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Optimization of transesterification of *Jatropha curcas* Oil to Biodiesel using Response Surface Methodology and its Adulteration with Kerosene

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Abstract
Biodiesel has emerged as an alternative to non-renewable diesel fuel. Growing demand for biodiesel has given birth to mal practices such as adulteration which degrade its quality. The present study has dealt with the optimization of biodiesel production from *Jatropha curcas* oil using a five-level-four-factorial central composite design based on response surface methodology in 54 experimental runs. A biodiesel yield of 98.3% is obtained with methanol/oil ratio (11:1 w/w) using NaOH as catalyst (1% w/w) in 110 min at 55^{o}C. ANOVA results revealed that catalyst concentration, reaction time and methanol/oil molar ratio had a significant effect on JCB yield. A model equation for predicting the yield of biodiesel is formulated which can be successfully adopted in oil industry to maximize the yield of methyl esters. The properties of the biodiesel, thus, produced conform to the ASTM and BIS specifications, making it an ideal alternative fuel for diesel engines. The adulteration of biodiesel with kerosene has been studied using viscosity and density measurement. A number of calibration curves and correlations are developed which can be used to find out the extent of adulteration in biodiesel and determine its quality.

Keywords: Adulteration, Biodiesel, Kerosene, Optimization, Response surface methodology, Transesterification.

1. Introduction
The world is presently confronted with energy crisis due to fossil fuel depletion and environmental degradation [1]. This has lead to the search for alternative energy sources such as bioethanol and biodiesel. Growing demand of biodiesel has given rise to mal practice of adulteration. Adulteration is the addition of unwanted chemicals in biodiesel to lower its quality and cost. The criteria for the addition of adulterants are that these should be miscible with and cheaper than biodiesel. The common adulterants used are kerosene and raw vegetable oils which can have a negative impact on the engine performance with regard to fuel consumption, power output and engine life. It is a malicious practice and should be seriously checked in order to meet the quality standards of biodiesel. With growing human population, more land is needed to produce food for human consumption, which poses a potential challenge to biodiesel production. *Jatropha curcas* oil (JCO) is a plant based feedstock that is unsuitable for human consumption and could be the best feedstock for biodiesel production [2]. For the conversion of high free fatty acid (FFA) JCO to biodiesel, two step acid-base catalyzed transesterification method is used [3]. It consists of acid catalyzed pretreatment step to reduce the FFA to less than 1% using H_2SO_4 as acid catalyst and transesterification of pretreated oil to biodiesel using alkali catalyst. This process involves many parameters that effect the reaction and optimizing so many reaction factors require large number of experiments, which is laborious, time consuming, and economically non-viable. Response surface methodology (RSM) is a useful statistical technique for the optimization of complex processes, as it reduces the number of experiments required to achieve ample data for a statistically pertinent result [4]. So, optimization of biodiesel production using RSM is of immense interest for meeting the growing fuel

requirements. Literature has revealed that only few papers are available on the use of Response Surface Methodology (RSM) for the optimization of process variables to maximize the biodiesel yield. Boonmee *et al.*[5] have studied the effect of three process variables viz. methanol/oil molar ratio, catalyst concentration and reaction time on the methyl esters yield of JCO. Central composite design (CCD) of 20 experiments was employed and 99.87% biodiesel yield was achieved. Similarly, Tiwari *et al.*[6] have optimized methanol quantity and reaction time using RSM based on central composite rotatable design (CCRD) of 21 experiments and obtained biodiesel yield of 99%. In view of the above, it can be seen that, no work is reported on the optimization of biodiesel production from JCO using four process variables. The present paper, therefore, reports the results of the optimization of four process variables viz. catalyst (NaOH) concentration (0-2% w/w), reaction temperature (35^{o}-55^{o}C), reaction time (30-180 min) and methanol/oil ratio (w/w) (6:1–12:1) for the maximization of *Jatropha curcas* biodiesel (JCB) yield. CCD of 54 experiments based on RSM with the help of Design Expert 8.0.6 software has been used. A model to predict the response (JCB yield (%)) has been formulated and validated by Analysis of Variance (ANOVA). The model can be employed in the oil industry to maximize the yield of methyl esters. Further, the adulteration of biodiesel with kerosene has been studied and correlations have been developed to check the adulteration of unknown samples of biodiesel.

