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(Research Article)

Heavea brasilienis (Rubber seed oil) as cost effective non edible feedstock for sustainable high quality biofuel production.

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Abstract

Biodiesel is renewable fuel acquired from biomass which has short chain alkyl esters derived from vegetable oil or animal fats. It has greater advantages over traditional diesel oil. In first level esterification, H_2SO_4 is used because the acid catalyst to decrease the FFA from 4. 5% to 0. 85 %. In 2nd stage, transesterification chemical process was carried with methanol and NaOH, the elevated temperature 60^{0}c and response time is 45 min to 75min. Only a few experiments have been carried out for evaluating the results of equation using a Scientific tool.

Keywords: Rubber seed oil; Free Fatty Acid (FFA); Transesterification; Central composite design; Statistical analysis.

1. Introduction

India is amongst the world's leading energy consumers As per international energy agency's energy demand in India is predict to grow up to 3% per annum till 2040 compared global growth rate of 1%. India's consumption would be about 5. 5-5. 6 million barrels per day [1]. The transport sector fuel consumption in India's expected to be double by 2030Due to emission of harmful gases like oxides of carbon, sulphur etc. The use of fossile fuel may become obsolete [2][3]. The economic development and energy consumption of a country are closely related to each other. The macro economic status of the country involves energy and electricity consumption, number of vehicles along with per capita CO_2 emission [4]. Biodiesel chemically defined as an alkyl ester can be produced from biomass which includes the vegetable oils (edible & non edible), fats of animal. However, non-edible oils are ideal and suitable feed stocks to produce biodiesel [5]. They have advantageous amongst the remaining sources because of their high lubricity which gain better fuel character during combustion in IC engine and biodegradability also gained significant and better attention in the engine performance as well [6]. As the neem, rice bran, cotton, rubber seed are focused for biodiesel production, these second generations non edible oils use can overcome problems of food versus fuel, environmental and cost-effective issues associated [7]. Feedstock alone can make much more contributions which is one third biodiesel production expense [8]. The economic manufacturing of biodiesel is particularly depending on procedure and its materials. The choice of feedstock and sort of alcohol is vital here to produce. Commonly methanol is favored on the grounds of its low price. The commercial biodiesel may be organized through the alkaline metal oxide, metallic hydroxide catalyst because of their low price and high reactivity [9]. Even though the alkali metal oxides and hydroxides have high reactivity and occasional price they're much less at risk of be carried out because of their solubility and issue in separation, purification of the final product.

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2. Rubber (*Heavea brasilienis*) seed oil suitability to biodiesel synthesis

The rubber seeds are crucial of the rubber trees and are considered as waste. The rubber tree is quickest developing plant and it belongs. Almost 99% of the natural rubber the trans form of isoprene is specified rubber within the world is synthetic via rubber tree. It's far determined in India, Indonesia, Malaysia and Sri lanka.

Table 1 indicates the percentage distribution of free fatty acids of the taken feed stock rubber seed oil. Gas chromatography (GC 57) became the tool to be used to locate the free fatty acids composition of oil. It includes Palmitic acid (10.3%), Stearic acid (7.5%) It gives (17.8%) of saturated acid and it has oleic acid (25. 6%), Linoleic acid (38.5%) Linolenic acid (15.4%) which contains (79.5%) of unsaturated acid and remaining are of others fatty acids.

