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Optimization of Vegetable Oil-Based Biodiesels by Multi-Response Surface Methodology (MRS) using Desirability Functions

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Abstract
Environmental concerns associated with petroleum resources have propelled the development of sustainable and renewable alternatives to petroleum based products. Vegetable oil is one amongst the foremost abundant bio-based feedstocks. The interest in using vegetable oils and low molecular weight alcohols by direct transesterification have shown great potential as alternatives to petroleum-based diesel, and the production of bio-based diesel continues to increase. Utilization of multi-response surface methodology (MRS) for the most effective combination effect or response from the uses of input to output variables to optimize the yield and higher heating values (HHV) of biodiesels was investigated. In this work, utilizing variety of non-edible vegetable oils like castor (*Ricinus communis L*), jatropha (*Jatropha curcas*), and neem (*Azadirachta indica*) seeds and several process variables or inputs, including mixing time, mixing speed, process temperature and catalyst dosage to formulate high quality renewable fuels were further explored. The outputs were yield, viscosity, higher heating value, density and turbidity. The proposed optimization scenarios for biodiesel using the statistical (MRS) models was aimed to optimize the processes to achieved high conversion and higher heating values, while reducing the reaction time, turbidity, density, and viscosity in the samples. The results showed catalyst dosage as the most important variable for all the three samples. For maximum yield of 100%, the molar ratio of 6.25, catalyst of 0.75 wt.%, reaction speed of 499.99 rpm, reaction time of 19.88 min and temperature of 24.50 ^{o}C were found as optimal conditions; while the molar ratio of 5.60, catalyst of 1.01 wt.%, the reaction speed of 499.5 rpm, reaction time of 20.00 min and temperature of 35.50 ^{o}C were optimal conditions for maximum biodiesel yield.

Keywords: biodiesel yields, optimization, statistical model, catalyst dosage.

1. Introduction

The environmental concerns associated with petroleum resources have propelled the development of sustainable and renewable alternatives to petroleum-based products. One of the renewable raw materials that have been widely used in chemical industries is vegetable oil; others are sugar, starch, and cellulose. Vegetable oils and low molecular weight alcohols have shown great potential as alternatives to petroleum-based diesel, and the interest in using them to produce bio-based diesel continues to increase. Vegetable oil is one amongst the foremost abundant bio-based feedstocks. Vegetable oils are utilized in numerous bio-based applications because of their important practicality, low toxicity, accessibility, biodegradability and low cost. A molecule of vegetable oil, known as a triglyceride, has three fatty acid chains connected to a glycerol chain. There are various forms of fatty acid within and among different triglyceride molecules [1]. Biofuels (biodiesel, bioethanol, biogas etc) are terribly enticing choices to overcome the energy crisis since waste feedstocks are obtainable freely for biofuels using different chemical and biological conversion technologies. The biodiesel production, which may be used as a mix or blend with diesel oil is increasing globally, which can grow in the coming years because of continuous dwindling of fuel reserves.

Recently, the worldwide crude costs are setting a record high within history because of heavy dependence on crude as a significant supply of fuel for transportation and electricity generation. On the opposite hand, the

exploitation of these standard energy resources is an additional reason for worldwide warming, which has to be tackled by adopting alternative energy sources. Biodiesel production from waste cooking oil (WCO) and non-edible indigenous seed oils is an attractive option, but the high free fatty acids (FFA) content in waste oils are severe bottlenecks for the trans-esterification.

The WCO oil will be processed to sophisticated refined cooking oil (RCO) to provide refined biodiesel (RBD), that is way more cost-effective than eatable edible fat, and may be a favourable different alternative to edible fat and oil [2]. Spent oil and fats cause substantial discarding issues in several countries of the world, whereas biodiesel is created from fats and oils either bio-chemically or with chemicals. There are generally four ways that oils and fats can be remodeled into biodiesel. Amongst these, transesterification is the best typically used method because it decreases the viscosity of the oil [3].