2. Materials and Methods

JCO was procured from Jatropha Vikas Sansthaan, New Delhi. All chemicals such as H_2SO_4, KOH, methanol, ethanol, Na_2SO_4 and NaOH were of Analytical Reagent grade and 99% pure. NaOH in pellet form was used as a base catalyst. Kerosene was purchased from local market. The fuel properties of JCO and kerosene determined by the methods described by Jain and Sharma [3] are reported in Table 1.

Table 1: Fuel properties of JCO and Kerosene

S.no	Properties	JCO	Kerosene
1	Density (g/c.c at 15^{o}C)	0.930	0.794
2	Viscosity (cSt, at 40^{o}C)	50	1.38
3	Flash point (^{o}C)	241	39
4	FFA contents (%)	14.6	-
5	Gross calorific value (MJ/kg)	37.05	46.2

2.1 Acid- Base catalyzed transesterification of high FFA JCO

Raw JCO was filtered to remove all the insoluble impurities followed by heating at 100^{o}C for 10 min to remove all the moisture. JCO had high FFA (14.60%), which is far above the 1% limit suitable for base catalyzed transesterification reaction. FFAs were, therefore, first converted to esters in a pretreatment process for the production of JCB [3]. The reaction was carried out at a temperature of 50^{o}C for 125 min. using conc. H_2SO_4 (1.5 % v/v) as acid catalyst with methanol/oil ratio of 6.5:1. The high FFAs were reduced to 0.34% and the resulting reaction mixture was subjected to base catalyzed transesterification process for biodiesel production using NaOH as base catalyst [3]. The methyl ester layer was separated, washed with water, heated to remove moisture and dried over anhydrous Na_2SO_4. The transesterification of JCO has been optimized using RSM for the maximization of JCB yield which was calculated using the following equation (1):

$$\text{Yield of JCB (\%)} = \frac{\text{Total weight of methyl esters}}{\text{Total weight of oil in the sample}} * 100\% \quad (1)$$

2.2 Analysis of JCB

The JCB was prepared in the laboratory under the operating conditions optimized by RSM and analyzed for fatty acid composition using Gas chromatograph (Model-Netal). The process is already reported by Jain and Sharma [3].

2.3 Physio-chemical properties of JCB

The physical and chemical properties of JCB produced under optimum conditions were determined by using standard methods [7].

2.4 Adulteration *of optimized JCB with Kerosene*

Different blends were prepared by mixing JCB with kerosene in varying proportions and denoted by KBx, i.e., kerosene biodiesel blend and x: % of biodiesel in blend.

2.5 Experimental design of Transesterification based on RSM

A five-level, four-factorial CCD was applied and the total number of experiments were 54 (2^k+2k+6+24); where k is the number of independent variables [8]. Twenty four experiments were augmented with two replications at axial and factorial points and six replicas at the centre point to evaluate the error for carrying out the optimization studies to maximize the JCB yield. Catalyst (NaOH) concentration (A) (% w/w), reaction temperature (B) (^{o}C), reaction time (C) (min) and methanol/oil molar ratio (D) (w/w) were the independent variables selected to optimize the yield of JCB. The coded and uncoded levels of the independent variables are given in Table 2.

Table 2: Independent variables and levels used for CCD in transesterification process

S.no	Variables	Symbols	Levels				
			-1	**-0.5**	**0**	**0.5**	**1**
1	Catalyst concentration (%w/w)	A	0	0.5	1.0	1.5	2.0
2	Temperature (^{o}C)	B	35	40	45	50	55
3	Time (min)	C	30	67.5	105	142.5	180
4	Methanol-to-oil ratio (w/w)	D	6	7.5	9	10.5	12

2.6 Statistical Analysis

The Design Expert 8.0.6 software was used for the regression and graphical analysis of the data. The maximum values of JCB yield were taken as the response of the design experiment. The experimental data obtained by the above procedure was analyzed by the response surface regression [9] using the following second-order polynomial equation (2):

$$y = \beta_o + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i_{i>j}}^{k} \sum_{j}^{k} \beta_{ij} x_i x_j \quad (2)$$

where; y is the response (JCB yield(%)), x_i and x_j are the uncoded independent variables, i and j are the linear and quadratic coefficients respectively, β_o is the regression co-efficient, k is the number of factors studied and optimized in the experiment. Statistical analysis of the model equation and evaluation of the analysis of variance (ANOVA) was carried out. Confirmatory experiments were also performed to validate the equation.