2.1. Characterization of rubber (*Heavea brasilienis*) seed oil (rso)

Table 1 Distribution (%) of fatty acids in rubber (*Heavea brasilienis*) seed oil (rso)

Sl. No	Components	RSO
1	Palmitic acid	10. 3
2	Steric acid	7. 5
3	Oleic acid	25. 6
4	Linoleic acid	38. 5
5	Linolenic acid	15. 4
6	Arachidonic acid	2. 1

Table 2 Physical properties of rubber (*Heavea brasilienis*) seed oil

Sl. No	Properties	Value
1	Colour	Dark Brown
2	State	Liquid
3	Viscosity (Cst)	8. 5
4	Flash point (^{0}C)	190
5	Calorific value (MJ/Kg)	40. 5
6	Density(Kg/m^3)	860
7	Specific gravity	0. 860
8	Moisture content (wt%)	0. 35%

2.2. Biodiesel production from *Heavea s brasilienis* seed oil

The oil from the rubber seed as a feed stock with free fatty acid which contain (FFA 4.5 %) is taken as a source material for the manufacturing of methyl ester of rubber seed oil. Here transesterification of two stage chemical process is effectively adopted to transform rubber seed oil into its methyl ester supported by methanol and catalyzed by H_2SO_4 and NaOH as a homogeneous catalyst. Inside the first stage esterification, with intension for minimizing the fatty acids composition H_2SO_4 acid is used as an catalyst, because the acid catalyst here will neutralize the degree of the rubber seed oil feed stock from 4.5% to 0.85%. This reaction became carried along with methanol at 60^{0}C, time numerous from 45 to 75 minutes . The system from here is totally closed to the atmosphere to prevent the loss of alcohol .

In this second stage of chemical synthesis was completed by transesterification reaction and treated with the RSO with methanol / catalyst mixture is fed to reactor for transesterificatoion process at 60^{0}C, 45 min to 75 min time interval, with aid of alkali catalyst the conversion rate is too high.

Table 2 Indicates the physical content of rubber seed oil like viscosity, flash point, calorific value and specific gravity values were estimated out with accordance to IS: 1448 standards.

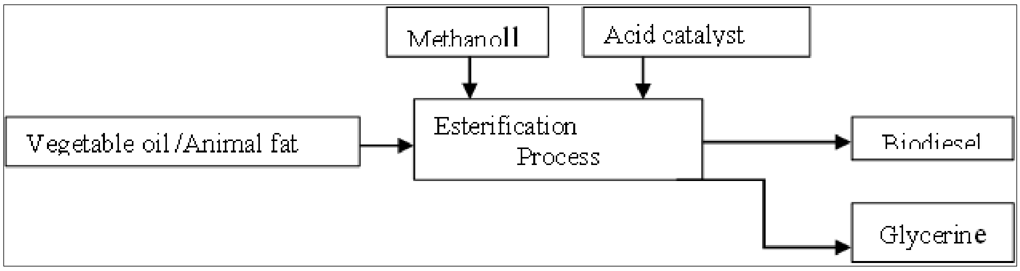

Figure 1 Biodiesel production using homogeneous acid catalyst method

The feed stock here used rubber seed oil with FFA (4.5%) this is above permitted level to apply base catalyzed transesterification chemical process. Therefore in this study attempt have been made to transform rubber seed oil into its methyl ester, having fuel character for the application in IC engine.

In the first level, esterification technique of chemical process, acid poured to oil of rubber seed to convert its FFA to required biodiesel. Here it is carried with aid of CH_3OH in catalyzed by H_2SO_4 (0.5% v/v) as to lower the free fatty acid degree to 0.8%. In the second level alkaline catalyzed supported transesterification chemical process has been executed via treating the pattern received from stage 1 supported with CH_3OH catalyzed by NaOH.

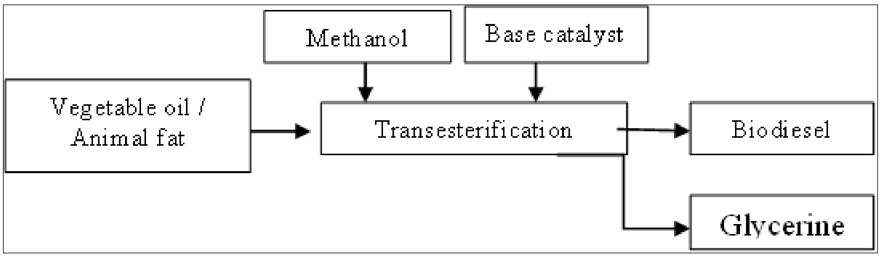

Figure 2 Biodiesel productions using homogeneous base catalyst method

3. Experimental methods

The rubber seeds were purchased from department of forest at Kundapur (Tq), Uttara kannada (Dist), Karnataka (India). From the collected seeds, oil was extracted in laboratory by using soxhlet extraction using hexane as solvent to determine the oil percentage in the seeds.

