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A multi-variant approach to optimize process parameters of two-step pretreatment of high FFA *Prosopis juliflora* oil

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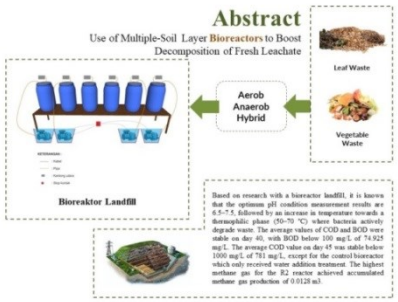
Graphical abstract



Abstract

A feasible alternative fuel for diesel engines in recent days is biodiesel, which can be produced from both edible and inedible feedstock. When considering the economic and environmental aspects, there is a considerable academic interest among researchers in the transesterification of non-edible oils to yield valuable Biodiesel, as compared to biodiesel production from edible oils. *Prosopis juliflora* oil was extracted using the solvent extraction technique. By using a two-step acid esterification method, the FFA acid value was reduced less than 1%. The acid value underwent a two-step reduction, initially decreasing from 44 KOH/gm to 8.6 mg KOH/gm, and subsequently reaching 2.7 mg KOH/gm. The implementation of the above procedure can effectively mitigate significant problems in diesel engines when using high viscous non-edible oils. The primary objectives of this research were to maximize the biodiesel output and simultaneously minimize the acid value. Response Surface Methodology (RSM) was employed in the current investigation to optimize different parameters. D-optimal design technique in Response Surface Methodology (RSM), was used for analyzing the methanol/oil volume ratio (factor A), reaction temperature (factor B), and reaction time (factor C) as process variables. The focus of the analysis was on the percentage of acid value (Y).

Keywords: *Prosopis juliflora,* acid esterification, response surface methodology (RSM), D-optimal design

1. Introduction

Numerous nations throughout the world still rely on petroleum fuel for transportation and electrification. While it is anticipated that the fossil fuel sources of oil, coal, and natural gas will run out in around 10 years. The estimated global use of vegetable oil as feedstock is 100 million tonnes (Balat 2011; Gopinathan 2009; Vasudevan and Briggs 2008). Following an effort by the European Commission to promote the use of biodiesel for transportation, the output of biodiesel in the European Union (EU) increased from 1066 million tonnes in 2002 to 10288 million tonnes in 2008 (Ramadhas *et al.*, 2005; Rajeshwaran *et al.*, 2018; Bankovi *et al.*, 2012). The development and modification of engines are given the highest priority due to the strict regulations on engine exhaust emissions and the intense concern for the environment. Less reliance on these fuels should be practiced since petroleum sources are finite (Vasudevan and Briggs, 2008; Rajeshwaran *et al.*, 2016; Baka, 2014). Because of the increase in the cost of conventional fuels, several nations are moving towards replacing them with biofuels (Rajeshwaran *et al.*, 2015; Ghadge and Raheman, 2005). India was ranked fifth in energy consumption in 2004, accounting for 3.47% of global energy consumption, and seventh in energy output in 2004, which represented around 2.48% of global annual energy production (Kannan *et al.*, 2011; Lin *et al.*, 2009; Berchmans and Hirata, 2008). India ranked fourth in the world for energy consumption in 2009 as a result of a rise in people's energy requirements. There are around 300 different types of oil-bearing seed-producing trees that make up India's natural flora. According to estimates, seeds or kernels from 75 different plant species contain 30% fixed oil (Bhanu Teja *et al.*, 2020; Sureshbabu *et al.*, 2023; Balu *et al.*, 2020). The various types of wasteland were classified in

accordance with the estimate provided by Wasteland Atlas of India. According to the "Waste Land Atlas of India 2015" research, there are currently 47.21 million hectares of wastelands in India, making up 14.91% of the country's total land area (Ramshankar *et al.*, 2023; Balasubramanian *et al.*, 2023; Balasubramanian *et al.*, 2022).