3. Results and Discussion

54 experiments were performed to get the experimental values of JCB yield. Experimental and predicted values for JCB yield responses at the design points are given in Table 3.

Table 3: CCD arrangement and responses for JCB yield

Run	Parameter 1 A: Catalyst	Parameter 2 B:	Parameter C: Time	Parameter 4 D:Methanol/oil	Experimental JCB yield	Predicted JCB yield
1	1	45	105	9	82.6	82.84
2	0	45	105	9	89.5	89.81
3	0.5	40	67.5	10.5	78.2	80.37
4	1.5	40	142.5	10.5	88.6	87.84
5	0.5	40	67.5	10.5	77.8	80.37
6	0.5	50	67.5	7.5	87.1	86.76
7	1.5	50	67.5	10.5	73.9	76.50
8	0.5	40	142.5	7.5	91	89.83
9	1	45	105	9	82.9	82.84
10	0.5	40	67.5	7.5	86.1	87.33
11	1	45	105	9	83.1	82.84

12	1	45	105	12	85.5	84.97
13	1	45	105	9	82.1	82.84
14	1	45	180	9	93.4	92.65
15	0.5	50	142.5	10.5	97.8	99.99
16	1	45	30	9	78.2	79.56
17	1.5	50	142.5	10.5	88.3	87.10
18	0.5	50	67.5	10.5	90	87.17
19	0.5	40	142.5	10.5	91.8	91.86
20	1.5	40	67.5	7.5	85.7	84.18
21	0.5	50	142.5	7.5	90	90.98
22	1	35	105	9	92.4	91.00
23	1.5	40	142.5	7.5	81.6	84.05
24	1.5	40	142.5	10.5	83.8	87.84
25	1	45	105	12	85.9	84.97
26	0.5	50	67.5	10.5	90.4	87.17
27	1.5	40	67.5	10.5	80	78.97
28	2	45	105	9	73	73.37
29	1	55	105	9	88.2	89.69
30	1.5	50	142.5	7.5	77	75.94
31	1.5	40	67.5	7.5	85.2	84.18
32	1	45	105	9	82.4	82.84
33	1	55	105	9	87.9	89.69
34	1.5	50	67.5	10.5	74.1	76.50
35	1.5	50	67.5	7.5	74.8	74.34
36	1.5	50	142.5	7.5	77.3	75.94
37	1.5	40	67.5	10.5	80.2	78.97
38	1	45	105	9	82.8	82.84
39	0.5	50	67.5	7.5	87.5	86.76
40	2	45	105	9	73.2	73.37
41	1	45	105	6	79.5	80.76
42	1.5	50	67.5	7.5	74.5	74.34
43	0	45	105	9	89.9	89.81
44	1.5	40	142.5	7.5	81.2	84.05
45	0.5	50	142.5	7.5	90.4	90.98
46	0.5	50	142.5	10.5	98.2	99.98
47	1	35	105	9	92.1	91.00
48	1	45	105	6	79.8	80.76
49	0.5	40	67.5	7.5	86.5	87.33
50	0.5	40	142.5	10.5	92.1	91.86
51	1	45	30	9	78.5	79.56
52	0.5	40	142.5	7.5	91.4	89.83
53	1.5	50	142.5	10.5	88.7	87.10
54	1	45	180	9	93.7	92.65

The summary of ANOVA is provided in Table 4. The associated Probability (P) value for the model is lower than 0.0001, implying the significance of the model. The value of regression coefficient R^2 for the model is 0.945, indicating the good fitness of the model. High values of predicted R^2 (0.890) and adjusted coefficient of determination (R^2_{Adj}:0.923) and low value of coefficient of variation (C.V) (2.09%), are an indication of precision of fitted model [10].

