Indian Journal of Chemical Technology
Vol. 28, November 2021, pp. 724-729

Response surface modelling and optimisation of biodiesel production from *Manilkara Zapota L.* seed oil

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Received 10 January 2020; accepted 22 August 2021

Biodiesel production from non-edible oils is one of the prominent research avenues being exploited in recent times to achieve energy and environmental sustainability. The aim of this study is to model and optimise the production of biodiesel from the reaction of ethanol with Sapota (*Manilkara Zapota L.*) seed oil using potassium hydroxide (KOH) as catalyst. A quadratic response surface model has been developed and validated**.** Analysis of variance (ANOVA) reveals that the model is significant. The standard deviation is 3.76% and the coefficient of determination (R^2) is 0.8438. Numerical optimisation reveal that the optimal biodiesel yield of 89.57% can be achieved at an ethanol to oil molar ratio is 6.58, catalyst amount of 1.07 wt% and temperature of 64.77°C. Parametric studies reveal that the yield of biodiesel initially increases with increasing ethanol-oil ratio and catalyst amount but drops off gradually beyond the region of optimality. Temperature has a slight positive effect on the process.

Keywords: Biodiesel, Modelling, Optimisation, RSM, Sapota

In view of the global drive towards energy and environmental sustainability, the use of renewable sources for the production of biofuels has been extensively investigated. Prominent among these research areas is the production of biodiesel by the transesterification of non-edible oils[6,9]. Biodiesel is non-toxic and environmentally friendly biofuel produced from the transesterification of oils and also yields a glycerol by-product [1]. Non-edible oils evaluated over the years for biodiesel production includes *Jatropha curcas*[3,20], *Euphorbia lathyris L.*[36,38], *Euphorbia lathyris L.*[5, 14] and *Persea americana*[19,31].

Sapota (*Manilkara Zapota L.*) is a drought resistant plant that grows in tropical and subtropical countries[12]. It can grow to about 30 meters in height and 1.5 meters in width[12]. The fruit is edible[25] but are sometimes fermented for alcohol production[27]. The seed of the plant contains about 25-30% non-edible oil[24] which can be harnessed for biodiesel production. The seed does not have any other competitive use except seedling of which only a little quantity is required[25].

Several studies have investigated Sapota seed oil for biodiesel production. Dewangan and Mallick 12 studied the oil using methanol reactant and Potassium hydroxide (KOH) catalyst in an ultrasonic assisted process. Maximum yield of 97% was achieved in 20 minutes, 1:6 oil to methanol molar ratio, 1 wt% of catalyst, and at 50°C. Karmee[21] studied the oil using methanol and several lipases as bio-catalysts. Kumar, *et al.*[26] optimised biodiesel production from the oil with methanol reactant and KOH catalyst using Taguchi method. Maximum yield of 94.83% was achieved in 90 min, 1:6 oil to methanol molar ratio, 1 wt% of catalyst, and at 50°C. From the synopsis of literature presented above, response surface methodology has not been utilised in optimising biodiesel production from Sapota (Manilkara Zapota L.) seed oil when ethanol is the alcohol used. Besides, only Kumar, *et al.*[26] utilised a statistical optimisation approach. Furthermore, methanol has been more frequently used in other studies. In this paper, ethanol was considered.

Methanol has been commonly use alcohol in the production of biodiesel with abundance of positive results[13,32]. In the recent time, the usage of ethanol in biodiesel production as a viable candidate of short chain ethanol is becoming appreciable. The usage of ethanol has been recently explored and found as suitable substitute for methanol in biodiesel production when compared in terms of similar process conditions employed. The usage of Soybean oil[33], *Mucor circinelloides*[11], and *Karanja*[35] had been explored in this regard. Also, the comparative study of methanol and ethanol in the trans-esterification of palm oil was carried out, and a close optimum (81.5% compared to

79.2%) yields were obtained respectively for both reactions except at lower reaction time for methanol based[34]. In the similar development, the process integration study on ethanol based by Gutiérrez *et al*[16] confirmed the option as very attractive taking into account high content of lignocellulosic biomass involved as substrate, making them very suitable materials for their conversion into ethanol and favours integrative process.

