oil molar ratio and catalyst amount, on Jatropha oil conversion (X_{JO}) and fatty acid ethyl esters yield's (Y_{FAEEs}). The modified central composite design that involved three independent factors (temperature, ethanol: oil molar ratio and the catalyst present) with two levels, but not included the non-linear stage, was employed to optimize the process. From the main factors and their interactions, the ethanol: oil molar ratio was found to highly affect the X_{JO} and Y_{FAEEs}. In this study, the statistical analysis showed that curvature is not significant ($p \leq 0.05$), and thus, from the model regression equations, linear model was found to be more suitable to optimize the responses. By using the regression analysis and the response surface plots, the optimum X_{JO} and Y_{FAEEs} of 37.63% and 36.31%, respectively were predicted to be obtained at the optimum temperature of 55 °C, ethanol: oil molar ratio of 35:1 and catalyst amount of 15%. Employing higher amount of catalyst reduced the X_{JO} and Y_{FAEEs}, particularly, when the variable interacted with the reaction temperature.

1. Introduction

Biodiesel is produced by the transesterification of triglycerides, which are one of the main constituents of both edible and non-edible vegetable oils, and an alcohol [1]. Biodiesel from non-edible and wasted oils is considered to potentially be a vital renewable energy alternative to current fossil based fuel as it is nontoxic, bio-degradable, with low greenhouse gas emission and higher lubricating quality [1–3].

Some of the promising alternative processes for biodiesel production are still unprofitable. This is due to their limitations, which includes long reaction times, difficulties in the separation of the products, unaffordable amounts of solvents and generation of large amounts of wastewater [4,5]. For instance, the homogeneous alkaline catalysts such as NaOH and KOH are generally used for the industrial production of biodiesel [1,4]. However, these catalysts require refined oil that contains less than 0.5% free fatty acids (FFAs), and anhydrous conditions as water favors the formation of FFAs by hydrolysis of the triglycerides of the oil. Oil with FFA higher than the indicated limit results in an undesired side reaction, saponification. It also allows emulsions to occur between the obtained biodiesel and the byproduct glycerol, which requires a long settling time for separation. Moreover, alkaline catalysts need to be neutralized with mineral acids, and this results in a dirty glycerol that requires an expensive washing and purification procedure [1,4,6].

The commonly used homogenous acid catalysts such as HCl and H_2SO_4 were found to be more efficient in terms of overcoming the problematic saponification side reactions [1]. However, homogeneous acid catalysts are difficult to recycle and operate at high temperatures and also cause serious environmental and corrosion problems, and thus, are not efficient [1,7,8]. The catalytic enzymes, such as lipase, have high reaction selectivity and can be immobilized in a support material. However, enzymes are very expensive, and have unstable activities and slow reaction kinetics [1,9]. A catalyst-free supercritical method of biodiesel production produces quality biodiesel, and with a very high rate of production. However, the method is expensive as it requires a higher temperature and pressure [1].

Using of heterogeneous catalysts for biodiesel production offers many advantages over homogeneous alternatives, such as simple catalyst recovery, catalyst reusability, simple product purification, less energy and water consumption, lower costs of purification, and simple glycerol recovery [1,4,10]. Thus, to minimize the drawbacks observed in the utilization of homogeneous catalysts, several heterogeneous

catalysts such as clays, zeolites, oxides and polymer resins (ion exchange resins) have been evaluated for transesterification of vegetable oils [8,11].

Ion exchange resins are suitable catalysts for etherification, esterification, and transesterification reactions [12–14]. The main advantage of using the resins over other heterogeneous catalysts is the opportunity to prepare tailor-made materials by controlling the polymerization conditions [8]. For instance, ion exchange resins can be prepared with different particle sizes and porosity degrees, and a wide variety of functional groups can also be introduced in these polymeric resins to prepare different materials [11]. Moreover, ion exchange resins can be easily separated from the biodiesel produced as they have relatively larger sizes [14].

From several literature reports on the catalytic activities of heterogenous catalysts in the transesterification of vegetable oils, only a few reports were found for that of ion exchange resins. Some of these investigations report that anionic ion exchange resins were more effective in the transesterification of oil than the cationic resins. For instance, Li et al. [14] and Shibasaki-Kitakawa et al. [1] investigated the transesterification of oil with methanol and ethanol respectively, using different types of ion exchange resins as catalysts and the catalytic activities of these resins were then compared. From these studies, it was reported that in general the anionic resins were more efficient in their catalytic activities than the cationic resins under the same conditions for the respective studies. Similarly, in the study of the catalytic activities of Amberlyst 15Wet (cationic resin) and Amberlyst A26 (OH) (anionic resin) on the transesterification reactions of Brazilian soybean oil with methanol and ethanol, the anionic resin was found to be more efficient than the cationic resin for the production of biodiesel under similar conditions [11].

The use of Amberlyst A26 (OH) to catalyze the transesterification of Jatropha (*Jatropha curcas* L.) oil to biodiesel is of interest due to the resin's ability to be recovered, regenerated, and reused. Amberlyst A26 (OH) resin can carry out both esterification and transesterification reactions consecutively, and it is very important to reduce the saponification side reactions in cases of biodiesel production from oils containing free fatty acids [15]. It is a macroporous ion-exchange resin with quaternary ammonium functional groups that impart a strongly basic and reactive surface [15]. The quaternary ammonium functional group in the resin is known to ease transesterification and to remove free fatty acids [15,16].

Only a few research reports were found, from literature, concerning the catalytic activities of Amberlyst A26 (OH) in the transesterification of vegetable oils. For instance, in the transesterification of sunflower oil with methanol using ion-exchange resins (anionic Amberlyst A26 (OH) and A27 (OH) and cationic Amberlyst 15), Vicente et al. [17] obtained a conversion that was less than 1% with each resin. By employing Amberlyst A26 (OH) in the transesterification of Brazilian soybean oil using ethanol, Oliveira et al. [11] obtained the oil conversion of 100% by using 50 mol % of resin, alcohol: oil molar ratio of 150:1 and a reaction time of 24 h. This shows that the catalytic activities of Amberlyst A26 (OH) in the transesterification of oil vary for different vegetable oils, the reaction conditions and needs much amount of alcohol and the catalyst. Moreover, to our knowledge, no research investigation has been performed on the transesterification of Jatropha oil using Amberlyst A26 (OH) in the presence of ethanol.