The increased FFA content of Mahua oil was reduced by two-step processing method. Experiments in both phases were conducted with a catalyst that had a contained 1% v/v H_2SO_4 and a molar ratio of 0.35-0.40 v/v methanol to oil (Mohanraj *et al.*, 2022; Vinayagar *et al.*, 2022; Krishnaraja *et al.*, 2022; Yamunadevi *et al.*, 2021). The process was carried out at a temperature of 60 ± 1 °C for 60 minutes. The experiment was followed by an hour of letting the liquid clarify and settle. The topmost layers of the water-methanol were then removed (Rajkumar *et al.*, 2020; Raja *et al.*, 2020; Premkumar *et al.*, 2020). Using 0.70% weight percent KOH as the base catalyst and 0.251% volume of methanol as the solvent, the material at the bottom was transesterified to create biodiesel. Alkaline catalyst-induced soap production is complicated by the presence of significant levels of FFA, which accounts for around 41%w/w of the oil (Shankar *et al.*, 2023; Raja *et al.*, 2023a; Raja *et al.*, 2023b). Finding the best response to certain factors in the experimental space is done using the response surface methodology. To fit a comprehensive second-order polynomial model for the process variables in the space, a special experimental design approach called D-optimal design is used. This technique works as a very effective combination, sufficiently representing response surfaces (Ranjith Kumar *et al.*, 2023).

The literature and research articles published in recent years make it abundantly clear that oil extracted from non-edible sources is best suited for the production of biodiesel. It is also clear that, despite having the potential to be an important source of oil for the production of biodiesel, no extensive experimental work has been done on the method of extracting oil using the fruit (seed) of the non-edible *Prosopis juliflora* plant. Furthermore, no information on the special *Prosopis juliflora* optimisation methods has been made available in the literatures so far.

2. Materials and methods

Prosopis juliflora, which is part of the Fabaceae group of plants, may reach heights of as much as 20 to 12 metres, depending on the species. *Prosopis juliflora*, which includes 44 species of thorny trees and shrubs, is widely distributed. The leaflets dimensions range from 1 to 7 mm in width and 2.5 to 230 mm in length. The 4-6mm long inflorescence is composed of tiny straw-yellow blooms. The plant almost always blooms throughout the year, with the exception of the months of March through July. *Prosopis juliflora* has fruit that resembles nearly flat pods. The pods have dimensions of 6-18mm in width, 5-10mm in thickness, and 5–31cm in length (Baka 2014).

3. Method of oil extraction

The swollen pulpy pods of *Prosopis juliflora* were physically gathered off the trees in wastelands in and around the Ramanathapuram district, which is located in the southern region of Tamil Nadu. It is essential to remove the moisture from *Prosopis juliflora* pods. The pods were washed, dried, crushed, and powdered in order to remove moisture. The oil from *Prosopis juliflora* has been extracted using a soxhlet apparatus and the common solvent-based extraction method. N-Pentane (36 to 40^{0}C), Ethyl acetate (70 to 80^{0}C), iso-propanol (80 to 85^{0}C), hexane (61 to 82^{0}C), methanol (64 to 67^{0}C), petroleum ether (67.9^{0}C), and ethanol (79^{0}C) were some of the well-known polar and non-polar solvents employed in the studies.

Polar and non-polar solvents produced an oil yield between 10 and 38%. The oil yield was high and it was it was challenging when Methanol was used as the solvent. A simplified representation of the Soxhlet device is shown in Figure 1.

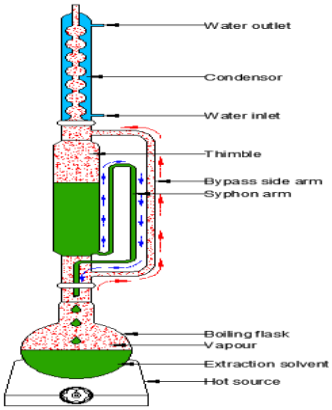


Figure 1. Schematic diagram of soxhlet extractor

4. Apparatus

A reaction flask with a condenser and a water bath with a fixed temperature make up the setup used for the experiment for oil pretreatment. Additionally, a mechanical stirrer was controlled by a digital rpm metre, which allowed a consistent stirring speed of 600 rpm to be maintained throughout the transesterification operations. Figure 2 depicts the schematic layout of a biodiesel production.

