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A multi-variant approach to optimize process parameters for biodiesel extraction from rubber seed oil

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ABSTRACT

Biodiesel is biodegradable, non-toxic and has the capacity for sustainable development, energy conservation and environmental preservation. Apart from yielding high value latex, the rubber plant supply large amount of rubber seed, which are currently underutilized. Extracting biodiesel from rubber seed is a viable option which demands attention for research to consolidate and optimize the process parameters. Design of experiments (DOE) is a powerful statistical approach which is used for optimizing the process parameters through two stage esterification process, relating acid and alkaline as catalyst. Reducing the acid value is the primary objective for process optimization in acid esterification process, whereas, maximizing the monoester yield is the objective for the alkaline-esterification process. Different saturated and unsaturated monoesters present in the biodiesel were quantified using gas chromatograph in order to determine the yield percentage, which ensures the quality of the biodiesel. The fuel was tested for properties such as viscosity, calorific value and carbon residue using standard test procedures and found to be analogous with diesel, which makes it possible to use this alternate fuel in the existing engine without any modification.

1. Introduction

The present world is confronted with twin crises of fossil fuel depletion and environmental degradation. Indiscriminate extraction and lavish consumption of fossil fuels have led to reduction in underground-based carbon resources. Increasing industrialization and motorization has led to a steep rise in the demand of petroleum-based fuels. With the exception of hydroelectric power and nuclear energy the majority of world's energy needs are supplied through petrochemical sources such as coal, oil and natural gas [1,2]. The search for alternative fuels, which promise harmonious correlation with sustainable development, energy conservation, efficiency and environmental preservation, has become highly pronounced in the present context.

The fuels of bio-origin can provide a feasible solution to this worldwide petroleum crisis. Gasoline and diesel-driven automobiles are the major sources of greenhouse gas (GHG) emission [3]. Scientists around the world have explored several alternative energy resources, which have the potential to quench the ever-increasing energy thirst of today's population. Various bio-fuel energy resources such as biomass, biogas, primary alcohols, vegetable oils and biodiesel are largely environment-friendly but they need to be evaluated on case-to-case basis for their advantages, disadvantages and specific applications [4]. Some of these fuels can be used directly while others need to be formulated to bring the relevant properties closer to conventional fuels.

To-date biodiesel research is carried out in more than 28 countries of which Germany and France are the pioneers. The United States department of energy has assessed that up to 50% of the total conventional diesel fuel could be potentially replaced by biodiesel [1]. At present bio-fuels are produced from edible crops like cotton seed, palm nut, linseed, and groundnut and also from non-edible crops such as *Jatropha curcas*, algae, eucalyptus, orange skin, *Eruca* sativa gars, neem, and rubber seed. In India, biodiesel production using edible oil is not much realistic because of the gap in its demand and supply, thereby limiting the use of edible oil in the production of biodiesel [5]. In fact, the price of crude oil is the most dominant factor in the cost of biodiesel fuel, and determines the competitiveness of biodiesel with fossil fuel in the fuel market [6,7]. Hence, search for a low-cost raw material with adequate fuel characteristics for biodiesel production is an important step towards establishing a successful biodiesel industry. Typically, rubber seed oil, which is non-edible, is considered as a prospective feedstock for biodiesel production.

The present study is the continuation and consolidation of the work initiated by researchers [8–11]. The computer software, Design Expert 7.0 is used in this work to design the prominent

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process parameter and there response is statistically analyzed and validated to derive objective inferences. Accordingly, acid and alkaline-esterification process parameters for biodiesel extraction were designed and the optimum process characteristics were found. The relative amount of different monoesters was quantified for the first time using gas chromatograph (GC) to estimate the percentage yield. Spate of research has been done in Jatropha based biodiesel [12–20], however rubber seed based biodiesel extraction is rather sparse and needs strenuous attention as they lend a hand both in economic and ecological aspects of insatiable demand for energy.

2. Experimental procedure

2.1. Potential and extraction of rubber seed oil

India is one among the top ten rubber producing countries in the world and Kerala state is the leading rubber plantation state of India. It originally belongs to Amazon basin (Africa) and later in the 19th century introduced to other countries in the tropical belts of Asia. The Para rubber tree (*Hevea brasiliensis*), belongs to the family Euphrobiaceae and the most economical member of the genus *Heavea*. The tree is deciduous in nature having trifoliate leaves with long stalks (see Fig. 1). Rubber plantation is of great economic value because of its sap-like extract, known as latex collected on the daily basis from its bark which is the primary source of natural rubber. In India they shed their leaves during December–February and refoliation starts quickly followed by copious flowering. Flowers are small but appear in large clusters. The main yield of rubber plantation is latex. However, the rubber tree also produces large volumes of seed, which is underutilized.