The objective of this study is to investigate the catalytic transesterification of Jatropha oil using Amberlyst A26 (OH) (a heterogeneous ion-exchange resin) and to determine the effects of reaction temperature, the ethanol: oil molar ratio and the catalyst percent on the conversion of the oil and the yield of biodiesel, and to optimize the process. For this purpose, a Design of Experiment (DOE) and Response Surface Methodology (RSM) have been implemented on the most significant operational variables.

2. Materials and methods

2.1. Reagents and materials

Jatropha oil that was extracted from Ethiopian seeds with Soxhlet extractor using hexane as solvent was used for the experiments. The oil's physico-chemical properties, such as density, iodine number, composition, etc., has already been carried out and the results were submitted elsewhere [18]. The Amberlyst A26 (OH). in wet form, was purchased from Dow Chemical Company, it was used as received, no pretreatment was done to it. The absolute ethanol, tetradecane, pyridine, acetone, methanol and hexane used were purchased from Sigma-Aldrich and with a purity of higher than 99% and used as received.

2.2. Experimental setup for the reactions

The reaction of Jatropha oil with absolute ethanol using Amberlyst A26 (OH) as the catalyst, was performed in a three-neck glass reactor from Quark Glass, with a volume capacity of 500 ml. A cooling condenser, connected to tap water, was inserted into the middle neck of the reactor to enable the refluxing of evaporated ethanol into the reactor. A thermostat attached to the digital heating plate on which the reactor was standing was inserted into the glass reactor, through one of the side necks, to measure the temperature of the reacting mixture. The third neck of the glass reactor was plugged with a rubber cork through which the samples of the reaction mixture were periodically taken using a syringe. The lower part of the reactor was connected to a thermostatic water bath that regulated the temperature of the reacting mixture by circulating the water through the reactor.

Before the reaction time was started, 50 g of Jatropha oil and the calculated amount of ethanol were added to the glass reactor and heated to the required temperature by vigorously stirring the mixture at a rate of 200 rotations per minute (rpm). When the mixture reached the pre-set temperature, a measured amount of Amberlyst A26(OH) was added to the mixture. This was registered as the starting time of the transesterification reaction. The stirring intensity of 200 rpm was maintained for all experiments to overcome the mass-transfer limitations. The aliquots (about 0.5 ml) of the reaction mixture were withdrawn using a syringe at specified time intervals (0, 5, 10, 15, 20, 30, 45, 60, 90, 120, 180, 240, 300, 420, 480 and 540 min) to investigate the progress of the reaction. This total amount of liquid removed from the reactor represents a small quantity in comparison with the total volume, and therefore a constant volume batch system can be assumed. After the reaction, the mixture was filtrated by placing the filter paper on the separatory funnel to separate the resin from the other constituents of the mixture. The filtrate mixture collected in the separatory funnel was then allowed to stand overnight to form different layers of the constituents of the mixture for separation. The resin remaining on the filter paper was washed by acetone and ethanol to be reused for another transesterification reaction [11]. After the separation of the resin, the samples were prepared for analysis, no pre analysis treatment was performed. The solid resin was used once, even though there is an established process to recover the catalysts, its reuses has not been tested so far.

2.3. Analysis of the reaction samples

The reaction samples were analyzed using the gas chromatography (GC) analyzer (Bruker scion 436 chromatograph) equipped with an autosampler (CP-8400), a flame ionization detector (FID) and using a 5-phenyl-methylpolysiloxane capillary column (DB-5HT column, Agilent Technologies). The GC column has a length of 15 m, a diameter of 0.32 mm and a thickness of 0.10 μm. The injection system was split-splitless, and helium was used as carrier gas with a flowrate of 1 ml min^{-1}. The temperature of the injector was set at 320 °C while that of detector was adjusted at 350 °C. The initial temperature in the

oven was 80 °C and it was programmed to raise with 10 °C per minute until it reached a final temperature of 360 °C. The GC samples were prepared following the AOAC (2003). Accordingly, tetradecane and pyridine were used as the internal standard and solvent for the GC samples, respectively. The GC analysis was performed by injecting 1 µl of the prepared samples into the equipment.

Using the area obtained for a given weight of the sample and internal standard from the chromatogram, the weight was converted to molar values with the help of standards and the response factors using equations (1) and (2) [19].

$$m_{EE} = \frac{m_{is} \times A_{EE}}{R_{EE} \times A_{is}} \qquad (1)$$

$$\eta_{EE} = \frac{m_{EE}}{M_{EE}} \qquad (2)$$

Where m_{EE} = mass of ethyl ester (g), m_{is} = mass of internal standard (g), A_{EE} = peak area of ethyl ester, R_{EE} = response factor of ethyl ester, A_{is} = peak area of internal standard, η_{EE} = number of moles of ethyl ester and M_{EE} = molar mass of ethyl ester (g mol^{-1}).

The equation used to calculate Jatropha oil conversion (X_{JO}) is expressed as:

$$X_{JO} = \frac{Initial\,moles\,of\,oil - Final\,moles\,of\,oil}{Initial\,moles\,of\,oil} x100 \qquad (3)$$

Moreover, the fatty acid ethyl esters yield (Y_{FAEEs}) obtained was calculated using the expression below following the study by Wang et al. [20].

$$Y_{FAEEs} = \frac{FAEE(\%)}{TG(\%) + DG(\%) + MG(\%) + FAEE(\%) + FAA(\%)} x100 \qquad (4)$$

Where FAEE, TG, DG, MG, and FAA refer to fatty acid ethyl ester, triglycerides, diglycerides, monoglycerides and free fatty acids, respectively.