5. Pretreatment-acid esterification process

Two-step acid esterification pretreatment techniques were employed to lower the acid content prior to the production of biodiesel. Experimental research was done to determine the impact of various process variables on the acid value of *Prosopis juliflora* oil. In all pretreatment stages, the effects of a methanol (alcohol) on oil with ratios (molar ratios) (v/v) of 3:1, 5:1, 7:1, and 9:1 and reaction times of 0.5, 0.75, 1.0, 1.25, 1.5, and 2.0 hours were investigated. Figure 3 shows the process organisational structure for acid esterification. In the initial pretreatment stage, 100 g of *Prosopis juliflora* were used to extract oil, which was then put into a flask and placed in a water bath that was heated to 50^{0}C. The H_2SO_4 1% (v/v) and methanol (alcohol) solution was progressively added to the hot *Prosopis juliflora* oil and

swirled continuously for several minutes. By putting the finished product from this pretreatment process into a separating funnel, extra methanol was separated from it. The impure layer at the top was eliminated by adding H_2SO_4 to the extra methanol. The product located at the bottom was then periodically tested for acidity using ASTM procedures.

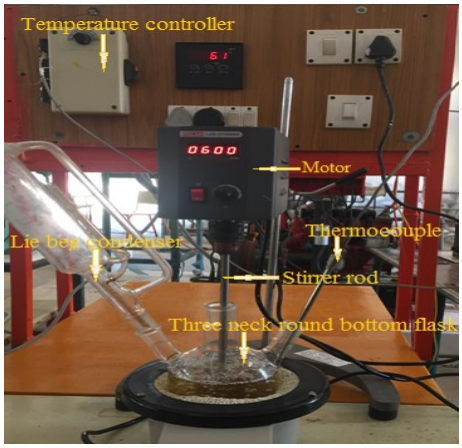


Figure 2. Schematic diagram of biodiesel plant

The first pretreatment stage source material was a substance having an acid level below 9 mg KOH/g. In order to investigate the impact of methanol/oil molar concentrations and response times, a number of tests were conducted (Lin *et al.*, 2009). The pretreatment stage's end result showed an acid value below 1 mg KOH/g. Similar to the previous step, excess methanol was removed, and the bottom layer of the product was separated using centrifugation. It was then cleansed using water from distillation, centrifuged once more, evaporated with a solution of anhydrous sodium sulphate, then utilised for further processing.

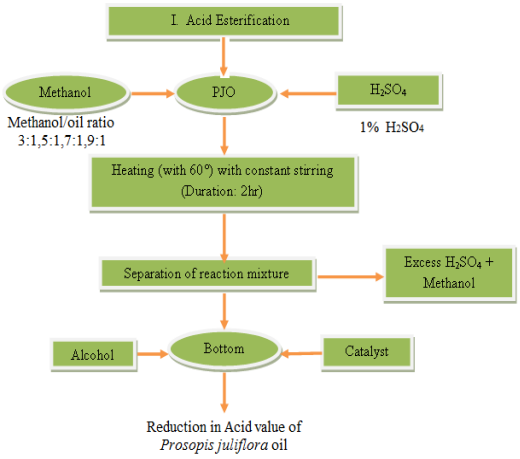


Figure 3. Layout of acid esterification process

6. Optimization of transesterification process

In accordance with the response surface method, a D-optimal design was developed to examine the influence of various factors on the rate of conversion of *Prosopis juliflora* Fatty Acid Methyl Esters. The dependent variable was based on the proportion of the final product produced by acid esterification, whereas the independent variables were the reaction temperature, reaction duration, and the methanol/oil ratio (Lin 2009). All the variables whose control limits are listed in Table 1 are those that significantly affect the rate of methyl ester conversion. The following equation was used to assess the independent variables as they are related to the quantity of acid esterification.

$$y = +17.97 - 12.71A + 0.030B - 4.30C.59AB + 0.51AC - 0.41BC + 0.75A^2 - 2.85B^2 + 4.50C^2$$

The alkaline value (response), percentage of acid esterification (Y), methanol/oil volume ratio, amount of reaction temperature, and reaction time were utilised to assess the model significance of the process variables using the method of analysis of variances (ANOVA). The process variables needed to optimise the transesterification process are listed in Table 2. It was determined how to perform statistical evaluation of experimental data performed using the RSM-based Deign expert 7.1.5 test programme.