In India alone there are around 2 lakhs hectares of rubber plantations. On an average 160 kg of rubber seed is produced per hectare of rubber plantation. The estimated availability of rubber seeds in India is about 30,000 tons per annum, which can yield oil to the tune of about 5000 tons per annum. The oil content in the rubber seed is roughly around 40–60 wt.% [10]. The seeds are three lobed, each holding three seeds, looks like castor seed in appearance but much larger in size (see Fig. 1). Rubber seeds are ellipsoidal in size varying from 25 to 30 mm long, mottled brown in colour, lustrous in look, weighing 2–4 g each. Rubber seeds are collected and kernels are separated by breaking them. These kernels are crushed and oil is extracted by screw pressing and then filtered. The rubber seed cake, which is the leftover after oil extraction is rich in protein and can be used as cattle and poultry feed. The entire process involved for the extraction of biodiesel from rubber seed is shown in a block diagram (Fig. 2).

Fig. 1. Photograph of rubber plantation in Kerala state of India along with rubber seed (inside picture).

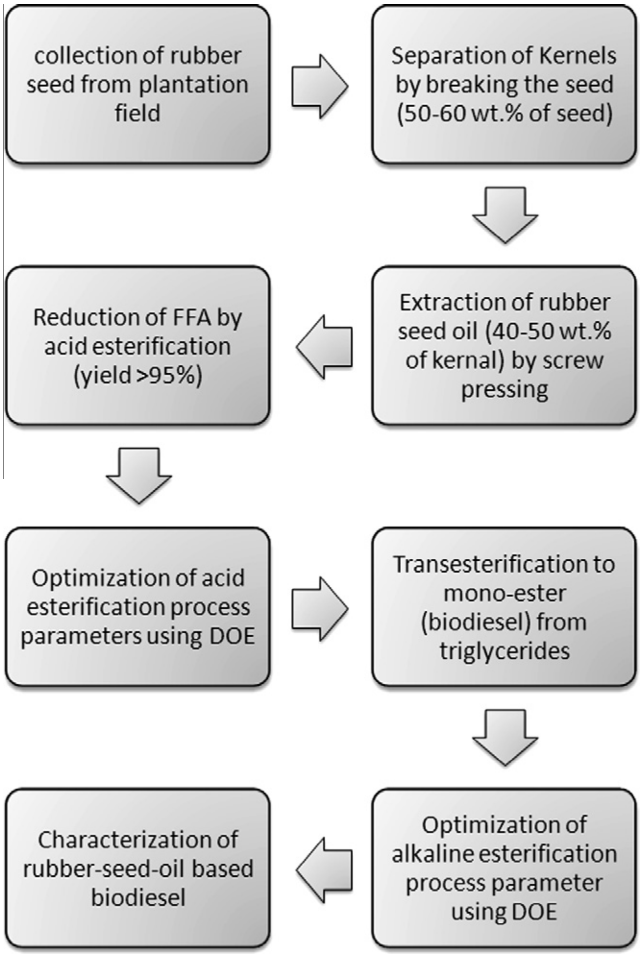


Fig. 2. Block diagram describing the entire process in the extraction of biodiesel from rubber seed.

The rubber seed oil varies in colour from light yellow to brown, depending on the Free Fatty Acids (FFA) content, yellow being on the lower side. Vegetable oils generally have different grades of fatty acids in the form of triglycerides. The fatty acids vary in their hydrocarbon chain length and the number of double bonds. The fatty acid profile and other important properties of rubber seed oil in comparison with other vegetable oil is given in Table 1 [8]. The type and percentage of fatty acids content in vegetable oil depends on the plant species and on the growth conditions of the tree. Rubber seed oil contains 18.9% saturated acids (palmitic and stearic) and 80.5% unsaturated acids (oleic, linolic and linolenic). Saturated fatty acid alkyl esters increase the cloud point, cetane number and improve stability. Rubber seed oil extracted and used for this analysis had an acid value of 35 mg KOH/g, which is equivalent to 17.5% FFA. The presence of high FFA hinders the transesterification process by single stage using a base catalyst due to its preference for saponification thereby forming soap [21]. Hence the amount of FFA must be reduced to its minimum by acid esterification before alkaline esterification.

2.2. Acid esterification to reduce FFA

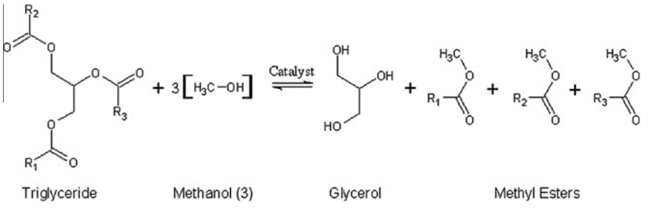
Vegetable oil has the potential to supplement petroleum-based fuels. However their high FFA, thereby its high viscosity deters its usage in internal combustion engine directly. The viscosity of the

Table 1
Properties of rubber seed oil in comparison with other edible oil [8,10].