2.4. Experimental design and statistical analysis

2.4.1. Response surface Methodology

Response Surface Methodology (RSM) is a collection of statistical and mathematical techniques that are useful for the modeling and analysis of problems in which a response of interest is influenced by several variables, and the objective of using RSM is to optimize this response [21,22]. It is used to evaluate operation variables that may or may not have a significant effect in the main responses [21]. The design procedures of RSM involve:

i) developing an original design of experiment for adequate and reliable measurement of the selected responses (the conversion of the oil to biodiesel and biodiesel yield in the current study),
ii) developing equations of a statistical model with best fittings,
iii) obtaining the optimal set of experimental parameters that results in the maximum value of responses, and
iv) presenting the direct and interactive effects of the parameters using response surface plots.

2.4.1.1. Experimental design.
In the present study, the modified central composite design (CCD) that excluded the star points (the non-linear stage) was applied to determine the influences of three different factors and their interaction on the conversion of Jatropha oil to FAEE (biodiesel) and the Y_{FAEEs}, and to optimize the process. The non-linear stage of the CCD was not included in the current experiment as the statistical analyses of the responses of factorial (linear) points and replicated central points showed that curvature was not significant, and thus, the linear model was used [23]. The design of the experiment involved three independent factors with two levels (2^3 factorial). The selected factors were reaction temperature (T), ethanol: oil molar ratio

Table 1
Values of the factors at different levels in the modified central composite design.

Factors	Levels		
	−1	0	1
Temperature (°C)	45	50	55
Molar ratio (-)	15	25	35
Catalyst amount (%)	15	20	25

(R) and the catalyst percent (C) whereas the X_{JO} and Y_{FAEEs} were the two chosen responses. The reaction time and stirring speed were kept constant at 540 min (9 h) and 200 rpm, respectively.

The selected factors have been chosen based on the previous transesterification reaction studies by Sánchez et al. [5] and Ayoola et al. [24], where the temperature, methanol: oil molar ratio and catalyst percent were found to be the most significant variables. The values for the factors were also selected based on the information from the product data sheet of the catalyst and a few related previous studies on ion-exchange resins [8,11,25]. As it was indicated on the product data sheet of the current catalyst (Amberlyst A26(OH)), its maximum operating temperature is 60 °C and thus, the maximum reaction temperature was kept below 60 °C. The design of the experiment consisted of eight factorial (linear) point and six center point experiments, respectively. Running replicated central points is important to measure the accuracy of the study, and it is also used in checking for the presence of curvature [23]. The values of the selected factors and their associated levels in the modified central composite design are presented in Table 1.

2.4.1.2. Statistical analysis.
The statistical analyses were performed by designing the sets of different experiments using the Statgraphics Centurion 17 (Statgraphics Technologies, Inc USA). The analyses allowed us to determine the influences of the main factors and their interactions on the conversion of Jatropha oil to biodiesel and yield of the biodiesel. The equations of the regression models were used to interpret the effects of the main factors and their interactions on the selected responses and predict the optimum conditions needed to maximize the responses.

The presence of curvature in the response surface when the selected model equation used was tested statistically using the responses of the factorial points and that of the replicated center points, by employing the statistical equations 5–7 [23,26]. Then, the p value associated with the calculated F value was determined to test the significance of the curvature ($p \leq 0.05$).

$$SS_{pure\,quadratic} = \frac{n_F n_C (\bar{y}_F - \bar{y}_C)^2}{n_F + n_C} \qquad (5)$$

$$MS_E = \frac{\sum_{Central\,points} (y_i - \bar{y}_C)^2}{n - 1} \qquad (6)$$

$$F = \frac{SS_{pure\,quadiratic}}{MS_E} \qquad (7)$$

Where: $SS_{pure\,quadratic}$ = sum of square for pure quadratic curvature, and MS_E = mean square error of central points. $\bar{y}_F$ and $\bar{y}_C$ are the average of responses of factorial and central points, respectively. n_F and n_C are number of factorial and central points, respectively. y_i refers to the responses of the central points and $n_C - 1$ is the degree of freedom for central points. F = F-statistic, the test statistic for F-tests.

3. Results and discussion

3.1. Design of the experiment and the experimental responses

As already mentioned, the present study investigated the influences

Table 2
Linear and central point experiments of the design of the experiments and the X_{JO} and Y_{FAEEs}.

Stage/types of experiments	Run number	Temperature (°C)	Molar Ratio	Catalyst (wt%)	X_T	X_R	X_C	X_{JO} (%)	Y_{FAEEs} (%)
Linear (factorial) stage	1	45	15	15	−1	−1	−1	16.91	16.14
	2	55	15	15	1	−1	−1	19.66	18.79
	3	45	35	15	−1	1	−1	31.61	30.41
	4	55	35	15	1	1	−1	38.12	36.81
	5	45	15	25	−1	−1	1	18.14	17.32
	6	55	15	25	1	−1	1	20.53	19.63
	7	45	35	25	−1	1	1	36.91	35.61
	8	55	35	25	1	1	1	34.55	33.29
Center stage	9	50	25	20	0	0	0	29.33	28.19
	10	50	25	20	0	0	0	32,22	31,01
	11	50	25	20	0	0	0	26.76	25.68
	12	50	25	20	0	0	0	27.03	25.94
	13	50	25	20	0	0	0	26.73	25.65
	14	50	25	20	0	0	0	28.42	27.31

of the three selected factors and their interaction on the conversion of Jatropha oil to biodiesel and the biodiesel yield. The modified central composite design (CCD) with three factors and two levels factorial (2^3) that consisted of only two stages (eight factorial/linear points and the central points that were replicated six times). Accordingly, the experiments of the linear stage and the central points were carried out randomly, and the obtained X_{JO} and Y_{FAEEs} were recorded. The natural and coded factors and the resulting X_{JO} and Y_{FAEEs} for the experiments were presented in Table 2.

As it can be seen from Table 2, the largest experimental X_{JO} (38.12%) and Y_{FAEEs} (36.81%) were obtained when the reaction was carried out at the reaction temperature of 55 °C, ethanol: oil molar ratio of 35:1 and 15% catalyst.