7. Results and discussion

7.1. Pre-treatment (first step method)

The initial acid values of non-edible oils used to make biodiesel were found to be high, ranging from 20 to 45 mg KOH/gm (Ramadhas *et al.*, 2005). In order to find the best technique to reduce the acid value around 1 mg KOH/gm, several pretreatment processes have gone through a number of steps. The key variables that affected the percentage of acid value in oil were the kind of feedstock, the amount of alcohol added, molar ratio of alcohol to oil, proportion of catalysts applied, reaction duration, and temperature. From Figure 4, it can be inferred that the response showed a rise in the early stages and sluggish response in the latter stages. Alcohol/molar ratio and reaction time had a significant impact on reaction intensity. Throughout the esterification process of FFA, which is the acid value continuously decreased as the methanol (alcohol) to molar concentration increased, and the rate of reaction remained relatively constant (Bankovi *et al.*, 2012). In order to acquire less than 1% FFA after the second pre-treatment stage, a free fatty acid (FFA) value of 5% should be attained in the first pre-treatment stage (Ghadge and Raheman, 2005). A 9:1 v/v methanol/oil ratio and a 2-hour minimum response time were the ideal values for the process variables, which caused the concentration of acid to drop from 44 mg KOH/g into 8.6 mg KOH/g.

Table 1. Process parameters level for the optimization of transesterification process

Factors	Process Parameters	Lower level (-1)	Middle level (0)	Upper level (+1)	Std. Dev.
A	Methanol/oil (v/v)	3:1	6	9:1	2.121
B	Extractiontemperature (deg C)	55	60	65	3.536
C	Extraction time (hrs)	0.5	1.25	2.0	0.530

7.2. Pretreatment (second step method)

Similar procedures were followed in succession to the first pretreatment step for the second pretreatment stage, as shown in Figure 5. A 9:1(v/v) methanol/oil molar concentration ratio and 120 minutes of reaction time were the optimum conditions for the reaction, which decreased the sulfuric acid level from 8.6 mg KOH/gm to a value of 2.7 mg KOH/gm. Problems also led to a further fall in acid value as the Methanol/oil concentration and the duration of reaction rose (Bankovi *et al.*, 2012). Following the two-step pretreatment procedures, *Prosopis juliflora* oil (PJO) was transesterified with methanol.

Table 2. Experimental design with process data and the response for transesterification process model

Std	Run	Methanol/oil (v/v)	Temperature (deg C)	Time (min)	Acid value (%)
4	1	9	65	0.50	13
8	2	9	65	2.00	4.7
18	3	6	60	1.25	19
15	4	6	60	1.25	19
2	5	9	55	0.50	13
5	6	3	55	2.00	29
19	7	6	60	1.25	17
7	8	3	65	2.00	25
9	9	3	60	1.25	33
1	10	3	55	0.50	37.7
6	11	9	55	2.00	2.7
20	12	6	60	1.25	19
17	13	6	60	1.25	19
3	14	3	65	0.50	39
14	15	6	60	2.00	21
12	16	6	65	1.25	15
13	17	6	60	0.50	22.7
10	18	9	60	1.25	3.2
11	19	6	55	1.25	14
16	20	6	60	1.25	17.3