The use of a statistical method of Multi-Response Surface Methodology (MRS) to model and maximize production processes can be adopted. Experimental designs for yield optimization require the design of experiments (DoE) that must be established using Response Surface Methodology (RSM) with design inputs to measure the outputs or response as shown in Figure 1: Design of Experimental Variables [4].

Theoretical Framework

Experimental designs for yield the planning of experiments (DoE) that has got to be established using RSM with design inputs to measure the outputs or response as shown in Figure 1

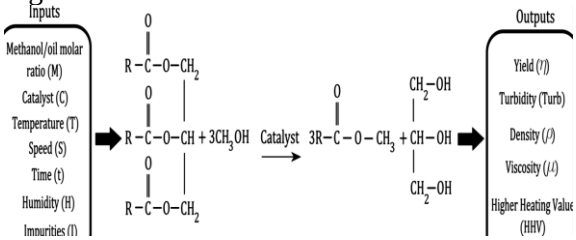


Figure 1: Design of Experimental Variables (Myers, 1971)

Optimization of biodiesel variables using Response Surface Methodology

Atapour *et al* [5] optimized biodiesel production using alkali-catalyzed transesterification of used cooking oil. Optimization of esterification of mixed oil with a high proportion of free fattyacid was similarly investigated [6, 7] showed the application of response surface methodology for optimization of biodiesel production by transesterification of vegetable oil with alcohol. Optimization of biodiesel production from the waste vegetable oil exploitation response surface methodology, response surface optimization of associate degree in transesterification of waste vegetable oil and used transesterification of neat and used cooking oil in the optimization for biodiesel production and response surface methodology as associate tools for optimized biodiesel production using rice bran and flower oils were reported by many authors [8 -13]. Using response surface methodology for the optimization and conversion of vegetable oils like castor (*Ricinus communis L*), jatropha (*Jatropha curcas*), and neem (*Azadirachta indica*) to biodiesel production has not been reported.

In this work, optimization and conversion of castor, jathropha and neem using oil/methanol molar ratio, reaction temperature, catalyst, speed and reaction time to generate a statistical model that can predict their conversion to biodiesel are now investigated.

2. Materials and Methods

2.1 Materials and Chemicals

Castor (*Ricinus communis L*), jatropha (*Jatropha curcas*), and neem(*Azadirachta indica*) seeds were purchased from Mandate Market, Ilorin, Kwara State, Nigeria. Methanol with a purity of 99.5% and Potassium Hydroxide (KOH) were purchased from Sigma Aldrich Company. Apparatus were supplied by Sigma Aldrich (Gillingham Dorset, UK). Biodiesel analyses were administered using separating funnel, micro-pipette, reflux set, digital hot plate/magnetic stirrer, thermostated water-bath, pycnometer (ASTM D941), pH meter (Hanna HI 4212 model), Cannon–Fenske viscometer Ostwald (Cannon Instrument Co., State College, PA, USA) and bomb calorimeter (Parr-1351 from Parr Instrument Company, Moline, IL, USA).

2.2 Biodiesel production

Refining and pretreatment processes of 100 mL of crude oils started with the removing impurities before economical trans-esterification and to bring the free fatty acid (FFA) levels to below 0.5%. Trans-

esterification processes were followed with the mixture of oils and methanol at the pre-set molar ratio, reaction temperature, reaction time, reaction speed heated and NaOH as dosage catalyst.

2.3 Response Surface Method (RSM) for Optimizing Biodiesel

RSM methodology seeks to establish the relationships between input variables (i.e. independent variables) and one amongst variables (i.e., response variables) for waste cooking oils [14]. RSM was developed originally by Box and Wilson [15] to model experimental processes. However it has been used with different techniques to optimize industrial processes and products [16, 17].. RSM consists of a group of statistical techniques that use a regression model that depends on a low-degree polynomial function. The development side of the R package appearance for a combination of essential factors that satisfies the strategy criteria of every response and [14, 18].