$$\% \text{ of oil extracted} = \frac{\text{Quantity of oil extracted}}{\text{Quantity of crushed seed sample}} \text{ X } 100$$

3.1. Stage : 1 Esterification by acid catalyst.

Table 3 Indicates factors with their levels for Stage 1 acid catalyzed process.

Table 3 Factors with their levels chosen for stage 1 esterification process catalyzed by acid

Factors	Units	Levels		
		1	2	3
CH_3OH(% v/v)	ml	5	10	15
Chemical reaction time	min	45	60	75

The experiments were executed according to the experimental matrix shown in Table 4.

Table 4 Layout of experimental design pattern first stage esterification chemical process

Expt No	Samples	CH_3OH	Reaction time	FFA
1	S_1	5	45	4. 5
2	S_2	5	60	3. 6
3	S_3	5	75	2. 7
4	S_4	10	45	2. 5
5	S_5	10	60	1. 5
6	S_6	10	75	0. 96
7	S_7	15	45	2. 2
8	S_8	15	60	1. 0
9	S_9	15	75	1. 5

3.2. Experimental procedure

The feed stock here i.e by adding rubber seed oil to a reactor and heated. The prepared methanoic sulphuric acid mixture is slowly poured with constant stirring to the heated oil at 60°C for different time intervals, similar processes continued for all other models. The collected excess methanol, H_2SO_4 and impurities were removed the acid value of the residue has to be measured.

3.2.1. Stage-2 alkaline catalyzed transesterification chemical process

Central composite design of three factors with a five-level used to analyze outcomes of the transesterification chemical process variables over the yield of rubber seed oil methyl ester (rsome). The independent variables; molar ratio, response time and catalyst concentration were decided as per Table V.

Here Table 5 represents the coded and uncoded degree of levels for independent variables. The sample S_6 as it contains lower value (FFA 0.96%) was selected as a most suitable source to carry the base catalyzed trans esterification chemical process. The selected sample was taken into the biodiesel digester process was implemented at 60^{0}C temperature using the required amount of sodium hydroxide solution along with methanol to the thermally treated rubber seed oil. The reaction proceeds to 60 minutes by transesterification chemical process. The experiments were conducted as per experimental design matrix which is shown by Table 5. On completing the process, the product of reaction is allowed to settled and the process product fall into two layer category one with rubber seed oil methyl ester (RSOME) on the upper layer while glycerol which is at the bottom. The crude methyl ester was washed twice with water to convert pH to7. To optimize the transesterification chemical process, the experiments were conducted as per the Table. 6 Because of its significantly reduced viscosity, the biodiesel generated by the transesterification process can replace petro-diesel in diesel engines. When vegetable oil's transesterification process was unknown in the past, its viscosity posed a significant barrier to its use as an engine fuel. This issue has been resolved by the transesterification process. The by-product of the transesterification chemical reaction is the glycerin that originally formed the bond between the chains of fatty acids. Glycerin can be used for various purposes. Thus during transesterification process nothing goes to waste. All the products and byproducts are utilized for various purposes.