Property	Rubber seed oil	Sunflower oil	Rapeseed oil	Cotton seed oil	Soybean oil
Fatty acid composition (%)					
(i) Palmitic acid C16:0	10.2	6.8	3.49	11.67	11.75
(ii) Stearic acid C18:0	8.7	3.26	0.85	0.89	3.15
(iii) Oleic acid C18:1	24.6	16.93	64.4	13.27	23.26
(iv) Linoleic acid C18:2	39.6	73.73	22.3	57.51	55.53
(v) Linolenic acid C18:3	16.3	0	8.23	0	6.31
Specific gravity	0.91	0.918	0.914	0.912	0.92
Viscosity at 40 °C (mm^2/s)	66.2	58	39. 5	50	65
Flash point (°C)	198	220	280	210	230
Calorific value (MJ/kg)	37.5	39.5	37.6	39.6	39.6
Acid value (mg KOH/g)	34	0.15	1.14	0.11	0.2

oil is usually reduced by blending, emulsification, pyrolysis, cracking and transesterification [11]. Among these methods, esterification process appears to be more effective and economical and the byproduct during the process, glycerol has commercial value.

Transesterification is the chemical reaction between triglyceride (rubber seed oil) and alcohol to produce monoester (biodiesel) facilitated by an acid or alkaline catalyst. During this process long and branched chain triglyceride is transformed into monoesterand glycerin [22]. Biodiesel does not contain any petroleum products; however it is compatible with conventional diesel. It can blend with diesel or used directly with no major modification in IC engines [23]. The more detailed explanation about the chemical processes involved is explained elsewhere [11,23–25]. The chemical reaction of the esterification process is given below:



Alkaline catalyzed transesterification is much faster and more effective as compared to that of the acid catalyzed transesterification process. However, alkaline catalyzed esterification is not possible before reducing the acid value of the oil below 4 mg KOH/g. Moreover, the higher acid value of the oil will reduce the percentage of yield. Since the raw rubber seed oil extracted has an acid value of 35 mg KOH/g, esterification is carried out first using acid as a catalyst.

In order to reduce the FFA content (i.e. reducing the acid value), the crude rubber seed oil is initially esterified by using acid (H_2SO_4) as a catalyst. Hundred milliliter of raw rubber seed oil is taken for each acid esterification process run. The oil is taken in round bottom flask and heated to the designed temperature. Proper proportion of methanol and sulphuric acid were added with the heated oil and stirred at atmospheric pressure using magnetic stirrer for 30–120 min depending on the experiment. After the stipulated time the process is stopped and the excess alcohol separates at the top surface along with the impurities in the separating funnel. The process parameter for acid esterification and the variation levels were finalized by pilot experiments over wider range in corroboration with literature (Table 2). The oil separates at the bottom and collected for characterization. The optimized acid esterification process was identified where the acid values of the raw rubber seed oil was below 3.8 mg KOH/g. The average yield for this process is above 95% by weight and hence this was not considered as the major criterion for the optimization of first stage.

Table 2
Process parameter levels for the optimization of acid esterification process.

Process parameter	Low (−)	High (+)	Centre	Axial (−α)	Axial (+α)
Oil/methanol (v/v)	2	4	3	2.5	3.5
H_2SO_4 (% v/v)	1.00	2.00	1.50	1.25	1.75
Temperature (°C)	30	60	45	37.5	52.5
Time (min)	30	120	75	52.5	97.5

2.3. Alkaline esterification to produce biodiesel

The objective of the first stage, i.e. acid esterification process, is to reduce the acid value of the raw rubber seed oil from 35 mg KOH/g to less than 4 mg KOH/g. Accordingly, sufficient quantity of oil having FFA less than 2% (3.8 mg KOH/g) were extracted through the established optimum process parameters. However, the percentage of yield during the alkaline-esterification process in which the triglycerides are converted to monoester (biodiesel) is considered as the major objective in the second stage.

Alkaline catalyzed esterification process uses the similar experimental setup used for acid esterification. By conducting pilot experiments and through literature the experimental parameters were carefully selected and the range for conducting experiments was finalized. The process parameter and their respective range for the conduct of experiment are shown in Table 3. For every experimental run in the second stage, 20 ml of the oil extracted from the first stage is taken in a flask and heated to designed temperature. The required amount of methanol and NaOH are then added into the flask and stirred using magnetic stirrer for definite period as per the design. After the stipulated time, the reaction is stopped and the products are allowed to separate. Because of its low specific gravity, methyl ester (yellow in colour, known as biodiesel) separates at the top surface, whereas glycerol settles down at the bottom. The biodiesel is collected and quantified for calculating the percentage yield for every run. The extracted biodiesel was analyzed for purity and in that way the relative amount of different saturated and unsaturated monoesters were quantified using GC 2003A gas chromatograph, CIC make. The process parameters were then optimized for higher yield of biodiesel based on gas chromatograph results.

Table 3
Process parameter levels for the optimization of alkaline-esterification process.

