

A KINETIC STUDY ON ACID CATALYZED ESTERIFICATION OF FREE FATTY ACIDS IN RICINUS COMMUNIS OIL FOR THE PRODUCTION OF BIODIESEL

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Abstract

The world economy is presently confronting an era of energy crisis as it primarily depends upon the conventional energy resources for meeting its demand that accounts for 80% of the energy expenditure [1]. Gradual depletion of conventional fossil fuel reserves, ambiguous fluctuations in its prices and the ever-increasing greenhouse gas emissions have intensified research on the scope for renewable fuels from alternative feedstocks towards mitigation of acute energy crisis. Recently biodiesel has withdrawn eminent interest as a vehicular fuel as it can be synthesized from a large variety of raw materials [2]. The present investigation emphasizes the optimization of acid esterification of non-edible castor (*Ricinus communis*) oil towards preparation of biodiesel under the influence of four process parameters viz. reaction time (0 to 4 h), reaction temperature (40 to 80°C), catalyst concentration (0.25 to 3.25 w/w) and molar ratio of methanol to oil (1:1 to 20:1). The effect of each parameter on the conversion of fatty acids into FAME has been discussed. Optimal conditions during which the FFA was reduced from 4.038 to 1.076 % were: 1 % w/w conc. H_2SO_4 , 15:1 molar ratio of methanol to oil, reaction temperature 50°C and reaction time 2.09 h. Among all the process variables, reaction temperature exhibited the most significant effect. Kinetic study of the optimized process parameters was performed. The experimental results were found to fit pseudo first order kinetics. These results were further fitted into the Arrhenius equation to determine the effect of temperature on rate constants. Activation energy and frequency factor were estimated as 22.148 KJ/mol and $A = 2.710 \text{ min}^{-1}$ respectively.

Keywords: Optimization; Acid-Esterification; Castor Oil; Activation Energy; Frequency Factor

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1. INTRODUCTION

The coming era of limited and expensive energy will be very difficult for everyone on Earth but it will be even more difficult if it is not anticipated. The majority of the oil reserves is located in some of the most politically and socially unstable countries. Moreover, the use of fossil fuel serves as an integral source of air pollution through greenhouse gas (GHG) and particulate matter emissions, which might also produce global warming, ground-level ozone and smog in the atmosphere [1]. Recently biodiesel has withdrawn eminent interest as a vehicular fuel as it can be synthesized from a large variety of raw materials. It offers reduced greenhouse gas and low sulphur emissions, due to its better combustion and lubricating effect. The European Union has issued a directive 2003/30/EC which proclaims that all its member states should use biofuels of up to 5.75% by 2010 and 20% by 2020 [2]. As per the American Society for Testing & Materials (ASTM), biofuel is a compound containing mono alkyl esters of long chain fatty acids obtained from the vegetable or animal fat based feedstocks [3]. Over the past few decades, the synthesis of biodiesel from renewable feedstocks like vegetable oils, animal fats, used oils and microbes, have been on the rise.

About 60-80% of the biodiesel production cost vests in feedstock selection [4]. Preparation of biofuel from refined vegetable oils is very common nowadays as they are available in abundance [5]. Higher demand for these feedstocks is responsible for the steady increase in their prices. Besides this, their usage would also create food insecurity which is also a major issue in the present decade [6]. It might also cause deforestation in certain countries due to widespread cutting down of forests for plantation purposes. This alarming situation has evoked the exploration of a wide variety of non-edible oils having high free fatty acid content such as: *Jatropha curcas* [6], waste cooking oil [7], neem oil [8], sea mango oil [9] croton oil [10], rocket seed oil [11] as feedstocks that are unfit for human consumption. Non-edible crops can be cultivated even on barren fields and wastelands and the cost of cultivation would be still lower as they can be grown sustainably without intensive care. But the major technical challenge lies in the reduction of FFA [12-14]. High FFA in the oil (>2% w/w) is undesirable as it hinders the process of conversion due to saponification with the alkali catalyst which further complicates the process of separation of the biodiesel from the glycerine fraction and causes difficulty in ester purification [5]. This results in significant yield loss. Acid catalyzed transesterification could overcome the

shortcomings by directly converting FFA and oil into biodiesel. However, it was discarded due to prolonged reaction time and poor yields [15]. Therefore, considering other economic aspects, the presence of high FFA necessitated a pre-treatment step for the reduction of FFA level to below 2% w/w which would improve product yields during base transesterification. However use of these non edible, high FFA feedstocks would require several steps for biodiesel production.

Currently, a number of methods are available that have been adopted for the synthesis of biodiesel. There are four main pathways for producing biodiesel, viz. direct use and blending with raw diesel [16 - 20], microemulsions [21], thermal cracking [22 - 27], and transesterification [28]. Several works have been reported on the two step biodiesel production from high FFA feedstocks.

Nowadays, the esterification pathway of free fatty acid in the presence of acid catalyst also yields fatty acid methyl esters or biodiesel [29]. Acid catalyzed simultaneous esterification and transesterification would convert the oil to biodiesel by a much simpler process. Esterification by means of acid catalyst would make the most utilization of free fatty acid in the oil and transform it to biodiesel. [30 - 32]. However, this one-step process is not suitable for high acid value, cheap feedstocks. Hence esterification followed by transesterification should be performed with cost effective, easily available catalyst. Solid acid catalyst forms the boost of today's research due to its formidable advantages like less corrosion, toxicity, ease of separation and eradication of environmental problems yet homogenous liquid acid catalyst has been used in the present experiment as solid acid catalyst has a slow reaction rate with the reaction occurring in three phases- solid, liquid and gas. This poses a kind of diffusional resistance that hinders the rate of reaction. Also, these heterogenous catalysts have low acid site concentrations, low microporosity and high costs.

The performance of the esterification depends on certain parameters like the free fatty acid content, amount of catalyst, the molar ratio of methanol to oil, reaction temperature and time [14]. One of the most important factors, yield is always determined by the selection of feedstock. Mostly the non-edible oils have low solubility with alcohol due to which more amount of alcohol is required to dissolve a particular amount of oil. This is also considered to increase the cost. Therefore, in this regard, castor oil seems to be an attractive solution feedstock for the preparation of biodiesel compared to other oils not only because its transesterification occurs at ambient temperature, but also it is cheap, high soluble in alcohol and abundantly available in India, where approximately 60% of the global castor seed production is recorded annually [24]. Understanding the kinetics of any chemical reaction is essential to know the extent of reaction at any time under particular conditions and to determine process design and parameter optimization [33]. Moreover, it also provides

further information on the research and design of industrial reactors for efficient biodiesel production [34].