Recently, Kumar[24] published a dataset of biodiesel yield from the transesterification of Sapota (*Manilkara Zapota L.*) seed oil without an associated research paper. Furthermore, no analysis or elaborations was conducted on the data published. The study extracted and characterised the oil and reported the biodiesel yield obtained using a 3-level experimental plan. Datasets such as these are published so they can serve as the foundational frameworks for more sophisticated analysis. This paper aims at building on the foundation of Kumar[24] by harnessing a statistical optimisation tool in studying biodiesel production from the reaction of ethanol with Sapota (*Manilkara Zapota L.*) seed oil using KOH as catalyst. By utilising the findings of Kumar[24], response surface methodology was employed in conducting a proper parametric study. Additionally, modelling of factor effects and interactions was conducted and detailed statistical information was given. A numerical optimisation was also performed.

Experimental Section

Response Surface Methodology

The details of response surface methodology has been elucidated in open literature over the years[18,22]. It is a group of statistical techniques used to investigate the functional relationship between input variables (x) and a response of interest (y). The relationship is unknown (ideally) but can be approximated via a low-degree polynomial model of the form given in equation 1.

$$y = f^I(x)\beta + \varepsilon \quad \text{... (1)}$$

Where $x = (x_1, x_2, \ldots, x_k)$, f(x) is a vector function p which consists of cross-products and powers of x_1, x_2, …, x_k up to a certain degree which is denoted by d ($\geq$ 1). Also from equation 1, β is a vector of p unknown constant coefficients referred to as parameters, and ε is a random experimental error assumed to have a zero mean[22]. There are two (2) important models commonly used in Response surface methodology (RSM); a first degree model and a second degree model. The first degree model is represented in equation 2.

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \varepsilon \quad \text{... (2)}$$

The second degree model is represented in equation 3

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum\sum_{i<j} \beta_{ij} x_i x_j + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \quad \text{... (3)}$$

There are 3 keys reasons for utilising RSM as explained by Khuri and Mukhopadhyay[22]

i. For the establishment of a relationship between inputs (x) and response (y)
ii. For the determination of the significance of the various factors (x_1, x_2, …, x_k)
iii. For the determine the optimum levels of the factors that will give the maximum response.

RSM optimisation have found applications in biodiesel production pyrolysis[29], steam reforming[2,4], solvent extraction[7,30], adsorption[8,15,23], biodiesel production[37,39] and a host of other processes[17,28]. Further elaborations on the of RSM for chemical and biochemical processes applications are presented elsewhere[10]. RSM is utilised in optimising biodiesel production from the reaction of ethanol with Sapota (*Manilkara Zapota L.*) seed oil using KOH as catalyst

Description of Dataset

The data utilised in this study was published and made openly available by Kumar[24]. The data is presented in Table 1. Results were obtained by the transesterification reaction of the oil with ethanol using KOH catalyst. For the study, all experiments were conducted at a process time of 90 minutes and at 500 rpm. Catalyst loading was varied between 0.5, 1 and 1.5 wt%. Ethanol-oil molar ratio was varied between 3, 6 and 9 mol/mol. Reaction temperature was varied between 50, 60 and 70°C. Results of biodiesel yield presented in Table 1 are average values of triplicate experiments

Results and Discussion

The data in Table1 was inputted into Design expert software version 10.0.1. Response surface methodology and historical data design was used. The results obtained are presented and discussed in this section.

Modelling

The software predicted the quadratic model as the best fit for the experimental data. The other models were either less accurate or they were aliased. The final equation in terms of actual factors is presented in equation 4.

$$Biodiesel\,Yield\,(\%) = -25.69 + 14.02A + 25.69B + 1.709C + 2.367AB - 0.0153AC + 0.03BC - 1.183A^2 - 20.13B^2 - 0.0127C^2 \quad ... (4)$$

Where A is ethanol-oil ratio in mol/mol, B is catalyst amount in wt% and C is temperature in degrees Celsius (^{o}C). The above correlation is an important design equation that applies specifically to the reaction of ethanol with Sapota (*Manilkara Zapota L.*) seed oil using KOH as catalyst. In evaluating the model, an analysis of variance (ANOVA) is presented in Table 2. The significance level was a p value <0.05. It can be observed that the model is significant. This informs that it is adequately able to capture the trend, relationship and interactions between the process factors and the studied response. However, of the model terms, the ethanol-oil ratio and the interaction of the ratio with catalyst loading are significant.