3. Experiments Design

Optimization model using RSM**:** The DoE input variables to be used are: time (t), speed (S), catalyst (C), temperature (T), and oil/ methanol molar ratio (M), The three factors and three levels of a Box-Behnken Design (BBD) would be adopted [14]. The experimental factors and their ranges for optimization are: reaction time (30 – 60), reaction speed (400–800 rpm), reaction NaOH catalyst (1–2 wt. %), reaction temperature (40 – 60 ^{o} C), and waste cooking oil/ methanol molar ratio (6:1 – 9:1). The expected measurable outputs are: yield, turbidity, density, viscosity, and higher heating value (HHV). Table 1 contains the variable ranges to cover the intervals popularly used in the literature.

Table 1: Experimental design levels with independent variables using the Box–Behnken Design (BBD) method

Inputs	Notation	Magnitude	Levels		
			-1	0	+1
Time	T	Min	30	45	60
Speed	S	Rpm	400	600	800
Temp	T	^{o}C	40	50	60
Catalyst	C	wt. %	1.0	1.5	2.0
Molar ratio	m	wt. %	6:1	7.5:1	9:1

Table 1 shows the inputs at various levels and combinations by applying the statistical software operating conditions from the from the planning matrix [14]. During this work, 45 experiments were accustomed to generate combination possibilities to determine the optimal conversion of biodiesel. Table 2 shows the design matrix of the transesterification of the three non-edible seed oils using combination variables of speed, time, temperature, catalyst and molar ratio for the experiments.

Table 2: The transesterification of non-edible seeds oils design matrix

Sample	Inputs				
	Molar Ratio	Catalyst (wt. %)	Time (min)	Speed (rpm)	Temp (^{O}C)
$N_{6:.1}$	6:1	1	30	400	40
$J_{6:1}$	6:1	1	30	400	40
$C_{6:1}$	6:1	1	30	400	40
$N_{7.5:1}$	7.5:1	1.5	45	600	50
$J_{7.5:1}$	7.5:1	1.5	45	600	50
$C_{7.5:1}$	7.5:1	1.5	45	600	50
$N_{9:1}$	9:1	2	60	800	60
$J_{9:1}$	9:1	2	60	800	60
$C_{9:1}$	9:1	2	60	800	60

After phase separation in each experiment, the biodiesel yield was calculated from the ultimate. Additionally, density (ρ), higher heating value (HHV), viscosity (μ) and turbidity (Turb) were similarly analysed in keeping with ASTM D6751-09 Quality Evaluations [19, 20]

4. Results and Discussions

4.1 Experimental Results

The physical properties of the biodiesels which were produced in the optimum conditions were measured and presented in Table 3 for yield (ŋ), density (ρ), higher heating value (HHV), viscosity (μ) and turbidity (Turb) analyses.

Table 3: Experimental results obtained for the output variables (η, Turb, ρ, μ, and HHV), according to the Box-Behnken DoE Design Matrix (Table 2).

	Outputs						
Sample	Yield % (η)	Turb (NTU)	Density ρ(g/mL)	Viscosity μ(mm^2/s)	SG	Kinematic	HHV (MJ/Kg)
$N_{6:1}$	53.8	38.5±0.07	3.69	32.2±0.14	0.97	6.69	41.72
$J_{6:1}$	29.5	119.50±0.7	6.09	14.60±0.14	0.96	8.46	44.14
$C_{6:1}$	55.5	19.50±0.7	3.52	52.0±0.00	0.97	14.74	43.27
$N_{7.5:1}$	50	77.5±0.7	3.87	31.2±0.00	0.96	8.04	41.82
$J_{7.5:1}$	84	91±1.41	1.89	14.65±0.07	0.94	7.75	45.34
$C_{7.5:1}$	41.1	68.5±0.7	4.50	52.1±0.00	0.98	11.56	41.23
$N_{9:1}$	58	73±0.00	3.43	32.90±0.14	0.96	5.61	40.89
$J_{9:1}$	87	77.5±0.7	1.04	14.95±0.07	0.94	14.20	44.20
$C_{9:1}$	91.1	83.5±0.7	2.39	51.85±0.07	0.93	21.63	43.54

The mean absolute error (MAE) and root mean square error (RMSE) are determined using the samples in Table 4 for the capacity of quadratic models as discussed (Marina *et al.*, 2017). Table 10 shows the prediction errors as minimum errors correspond to **η** (MAE equal to 9.337 and RMSE equal to 11.706), and the minimum error correspond to **ρ** (MAE equal to 0.009 and RMSE equal to 0.012).