Therefore, to find out the best parametric condition for the conversion of castor oil to biodiesel, the experiments were designed by response surface methodology (RSM). RSM has been used to find out the level of significance of each parameter affecting the esterification process. Second order regression model equation is formulated to check the significance of individual parameters which has been analyzed statistically by means of Analysis of Variance tests in order to find out common relationships among various parameters. The inevitable need to convert FFA and the motive of characterizing the kinetics of reaction has induced us to undertake the present study to determine the effect of process variables on the kinetics of esterification of FFA in castor oil using sulphuric acid as a catalyst. The produced fatty acid methyl esters were examined by comparing the standard properties with ASTM standard specifications.

2. EXPERIMENTAL

2.1 Materials

In the present study, industrial grade castor oil was collected from J.C Kundu and Bros, Kolkata, India. Methanol (99.5%, Merck, India) and iso-propanol (Qualigens, Mumbai, India) were used as solvents. Pure potassium hydroxide pellets used during standard titrations along with conc. Sulphuric acid (98%) was obtained from Merck, India. Deionized water was obtained from Arium 611 DI ultra-pure water system (Sartorius A.G., Gottingen, Germany). Methyl ester reference standard 37 % FAME mixture containing methyl oleate, methyl linoleate, methyl palmitate, methyl stearate of purity > 99 % was purchased from SUPELCO, India.

2.2 Characterization of the Feedstock

Castor oil, which is used as feedstock in the present investigation was characterized in terms of free fatty acid content, acid value, relative density, viscosity, saponification value, ester value, glycerol value and iodine value. The fatty acid composition of castor oil was also determined. The rate of conversion of FFA or the acid value of oil signifies the completion of esterification reaction. The initial FFA content of the feedstock was determined by means of the standard titrimetry method that conformed to the EN 14104 Standard. 50 mL of 0.1 N aqueous KOH was prepared for use as a standard solution. 1g of the oil was weighed in a beaker and 50 mL of isopropanol was added to it and warmed on a hot plate. This solution was cooled and two drops of phenolphthalein indicator were added before titrating against the standard KOH solution. The FFA value was calculated by equation 1

$$FFA(\%) = \frac{t \times 0.1 \times 28.1}{W}$$

(1)

t = volume of titrating solution used, W = weight of oil used.

2.3 Design of Experiment

Response surface methodology is an empirical modeling system generally used for optimizing complex processes [35]. DOE is an approach that gives a possible approximation of the cause and effect relationships. An experimental design methodology should be able to yield maximum complex information within minimum time that would result in lesser material and personnel cost. Some of the primary response surface techniques viz. Central composite design, Box Behnken design and the Doehlert design are generally used. Amongst them, CCD has been employed in the present study as it suitably fits into a quadratic surface and helps in optimizing, analyzing and modeling the interactions among the process parameters within the minimum number of experimental runs [36]. Moreover, it can give appropriate predictions at points lying equidistant from the center. Each variable is analyzed at two levels; the upper level (+ α) and the lower level (- α) respectively. The four process variables studied are: reaction time (A) (0-4h), reaction temperature (B) (40-80 °C), catalyst concentration (C) (0.25 to 3.25% by wt of oil) w/w and molar ratio of oil to methanol (D) (1:1 to 1:20). The factors are coded within the interval (- α , + α). Table 1 gives an account of the range and levels of the four independent variables evaluated.

Table -1: Factors and their levels as used in the design of esterification

Variable	Coding	Unit	Level	
			Lower	Higher
Reaction time	A	Hours	0	4
Reaction temperature	B	Celsius	40	80
Catalyst concentration	C	Wt%	0.25	3.25
Methanol to oil ratio	D		0.0	20

The design matrix for the acid-esterification of castor oil was obtained using Design-Expert software, package version 8.0.7.1 (STAT-EASE Inc., Minneapolis, USA) by central composite design (CCD) approach. For each variable, 2^4 full factorial two level CCD consisting of sixteen factorial points, eight axial points and six replicates at center points were designed which indicated the necessity of 30 experiments as computed from equation 2 [37]:

$$N = 2^n + 2(n) + n_c = 2^4 + 2(4) + 6 = 30 \quad (2)$$

Where N refers to the total number of experimental runs performed and n is the number of process parameters studied during acid esterification. Coded and uncoded variable can be correlated to each other using equation 3

$$x_i = \frac{X_i - \bar{X}_i}{\Delta X} \quad (3)$$

In Eq. 3, X_i is the actual value of the i^{th} factor in the uncoded units, \bar{X}_i is the average of the low and high values for the i^{th} factor, and ΔX represents the step change.

2.4 Development of Empirical Model

Basically, RSM optimization process consists of performing the designed experiments, evaluating the coefficients in a mathematical model, predicting the response and validation of the model. A mathematical model, useful in correlating the conversion of castor oil into FAME can be designed by means of RSMCCD. This model was examined through first, second order, and interaction terms, according to the second order polynomial equation cited in equation 4 [9]:

$$Y = b_0 + \sum_{i=1}^4 b_i x_i + \sum_{i=1}^4 b_{ii} x_i^2 + \sum_{ij=1}^4 b_{ij} x_i x_j \quad (4)$$

Where Y is the predicted conversion of castor oil into FAME (%) value of the response FFA, b_0 is the constant coefficient, b_i is the linear effect, b_{ij} is the first order interaction effect, b_{ii} gives the square effect and x_i , x_j are coded values of the acid esterification variables. Eq. 4 was expanded to obtain the following quadratic form in equation 5:

$$Y = b_0 + b_1 x_1 + b_2 x_2 + b_3 x_3 + b_4 x_4 + b_{12} x_1 x_2 + b_{13} x_1 x_3 + b_{14} x_1 x_4 + b_{23} x_2 x_3 + b_{24} x_2 x_4 + b_{34} x_3 x_4 + b_1^2 x_1^2 + b_2^2 x_2^2 + b_3^2 x_3^2 + b_4^2 x_4^2 \quad (5)$$

The coefficient of the proposed model is found out by multiple regression analysis technique.

2.5 Acid Catalyzed Esterification

Esterification of castor oil was done in a three necked flat bottomed flask well-equipped with a thermometer to measure temperature and a reflux condenser on the other neck to reduce evaporative methanol loss. The third neck is used for adding chemicals. The reaction mixture consisting of oil, methanol and acid catalyst was taken in the flask in requisite amount as mentioned in the design matrix and heated to the specified temperature by placing it on a magnetic stirrer hot plate with temperature controller. The speed of the stirrer was set at 700 revolutions per minute (rpm) to ensure complete mixing. The reaction was monitored during the time period specified in the experimental design matrix. The reaction mixture was cooled and poured into a separating funnel. It was left to stand overnight for the separation of mixtures into two distinct layers viz. aqueous phase and the oil-rich phase. Water was drained out of the funnel and the oil was decanted in a beaker and was heated for 5 minutes to eliminate excess of methanol prior to the determination of free fatty acid value. The optimal condition that yielded the minimum FFA value of the oil was then recorded.