For a more detailed evaluation of the model, a parity plot between the experimental values obtained and a model prediction is presented in Fig. 1. The diagonal represents a line of perfect prediction where model values completely matches experiments. It can be observed that most of the data points fall very close to the diagonal with no major outliers. We can deduce that the model is accurate for predicting the yield of biodiesel

Table 1 — Dataset on biodiesel production from Sapota seed oil [24]

S/N	Ethanol-Oil ratio (mol/mol)	Catalyst amount (wt %)	Reaction temperature (°C)	Biodiesel yield (%)
1	3	0.5	50	68
2	3	0.5	60	69.5
3	3	0.5	70	70
4	3	1	50	74
5	3	1	60	76.3
6	3	1	70	78.2
7	3	1.5	50	64.3
8	3	1.5	60	66
9	3	1.5	70	65.4
10	6	0.5	50	81
11	6	0.5	60	83.1
12	6	0.5	70	84.8
13	6	1	50	87.2
14	6	1	60	89.8
15	6	1	70	93.2
16	6	1.5	50	78.7
17	6	1.5	60	81.2
18	6	1.5	70	82.8
19	9	0.5	50	73.4
20	9	0.5	60	76.8
21	9	0.5	70	69.8
22	9	1	50	73.2
23	9	1	60	76.4
24	9	1	70	79.8
25	9	1.5	50	82.8
26	9	1.5	60	86.4
27	9	1.5	70	81.6

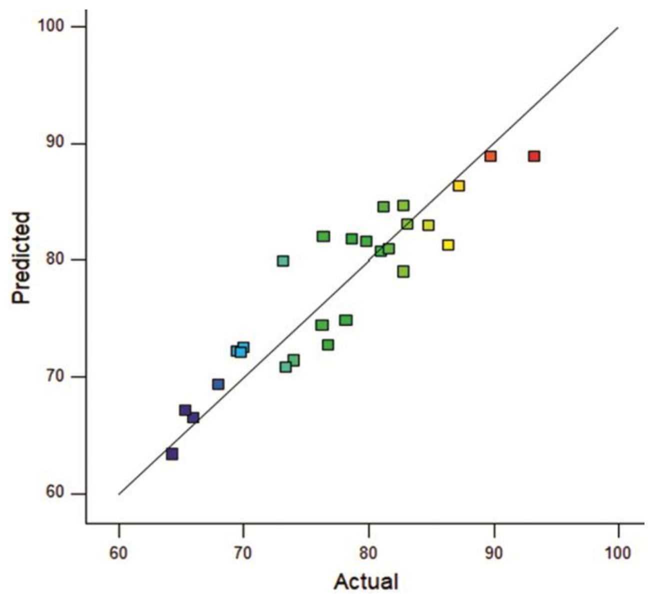

Fig. 1 — Parity plot between model predictions and experiments

Table 2 — Analysis of variance (ANOVA) of the developed RSM model

Source	Sum of squares	df	Mean square	F value	P-value Prob>F	
Model	1295.36	9	143.93	10.20	< 0.0001	significant
A-Ethanol-Oil ratio	260.68	1	260.68	18.48	0.0005	
B-Catalyst amount	9.10	1	9.10	0.65	0.4329	
C-Temperature	29.39	1	29.39	2.08	0.1671	
AB	151.23	1	151.23	10.72	0.0045	
AC	2.52	1	2.52	0.18	0.6778	
BC	0.27	1	0.27	0.019	0.8916	
A^2	680.53	1	680.53	48.24	< 0.0001	
B^2	152.01	1	152.01	10.77	0.0044	
C^2	9.63	1	9.63	0.68	0.4202	
Residual	239.85	17	14.11			
Cor Total	1535.21	26				

from the reaction of ethanol with Sapota seed oil using KOH as catalyst. Furthermore, it can be deduced that this premise is accurate in all domains of factor levels studied.