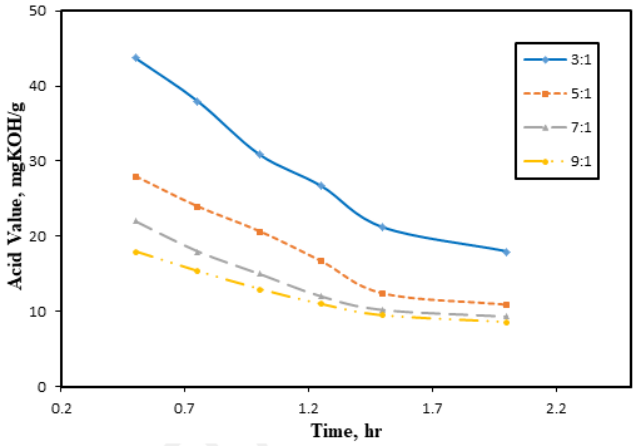


Figure 4. Influence of alcohol/oil molar ratio and time taken for decrement in PJO acid value in the primary pre-treatment step to obtain biodiesel. Initially the acid value was 43.7mg KOH/g of oil.

7.3. Analysis and evaluation of acid-esterification process parameters

Biodiesel was produced using an Alkaline Transesterification method followed by an acid esterification procedure. Percentage of acid esterification (factor Y) was utilized to investigate the connection between the dependent as well as independent process variables methanol/oil ratio of volume (factor A), the quantity of reaction temperature (factor B), and reaction duration (factor C). To evaluate the model's relevance, variance analysis was done. Table 3 shows the ANOVA response.

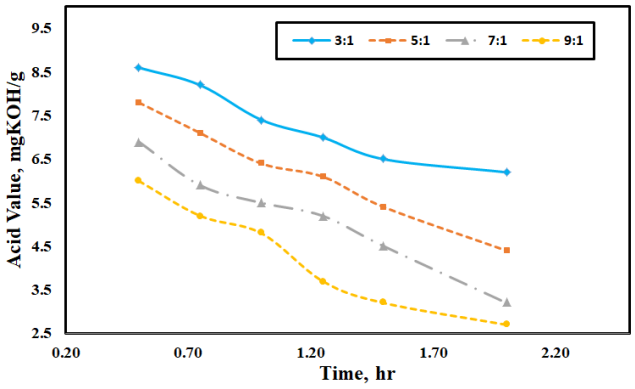


Figure 5. Influence of alcohol/oil molar ratio and time taken for decrement in PJO acid value in the secondary pre-treatment step to obtain biodiesel. Acid value in this stage was 8.6mg KOH/g of oil

Greater methyl ester production was achieved by optimising process parameters using a response surface technique with D-optimal design, with the findings showed a coefficient of determination (F-value) of 36.63686 and an associated p-value at 0.0001. The results demonstrate that the model significance threshold had a

probability of 0.01%. During alkaline esterification, the methanol/oil ratio of volume (factor A) was proven to be significant in the reduction of acid value and enhancement of biodiesel generation. For factor A, a large F-value of 283.1074 presented evidence in favour of the same.

Table 3. ANOVA result for Pretreatment (Acid value) method

Source Model	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
	1881.484	9	209.0538	36.63686	< 0.0001	significant
A-Oil/Methanol (v/v)	1615.441	1	1615.441	283.1074	< 0.0001	
B-Temperature(deg C)	0.009	1	0.009	0.001577	0.9691	
C-Time(hrs)	184.9	1	184.9	32.40388	0.0002	
AB	2.76125	1	2.76125	0.483911	0.5025	
AC	2.10125	1	2.10125	0.368246	0.5575	
BC	1.36125	1	1.36125	0.23856	0.6358	
A^2	1.528182	1	1.528182	0.267815	0.6161	
B^2	22.40818	1	22.40818	3.927053	0.0757	
C^2	55.57506	1	55.57506	9.739575	0.0109	
Residual	57.06107	10	5.706107			
Lack of Fit	52.45273	5	10.49055	11.38215	0.0092	significant
Pure Error	4.608333	5	0.921667			
Cor Total	1938.546	19				

The high acid value of the extracted oil decreased as a result of other parameters, including Reaction Temperature (Factor B) with the duration of the reaction (Factor C). The amount of acid esterification (Y), according to studies on the effects of temperature, varied very little. The interaction of two major variables involved in the process, methanol /oil ratio of volume (factor A) and reaction temperature (factor B), was indicated by the p-value of 0.9691, which is less than 0.05.