2.6 Base Catalyzed Transesterification of Castor Oil

Castor oil (10 ml) was pre-treated using the optimized conditions obtained using response surface methodology. Potassium hydroxide pellets (1% by wt), to be used as catalyst, were dissolved in the required amount of methanol. Catalyst solution has to be freshly prepared to ensure effective catalyst activity. This solution, along with the pre-treated oil, was poured into the reaction flask and heated to 60 °C by means of magnetic stirrer where the contents were constantly agitated at 500 rpm to carry out base transesterification. At the end of the reaction process, the products were emptied into a separating funnel for separation of castor biodiesel (COB) and glycerols. The glycerol was removed, but the product layer obtained may still contain unreacted catalyst, methanol and residual glycerol. Hence, the hot water washing method was used to eliminate these impurities and it is done for 4 to 6 times until a clear aqueous layer is obtained. Traces of water and methanol, which would have reduced the flash point of the biodiesel obtained is therefore eliminated by heating the ester layer for about 15 minutes at 60 °C.

2.7 % FAME Estimation by GC (Gas Chromatography) Method

The fatty acid profile of COB was determined by means of gas chromatography (HP 6890 powered with HP ChemStation Rev. A 09.01 (1206) software, Agilent Technologies Inc., Santa Clara, CA, USA) equipped with a flame ionization detection system. The column was DB-1 (length 28 m, internal diameter 0.32 mm, film thickness 0.25 µm). The oven temperature program was as follows: initial temperature at 90 °C, ramping occurred at 10 °C/min to 240 °C for 20 min. Hydrogen was used as a carrier gas and a sample volume of 0.2 µl was injected using a split ratio of 10:1. The retention time of the methyl esters produced were compared to those of the standard methyl ester of fatty acids (Supelco FAME standard of 37 components) for identification. Estimated % FAME has been used to obtain the yield of biodiesel by the following equation 6

$$Yield(\%) = \frac{\text{Total wt of biodiesel produced} \times \text{total wt \% of FAME}}{\text{Total wt of oil}} \times 100 \quad (6)$$

2.8 Biodiesel Characterization

The physical and chemical properties of the final product were determined by performing standard experiments suggested by American Society for Testing and Materials (ASTM) as follows viscosity at 40°C (ASTM D445-06) [38], flash point (ASTM D93-07) [39], calorific value, fire point. Viscosity of a liquid tells its ease of atomization and flow properties. While flash point signifies the minimum temperature at which the fuel flashes into vapour. Fire point implies the point at which the fuel forms an ignitable mixture. This temperature gives an idea regarding the storage and transportation conditions. Cetane number of diesel signifies amount of ignition delay in compression

engines. The calorific value of the fuel denotes the amount of heat obtained after combustion of fuel. Apart from these, the other fuel properties that were subsequently tested by comparing them with ASTM D6751 biodiesel standards are:

- (i) Fatty acid composition (ii) Density (iii) Acid value
- (iv) FFA content (v) Moisture content
- (vi) Iodine value (vii) Kinematic viscosity (viii) Oxidation stability (ix) Flash point (x) Pour point (xi) Cloud point

3. RESULTS AND DISCUSSIONS

3.1 Characterization of Castor Oil

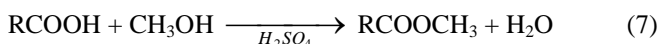
Commercial grade castor oil, pale yellow in colour, had an initial FFA content of 4.038 % that corresponded to an acid value of 8.076 mg KOH/g oil. The fatty acid composition and few other important properties have been reported in Table 2. With respect to other oils, castor oil has high viscosity and moisture content which make it inappropriate for direct use in diesel engine. Thus the castor oil is finally transformed into biodiesel to enhance its performance.

Table -2 : Characteristics of castor oil feedstock

Property	Castor oil
Fatty acid composition(%)	
(i) Ricinoleic	83.97
(ii) Oleic	2.28
(iii) Linoleic	0.61
(iv) Linolenic	0.33
(v) Stearic	0.52
(vi) Dihydroxylstearic	0.24
(vii) Palmitic	0.46
Acid Value (mg KOH/g)	8.076
Free fatty acid (%)	4.038
Relative density	0.964
Saponification value (mgKOH/g)	226.5
Viscosity (20 °C)	260
Ester value	218.47
Glycerol value (%)	11.95
Iodine value	87

3.2 Acid Esterification Process

Acid esterification is a process by which high acid value oils can be made suitable for base transesterification by their reaction with alcohol in the presence of acid acting as a catalyst thereby converting the free fatty acid to methyl esters [35].



Eq. 7 is a reversible reaction and therefore it requires methanol in excess to drive the equilibrium towards the formation of esters. The complete experimental design matrix with the response has been shown in Table 3. It was found that the reduction of FFA value in oil was highly successful as implied from the FFA range of 3.49 to 0.78%. The maximum reduction of free fatty acid was observed at 40 °C when the reaction took place at 10:1 methanol to oil ratio for 2h in the presence of 1.75% H₂SO₄ w/w. The minimum reduction was found at 60 °C for 4h, 1.75% H₂SO₄ by wt of oil, 10:1 methanol to oil ratio. The optimum reduction was predicted at 50 °C in the presence of 1 % w/w of catalyst with 15:1 methanol to oil ratio for 2h. The excess amount of methanol was essential to prevent the occurrence of backward reaction since the esterification process is reversible. Besides this, minimum use of catalyst is highly recommended as it would reduce the operating cost to some extent. Also, it would restrain the risk of more wastewater discharge due to sulphuric acid which was used in our present investigation for its cheapness and easy availability. Hence judicious use of catalyst is highly recommended.

3.3 Development of Regression Model equation

Response surface methodology enables the evolution of mathematical models in terms of FFA and the four independent variables affecting the esterification process by means of regression technique without actually considering the detailed reaction mechanism involved in the process. The models were selected based on the highest order polynomials where they were not aliased. The quadratic model was selected according to the suggestions by the DOE software for the response obtained in this case. Model summary statistics for reduction of FFA value in oil has been tabulated in Table 4.