Process parameter	Low (−)	High (+)	Centre	Axial (−α)	Axial (+α)
Methanol/oil (v/v)	0.2	0.5	0.35	0.275	0.425
NaOH (% w/v)	0.5	1.5	1.0	0.75	1.25
Temperature (°C)	30	60	45	37.5	52.5
Time (min)	30	120	75	52.5	97.5

2.4. Characterization of fuel

The collected methyl ester (biodiesel) is then purified by warm water washing, where entrained glycerol, catalyst, and excess methanol were removed. Usually three or four times the water wash is done with a time interval of 1 h between each wash. While water washing care should be taken to avoid vigorous shaking as it may tend to emulsify. Drying is done by using silica gel to ascertain that no moisture is present in the fuel. The purified biodiesel is then quantified for fuel properties.

Reduction of acid number is the chief objective of the acid esterification process. One gram of oil after initial esterification was titrated against standard potassium hydroxide solution using phenolphthalein as indicator. The acid number of the oil is quantified as mg KOH/g, (which is also a measure of FFA) using the titrated value.

The density of the fuel is determined by weighing the known volume of the fuel. Specific gravity is the ratio of the oil to the density of water. The percentage yield of biodiesel is calculated on volume basis. Viscosity is the most important property for using biodiesel in IC engines because high viscosity and high molecular weight cause poor fuel atomization and low volatility, leading to incomplete combustion in IC engine. The higher viscosity provides greater opportunity for the fuel to cause such problems [25]. The viscosity of the oil is measured using BROOKFIELD LV-DV-II + Pro viscometer, Middleboro, USA at a constant temperature of 40 °C. The flash point and fire point of biodiesel is determined by using the Pensky Marteins closed cup apparatus. Flash point of the biodiesel gets lowered after esterification and the cetane number gets improved. The calorific value of biodiesel is measured with Parr-6772 calorimetric thermometer and found to be very close to that of the diesel. The closeness of biodiesel properties with diesel made it possible for the diesel engine to perform satisfactorily with the existing engine. TANAKA ACR-M3 micro carbon residue tester is used in the determination of the amount of carbon residue which forms after evaporation.

3. Design of experiment – an overview

The design of experiment (DOE) is a test or a series of tests conducted in which designed changes are made in the process parameters to observe and identify the reasons for the observed changes in the output (response). The experimentation procedure extensively adopted in practice is the one-factor-at-a-time approach. In this method, each factor is varied over its range while other factors are held at the baseline level. The major disadvantage of this strategy apart from requiring more number of experiments is that it fails to consider any possible interaction between factors. That is, the effect on the response (output) at different levels of other factors with respect to the one factor that is varied [26].

The analysis of variance (ANOVA) is a collection of statistical models, and their associated procedures, in which the observed variance is partitioned into components due to different explanatory variables. The fundamental technique is, partitioning of the total sum of squares into components related to the effects used in the model.

4. Result and discussion

4.1. Optimization of acid esterification process parameter

Poor choice of factors and ranges results in unsatisfactory solution – no matter how good the experimental plan and ingenuity in data analysis. Accordingly, central composite design is employed in the first stage for acid esterification process to evaluate the relevance of these process parameters on the acid value. The planned experimental parameter for conducting experiments as per the procedure mentioned in Section 2.2 and their acid value (response) is given in Table 4. An analysis of variance (ANOVA) is then carried out for the response (acid value) in order to test the model signification and suitability. The ANOVA table for the same is given in Table 5.

The model *p*-value of 0.0099 indicates that the model terms are significant. In this model, factor A, which is the volume ratio of oil to methanol is the most significant model term. However the other parameters have less influence on the acid value of the oil extracted from raw rubber seed oil. The "Pred *R*-Squared" value of 0.1715 is in reasonable agreement with the "Adj *R*-Squared" value of 0.3648. The "Adeq Precision" measures the signal to noise ratio and ratio greater than 4 is desirable, whereas the model ratio is 6.746 indicates an adequate signal. With these statistical validation the model is used to navigate the design space to get inference from the graph.

The perturbation plot compares the effect of all the factors about a particular point in the design space. The response (acid value) is plotted by changing only one factor (process variable)

Table 4
Experimental design with process data and the response for acid esterification process.