The R- Squared score for the statistical regression of fit was determined to be 0.9706. This Figure suggests that when the relevant factor was taken into account, the complete change in reaction was represented. Modified R^2 value was found to be 0.9441. This value is known as the "goodness of prediction value" since it indicates how many predictors are included in the model. The RSM-based quadratic model was flawless since both the R^2 and corrected R^2 values indicated that the data and model suited one another. Table 4 displays the recorded R^2 and corrected R^2 responses.

Table 4. R Squared results for Acid value

Factor	Optimum value	Factor	Optimum value
Std. Dev.	2.39	R-Squared	0.9706
Mean	19.16	Adj R-Squared	0.9441
C.V. %	12.16	Pred R-Squared	0.7397
PRESS	504.58	Adeq Precision	20.348

The perturbation chart displayed an unfavourable irregular sharp curvature for the methanol/oil ratio of volume and acid concentration. In comparison to other variables, the methanol (alcohol)/oil volume ratio (factor A) in the Figure was the most crucial process variable. The Perturbation chart made it clear that the acid values for the actual process parameters were 6 (v/v) methanol/oil, 60^0C for the reaction, and 75 min for the reaction. The curves for the other process variables, such as the ratio of methanol to oil, period of time, and the temperature, were plateau-shaped, suggesting that they had no effect on the acid value percentage.

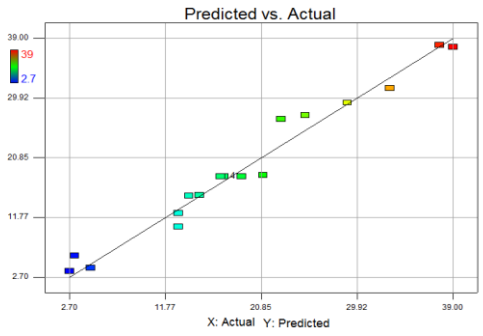


Figure 6(a). Predicted and Actual Acid value

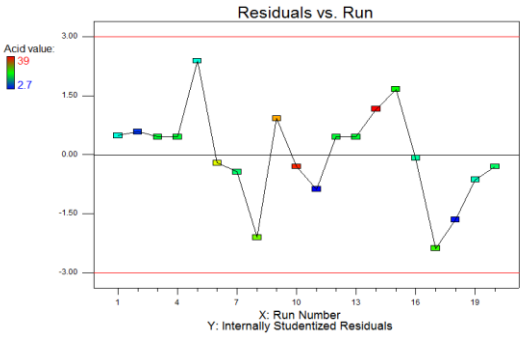


Figure 6(b). Residuals vs Run

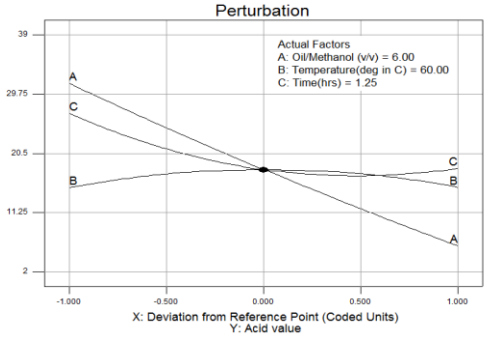


Figure 6(c). Perturbation chart and Actual Acid value

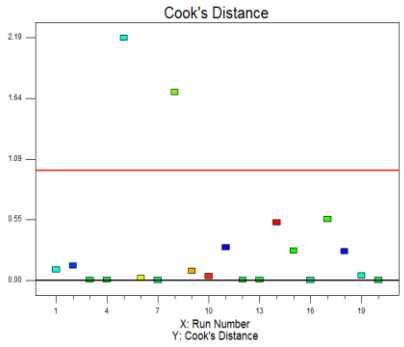


Figure 6(d). Cook's Distance vs Run number

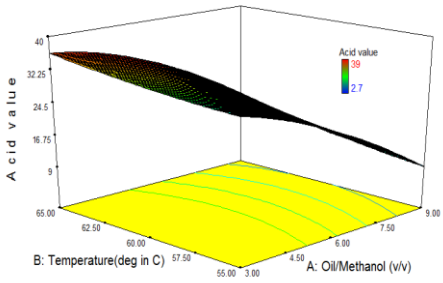


Figure 6(e). Response surface plot of PJO Acid value as a function of Reaction temperature and Methanol/oil ratio concentration