Table 3 presents the summary statistics of the model in Equation 4. The standard deviation is 3.76%. The standard deviation is an indicator of the amount of dispersion or variation of the data values. The R^2 value is 0.8438. The coefficient of determination (R^2) is the extent to which the variance of the experimental variables is predictable by the correlation. The closer the R^2 value to 1, the better the model**.** Considering that 27 data points were evaluated in this study, the R^2 value of 0.8438 can be considered to be very good. It can also be observed that predicted R^2 is in reasonable agreement with the adjusted R^2 as their difference is less than 0.2.

Numerical optimisation

A numerical optimisation was conducted using Design expert software version 10.0.1 to evaluate the best combination of factor that can be used to attain the highest biodiesel yield. The results obtained are presented in Table 4. It can be observed that the optimal ethanol to oil molar ratio is 6.58. This is quite similar to the needed ration of 6 mol/mol observed by Dewangan and Mallick[12] and Kumar, *et al*.[26] albeit for methanol. The optimal KOH catalyst loading was 1.07 wt%. This is in good agreement with 1 wt% KOH catalyst observed by Dewangan and Mallick [12] and Kumar, *et al*.[26] albeit with the use of methanol. The optimal temperature observed for the reaction of ethanol with Sapota seed oil using KOH as catalyst was 64.77°C which is relatively higher than 50°C observed by Dewangan and Mallick[12] and Kumar, *et al*.[26] for methanol. This informs that a higher energy requirement is needed for the process compared to the use of methanol. Using the combination of these factors, the optimal yield of biodiesel was observed to by 89.57%. This is relatively lesser than for methanol. However, it is still a good yield nonetheless when compared with other non-edible oils.

Parametric studies

In this section, three key process parameters were evaluated to understand how they affect the biodiesel production process. Response surface plots were used to elucidate the effect of the factors on the on biodiesel yield.

Figure 2 presents the factor interactions of catalyst amount and ethanol-oil ratio on biodiesel yield. Yield of biodiesel initially increases with increasing ethanol-oil ratio but drops off gradually beyond the region of optimality. A similar observation can be made for the catalyst loading which tails off beyond the optimal region of 1 wt%. The drop in biodiesel yield beyond the optimal level of catalyst is due to the synthesis of excess soap over time (due to the interactions between the KOH catalyst and the base oil). The region of optimality is clearly noticed as a bright orange patch at the middle of the rise on the response surface.

Figure 3 presents the factor interactions of temperature and ethanol-oil ratio on biodiesel yield. It