Run	Oil/methanol (v/v)	H_2SO_4 (% v/v)	Temperature (°C)	Time (min)	Acid value (mg KOH/g)
1	3.0	1.50	45.0	75.0	21.762
2	4.0	1.50	45.0	75.0	24.324
3	2.5	1.75	37.5	97.5	13.247
4	2.5	1.25	52.5	97.5	10.694
5	3.5	1.75	52.5	97.5	15.410
6	2.5	1.25	37.5	52.5	14.012
7	3.5	1.25	52.5	52.5	20.419
8	3.0	1.50	45.0	30.0	15.499
9	3.5	1.25	37.5	52.5	33.076
10	3.0	2.00	45.0	75.0	18.719
11	3.0	1.50	45.0	75.0	21.633
12	3.0	1.50	45.0	75.0	20.453
13	2.5	1.75	52.5	52.5	4.520
14	3.5	1.25	52.5	97.5	32.829
15	2.0	1.50	45.0	75.0	3.823
16	3.0	1.50	30.0	75.0	13.062
17	3.0	1.50	45.0	75.0	21.034
18	3.0	1.50	60.0	75.0	7.707
19	2.5	1.25	37.5	97.5	21.322
20	3.0	1.50	45.0	120.0	11.472
21	3.0	1.50	45.0	75.0	20.987
22	3.5	1.75	37.5	52.5	17.442
23	3.0	1.50	45.0	75.0	21.582
24	3.5	1.25	37.5	97.5	16.302
25	3.5	1.75	37.5	97.5	20.319
26	3.5	1.75	52.5	52.5	11.247
27	2.5	1.75	37.5	52.5	10.875
28	2.5	1.75	52.5	97.5	22.083
29	3.0	1.00	45.0	75.0	17.193
30	2.5	1.25	52.5	52.5	9.328

Table 5
ANOVA results for acid value model by acid esterification method.

Source	Sum of squares	*df*	Mean square	*F*-value	*p*-Value prob. > *F*
Model	9.90	4	2.47	4.45	0.0099
A-Oil/methanol	7.60	1	7.60	13.65	0.0014
B-H_2SO_4	0.90	1	0.90	1.61	0.2193
C-Temperature	0.95	1	0.95	1.70	0.2067
D-Time	0.46	1	0.46	0.82	0.3765
Residual	11.13	20	0.56		
Total	21.03	24			

over its range while holding the other factors constant. Fig. 3 is the perturbation chart for the acid value of the oil after acid esterification process. A steep slope or curvature in a factor shows that the response is more sensitive to that factor. The perturbation chart strengthen the claim that the factor A, oil/methanol ratio is the most influencing factor in decreasing the acid value, by its steep positive slope. Obviously, since alcohol is the one which reacts with ester, called triglycerides in the presence of a catalyst (either acid or alkali) it has more influence in the reaction product. The three-dimensional response plot of acid value in relation to oil/methanol ratio and volume percentage of H_2SO_4, where the other two process parameters are kept at the center point is shown in Fig. 4. The constant response contour lines indicate that lower acid values are achieved by decreasing the oil/methanol ratio and at a higher value of sulphuric acid addition.

Acid value reduction is the primary objective in the first stage. The acid value (response) after the first stage depends on four process variables (factors) of the acid esterification process. Moreover, factors may influence each other and if they are optimized separately, the overall result may be suboptimal. Therefore, multivariant approach, called response surface design is adapted, where optimized setting of process parameters were obtained statistically by design expert software. With the optimized process parameters enough quantity of oil was prepared for the second stage, called alkaline-esterification process. The average acid value of the extracted oil with optimum process is around 3.8 mg KOH/g. The optimum values obtained are in corroboration with the results published by other researchers [8,9].

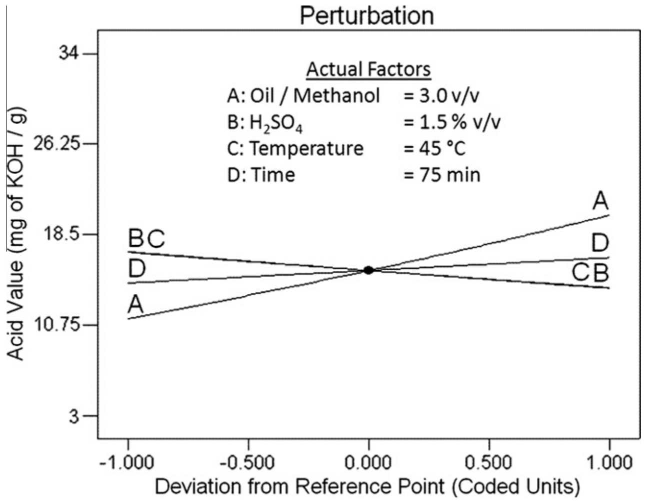


Fig. 3. Perturbation chart of acid esterification process for acid value model.

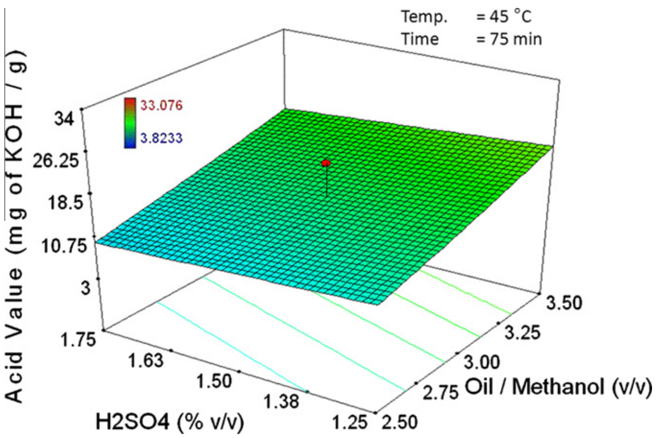


Fig. 4. Response surface model in graphical form for the acid value.