Table 5 Coded and un-coded levels of independent variables

Parameters	Units	Symbols	Levels				
			-1. 68	-1	0	+1	+1. 68
CH_3OH	ml	A	11. 6	15	20	25	28. 4
NaOH	gm	B	0. 16	0. 5	1	1. 5	1. 84
Reaction time	min	C	34. 8	45	60	75	85. 2

Table 6 Experimental matrix for ccd and experimental results

Sl. No	A	B	C	CH_3OH (%v/v)	NaOH (%w/v of oil)	Reaction time	Yield (%)	Yield (%) Predicted
1	-1	-1	-1	15	0. 5	45	90. 5	82. 51
2	-1	-1	1	15	0. 5	75	85	82. 13
3	-1	1	-1	15	1. 5	45	32	43. 20
4	-1	1	-1	15	1. 5	75	56	61. 07
5	1	-1	-1	25	0. 5	45	80	80. 89
6	1	-1	1	25	0. 5	75	78. 0	72. 76
7	1	1	-1	25	1. 5	45	50	58. 83
8	1	1	1	25	1. 5	75	55	68. 95
9	0	0	-1. 68	20	1. 0	34. 8	75	70. 19
10	0	0	1. 68	20	1. 0	85. 2	82	78. 39
11	0	-1. 68	0	20	0. 16	60	74	85. 92
12	0	1. 68	0	20	1. 84	60	70	49. 66
13	-1. 68	0	0	11. 6	1. 0	60	65	64. 66
14	1. 68	0	0	28. 4	1. 0	60	78	69. 92
15	0	0	0	20	1. 0	60	86	86. 24

4. Statistical analysis

The experimental results studied for quadratic least square approach method. The results were obtained with scientific tools to obtain ANOVA. The surface plots the usage of the fitted quadratic polynomial equation acquired from regression evaluation were plotted by applying the XLSTAT software. Experiments were carried in order to prove the equation the usage of aggregate of independent variables, the variable which has been selected are in the range of experiment for % RSOME yield in terms of coded and un coded factors are given in the equation below. Applying the method of least square. The R^2 value of 0.894 as shown by the ANOVA is confirmed the goodness of fit with the model.

The obtained RSOME yield range of predicted and experimental yield demonstrates acceptable correlation between predicted biodiesel yield and experiments, indicated reliability of the model. The RSOME yield was predicted by second-order polynomial equation in terms of coded factors as in below equation.

$$Y=\beta_0 + \beta_1X_1+ \beta_2X_2 + \beta_3X_3+ \beta_{11}X_1^2+ \beta_{22}X_2^2+ \beta_{33}X_3^2+ \beta_{12}X_1X_2 + \beta_{13}X_1X_3 + \beta_{23}X_2X_3$$

$$Y =86.24+1.56X_1-10.78X_2+2.44X_3-6.70X_1^2-6.52X_2^2-4.23X_3^2+4.31X_{12}-1.94 X_1X_3+4.56 X_2X_3$$

Table 7 Indicates regression co-efficient of predicted quadratic polynomial model

Terms	Coefficients	Standard Errors	Computed t-value	P value
Linear				
β_0	86. 24	4. 43	19. 45	0. 000
β_1	1. 56	2. 94	0. 53	0. 606
β_2	-10. 78	2. 94	-3. 66	0. 004
β_3	2. 44	2. 94	0. 83	0. 427
Quadratic				

β_{11}	-6. 70	2. 86	-2. 34	0. 041
β_{22}	-6. 52	2. 86	-2. 28	0. 046
β_{33}	-4. 23	2. 86	-1. 48	0. 171
Interaction				
β_{12}	4. 31	3. 84	1. 12	0. 288
β_{13}	-1. 94	3. 84	-0. 50	0. 625
β_{23}	4. 56	3. 84	1. 19	0. 263
R^2	0. 894			

Table 8 ANOVA for the quadratic polynomial model

Sources	**df**	**SS**	**MS**	**F**	**Probability**
Model	9	3328. 45	369. 83	3. 13	0. 045
Error	10	1181. 68	118. 17		
Corrected total	19	4510. 14			