3.2. Effects of the reaction variables

During the experiment, four reactions were carried out by varying the temperature, ethanol: oil molar ratio and catalyst amount one at a time and keeping the other reaction conditions constant (at the value of the central points) to investigate the effects of the respective factors on the responses. Fig. 1a-c shows the effects of temperature, ethanol: oil molar ratio and catalyst amount on the X_{JO} and Y_{FAEEs} by keeping two of the three factors constant. As it can be seen from Fig. 1a, the raising of reaction temperature from 41.6 to 55 °C resulted in the increase of X_{JO} and Y_{FAEEs} by 5.39% and 5.27%, respectively. The raising of the ethanol: oil molar ratio from 8.18:1 to 35:1 found to increase the X_{JO} and Y_{FAEEs} by 33.71% and 32.88%, respectively (Fig. 1b). Moreover, increasing the catalyst amount from 11.6 to 25% resulted in the increase of X_{JO} and Y_{FAEEs} by 2.42 and 2.37%, respectively (Fig. 1c). Thus, the results of these experiments showed that from the influences of the three investigated reaction factors, the effects of ethanol: oil molar ratio on both responses are the largest.

3.3. Results from the statistical analysis

The statistical analysis was performed by considering the reaction temperature, ethanol: oil molar ratio and the catalyst amount. The effects of the main factors and their interactions on X_{JO} and Y_{FAEEs} were determined using Statgraphics Centurion 17, and the $SS_{pure\ quadratic}$, MS_E and the value of F statistics were determined using equations 5–7 [23,26] to test the presence (significance) of curvature ($p \leq 0.05$) in the response surface plot as previously mentioned. Table 3 shows the results obtained from the statistical analysis of the experimental responses. From the results depicted in Table 3, ethanol: oil molar ratio was found to be the factor with the highest positive impact. The reaction temperature and the catalyst percent were found to have a very small positive impact on the transesterification process compared to that of ethanol: oil molar ratio. Moreover, the effects of all the binary

interactions on the transesterification process were found to be small and negative.

The experimental results from Fig. 1 and Table 3 showed that ethanol: oil molar ratio has the highest positive impact on the transesterification Jatropha oil. According to the stoichiometry, three molecules of ethanol react with one molecule of triglyceride to produce three moles of FAEE. However, an excessive amount of alcohol is generally employed to promote the forward reaction to increase the oil conversion and yield of the esters [27,28] and to facilitate the glycerin separation [27]. This is in line with literature reports for transesterification of different vegetable oils using ion-exchange resins as catalyst, in which an increase in the molar ratio of alcohol to oil ratio highly influenced the transesterification of the oils. For example, in the transesterification of soybean oil with ethanol, Oliveira, et al. [11] reported an increase of oil conversion from 50% to 100% when the alcohol to oil molar ratio raised from 50:1 to 150:1.

There are also reports from literature about the requirement of very high alcohol: oil molar ratio for the transesterification of soybean oil with ethanol and methanol by using ion exchange resins. In the study of the influence of methanol: oil molar ratio on the conversion of babaçu coconut oil by using Amberlyst 15 wet as catalyst, Reis et al. [25] found the need of a high alcohol amount to produce ester. Accordingly, the authors reported that the conversion of oil to biodiesel reached around 70% only by employing an alcohol: oil molar ratio of 300:1, which is very high.

From an industrial perspective, increasing the amount of alcohol has several disadvantages, technical as well as economical. The higher amount of alcohol produced that the reaction equipment is of bigger size, increasing the investment cost, there is more energy consumed due to heating of reactors, pumping of streams, storage of products, etc. as well more time and money consumed separating the alcohol from the products, recirculation of the unreacted material, among other disadvantages.

In order to make this new technology more commercially attractive, it is imperative to improve the reaction, decreasing the amount of alcohol to almost stoichiometric quantities, reducing the cost of reactant, the cost of recycling material as well as making the equipment as efficient as possible. However, this needs to go hand in hand with producing the desired product at the desired quality and with the desired conversion and selectivity.

In the current study, compared to the influence of ethanol: oil molar ratio, the impacts of the reaction temperature and catalyst amount on the oil conversion and biodiesel yield are very low (Fig. 1 and Table 3). According to Yatish et al. [29], generally, temperature has a positive impact on the transesterification of different vegetable oils although this depends on the type of catalyst and the experimental range studied.

The natural values of the experimental variables were used to predict the suitable mathematical regression models for the described
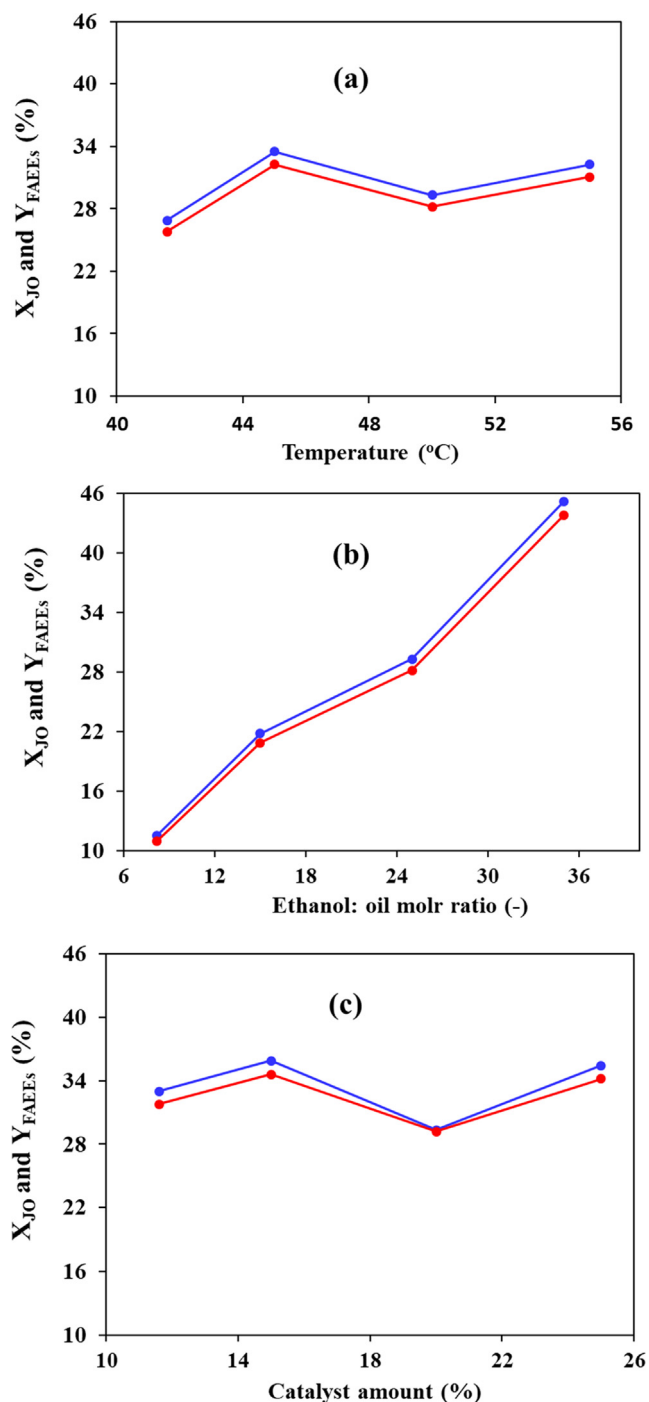
Fig. 1. (a) Effect of reaction temperature (•) on X_{JO} and (●) Y_{FAEEs} at ethanol: oil molar ratio of 25:1, catalyst amount: 20 wt%. (b) Effect of ethanol: oil molar ratio (•) on X_{JO} and (●) Y_{FAEEs} at reaction temperature: 50 °C and catalyst amount: 20 wt%. (c) Effect of catalyst amount (•) on X_{JO} and (●) Y_{FAEEs} at reaction temperature: 50 °C and ethanol: oil molar ratio: 25:1. The stirring intensity: 200 rpm and reaction time: 540 min were common for all the three cases.