4.2. Optimization of alkaline-esterification process parameter

It was possible to produce monoesters (biodiesel) by alkaline catalyzed esterification process only after reducing the FFA content of the unrefined oil by acid esterification process to less than 2%. The objective of the second step is to maximize the yield of monoester. The percentage yield was calculated by quantifying the different fatty acid composition present in the ester by gas chromatography, which is the most accurate method. The planned experimental process parameter for conducting experiments as per the procedure mentioned in Section 2.3 and their corresponding yield percentage of biodiesel (response) based on weight percentage as well as through gas chromatograph study is given in Table 6.

An analysis of variance (ANOVA) is then carried out for the response (percentage of monoester yield) based on the gas chromatograph to test the model signification and suitability. The ANOVA table for the same is given in Table 7. The response surface quadratic model for percentage of yield has *F*-value of 12.12 and the corresponding *p*-value of 0.0001 indicates that the model is significant with only 0.01% chance that a 'Model *F*-value" could have occurred due to noise. In this model, the factor A, methanol/oil volume ratio is the major deciding factor for the monoester yield, where maximizing the yield is the objective. This is confirmed by the very high *F*-value (127.14) for that factor. The other process parameters such as the amount of alkaline catalyst, sodium hydroxide also has significant influence on the yield followed by the duration of the process. However, the yield has not varied much for the selected range of temperature in experimentation. There is a significant interactive effect between the two process variables (i.e. *AB*), such as methanol/oil volume ratio and the amount of sodium hydroxide as seen by the *p*-value of 0.0195, which is lower than 0.05.

In addition to the basic analysis of variance, the program displays some additional useful information indicating the precision of the model. The quantity "*R*-Squared", which is loosely interpreted as the proportion of the variability in the data is 0.9289. The "adjusted" R^2 is the variation of the ordinary R^2 statistics that reflects the number of factors in the model and will get adjusted for the "size" of the model is 0.8522. Similarly other diagnostic tools are used to check the validity and the adequacy of the model. The biodiesel yield model by the surface response methodology is shown in Fig. 5 and the corresponding perturbation chart in Fig. 6.

The negative non-linear steep curvature of methanol/oil volume ratio with the percentage of yield is depicted in the perturbation chart (see Fig. 6). Once again, the factor A, which is the ratio of methanol to oil, is the major significant process parameter in comparison with the other three process parameter. The plateau shape of the curves for other process parameters such as the amount of NaOH, time and temperature have very less significant influence as shown in Fig. 6. The surface response model for the yield in comparison with the amount of methanol/oil ratio and sodium hydroxide is shown in Fig. 5 where the other two process parameter such as time and temperature are kept at middle level. The maximum yield is obtained when the methanol/oil ratio is kept at low level of 0.2% v/v and the amount of sodium hydroxide is at minimum level of addition. The interaction between methanol/oil ratio and amount of NaOH addition is significant, which is taken care by the response surface model. The equations of the response surface model for the percentage of yield (% summation of all monoesters) with coded factors (Eq. (1)) and with actual factors (Eq. (2)) by accounting only the major influencing terms are given below:

Table 6
Experimental design with process data and the response for alkaline-esterification process model.