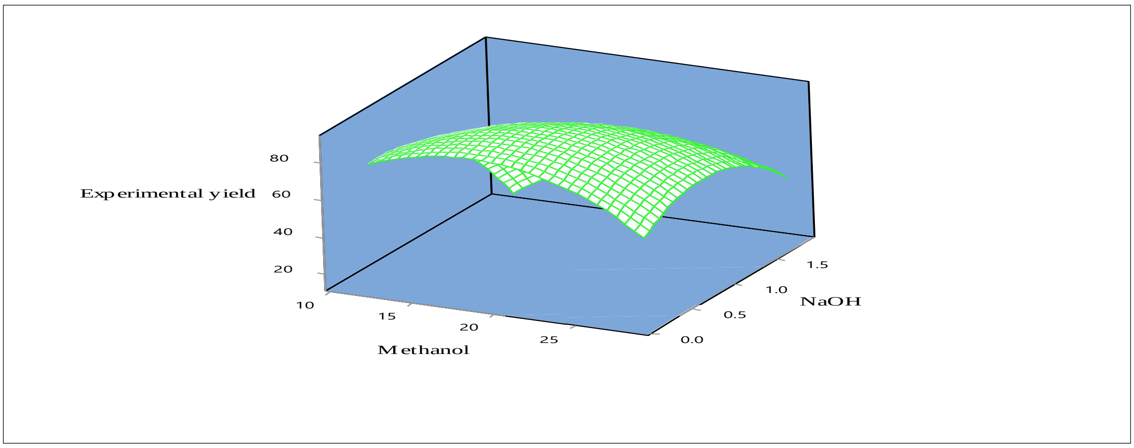

Figure 3 Response surface 3d plots for methanol quantity and NaOH concentration for different fixed parameters

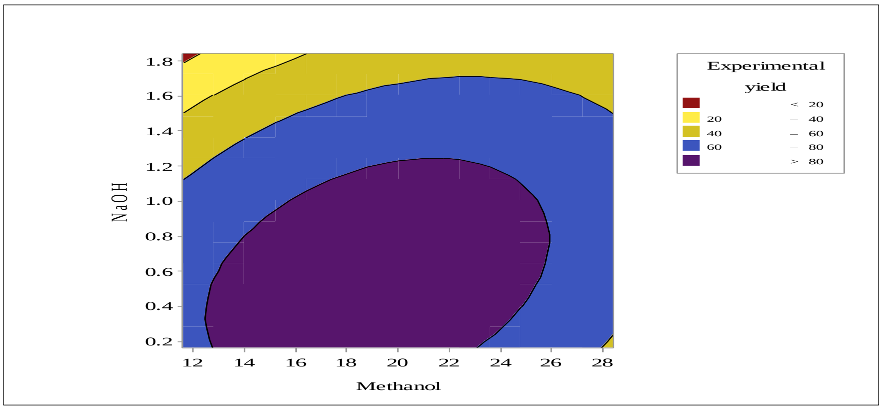

Figure 4 2D Contour Plots Between Methanol Quantity And Concentration Of NaOH For Different Fixed Parameters

The Figure 3 & 4 obtained here represents the 3D regression surface and 2D contour plots between the methanol quantity and NaOH concentration at different parameters. The enhance in volume of methanol increases the yield (%) of biodiesel for the different parameters. The Figure 3 shows that yield of biodiesel (%) Increases with increasing amount of methanol to concentration of NaOH. It reached a maximum yield 90.5% for 0.5(w/v) grams of NaOH with 15ml (v/v) methanol. The yield of the desired product decreases with the increase in concentration of NaOH in the amount of methanol i.e sodium methoxide solution. The desired yield reached to the lowest value 32% with for NaOH 1.5 gr (w/v), 15 ml(v/v) of methanol, because of no significant interaction between the methanol and catalyst the yield decreases.