transesterification of Jatropha oil using Amberlyst A26 (OH). As the curvature for both responses is not significant (Table 3), the first order mathematical model (linear model) was found to be suitable to be used for the optimization of the transesterification process [23,26]. Accordingly, the linear regression models that express the X_{JO} and Y_{FAEEs} under the current experimental range are presented in equation (8) and (9), respectively.

Table 3
Results from the statistical analysis of the experiments.

Parameters	Responses	
	Oil conversion	Biodiesel yield
Main effects and interactions	$\bar{y} = 27.63$	$\bar{y} = 26.55$
	$I_T = 2.32$	$I_T = 2.26$
	$I_R = 16.48$	$I_R = 16.06$
	$I_C = 0.95$	$I_C = 0.92$
	$I_{TR} = -0.24$	$I_{TR} = -0.22$
	$I_{TC} = -2.31$	$I_{TC} = -2.26$
	$I_{RC} = -0.092$	$T_{RC} = -0.08$
Significance of curvature (at $p \leq 0.05$)		
Mean response (factorial points, $\bar{y}_F$)	27,053	26.00
Mean response (center points, $\bar{y}_C$)	28.415	27.29
Curvature	−1.36	−1.29
$SS_{pure\ quadratic}$	6.35	5.76
MS_E	4.56	4.35
F calculated	1.39	1.32
p value	0.291	0.301
Significance of curvature ($p \leq 0.05$)	Not significant	Not significant

Where: T = temperature, R = ethanol: oil molar ratio, C = catalyst percent, I_{TR} = interaction of temperature and molar ratio, I_{TC} = interaction of temperature and catalyst percent and I_{RC} = interaction of molar ratio and catalyst percent.

X_{JO}

$$= -56.20 + 1.21T + 0.96R + 2.42C - 0.0024TR - 0.046TC - 0.00092RC \tag{8}$$

Y_{FAEE}

$$= -55.14 + 1.18T + 0.93R + 2.37C - 0.0022TR - 0.045TC - 0.00085RC \tag{9}$$

Based on the regression models, three-dimensional (3D) response surface plots were produced to illustrate the binary interaction effects of the reaction temperature, ethanol: oil molar ratio and catalyst percent (Figs. 2-4). From the binary factor interactions (I_{TC}, I_{TR} and I_{RC}), the effect of the interactions of temperature and catalyst percent on the responses was relatively larger and negative while that of the interaction of ethanol: oil molar ratio with catalyst amount was the smallest (Table 3). As aforementioned, generally, the effects of the binary interactions of the experimental factors on the X_{JO} and Y_{FAEEs} were found to be low. The negative impact of the interaction of the temperature and catalyst amount on the responses might be due mass-transfer limitation at higher concentration of the catalyst (Table 3 and Fig. 4a and b).

As it can be seen from Fig. 2a and b and Fig. 3a and b, in the interactions of temperature and ethanol: oil molar ratio (at catalyst amount of 20%) and those of the catalyst percent and ethanol: oil molar ratio (at constant temperature, 50 °C), the effects of the factors on both responses were dominated by the alcohol: oil molar ratio. As the ethanol: oil molar ratio raised from its minimum (15:1) to the maximum (35:1) of the experiment, the X_{JO} and Y_{FAEEs} increased linearly whereas the impacts of the temperature and catalyst amount, respectively were relatively lower. Accordingly, when the ethanol: oil molar ration raised to 35:1, both responses were predicted to reach above 33% even at the minimum experimental temperature (45 °C) and catalyst amount (15%), respectively (Fig. 2a and b and Fig. 3a and b). Moreover, the linearity and continuous increasing of both responses with the raising of the alcohol: oil molar ratio up to the maximum value of the experiment suggested that further increasing of ethanol: oil molar ratio than the experimental maximum could result in higher X_{JO} and Y_{FAEEs} compared to those obtained in the current experiments.