Run	Methanol/oil (v/v)	NaOH (% w/v)	Time (min)	Temperature (°C)	Percentage of monoesters in biodiesel (by GC analysis)						Yield (wt.%)
					Oleic	Linoleic	Linolenic	Palmitic	Stearic	Total	
1	0.4	1.25	97.5	37.5	3.5	4.9	1.4	0.8	0.7	11.3	80.9
2	0.4	1.00	120.0	45.0	15.1	17.3	3.8	2.9	2.5	41.6	86.1
3	0.3	0.75	97.5	52.5	23.8	25.5	5.6	4.8	3.9	63.6	91.6
4	0.4	0.75	97.5	52.5	6.4	7.8	2	1.2	1	18.4	82.2
5	0.3	1.25	97.5	37.5	12.1	13.5	3.4	2.5	2.2	33.7	84.8
6	0.4	1.00	75.0	45.0	20.5	21.75	4.5	3.6	3.4	53.7	87.8
7	0.4	0.75	52.5	37.5	6.1	7.3	1.9	1.1	1	17.4	82.3
8	0.4	1.00	75.0	45.0	20.8	21.9	4.61	3.71	3.14	54.2	89.4
9	0.3	0.75	52.5	37.5	23.3	24.1	5.2	4.3	3.6	60.5	90.4
10	0.3	1.25	97.5	52.5	20.7	22.1	4.6	3.7	3.1	54.2	88
11	0.4	1.00	75.0	45.0	20.8	22.1	4.7	3.8	3.9	55.3	88.2
12	0.4	0.75	97.5	37.5	4.3	5.5	1.5	1	0.9	13.2	81.5
13	0.4	1.00	75.0	45.0	20.9	21.9	4.6	3.7	3.05	54.2	88.8
14	0.4	1.00	75.0	45.0	20.3	21.65	4.45	3.55	3	52.9	87.6
15	0.4	1.00	75.0	30.0	14.2	16.5	3.7	2.8	2.4	39.6	85.4
16	0.3	1.25	52.5	52.5	14	16.5	3.6	2.8	2.4	39.3	85.1
17	0.4	1.25	52.5	52.5	5.6	6.8	1.8	1.1	1	16.3	81.9
18	0.2	1.00	75.0	45.0	30.7	32.6	9.7	7.5	6.4	86.9	97.1
19	0.3	0.75	97.5	37.5	21.5	22.4	4.8	3.9	3.2	55.8	89
20	0.4	1.00	75.0	60.0	16.6	18.5	4	3.1	2.7	44.9	86.3
21	0.4	1.25	52.5	37.5	15	17.3	3.8	2.9	2.4	41.4	86
22	0.4	1.00	75.0	45.0	20.8	21.8	4.6	3.7	3.05	53.9	87.7
23	0.3	1.25	52.5	37.5	20.1	21.4	4.3	3.4	2.9	52.1	87.5
24	0.4	1.25	97.5	52.5	3.8	5.3	1.5	1	0.8	12.4	81.1
25	0.4	0.50	75.0	45.0	21.7	22.4	4.9	4	3.2	56.2	91.3
26	0.5	1.00	75.0	45.0	3.1	4.1	1	0.6	0.3	9.1	80.2
27	0.4	1.50	75.0	45.0	9.3	11.3	2.6	1.9	1.7	26.8	83.1
28	0.4	0.75	52.5	52.5	6.7	8	2.1	1.2	1	19.0	82.6
29	0.3	0.75	52.5	52.5	26	27.7	6.2	5.1	4.2	69.2	92.5
30	0.4	1.00	30.0	45.0	19.9	21.2	4.3	3.4	2.9	51.7	87.2

Table 7
ANOVA results for ester yield model by alkali esterification method.

Source	Sum of squares	*df*	Mean square	*F*-value	*p*-value prob. > *F*
Model	10529.92	14	752.14	12.12	<0.0001
A – Methanol/oil	7888.00	1	7888.00	127.14	<0.0001
B – NaOH	561.63	1	561.63	9.05	0.0101
C – Time	226.32	1	226.32	3.65	0.0784
D – Temperature	11.62	1	11.62	0.19	0.6723
AB	439.95	1	439.5	7.09	0.0195
Residual	806.52	13	62.04		
Total	11336.43	27			

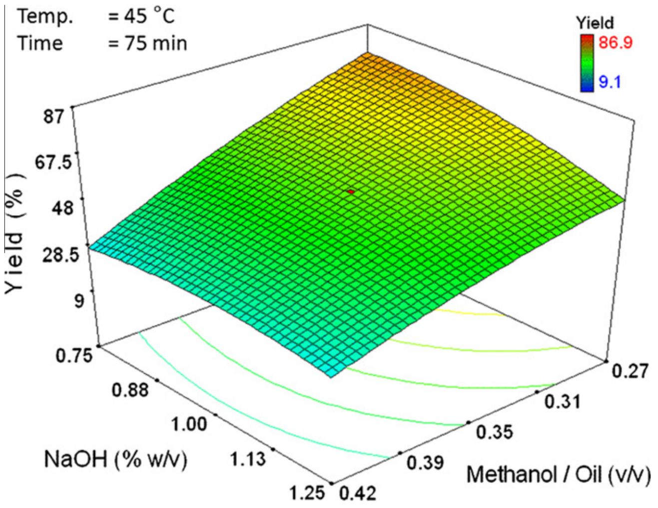


Fig. 5. Response surface model in graphical form for biodiesel yield by alkaline esterification method.

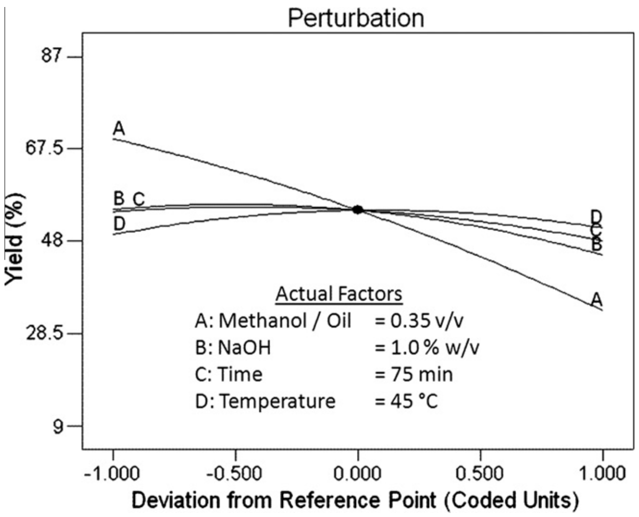


Fig. 6. Perturbation chart of alkaline-esterification process for percentage biodiesel yield model.