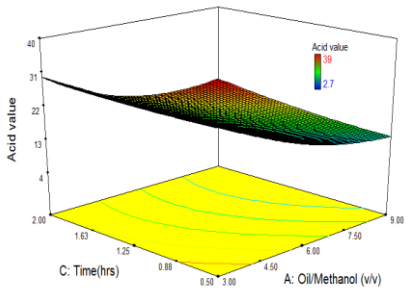


Figure 6(f). Response surface plot of PJO Acid value as a function of Reaction time and Methanol/oil ratio concentration

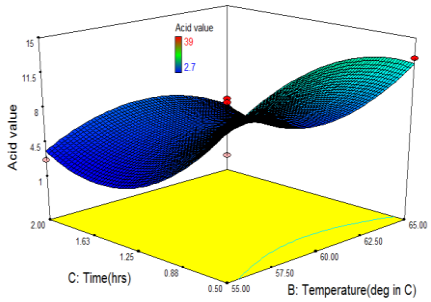


Figure 6(g). Response surface plot of PJO Acid value as a function of Reaction time and Temperature concentration

The RSM-based predicted acid value and actual acid value, the amount of residuals vs run, as well as the effect of perturbation chart are shown in Figures 6(a), 6(b) and 6(c). Figure 6(d) demonstrates the value of the Cooks distance vs Run number was much lower than the control limits of 0.2, at less than 0.55. The resulting response surface model (RSM) of the value of acid is shown in Figures 6(e), 6(f) and 6(g) and compares different process parameters (AB, AC, and BC). The percentage of acid value was recorded at its maximum when the methanol/oil volume ratio was maintained at a minimum of 3:1(v/v) and less amount of H_2SO_4 addition. The acid value may be calculated using the empirical formula.

$$\text{Acid value} = -337.82854 - 7.86533\ \text{X Oil/Methanol}\ (\text{v/v}) + 13.61032\ \text{X Temperature}\ (\text{deg C}) - 20.47980\ \text{X Time}(\text{hrs}) + 0.039167\ \text{X Oil/Methanol}\ (\text{v/v})\ \text{X Temperature}(\text{deg C}) + 0.22778\ \text{X Oil/Methanol}\ (\text{v/v})\ \text{X Time}(\text{hrs}) - 0.11000\ \text{X Temperature}\ (\text{deg C})\ \text{X Time}\ (\text{hrs}) + 0.082828\ \text{X Oil/Methanol}\ (\text{v/v})^2 - 0.11418\ \text{X Temperature}(\text{deg C})^2 + 7.99192\ \text{X Time}(\text{hrs})^2$$

8. Conclusion

Experiments based on two step acid esterification and optimisation of *Prosopis juliflora* oil were carried out, and the outcomes were recorded for various concentrations, methanol/oil molar ratios, reaction temperatures, and reaction periods.

The following is a summary of the data analysis from the present study:

- An acid esterification process utilising 1% anhydrous sulphuric acid (H_2SO_4) at a reaction temperature of 60 ± 1 °C for 120 min at a 9:1(v/v) and methanol/oil molar volume ratio with a continuous stirring rate of 600 rpm was the most efficient way to convert free fatty acids (FFA) to triglycerides. It is important to emphasize that there has been a decrease in the concentration of acid level in *Prosopis juliflora* oil during this reaction. The value reduced from 44 to 2.7 mg KOH/g.
- Recorded responses of R^2 and adjusted R^2values of 0.9706 and 0.9441 suggest that the data and model match each other which led to the confirmation that the RSM based quadratic model was ideal using the Response Surface Methodology D-optimal Design approach.
- The utilization of low viscosity *Prosopis juliflora* oil in the production of Biodiesel holds significant potential as a viable alternative fuel for Direct injection (DI) diesel engines.

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