In the binary interactions of reaction temperature and catalyst amount (Fig. 4a and b), the maximum X_{JO} and Y_{FAEEs} were predicted to be obtained when the reaction temperature raised form the minimum (45 °C) to the maximum (55 °C) experimental ranges but at the
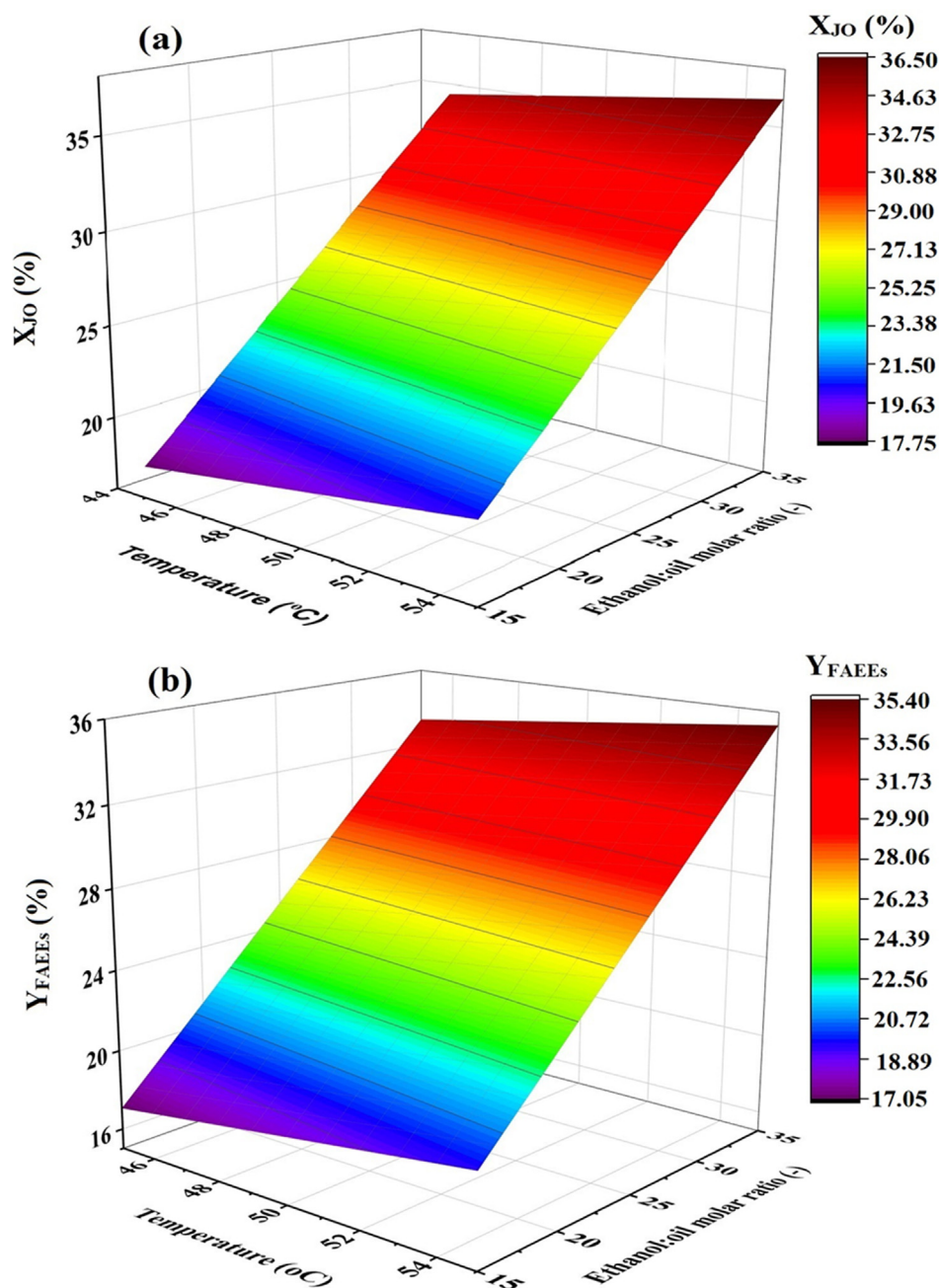
Fig. 2. Response surface 3D plot indicating the influence of temperature and ethanol: oil molar ratio on (a) the X_{JO} and (b) Y_{FAEEs}. Catalyst amount = 20% (temperature and ethanol: oil molar ratio refer to the actual values).

minimum catalyst amount (15%). The amount of catalyst utilized in the present experiment varied from 15 to 25%. Although the variable, generally, has slight positive effects on the transesterification process of the oil (Table 3), its interaction with temperature at the average ethanol: oil molar ratio (25:1) had a negative impact on both responses. As it can be seen from Fig. 4a and b, when the catalyst amount raised from the minimum (15%) to the maximum (25%) range of the experiment, both the X_{JO} and Y_{FAEEs} slowly decreased. The decreasing of the X_{JO} and Y_{FAEEs} with the simultaneous raising of the catalyst amount and temperature at the average ethanol: oil molar ratio (25%) might be due to the lower ethanol: oil molar ratio than the optimum alcohol: oil molar ratio value predicted (35:1) (Table 4) and the mass-transfer limitation that could be occurred as the catalyst amount increased.

By using the linear model equations and the response surface plots, the optimum X_{JO} and Y_{FAEEs} of 37.63% and 36.31%, respectively were

predicted to be obtained at the optimum temperature of 55 °C, ethanol: oil molar ratio of 35:1 and catalyst amount of 15% (Table 4). During the experiment, the X_{JO} and Y_{FAEEs} of 38.12% and 36.81%, respectively were obtained at the same reaction conditions (reaction temperature of 55 °C, ethanol: oil molar ratio of 35:1 and catalyst amount of 15%) (Table 2), and thus, the experimentally obtained values are in agreement with those predicted for the optimal operational conditions.