Moreover, from Table 4 it can be seen that the difference between adjusted and predicted R-squared (R²) value is less than 0.1 in case of the quadratic model. Therefore, this model could be a suitable one for the determination of optimized conditions during esterification. The individual FFA response, which was obtained by applying multiple regression analysis, has been compared to the independent variables of the acid catalyzed esterification process with the help of second degree polynomial equation as cited in Eq. 5. From the experimental study it can be seen that temperature is the most important parameter showing the most significant effect followed by molar ratio and catalyst concentration. Similar results were obtained by Khan et. al who had used a blend of rubber seed oil and crude palm oil for the optimization and parametric analysis of acid

esterification [40]. The experimental design matrix along with its actual and predicted responses has been shown in Table 3. The center runs were performed six times as they estimate the quadratic terms in the model. The values of all coefficients given in Eq. 5 have been evaluated from the design matrix to fabricate the regression equation for FFA which has been cited as Eq. 8

$$\begin{aligned} Y(\text{FFA} \%) = & 1.61 + 0.031 \times A + 0.16 \times B + 0.025 \times C - 0.047 \times D + 0.086 \times A \times B \\ & - 0.014 \times A \times C - 0.017 \times A \times D - 0.014 \times B \times C + 3.125 \times 10^{-3} \times B \times D \\ & + 0.021 \times C \times D + 0.43 \times A^2 - 0.15 \times B^2 - 0.048 \times C^2 - 0.065 \times D^2 \end{aligned} \quad (8)$$

Eq. 8 also indicates that the reduction of FFA has linear, square and interactive effect on the four variables studied. However, all the terms in Eq. 8 are not equally significant and this necessitated the validation of model equation which has been discussed in the subsequent section.

Analysis and Adequacy of Acid Esterification

Model

Analysis of variance (ANOVA) technique was used to determine the significance of variables and check the adequacy of the quadratic regression model obtained from response surface modeling. ANOVA basically comprises classifying and cross-classifying statistical values which were tested by means of F test to assure the significance of the model. F value stands for the ratio of mean square of regression to the mean error. Lower p-value of LOF test corresponding to 95% confidence level denotes the greater significance of the model terms as it signify higher interaction among the parameters. Likewise, a higher F-value represents an appreciable prediction over the experimental results which finally estimate the variance of data about the mean. Lack of Fit (LOF) has been yet another diagnostic test that enables us to determine the adequacy of the model. In the present study, the ANOVA obtained from the regression analysis validated the fitness of the model as illustrated from the model F-value of 30.54 having a low probability value (p<0.0001) and a high sum of a square of 7.52. The efficacy of the RSM optimization tool was verified by relating the experimental responses with that of the predicted results. F-test also estimates the magnitude of the coefficient of R by Eq. 9

$$R^2 = 1 - \frac{\sum_{i=1}^n (FFA_{i,\text{cal}} - FFA_{i,\text{exp}})^2}{(FFA_{\text{avg},\text{exp}} - FFA_{i,\text{exp}})^2} \quad (9)$$

FFA_{i,cal} is the calculated value of the response for ith run, FFA_{i,exp} are the experimental values for individual run, FFA_{avg,exp} is the average value obtained. The value of R² ensured the accuracy of the proposed model. It signifies the degree of reduction in the variation of the response in the model. The value of R² should approach unity. Predicted R² of 0.8772 is in reasonable agreement with an adjusted R² of 0.9366. Acceptable values of R² imply that the model

equation yields true representation of the system and can be used in case of interpolation within the experimental domain. The results of ANOVA have been shown in Table 5.

Table 5 demonstrates that the linear effect (B), the quadratic effects of A, B and D and the interaction term between reaction time and temperature constitute the most significant terms influencing the acid catalyzed esterification process. The efficiency of the model was ascertained from the R^2 value and standard deviation values which was found to be

0.9683 and 0.13 respectively. model has a good fit. Thus, the

Fig. 1 further implies that an appreciable agreement exists between the predicted and experimental results. It becomes clear that the proposed model for acid-esterification was validated by the parametric conditions outlined in Table 6.

Table -3: Experimental design matrix and response to the acid catalyzed esterification reaction

Order no.	Reaction time (hours)	Reaction temperature(Celsius)	Catalyst conc. (wt%)	Methanol:oil ratio	Observed FFA (%) (Actual)	Predicted FFA (%) (Predicted)
1	2	60	1.75	10:1	1.9	1.61
2	1	50	1	5:1	1.61	1.67
3	1	50	2.50	5:1	1.69	1.74
4	3	50	2.50	15:1	1.48	1.54
5	3	70	2.50	5:1	1.98	2.10
6	2	60	1.75	10:1	1.6	1.61
7	1	70	1.00	15:1	1.75	1.75
8	2	60	1.75	20:1	1.37	1.26
9	3	70	1.00	5:1	2.14	2.15
10	2	60	1.75	10:1	1.52	1.61
11	2	60	0.25	10:1	1.46	1.37
12	4	60	1.75	10:1	3.49	3.38
13	1	70	2.50	15:1	1.72	1.85
14	2	60	1.75	10:1	1.48	1.61
15	3	70	1	15:1	1.89	1.98
16	1	70	2.50	5:1	1.89	1.86
17	3	70	2.50	15:1	2.03	2.02
18	3	50	1	5:1	1.61	1.62
19	0	60	1.75	10:1	3.34	3.26
20	1	70	1	5:1	1.77	1.85
21	1	50	2.50	15:1	1.67	1.71
22	2	60	1.75	10:1	1.57	1.61
23	2	40	1.75	10:1	0.78	0.69
24	3	50	1	15:1	1.37	1.45
25	3	50	2.50	5:1	1.59	1.63
26	2	80	1.75	10:1	1.45	1.35
27	2	60	3.25	10:1	1.57	1.47
28	1	50	1	15:1	1.54	1.56
29	2	60	1.75	0	1.52	1.45

Table -4: Model summary statistics for acid catalyzed esterification towards reduction of FFA level

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	
Linear	0.54	0.0955	-0.0553	-0.4044	10.90	
2FI	0.62	0.1129	-0.3799	-0.3955	10.83	
<u>Quadratic</u>	<u>0.13</u>	<u>0.9683</u>	<u>0.9366</u>	<u>0.8772</u>	<u>0.95</u>	<u>Suggested</u>
Cubic	0.19	0.9713	0.8660	-1.1026	16.32	Aliased