P-values < 0.05 indicate that the model terms are significant [11]. In this case, A (catalyst concentration), C (time), D (ratio of methanol/oil), interaction effect of AB (catalyst concentration with reaction temperature), AC (catalyst concentration with reaction time), BD (reaction temperature with methanol/oil ratio), CD (time with methanol/oil ratio), B^2 (quadratic effect of temperature), C^2 (quadratic effect of time) have significant effect on the JCB yield.

The regression equation (3) for the determination of predicted values of output parameter (i.e. JCB yield) is given as follows:

$$JCB\ (\%) = 343.90 + 34.43A - 8.34B - 0.46C - 15.19D - 0.93AB - 0.035AC + 0.58AD + 0.0023BC + 0.25BD + 0.04CD - 1.25A^2 + 0.075B^2 + 0.0006C^2 + 0.0023D^2 \quad (3)$$

The graph between the predicted and actual JCB yield (%) given in Figure 1 shows that the predicted values are quite close to the experimental values, thereby, validating the reliability of the model developed for establishing a correlation between the process variables and the JCB yield.

Table 4: ANOVA for response surface quadratic model

Source	Sum of Squares	Degree of freedom (df)	Mean Square	F-value	P-value Prob>F
Model	2078.70	14	148.48	47.43	<0.0001
A-Catalyst concentration	815.10	1	815.10	260.35	<0.0001
B-Temperature	6.75	1	6.75	2.16	0.1500
C-Time	520.08	1	520.08	166.12	<0.0001
D- Methanol/oil molar ratio	53.76	1	53.76	17.17	0.0002
AB	172.05	1	172.05	54.95	< 0.0001
AC	13.78	1	13.78	4.40	0.0424
AD	6.13	1	6.13	1.96	0.1698
BC	5.78	1	5.78	1.85	0.1820
BD	108.78	1	108.78	34.75	<0.0001
CD	162.90	1	162.90	52.03	<0.0001
A^2	4.19	1	4.19	1.34	0.2541
B^2	149.83	1	149.83	47.86	<0.0001
C^2	28.97	1	28.97	9.25	0.0042
D^2	0.000115	1	0.000115	0.000036	0.9848
Residual	122.10	39	3.13		
C.V:2.09% R^2_{model} : 0.945, $R^2_{Adj.}$: 0.923 Predicted R^2_{model}: 0.890					