The graphical representation for the predicted values and experimental results of X_{JO} and Y_{FAEEs}, are presented in Fig. 5a and b, respectively. As it can be seen from Fig. 5a and b, the predicted X_{JO} and Y_{FAEEs} generally banded around the predicted straight line and this shows the better correlation of the predicted values with the experimental results.
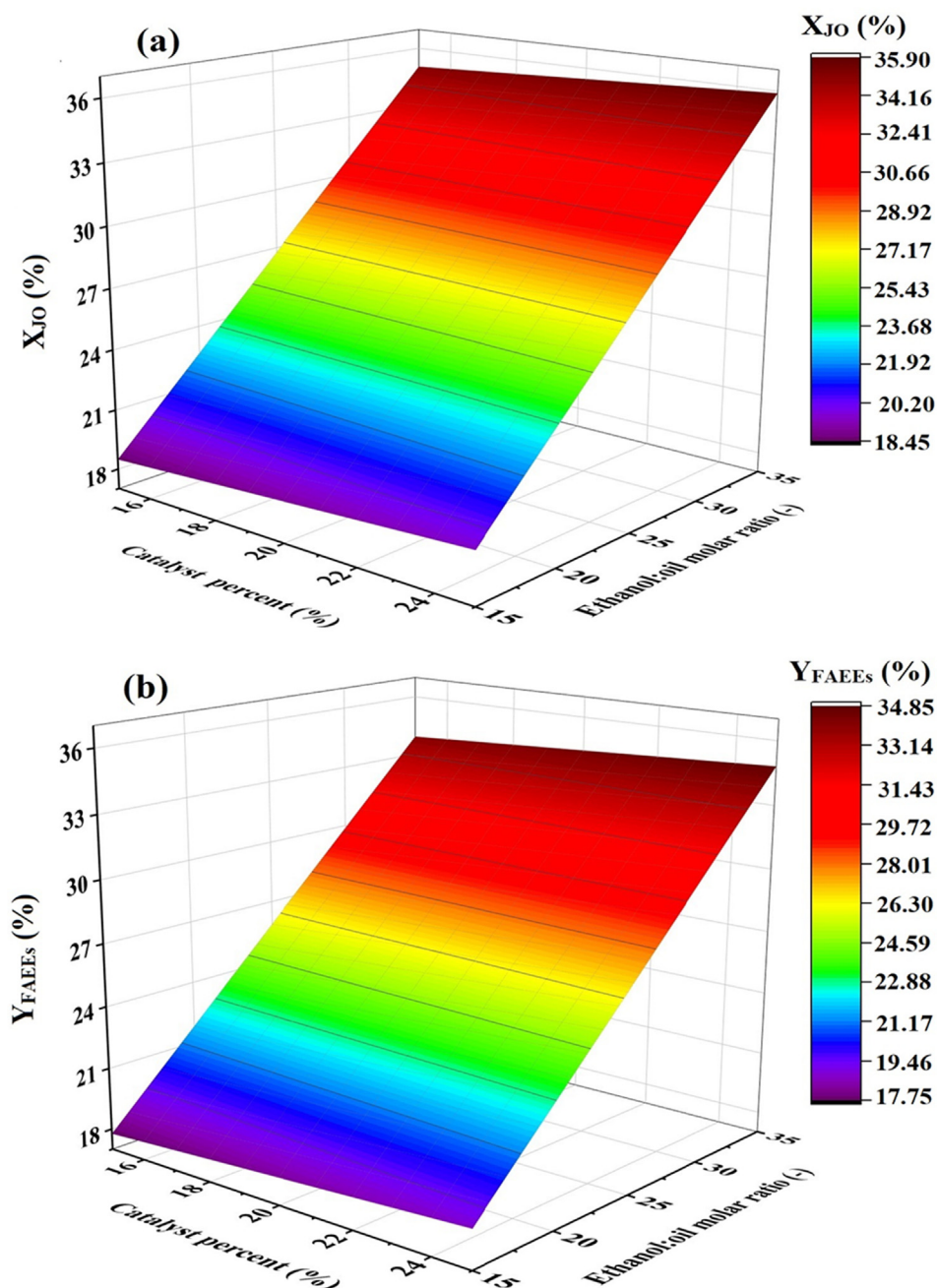
Fig. 3. Response surface 3D plot indicating the of influence of catalyst percent and ethanol: oil molar ratio on (a) the X_{JO} and (b) Y_{FAEEs}. Temperature = 50 °C (catalyst percent and ethanol: oil molar ratio refer to the actual values).

4. Conclusion

This study was carried out to investigate the catalytic transester-ification of Jatropha oil using Amberlyst A26 (OH) wet (a hetero-geneous ion-exchange resin) as catalyst and determine the impacts of the reaction temperature, ethanol: oil molar ratio and catalyst amount on the X_{JO} and Y_{FAEEs}, and to optimize the process. Accordingly, the modified central composite design from which the non-linear stage excluded was used to optimize the reaction process. From the main factors and their interactions, ethanol: oil molar ratio was found to highly influence the X_{JO} and Y_{FAEEs}. From the model regression equa-tions, the linear model was found to be suitable to optimize the re-sponses. The optimum X_{JO} and Y_{FAEEs} of 37.63% and 36.31%, respec-tively were predicted to be obtained at the optimum temperature of 55 °C, ethanol: oil molar ratio of 35:1 and catalyst amount of 15%.