Table -5: ANOVA for Response Surface Quadratic Model

Source	Sum of squares	Mean square	F-value	p-value	
Model	7.52	0.54	30.54	< 0.0001	significant
A-Reaction time	0.023	0.023	1.33	0.2676	
B-Reaction temperature	0.65	0.65	36.97	<0.0001	
C-Catalyst concentration	0.015	0.015	0.82	0.3791	
D-methanol to oil ratio	0.053	0.053	3.03	0.1039	
AB	0.12	0.12	6.67	0.0217	
AC	3.306E-003	3.306E-003	0.19	0.6712	
AD	4.556E-003	4.556E-003	0.26	0.6187	
BC	3.306E-003	3.306E-003	0.19	0.6712	
BD	1.563E-004	1.563E-004	8.886E-003	0.9262	
CD	6.806E-003	6.806E-003	0.39	0.5438	
A ²	4.73	4.73	269.06	<0.0001	
B ²	0.57	0.57	32.31	<0.0001	
C ²	0.060	0.060	3.40	0.0866	
D ²	0.11	0.11	6.33	0.0247	
Residual	0.25	0.018			
Lack of Fit	0.14	0.014	0.49	0.8361	Not significant

Table -6: Model validation of acid esterification process

Parameters	Predicted values	Experimental values
Reaction time	2.09 hrs	2.09
Reaction temperature	50 °C	50 °C
Catalyst concentration	1.00 % w/w	1 % w/w
Methanol to oil ratio	15:1	15:1
FFA Predicted	1.076 %	1.144 %

Design-Expert® Software
FFA

Color points by value of
FFA:
3.49
0.78

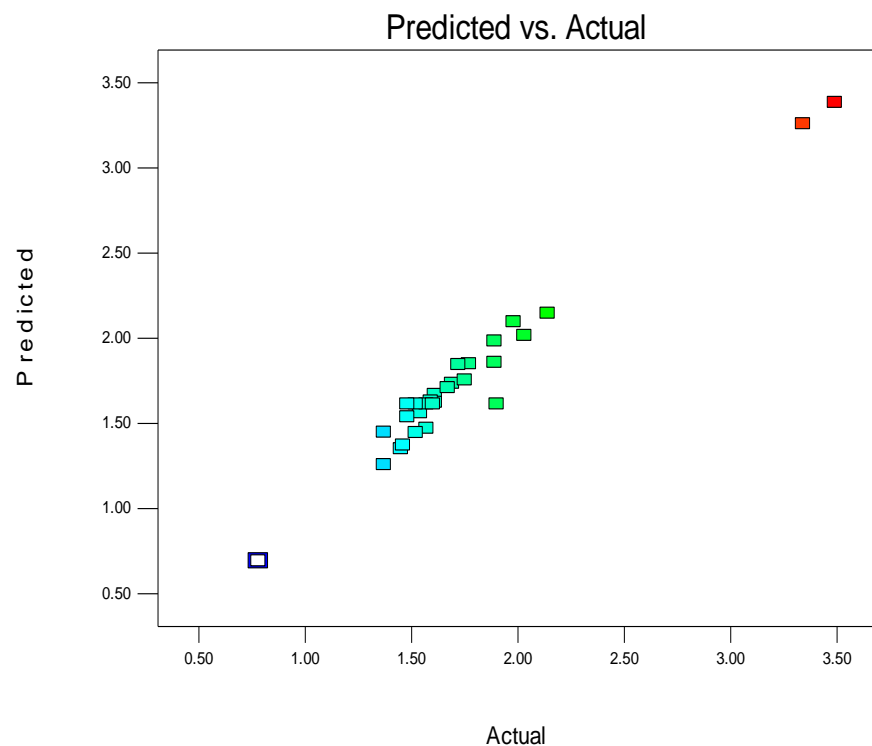


Fig -1: Plot showing comparison between predicted and actual (experimental) values of FFA

3.4 Effects of Individual Process Parameters

The reduction of FFA in oil depends much on the process variables like catalyst concentration, molar ratio methanol to oil, reaction time and temperature. A detailed study was undertaken with an objective to derive optimum conditions for the esterification reaction between FFA in castor oil and methanol in the presence of sulfuric acid catalyst.

3.5.1 Effect of reaction temperature

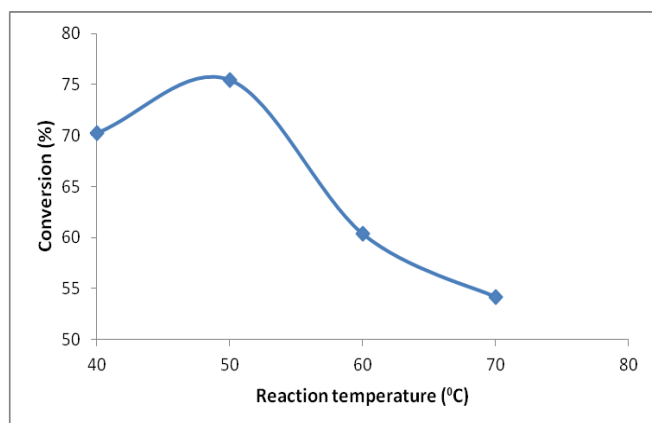


Fig -2: Effect of temperature on the conversion of free fatty acid into castor FAME

Keeping the other parameters fixed, temperature was varied within the range 40 to 70°C. Optimization of low temperature is essential as it would minimize thermal energy consumption. Maximum reduction of FFA to 0.78% was obtained at a temperature of 40°C. Apparently, high temperature favours forward reaction. From Fig. 2 it can be seen that the conversion of free fatty acid initially increased when the temperature was changed from 40°C to 50°C perhaps due to the high reaction rate[41]. A further rise in temperature, however, did not improve the conversion process due to greater methanol loss from the system. The conversion would have been better under a pressure greater than 1atm, which was not used in our study due to impending risks of methanol loss [42]. Hence it was inferred that an increase in temperature beyond 50°C would exhibit a negative impact on the reduction of FFA. This is probably due to the presence of water content. Similar results were reported by Leung and Guo[43] who used neat and frying oil for biodiesel production. In our study, the optimum FFA content of around 1.076 % was predicted at 50°C.

3.5.2 Effect of reaction time

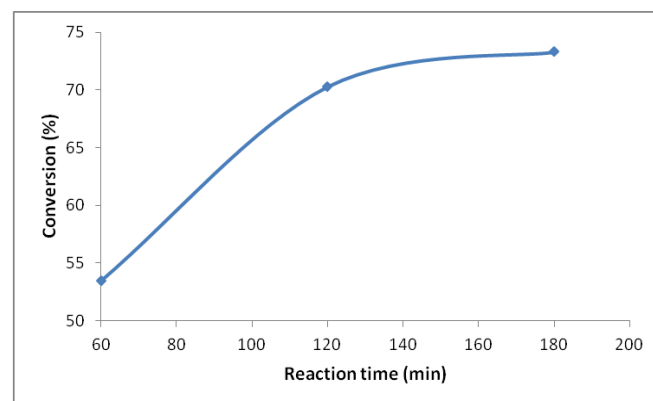


Fig -3: Effect of reaction time on the conversion of free fatty acid into castor FAME

From Fig. 3 it can be seen that initially the FFA decreases and conversion into FAME goes up with time, the maximum reduction occurring at 2h after which conversion starts deteriorating. This is due to the fact that the conversion rate is higher initially and it steadily attains equilibrium at a later stage. Further reaction time does not significantly influence the conversion. The inhibitive effect on the conversion of FFA with time is in conformance with the results of Perna et. al [44]. Prolonged reaction time is usually not favoured due to high production cost[45]. Optimum temperature was reported as 2 hr 9 mins.