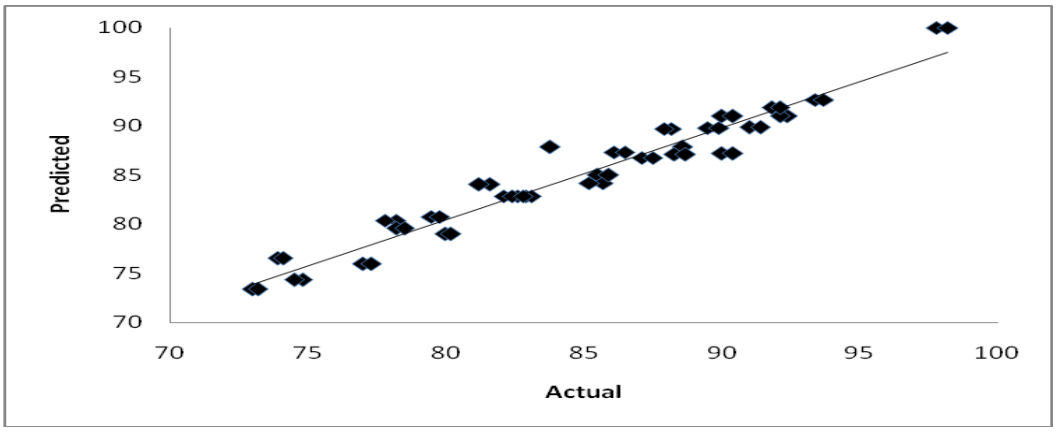

Figure 1: Predicted versus actual JCB yield (%) values

3.1 Effect of process parameters on JCB yield (%)

Figure 2 shows the effect of catalyst concentration, reaction temperature, reaction time and methanol/oil ratio on JCB yield. It can be seen from the figure that the JCB yield decreases significantly with increase in catalyst concentration. This may be due to the fact that addition of excessive catalyst causes more triglyceride to react with the alkali catalyst leading to the formation of soap, which decreases the biodiesel yield [12]. JCB yield decreases with increase in temperature till the middle point is reached, after that it increases. This may be due to the fact that viscosity of oils decreases at high temperature resulting in an increased reaction rate and shortened reaction time, thereby, increasing the biodiesel yield [12]. Reaction time has a positive effect on the JCB yield, as it increases with increase in time [13]. Yield of JCB is found to increase with the increase in methanol/oil ratio; since the transesterification reaction is reversible in nature, so excess alcohol is added to ensure the total conversion of triglycerides [12]. Thus, the yield of biodiesel increases with increase in temperature, time and methanol quantity and decreases with increase in catalyst concentration.

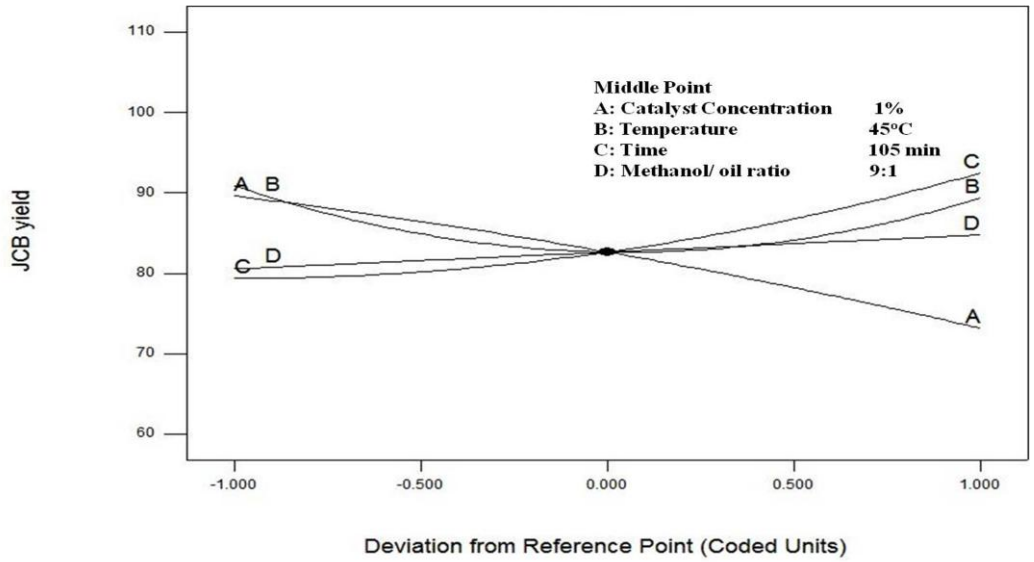

Figure 2: Effect of catalyst concentration, temperature, time and methanol/oil ratio on JCB yield (%)

3.2 Optimization of response parameters

Optimization of individual responses was performed to achieve the desired maximization of JCB yield based on equation 3. Design Expert 8.0.6 software was used to optimize the response and the value of the response (JCB yield) was set at maximum. The optimal value of input process parameters is given in Table 5. An experiment was carried out at the optimal parametric settings for JCB yield to obtain the targeted value of response parameter.

Table 5: Optimized input process parameters and optimum value of JCB yield

Response	Optimum value of process parameters				Predicted value	Experimental value
	A	B	C	D		
JCB yield (%)	1.0	55	110	11	98.89	98.3

3.3 Analysis of JCB

The Fatty acid (FA) composition of JCB prepared using the above optimum parameters given in Table 5 and determined by Gas Chromatography (GC) is given in Table 6 which shows that JCB mainly contained Oleic and *Linoleic* acid. The FA composition is in good agreement with the composition reported by Jain and Sharma [7]. The physio-chemical properties of JCB are reported in Table 7. The properties of JCB were found to be in good accord with ASTM and BIS specifications and with the work of Rashid *et al.* [14].