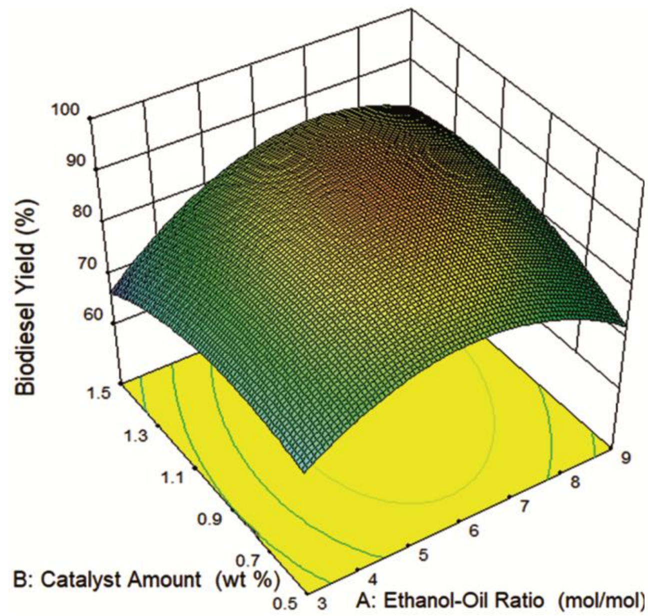

Fig. 2 — Effect of catalyst amount and ethanol-oil ratio on biodiesel yield

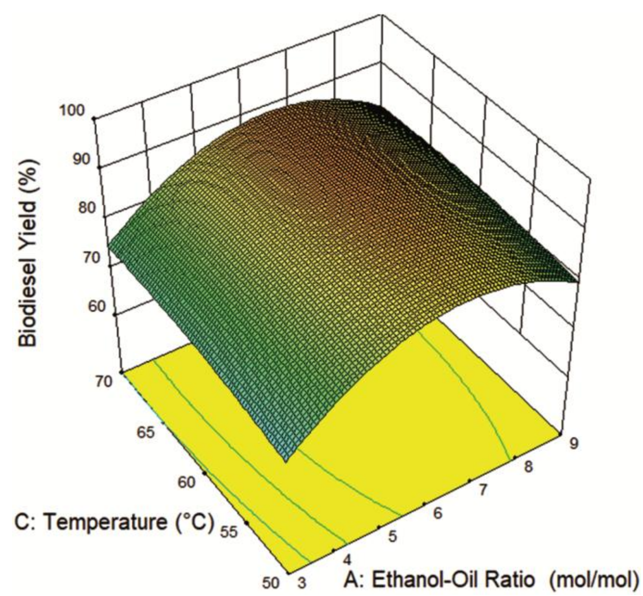

Fig. 3 — Effect of temperature and ethanol-oil ratio on biodiesel yield

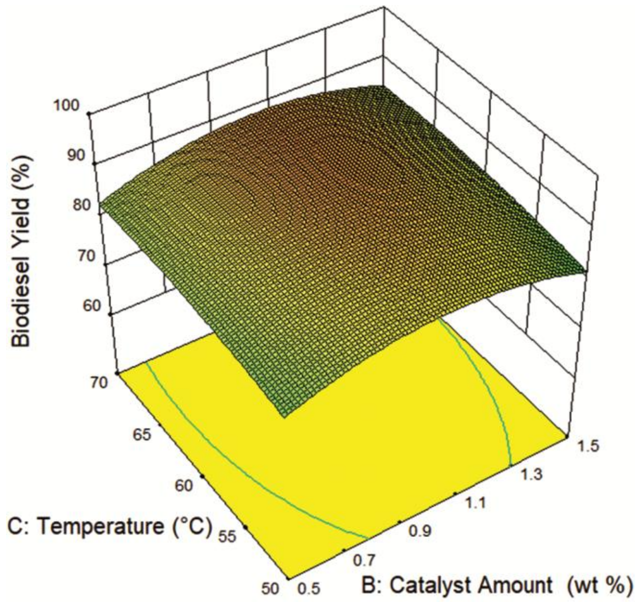

Fig. 4 ─ Effect of temperature and catalyst amount on biodiesel yield

can be observed that increasing temperature favours biodiesel yield. However, the effect of temperature on the process is rather minimal. Furthermore, there are no significant combinatorial effects of both factors on the biodiesel yield. Figure 4 presents the factor interactions of temperature and catalyst amount on biodiesel yield. The previously elucidated factor effects can also be observed.

Conclusion

A quadratic response surface model was developed for the prediction of biodiesel yield by the reaction of ethanol with Sapota (*Manilkara Zapota L.*) seed oil using KOH as catalyst**.** ANOVA revealed that the model was significant. The standard deviation was 3.76% and the coefficient of determination (R^2) was 0.8438. Considering that 27 data points were evaluated in this study, the R^2 value can be considered to be very good. Furthermore, it was observed that predicted R^2 is in reasonable agreement with the adjusted R^2 as their difference is less than 0.2. The suitability of the model was thus justified. Numerical optimisation revealed that the optimal biodiesel yield of 89.57% can be achieved at an ethanol to oil molar ratio is 6.58, catalyst amount of 1.07 wt% and temperature of 64.77°C. Parametric studies revealed that the yield of biodiesel initially increases with increasing ethanol-oil ratio and catalyst amount but drops off gradually beyond the region of optimality. Temperature has only a slight positive effect on the process. Based on the yield obtained, Sapota (*Manilkara Zapota L.*) seed oil can be harnessed and valorised for biodiesel production using the current experimental approach. The developed model can afford for quick simulation given a known set of process inputs. It can also serve as a basis for other optimisation approaches and will enable for early estimates and budgeting at the preliminary design stage for research and development towards greater energy sustainability.

Abbreviations

ANOVA - Analysis of variance
KOH - Potassium hydroxide
RSM - Response surface methodology

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