3.5.3 Effect of catalyst concentration

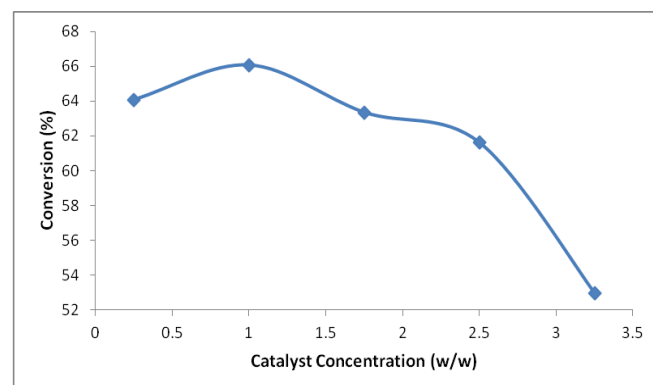


Fig -4: Effect of catalyst concentration on the conversion of free fatty acid into castor FAME

Today's trend is on the development of heterogenous catalysts because they are proclaimed as eco-friendly and recyclable. Nevertheless, some of their associated disadvantages are: low microporosity, diffusion limitations and high cost. Thus, concentrated sulphuric acid was chosen for our present study keeping in mind its low cost, abundant availability, high temperature effectiveness and less tendency to undergo soap formation [6]. The dosage of acid was varied from 0.25% to 3.25%. From Fig. 4, it is evident that sulphuric acid was an efficient catalyst in acid-esterification. It can be seen that conversion into FAME is initially influenced by the changes in catalyst concentration

i.e. upto 1% w/w. Further addition of catalyst does not appreciably change the conversion. Similar results were reported by Wiratni et. al [46] and Prerna et. al [44]. Besides, 1% w/w use of catalyst is predicted as more use of catalyst would add to the operating cost.

3.5.4 Effect of molar ratio of methanol to oil

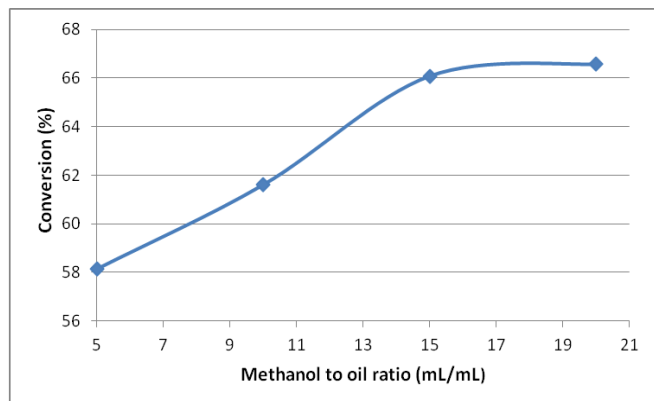


Fig -5: Effect of methanol to oil ratio on the conversion of free fatty acid into castor FAME

The molar ratio of methanol to oil is one of the most influencing factors of esterification as excess of it would bring about difficulties in heating. It is said that one mole of FFA reacts with one mole of methanol to yield esters. Excess methanol is required to drive the equilibrium towards forward reaction and increase the rate of formation of esters as esterification is a reversible process [34]. At the same time, the increased molar ratio would increase the rate of esterification reactions, thereby resulting in the formation of large amounts of water as byproducts that would further cause a reduction in reaction rate. Thus it is quite important to decide the optimum level of methanol to oil ratio. From Fig. 5 it can be said that conversion into FAME goes higher with more methanol to oil ratio. However, beyond 15:1, there is a slight increase in conversion. Thus the amount of methanol is reasonably maintained in order to obtain appreciable results. In the present study the optimum level of methanol to oil was predicted to be 15:1.

3.6 Numerical Optimization

In the esterification process of castor oil towards generation of biodiesel, the minimum FFA obtained was observed to be most influenced by reaction temperature and reaction time. The numerical optimization as provided in the Design Expert 8.0.7.1 software was performed on the model. This software provides selection of the desired result for each factor and response from the matrix with five possible, desirable steps as maximize, minimize, target, within range, none (for responses only) or set to an exact value (factors only) where a minimum and a maximum level is to be provided for each variable included in the optimization. Hence, from the overall results, the entire esterification process was optimized to get optimum values for minimum values of FFA. Optimized values of outputs are shown in Fig. 6.

3.7 Characterization of Castor Biodiesel & its Fatty

Acid Profile

The biodiesel that was obtained from transesterification of castor oil was subjected to GC analysis. Fig. 7 represents the fatty acid composition of the transesterified fuel sample. Fig. 7 reveals that castor biodiesel primarily consists of methyl esters of ricinoleic acid (89.5 %), stearic acid (4.3 %), palmitic acid (0.9 %), oleic acid (2.7 %) and linoleic acid (1 %). However the original castor oil contains methyl esters of ricinoleic acid (83.97 %), oleic acid (2.28 %), linoleic acid (0.61 %), linolenic acid (0.33 %), stearic acid (0.52 %), palmitic acid (0.46 %) and dihydroxylstearic acid (0.24 %). Density, viscosity and moisture content of the produced biodiesel were measured by ASTM methods. Table 7 represents the obtained results and the corresponding ASTM methods. According to the ASTM D6751 standards, the range of kinematic viscosity of biodiesel lies within 1.6-9 mm²/s which is found to contradict in this case viz. 19.58, due to the presence of ricinoleic acid with hydroxyl group. Standard density usually is within the range of 0.85-0.9 g/mL. ASTM D 613 is a method to calculate the cetane number of biodiesel. Cetane number of pure castor biodiesel is lower than the minimum range of ASTM D 6751. However, this oil, when blended with diesel might yield acceptable values of cetane number and viscosity. Certain advantages associated to castor biodiesel like lubricity, high flash point and pour point makes the oil safe for transportation and use in cold countries.