Using a catalyst amount higher than 15% reduced the X_{JO} and Y_{FAEEs}, particularly, when the variable interacted with the reaction tempera-ture, and this might be due to the mass-transfer limitation. The result hereby presented are limited to the domain where they have been ob-tained. Any extrapolation based on the models needs to be done care-fully since the models are valid for the domain used to developed them.
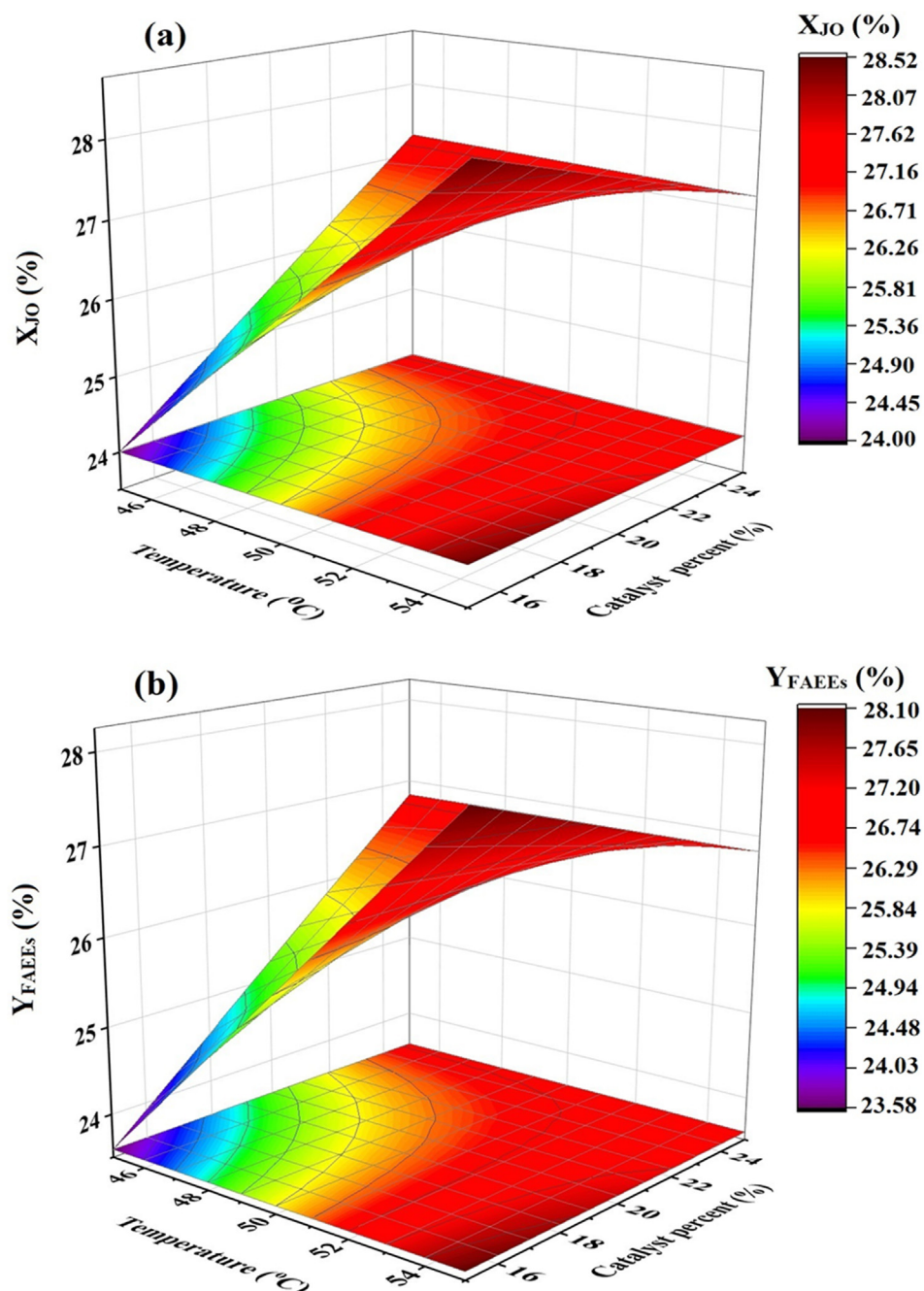
Funding

Fig. 4. Response surface 3D plot indicating the influence of temperature and catalyst percent on the X_{JO} and (b) Y_{FAEEs}. Ethanol: oil molar ratio = 25 (temperature and catalyst percent refer to the actual values).

Table 4
Optimum conditions predicted for maximum conversion of Jatropha oil and Y_{FAEEs}, and the optimum responses.

Factors	Conversion Optimum factors	Optimum response (%)	Yield Optimum factor	Optimum response (%)
Temperature (°C)	55.00		55.00	
Molar ratio (-)	35.00	37.63	35.00	36.31
Catalyst amount (%)	15.00		15.00	

CRediT authorship contribution statement

Yadessa G. Keneni: Conceptualization, Methodology, Investigation, Data curation, Formal analysis, Software, Validation, Writing - original draft, Writing - review & editing, Visualization. **Anne Kathrine (Trine) Hvoslef-Eide:** Conceptualization, Methodology, Validation, Visualization, Supervision, Project administration, Funding acquisition. **Jorge M. Marchetti:** Conceptualization, Methodology, Investigation, Data curation, Formal analysis, Software, Validation, Writing - review & editing, Visualization, Supervision, Project administration.
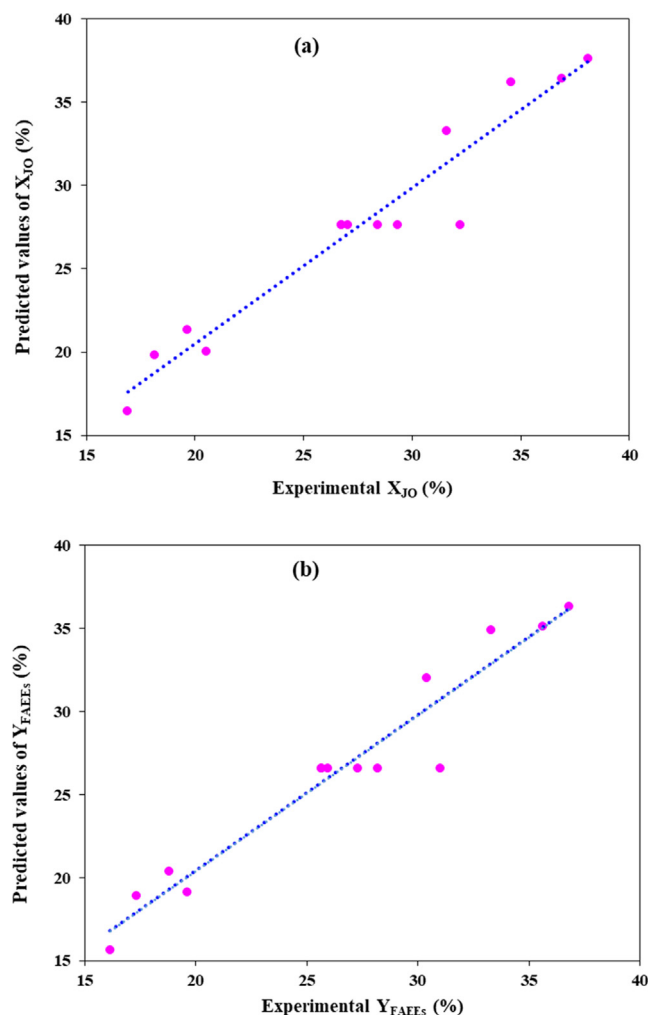
Fig. 5. Predicted versus experimental values of (a) X_{JO} and (b) Y_{FAEEs}, respectively.

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.

Acknowledgments

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