4.2 Analysis of variance

These equations show the second-order polynomial functions and combinations of input variables that were obtained to model yield, Turbidity, density, viscosity, and HHV [14]

$$\eta = 2217 + 0.8937.M - 12.79.A2 - 3.572.M.C - 2163.C2 - 2.689.T - 0.01284.Q2 + 2.860.H + 0.05896.C.H \quad (1)$$

$$Turb = 2565 - 1.43.M^3 + 2.2.A^2 - 0.23M.C - 2508.C^2 - 0.60.T \quad (2)$$

$$Density = 63.9 - 0.0990.M^3 + 0.00065.M + 0.0251.M.C - 57.6.C^2 - 0.0155.T \quad (3)$$

$$Viscosity = -1561 + 1.85.M^3 - 0.047.M + 17.7.A^2 + 1471.C^2 + 1.61.T \quad (4)$$

$$Specific\ gravity = 1.0566 - 0.001118.M^3 - 0.000108.M - 0.00841.A^2 + 0.000304.M.C - 0.000492.T \quad (5)$$

$$HHV = 426 - 0.258.M^3 - 0.022.M - 1.92.A^2 + 0.283.M.C - 419.C^2 \quad (6)$$

Tables of ANOVA results for each of the final quadratic models are given in Tables 4 – 8. The p-value is less than 0.05 for most variables and is statistically significant for each quadratic model. The regression model provided the multiple correlation coefficients (R^2) as a measure of variation of the mean and is close to 1 indicating the predictive capability of these models is excellent.

Table 4: Analysis of Variance (ANOVA) Table for the "**η**" quadratic model

Source	Degree of freedom	Sum of Square (Adj)	Mean Square (Adj)	F Value	P-Value
K	*5*	3670.34	734.067	53.83	0.004
M	1	2.34	2.343	0.17	0.706
A^2	1	304.26	304.261	22.31	0.018
M×C	1	31.61	31.606	2.32	0.225
C^2	1	137.08	137.082	10.05	0.050
T	1	2.07	2.070	0.15	0.723
Error	*3*	40.91	13.638		
R^2	*8*	3711.25			

Significance code 0.05

Table 5: Analysis of Variance (ANOVA) table for the "**Turb"** quadratic model

Source	Degree of freedom	Sum of Square (Adj)	Mean Square (Adj)	F Value	P-Value
K	5	5159.03	1031.81	2.01	0.301
M^3	1	88.33	88.33	0.17	0.706
A^2	1	2.24	2.24	0.00	0.952
M×C	1	16.84	16.84	0.03	0.868
C^2	1	573.10	573.10	1.11	0.369
T	1	20.50	20.50	0.04	0.855
Error	3	1542.69	514.23		
R^2	8	6701.72			

Significance code: 0.05

Table 6: Analysis of Variance (ANOVA) table for the "**ρ"** quadratic model

Source	Degree of freedom	Sum of Square (Adj)	Mean Square (Adj)	F Value	P-Value
K	5	17.1774	3.43549	22.64	0.014
M^3	1	3.3849	3.38494	22.31	0.018
M	1	0.0007	0.00066	0.00	0.952
M×C	1	0.3635	0.36351	2.40	0.219
C^2	1	0.4285	0.42850	2.82	0.191
T	1	0.0140	0.01397	0.09	0.781
Error	3	0.4552	0.15172		
R^2	8	17.6326			