5. Kinetic study

The chemical reaction which proceeds between triglycerides of rubber seed oil with methanol in presence of catalyst gives rubber seed oil methyl ester with properties similar to conventional diesel along with glycerol which can be identify by Eq. 4. The Eq. 5 can be studied as rate or velocity of the reaction (r).

$$\mathrm{RSO} + 3\mathrm{M} \underset{k_2}{\overset{k_1}{\rightleftarrows}} 3\mathrm{RSOME} + \mathrm{GL} \qquad \text{-- Eq. (1)}$$

$$r = \frac{-d[\mathrm{RSO}]}{dt}\; k_1[\mathrm{RSO}][\mathrm{M}]^3 - k_2\,[\mathrm{RSOME}]^3[\mathrm{GL}] \qquad \text{-- Eq. (2)}$$

Where M indicates methyl alcohol and GL as glycerol. The equation 1, which represents the reversible nature in the reaction it has been ignored because of excess amount of methyl alcohol in reaction mixture which will shift the reaction towards the forward side according to Lechatelier principle. Hence the reaction rate comes to be as equation3.

By assuming a pseudo-first order kinetic mode the rate constant (k) can be calculated. Calculation of rate constant (k) is as follows (Eq. 4 – Eq. 6).

$$r = \frac{-d[\mathrm{RSO}]}{dt} = k[\mathrm{RSO}] \qquad \text{--Eq. (3)}$$

$$\frac{d[\mathrm{RSO}]}{[\mathrm{RSO}]} = -k dt \qquad \text{--Eq. (4)}$$

The conversion rate of RSO into RSOME can be written as $[\mathrm{RSO}] = [\mathrm{RSO_i}][1 - x]$ where xrepresentsis the initial concentration and conversion of$[\mathrm{RSO_i}]$ of RSO. Substitute this in equation 7 we may get,

$$\frac{d[\mathrm{RSO_i}][1-x]}{[\mathrm{RSO_i}][1-x]} = -K dt \qquad \text{---Eq. (5)}$$

On simplification of equation 8, we get the rate constant as equation 9.

$$K = \frac{-\ln[1-x]}{t} \qquad \text{---Eq. (6)}$$

The velocity constant of the chemical reaction and the slope is determine with which is drawn between $-\ln[1 - x]$ against t, the temperature have significance over the rate constant or velocity constant of reaction. Hence, for Chemical transesterification chemical process the activation energy which is the minimum amount of energy that must be required for reactant molecules to react and form the desired product is estimatedusingArrhenius equation (Eq. 7) and this equation adapted as equation 8.

$$k = Ae^{[-E_a/RT]} \qquad \text{---Eq. (7)}$$

$$\ln k = \ln A - \frac{E_a}{RT} \qquad \text{---Eq. (8)}$$

Here velocity constant (K), Arrhenius constant (A) Activation energy (Ea), Universal gas constant(R) and Absolute temperature (T) have their significances. The activation energy (Ea) was estimated using graph of ln (k) vs 1/T. It identified that Ea can be used to determine whether a reaction is controlled by kinetic factors or mass transfer.

6. Results and discussion

The rubber seed oil turned into an appropriate feedstock to convert into its methyl ester with intension to limit production cost. RSO was recognized as a critical feedstock for biodiesel manufacturing. The layout of experiments had been carried through the response surface methodology, CCD used for the optimization of biodiesel production parameters have the values 90. 5 % yield received at the 15ml CH_3OH (% v/v), NaOH 0.5 (%w/v) and 45 minutes of response time. From the above results we can conclude that RSO can contribute more for sustainable bio fuel in future.

7. Conclusion

In this study the biodiesel is produced from rubber seed oil, its oil is non edible and considered as waste that mainly employed in the context of minimizing the production cost. The design of experiments through the response surface methodology was successfully employed for the optimization of process parameters. Therefore, the rubber seed oil can be viewed as a viable green source for the synthesis of efficient biodiesel production.

Compliance with ethical standards

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All the authors mentioned in the manuscript have agreed for authorship, read and approved the manuscript, and given consent for submission and subsequent publication of the manuscript.

Discloser of conflict of interest

There is no potential conflict of interest in publishing this article.

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