Table -7: Properties of COB with biodiesel specifications

Name of the parameters	COB	ASTM
Moisture content	0.05	0.053(max)
FFA	1.144	<2
Relative Density at 25 ^o C	0.899	N/A
Flash point	180	>130
Kinematic viscosity (40 ^o C)	19.58	1.6-9.0
Oxidation stability	1.1	-----
Cloud point	-13.4 ^o C	ASTM D2500
Pour point	-26 ^o C	
Cetane number	38 ^o C	ASTM D 613

3.8 Determination of Reaction Kinetics

Acid catalyzed esterification of FFAs using methanol as solvent can be represented by the following equation:



R₁ is a long chain carbon. Methanol was used in excess (15:1) to avoid the tendency of backward reaction and to maintain a constant concentration throughout the reaction. (Berrios et. al). Under this condition, the order of the reaction is however not affected by methanol concentration. Therefore esterification is assumed to occur by pseudo first order reaction as a function of FAME content [47]. In our present investigation, the rate constants of reaction were determined at various temperatures based on the change in FAME content as a function of time. Samples taken out at

regular intervals, were subjected to evaluation of FFA values. The reaction rate constant (k) was determined based on Eq. 11.

$$r = \frac{d[FAME]}{dt} = k[FFA] \quad (11)$$

Where r is the reaction rate, $[FAME]$ and $[FFA]$ is the concentration of methyl esters and free fatty acid respectively, t is the time.

With the help of esterification conversion data, reaction time was plotted against $\ln(1 - X_a)$ at different temperatures to determine the corresponding rate constants as shown in Fig. 8. The results point out that the esterification reaction follows pseudo first order kinetics. It was found that within the experimental conditions, an increase in reaction temperature causes the rate constant to increase as well. The value of rate constant was 0.003 min^{-1} ($R^2 = 0.998$), 0.004 min^{-1} ($R^2 = 0.888$) and 0.005 min^{-1} ($R^2 = 0.946$) at 313 K, 323 K and 333K respectively. The value of activation energy can be determined from the Arrhenius equation expressed below:

$$k = Ae^{-E_a/RT} \quad (12)$$

where A is the exponential factor, E_a is the activation energy, R is the universal constant and T is the temperature (K).

Activation energy (E_a) can be determined from the Arrhenius plot of $\ln k$ vs $(1/T)$ as depicted in Fig. 9 The activation energy (E_a) obtained was 22.148 KJ/mol and the pre-exponential factor was 2.710 (slope = -2664 and intercept = 2.710). With H_2SO_4 as catalyst, the activation energy should range between 20.7 – 45.9 KJ/mol. The value of E_a obtained from our results complied with those of Chai et.al[45]. The R^2 values for all such calculations shown in Fig. 9 are between 0.85 and 0.99 that indicate good fit of experimental value with the equation.

3.9 Factors Affecting the Yield of Biodiesel

Esterification process is usually followed by a transesterification that finally gives an appreciable yield of biodiesel. Certain factors like catalyst concentration, time, temperature and molar ratio have an influencing effect on the yield of biodiesel. The catalyst used in this process is potassium hydroxide.