Significance code: 0.05

Table 7: Analysis of Variance (ANOVA) table for the "**μ"** quadratic model

Source	Degree of freedom	Sum of Square (Adj)	Mean Square (Adj)	F Value	P-Value
K	5	1764.67	352.934	3.29	0.178
M^3	1	248.29	248.285	2.32	0.225
M	1	3.51	3.509	0.03	0.868
A^2	1	256.69	256.687	2.40	0.219
C^2	1	260.07	260.069	2.43	0.217
T	1	268.83	268.834	2.51	0.211
Error	3	321.40	107.135		
R^2	8	2086.07			

Significance code: 0.05

Table 8: Analysis of Variance (ANOVA) table for the "**HHV"** quadratic model

Source	Degree of freedom	Sum of Square (Adj)	Mean Square (Adj)	F Value	P-Value
K	5	154.570	30.9139	1.64	0.363
M^3	1	2.860	2.8596	0.15	0.723
M	1	0.751	0.7508	0.04	0.855
A^2	1	1.735	1.7350	0.09	0.781

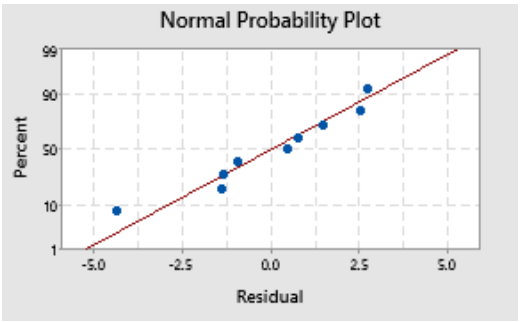
M×C	1	47.269	47.2690	2.51	0.211
C^2	1	14.666	14.6664	0.78	0.443
Error	3	56.512	18.8375		
R^2	8	211.082			

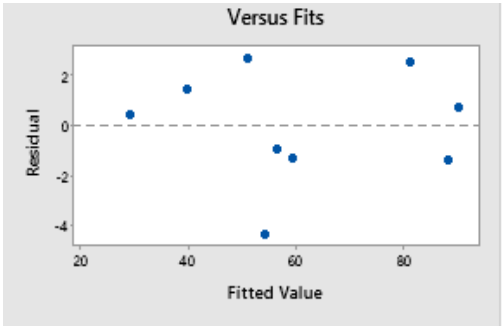
Significance code: 0.05

Table 9**:** Predicted error process critical for yield, turb, density, viscosity, HHV, using quadratic models.

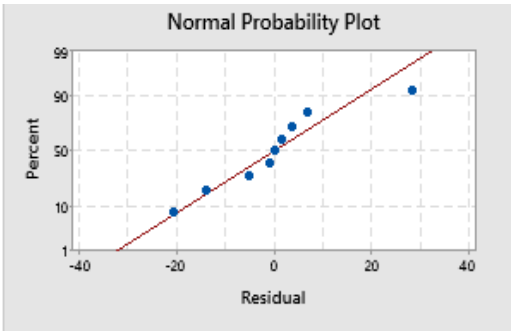
ERROR	η	Turb	ρ(g/mL)	μ	HHV
MAE	9.337	5.00	0.090	0.998	0.310
RMSE	11.706	8.622	0.012	1.450	0.398

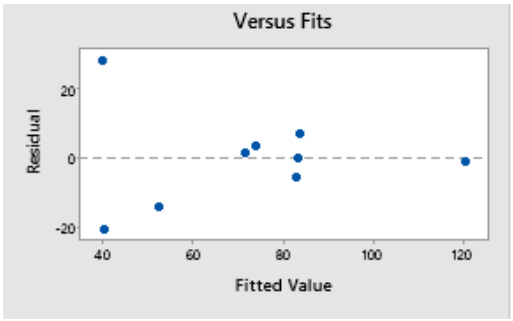
Figure 2 shows the link between the experimental values that were obtained (Table 1) and also the predicted (quadratic models) values of η (Figure 2a), Turb (Figure 2b), ρ (Figure 2c), μ (Figure 2d), and HHV (Figure 2e). The figures show that these models suffice for the prediction of these values, because the residuals that were obtained were small and also the correlations between actual and predicted values were high [14].