Table 6: Fatty acid composition of JCB

S.no	Fatty acid	Formula	% Composition
1	Palmitic acid	$C_{16}H_{32}O_2$ $CH_3(CH_2)_{14}COOH$	16.2
2	Stearic acid	$C_{18}H_{36}O_2$ $CH_3(CH_2)_{16}COOH$	8.2
3	Oleic acid	$C_{18}H_{34}O_2$ $CH_3(CH_2)_7$-CH=CH-$(CH_2)_7COOH$	38.4
4	Linoleic acid	$C_{18}H_{32}O_2$ $CH_3(CH_2)_4CH$=CH-CH_2-CH=CH-$(CH_2)_7COOH$	36.8
5	Linolenic acid	$C_{18}H_{30}O_2$ $CH_3(CH_2)_4CH$=CH-CH_2-CH=CH-CH_2-CH=CH-$(CH_2)_4COOH$	0.4

Table 7: Physio-chemical properties of JCB

S.no	Property (unit)	ASTM D6751	IS 15607	JCB	ASTM D6751 limits	IS 15607 limits
1	Viscosity (cSt; 40°C)	ASTM D445	IS 1448	4.9	1.9-6.0	2.5-6.0
2	Density (g/c.c at 15°C)	ASTM D4052	IS 1448	0.862	-	0.860-0.900
3	Flash point (^oC)	ASTM D93	IS 1448	174	Min 130	-
4	Ester content (%)	-	EN 14103	98.3	-	Min 96.5

3.4 Adulteration of JCB with Kerosene

The JCB prepared under optimum conditions was adulterated with kerosene in different proportions and change in the properties of JCB was observed with respect to kerosene. The various properties that were analyzed are given as follows:

3.4.1 Viscosity of Blends:

Figure 3 shows the plot of viscosities of biodiesel blends. The plot can be used as a calibration curve to find out the extent of adulteration of kerosene in biodiesel on the basis of viscosity. The figure indicates that the viscosity of biodiesel blends decreases from KB_{100} to KB_{10} due to lower viscosity of kerosene than biodiesel.

Based on the curve shown in Figure 3, a correlation (Equation (4)) is developed to measure the viscosity of any adulterated sample of biodiesel blend. The correlation can be used to keep a check on the mal practice of adulteration by finding out the extent of blending of biodiesel with kerosene. The value of the regression coefficient (R^2) is quite high for equation 4, thus, indicating the validity of the correlation developed.

$$v = 0.030\ b + 1.441\ ;\ R^2 = 0.996 \quad (4)$$

where; v – Viscosity of blends in cSt

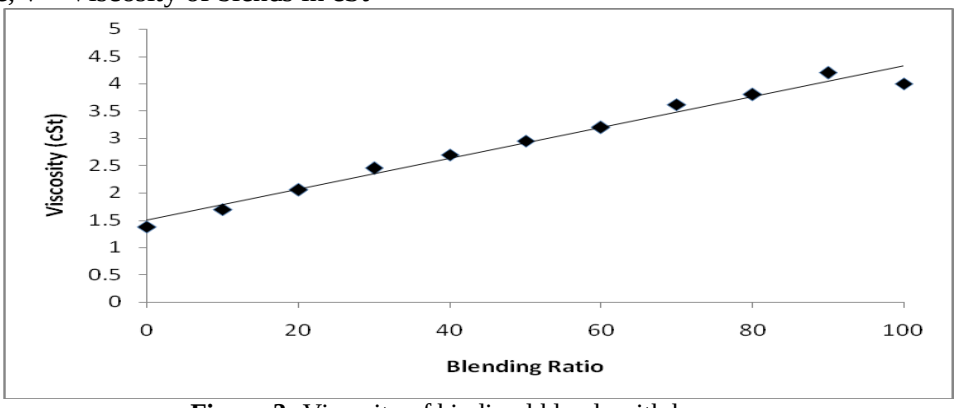

Figure 3: Viscosity of biodiesel blends with kerosene

3.4.2 Density of *Blends*

Figure 4 shows the plot of density of biodiesel blends that can be used as calibration curve to know the density of unknown adulterated biodiesel sample. The density of biodiesel blends also decreases from KB_{100} to KB_{10}. This is again due to lower density of kerosene than biodiesel.