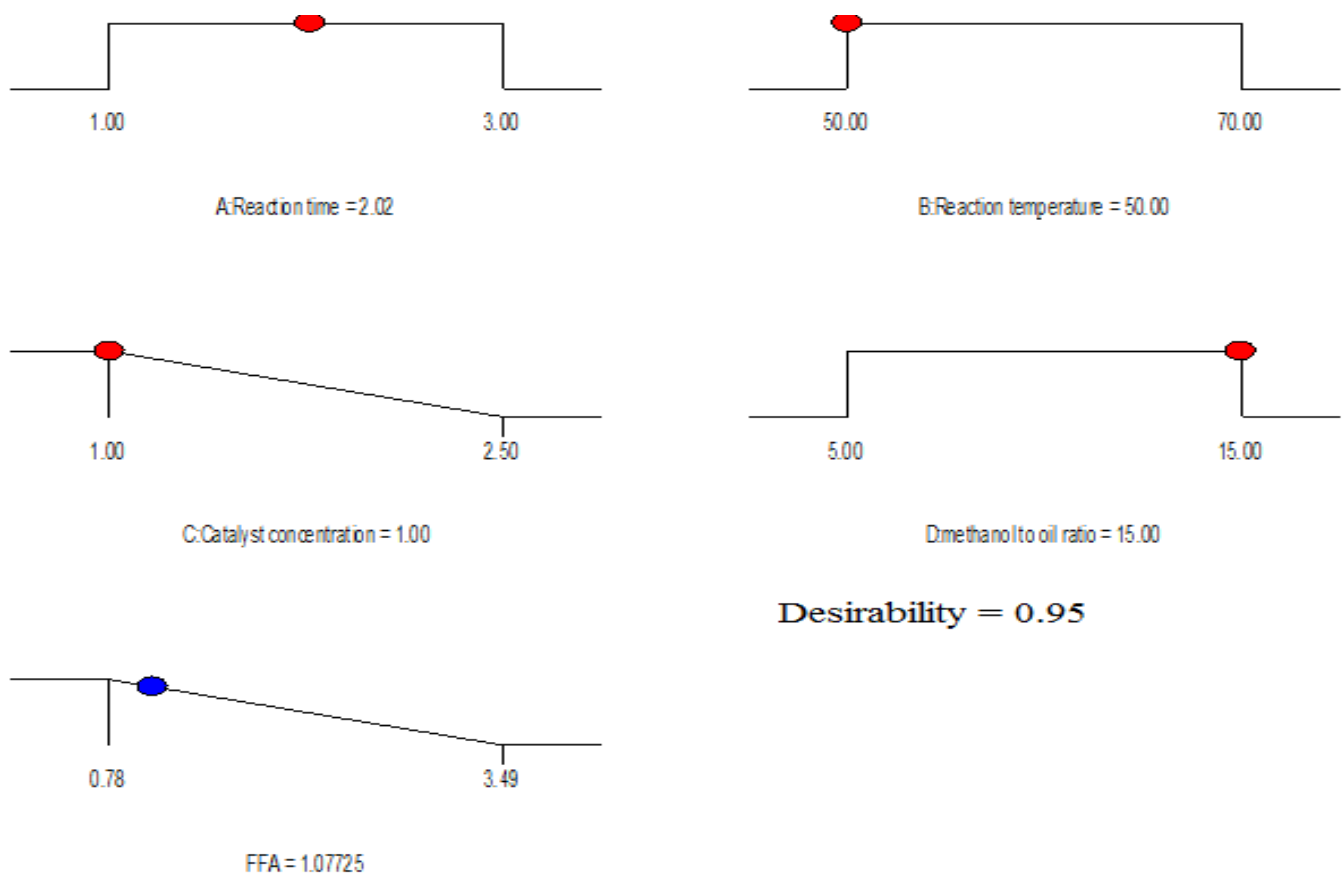


Fig -6: Optimized process condition

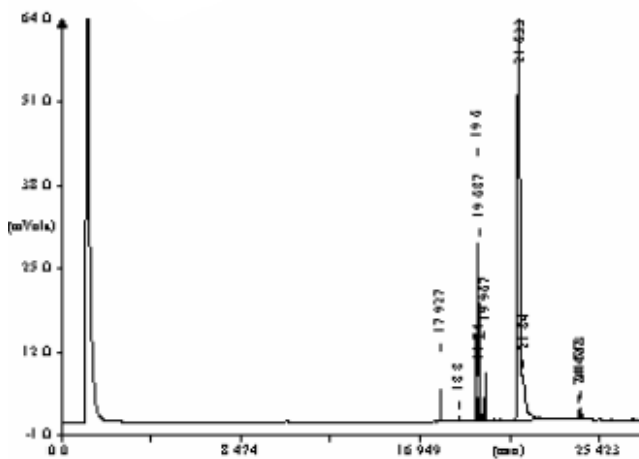


Fig -7: Gas chromatographic analysis of castor biodiesel

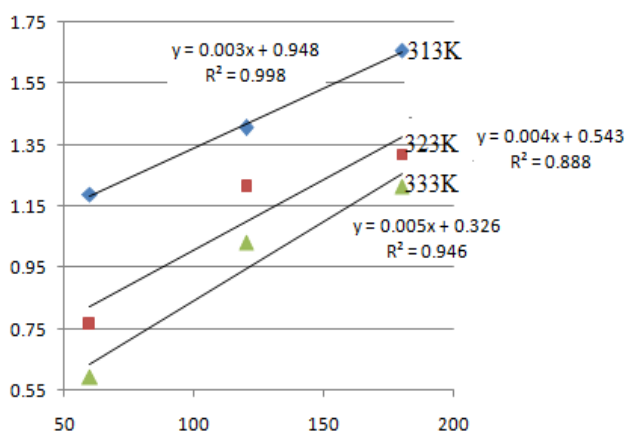


Fig -8: First order kinetic fit for the esterification of FFA at various temperatures : 313 K, 323 K and 333 K

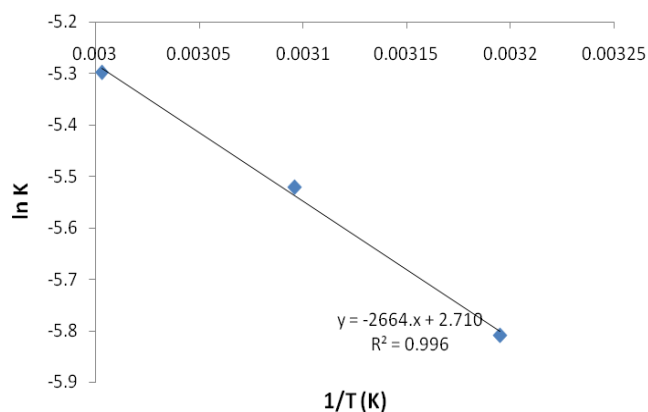


Fig -9: Arrhenius plot of pseudo first order kinetics

3.9.1 Effect of catalyst concentration on yield

The biodiesel yield increases significantly with that of catalyst loading during the initial stages. However, as time progresses, the yield decreases due to soap formation. The process occurs for 1h at a temperature of 60°C with a molar ratio of 15:1 during which yield of 90 % is achieved. The catalyst concentration was varied between 0.5 to 2 %. It was observed that an increase in the amount of catalyst also increases yield. However, beyond 1.5 %, the yield starts

decreasing as high catalyst concentration maximizes the tendency of soap formation during transesterification that further increases the viscosity of the reactants and lowers the amount of methyl esters formed.

3.9.2 Effect of temperature

In the available literature, it can be seen that the temperature of 60°C is the most desirable one for transesterification. Usually the rate of the reaction is slow and takes much time to complete if the temperature is below 60 °C. On the contrary, when the temperature is beyond 60°C, the yield of biodiesel decreases due to evaporative methanol loss since its boiling point is 64.7 °C. The process was carried out at four temperatures viz. 40, 50, 60 and 70 °C. At 40 °C, low yield of (82%) was obtained. The reaction was slowest at this temperature. The reaction occurred most satisfactorily at 60 °C when 90 % of methyl ester content was obtained within 1 h. This is in conformance with the work of other researchers [48].

3.9.3 Effect of reaction time

It has been studied from previous works that 1 h would be sufficient for the completion of transesterification using base catalyst. Higher temperature would take less time due to high reaction rate compared to low temperature that would take more time to give the same yield. Longer reaction time does not however improve the yield, but only raises operational cost. Hence 1 hour was chosen in our study.

3.9.4 Effect of methanol to oil ratio

Methanol to oil ratio is one of the most influencing factors that affects the yield of esters. The yield of biodiesel would considerably improve on increasing the molar ratio as they imply better conversion into methyl esters. The reaction remains incomplete if an insufficient amount of methanol is added to the reaction media. This also lowers yield significantly. In our study the molar ratio was varied between 5:1 – 20:1. It was found that the yield of biodiesel improved from 82 % to 92 % on increasing the molar ratio from 5:1 to 15:1. At the ratio of 20:1, the yield was not found to alter appreciably. Therefore 15:1 methanol to oil ratio was chosen for our study.

4. CONCLUSION

The present investigation has illustrated the feasibility of successfully converting castor oil into FAME in two steps – acid esterification followed by base transesterification. RSM was used to analyze the optimum conditions for acid catalyzed esterification of castor oil. The kinetic study for esterification process was carried out in this case and the kinetic parameters were determined. The results have shown that the temperature had the highest effect over free fatty acid reduction followed by methanol to oil ratio. In contrary to other models, the proposed one was found to accurately fit into the experimental data. The optimum values suggested for each parameter were: reaction temperature - 50 °C, catalyst concentration- 1 % w/w, reaction time-2.09 h, molar ratio 15:1. Under these conditions the FFA was

actually reduced to 1.144%. This was followed by base transesterification in presence of KOH as catalyst. The small error percent of 0.068% substantiate the validity of the model in representing the actual experimental values within the studied range. In this study, the optimum conditions found for acid catalyzed esterification of castor oil can be commercially practiced in the oil sector in future. Thus, the major hindrance to the use of biodiesel in the form of its high operating cost can be easily overcome. Henceforth, new trends towards utilization of biodiesel can be expected to take a green turn for tomorrow.

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