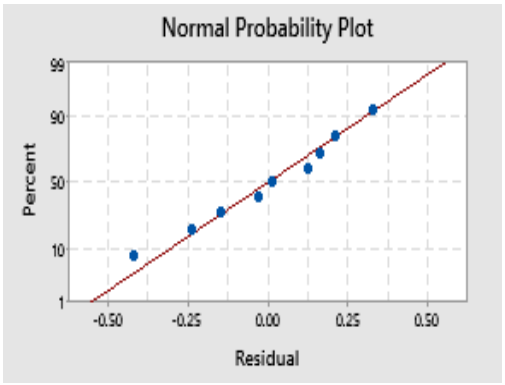


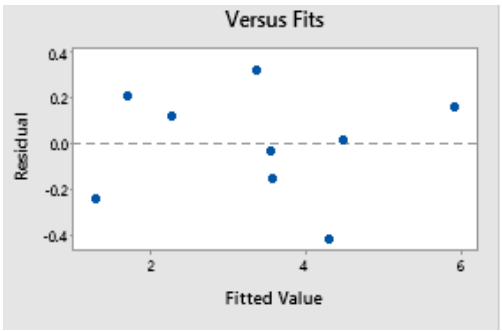
(a) Yield



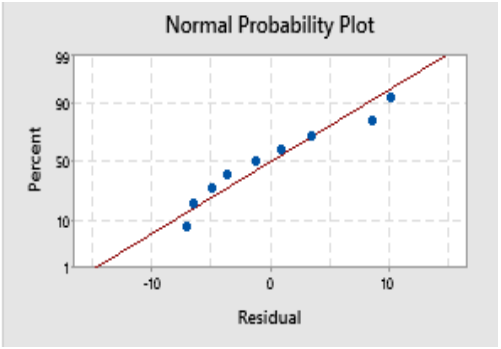


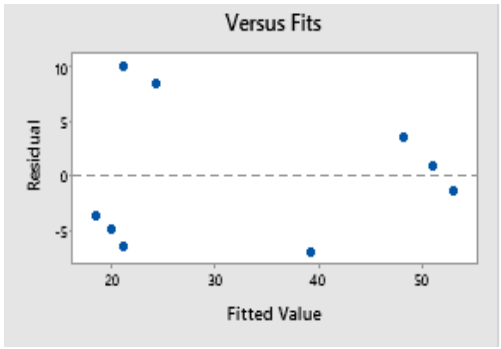
(b) Turbidity



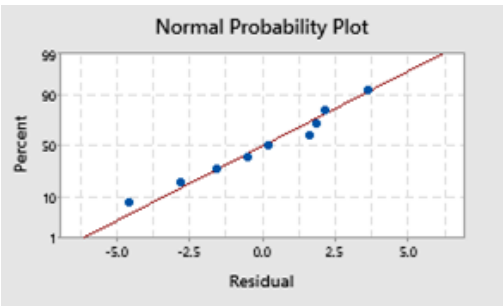


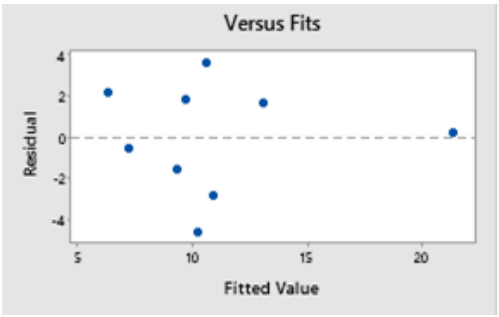
(c) Density





(d) Viscosity





(e) High heating value (HHV).

Figure 2: Scatter diagram of: (a) Yield (ɳ); (b) turbidity (Turb); (c) density (ρ); (d) viscosity (μ); and (e) high heating value (HHV).