Based on the curve shown in Figure 4, a correlation (equation 5) is developed to measure the density of any unknown adulterated sample of biodiesel blend. The value of the regression coefficient is quite high for correlation, thus, indicating the validity of the correlation developed.

$$\rho = 0.766\ e^{0.001b}\ ;\ R^2 = 0.937 \quad (5)$$

where; ρ - density of blends in g/c.c

The present study has provided the optimum range of parameters to maximize the JCB yield to a high value of 98.3%. Moreover, the low reaction temperature condition and less reaction time, that has been optimized using RSM, is a new work in the field of transesterification of JCO to produce biodiesel. The esterified oil with reduced FFA of < 1% was subjected to base-catalyzed transesterification to produce biodiesel. A biodiesel yield of 98.3% has been achieved with methanol/oil molar ratio of 11:1 (w/w) using NaOH as catalyst (1% w/w) in 110 min at 55^{o}C. Further, the adulteration of biodiesel with kerosene has been studied and correlations have been developed to check the adulteration of unknown samples of biodiesel.

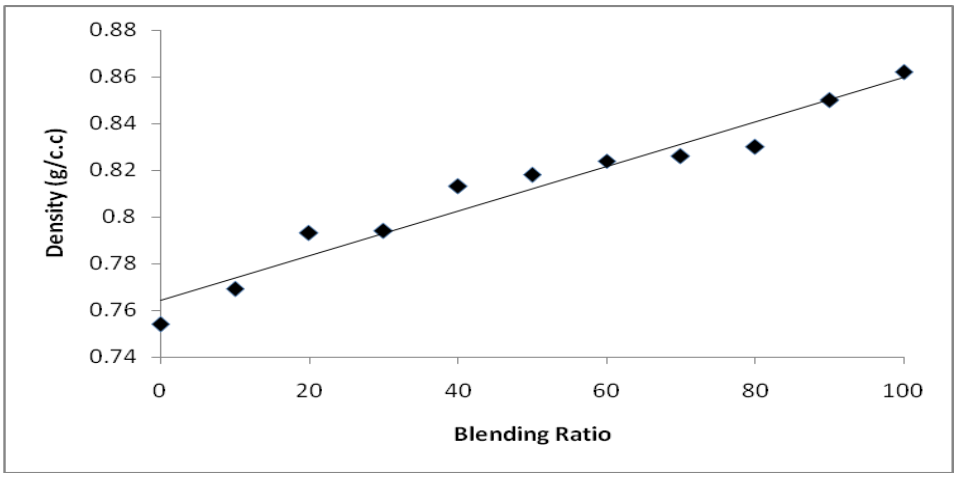

Figure 4: Density of biodiesel blends with kerosene

Conclusions

Optimization of transesterification process of JCO was achieved by four-factorial CCD using RSM in 54 experimental runs. A second-order model has been obtained to predict the JCB yield as a function of process variables. A biodiesel yield of 98.3% has been achieved with methanol/oil molar ratio (11:1) using NaOH as catalyst (1% w/w) in 110 min time at 55^{o}C temperature. The prepared JCB conformed to the ASTM and BIS specifications. On the basis of ANOVA; the catalyst concentration, reaction time and methanol/oil ratio had a significant effect on JCB yield. Based on the analysis of blends of biodiesel with kerosene by viscosity and density measurement, curves and correlations have been developed to check the extent of adulteration of kerosene in unknown samples of biodiesel. The study postulates that the regression coefficient (R^2) of correlations has a value above 0.93 indicating their usefulness in curbing the mal practice of biodiesel adulteration. This study will be helpful in characterizing the biodiesel for its adulteration with kerosene. This would lead to customer acceptance, standardization and quality assurance of biodiesel and its blends in the market. The model for predicting the biodiesel yield can be successfully employed in the biodiesel industry to maximize the yield of methyl esters.

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