Table 8
The optimum predicted parameters for maximum ester yield by alkali esterification method using design of experiment methodology.

Parameter	Optimum value
Methanol/oil	0.28 v/v
NaOH	0.75% w/v
Temperature	51.23 °C
Time	82.52 min

$$\text{Yield} = 54.50 - 18.13 \times A - 4.84 \times B - 3.07 \times C + 0.70 \times D + 5.24 \times AB \qquad (1)$$

Table 9
Properties of rubber seed oil biodiesel in comparison with standard biodiesel and diesel [8,10].

Property	Test procedure	Biodiesel – Standard ASTM D6751-02	Rubber seed oil – biodiesel	Diesel
Specific gravity at 30 °C	ASTM D4052	0.87–0.90	0.837	0.839
Kinematic viscosity at 40 °C (mm^2/s)	ASTM D445	1.9–6.0	3.12	3.18
Heating value (MJ/kg)	ASTM D240	–	38.20	42
Flash point (°C)	ASTM D93	130	128	68
Cloud point (°C)	ASTM D2500	−3 to 12	5	17
Pour point (°C)	ASTM D97	−1.5 to 10	−7	−20
Carbon residue (%)	–	<0.3	0.14	0.17

$$\begin{aligned}\text{Yield} = {} & -168.06 + 125.48 \times \text{methanol/oil} + 108.1 \times \text{NaOH} \\ & + 0.369 \times \text{time} + 8.34 \times \text{temperature} + 279.67 \\ & \times \text{methanol/oil} \times \text{NaOH} \end{aligned} \tag{2}$$

This empirical model can be used to predict the percentage of yield for the given process parameter. Considering the probability of error in the experiment into account the optimum process parameters for maximum biodiesel yield in the second stage, called alkaline esterification is tabulated in Table 8. The optimum values obtained are showing similar trends published by other researchers [8,9]. However, the optimum value of NaOH is slightly on the higher side, whereas the methanol/oil ratio is slightly on the lower side. These results are significant considering the fact that the interactive effect of the process parameters are taken into account to arrive at this optimum value.

4.3. Fuel properties

The properties of the extracted rubber seed oil biodiesel was determined using the standard test procedure described in Section 2.4. The conversion of triglycerides (raw rubber seed oil) into methyl ester (biodiesel) through two stage esterification process reduces the acid value from around 35 mg KOH/g to less than 3 mg KOH/g. The viscosity of the oil was reduced from 37.06 mm^2/s to 3.12 mm^2/s, which is similar to that of diesel. The comparison of some fuel properties with that of standard biodiesel and diesel is shown in Table 9. Identical viscosity of biodiesel is the added advantage of this fuel, which demands no hardware modifications for using it in the existing diesel engines. The heating value is the measure of energy content of the fuel and the present result shows that the biodiesel has a value around 91% of that of diesel. The presence of oxygen in the fuel enhances combustion process while using in internal combustion engine. The cloud point and pour point temperature of biodiesel are high enough for low temperature applications. The tested properties of rubber seed based biodiesel are comparable with that of the standard biodiesel.

5. Conclusion

The discarded rubber seed from the hefty rubber plantation of southern India is considered as the potential source for extracting biodiesel. Since extracted raw rubber seed oil cannot be used for edible purposes, utilizing this waste oil as an alternate fuel will lend a hand in conserving petroleum reserves. Two stage esterification processes is needed to reduce the high FFA content of the raw rubber seed oil. The major influencing process parameter and their ranges were identified to optimize the acid and alkaline catalyzed esterification process. Design of experiments is employed in this work, since it takes into account the interactive effects between the input parameters. It is found that oil/methanol ratio is the major factor in deciding the acid value of the first stage esterification process. In the same way, the methanol/oil ratio has the major influence for maximizing the monoester yield in the second stage. It is found that the biodiesel yield is optimum when methanol/oil ratio is around 0.2% v/v and sodium hydroxide is kept at a minimum level of 0.5% w/v. However, for the first time process optimization was done based on the percentage yield calculated by the use of gas chromatograph. The yield varied from 9.1% to 86.9% with GC analysis, whereas the variation of yield by weight percentage is from 80.2% to 97.1% which makes the process optimization more appropriate by means of GC. The biodiesel obtained constitutes monoester, a volatile substance which increases the suitability of substituting it for diesel in automobiles. Further testing of its usage and performance study on IC engine is needed to consolidate these claims.

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