5.3 Multi-response optimization

The combination of process variables were studied in examining the biodiesel production process by means of desirability package according to nine different criteria. From the results, it shows that the optimal process variables for various design requirements were found in an exceedingly relatively narrow range. Once the various biodiesel optimization scenarios were obtained, nine new experiments in keeping with the mix of process variables were prepared so as to work out the accuracy of the proposed methodology. Table 10 shows the values of various biodiesel outputs in step with the nine biodiesel optimization scenarios that were studied. These tables' shows that the experimentally-obtained values for the nine biodiesel optimization scenarios failed to differ significantly from those who application of the MRS methodology produced. The error that appears within the last two columns represents the MAE and RMSE that were normalized for every variable in each of the nine biodiesel optimization scenarios that were studied. However, the normalized MAE and RMSE within the last two rows correspond to the error in each of the outputs that were studied. as an example, when minimize the turbidity is taken into account to be an optimization variables for biodiesel production, the errors obtained are the tiniest (MAE = 0.02 and RMSE = 0.02), but when minimizing the viscosity and density the error considered is that the largest (MAE = 0.10 and RMSE = 0.07). In contract, the most error obtained for every of the outputs are lower when predicting viscosity (MAE = 0.01 and RMSE = 0.00) and greater when predicting turbidity (MAE = 0.03 and RMSE = 0.08).

Table 10: Experimental outputs according to the nine biodiesel optimization scenarios.

Experimental Values Obtained							
Optimization Scenarios	η	Turb(NTU)	P(g/mL)	μ(mm/s)	HHV(MJ/Kg)	MAE	RMSE
1st Scenarios	0.97	0.03	0.87	0.30	0.22	0.04	0.02
2nd Scenarios	0.98	0.01	0.67	0.29	0.18	0.07	0.04
3rd Scenarios	0.97	0.02	0.87	0.30	0.21	0.02	0.02
4th Scenarios	0.00	0.94	0.00	0.00	0.00	0.10	0.07
5th Scenari	0.97	0.01	0.78	0.99	0.98	0.06	0.04
6th Scenarios	0.97	0.01	0.97	0.32	0.21	0.09	0.03
7th Scenarios	0.96	0.00	0.87	0.34	0.21	0.02	0.04
8th Scenarios	0.97	0.03	0.96	0.36	0.21	0.10	0.06
9th Scenarios	0.97	0.01	0.98	0.39	0.21	0.04	0.02
MAE	0.03	0.03	0.01	0.01	0.01	0.09	0.03
RMSE	0.07	0.08	0.07	0.00	0.03	0.34	0.12

Conclusions

This work was investigated to analyze yield, turbidity, density, viscosity and HHV of biodiesel from some non-edible seeds oils. Response surface methodology supported the Box-Behnken design was employed to study the effect of the method variables on the biodiesel production from non-edible seeds oils. According to the ANOVA the results obtained demonstrated that, although non-edible seeds oil were different seeds, the molar ratio and dosage of catalyst were one among the foremost vital factors within the yield of biodiesel production.(see Table 4), whereas the HHV was the least factors. Additionally, temperature was one of the foremost important factors that increased turbidity (see Table 5), whereas for the HHV, the dosage of catalyst was the most significant factor (see Table 9). Finally, the dosage of catalyst was one in every of the foremost important factors within the biodiesel production. The optimal conditions for optimum yield were found to be: molar ratio of 6.25, catalyst loading of 0.75 wt. %, response time of 19.88 min, reaction speed of 499.99 rpm, temperature of 24.50^{o}C, the most biodiesel yield under these conditions was 100%. Also, the optimal condition for maximum heating value was found to be: molar ratio of 5.60, catalyst loading of 1.01 wt. %, interval of 20 min, reaction speed of 499.59 rpm, temperature of 35.50^{o}C. The utmost biodiesel yield under these conditions was 100%. Biodiesel has become more attractive due to its economic and environmental benefits.

Conflict of Interest

The authors declare that there is no conflict of interest.

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