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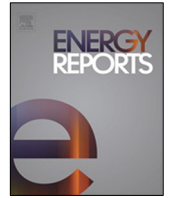
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Research paper

Optimization of ethyl ester production from arachis hypogaea oil

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HIGHLIGHTS

- Biodiesel from Arachis Hypogaea oil with biodegradable ethanol is produced and characterized.
- Esterification of oil with ethanol and concentrated sulphuric acid is carried out to reduce the FFA value from 4.85% to 0.86%.
- Optimization of four major influencing transesterification process parameters of Arachis Hypogaea oil with biodegradable ethanol.
- Physicochemical properties of the new ethyl ester biodiesel meeting the requirements of EN 14214 standards for biodiesel.

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ABSTRACT

Increased rate of use of fossil fuels have greatly polluted the earth through harmful by-products. Biodiesel is an attractive substitute to fossil fuel in compression ignition engine applications. In this research work, vegetable oil namely Arachis Hypogaea Oil (AHO) is used along with ethanol for biodiesel production. Since the amount of free fatty acid of AHO is 4.85%, two step transesterification process was adopted for biodiesel production. In the first step, 6:1 ethanol to oil ratio, 1% w/w concentrated H_2SO_4 with 60 ° C process temperature and one hour process time were followed for esterification and the FFA value was found to be 0.86% after esterification. As ethanol is very rarely used for biodiesel production, optimization of transesterification process has been carried out using orthogonal array based experimental design. The four most influencing parameters, molar ratio of ethanol to oil, catalyst amount, process temperature and process time were considered for optimization. Ethanol to oil molar ratio of 9:1, 1% (w/w) concentration of catalyst, 90 min of process time and 70°C temperature of reaction were found to be the optimal values of parameters for maximizing the yield of Arachis Hypogaea Ethyl Ester (AHEE) and the corresponding maximum yield was 95.49%. The biodiesel produced with optimum values of transesterification process parameters has been characterized and found to meet the biodiesel requirements of EN 14214 standards.

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1. Introduction

Energy is the primary requirement in several sectors such as power, transport, industrial, commercial and residential. The development of any country depends upon the availability of various natural energy resources. Per capita energy consumption of any nation is the measure of the development of the nation (Hariram et al., 2018; Sathish Kumar et al., 2015). The rate of consumption of fossil fuel in transport sector is increased many folds in recent two decades. Due to this two major illness are encountered such as fossil resource depletion and increase in amount of greenhouse gases in the earth. Human health illness, reduced life span of animals, increased acidity level of rain water, raise in the atmospheric temperature of the globe and diminution

of ozone layers are identified as major problems of greenhouse gases (Antony Miraculas et al., 2018; Karmakar et al., 2018; Kudre et al., 2017).

Biofuels are the most attractive alternative for fossil fuel to address the above mentioned twin problem. The expected contributions from the biofuel are to reduce the dependency of fossil fuels, sustainable usage and less harmfulness to the earth. Identification of renewable, biodegradable and sustainable resource for producing substitute to the fossil based oils is a key challenge among researchers. Sustainable resources such as biodiesel (synthesized from vegetable oils and animal fats), biogas (produced from agricultural and domestic wastes) and alcohols (produced from bio products) are some of the potential substitutes for the petroleum fuels. Out of which, biodiesel is best suitable substitute for diesel in diesel engine applications (Kudre et al., 2017; Hoseini et al., 2019; Venu and Madhavan, 2017; Yilmaz and Sanchez, 2012).

Many researchers have produced biodiesel from many resources and optimized the yield. From the extensive literature

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review, it was found that predominantly biodiesels were synthesized from vegetable oils of edible and nonedible nature and some animal fats (Hariram et al., 2018; Sathish Kumar et al., 2015; Antony Miraculas et al., 2018; Karmakar et al., 2018; Kudre et al., 2017; Hoseini et al., 2019; Nautiyal et al., 2014; Gupta et al., 2016; Adewale et al., 2017; Karabas, 2013; Wu and Leung, 2011; Kafulku and Mbarawa, 2010; Melvin Jose et al., 2011; Kafuku and Mbarawa, 2010; Rashid et al., 2008; Nakpong and Wootthikanokkhan, 2010; Sánchez et al., 2013; Schinas et al., 2009; Eevera et al., 2009). Out of the above resources edible vegetable oils are having many advantages such as available in plenty, easily cultivatable in short period, less viscosity in comparison with nonedible vegetable oils, less content of free fatty acid (FFA) and desirable quality to convert as biodiesel. The edible vegetable oils as biodiesel resources are commonly known as first generation biodiesel resources, to name a few, sunflower oil, peanut oil, coconut oil, rice bran oil, gingelly oil, mahua oil, and mustard oil (Yilmaz and Sanchez, 2012; Nautiyal et al., 2014; Gupta et al., 2016; Adewale et al., 2017; Sathik Basha and Anand, 2014; Mojifur et al., 2014; Wang et al., 2018).

At the same time nonedible vegetable oils such as jatropa, pongamia, rubber seed oil, soap seed oil, cotton seed oil, simarouba oil, camelina oil, jojoba oil, polanga oil, calophyllum inophyllum oil, poon oil, Manilkara zapota seed oil, custard apple seed oil, wild apricot seed oil, neem oil, eucalyptus oil, etc. are also attracted the attention equally in production of biodiesel in spite of their few disadvantages such as non-availability in bulk quantity, high free fatty acid and high viscosity. They are commonly known as second generation biodiesel resources (Khond and Kriplani, 2016; Chen et al., 2018; Gogoi and Baruah, 2010; Karabas, 2013; Wu and Leung, 2011; Kafulku and Mbarawa, 2010).

Conversion of triglycerides in to stable mono alkyl esters through transesterification is the best suitable method to synthesize biodiesel from both edible and non-edible vegetable oils because of high yield, easy chemical kinetics, economical, fast process etc. Transesterification can be either single step, two step or sometimes three step with respect to the amount of free fatty acid of the vegetable oils. In single step, base catalyst such as KOH or NaOH will be commonly used, when the FFA value is less than 2%. If the FFA value is greater than 2% then two step transesterification process will be used, in that esterification with acid catalyst will be performed first to reduce the FFA value less than 2% and then base catalyst transesterification will be carried out (Melvin Jose et al., 2011; Kafuku and Mbarawa, 2010; Meng et al., 2009; Hanh et al., 2009; Saydut et al., 2008).

Methanol is the extensively used alcohol for biodiesel production because of its high reactivity with fatty acids due to simple chemical structure. At the other hand it is toxic in nature to human health and it is chemically synthesized not biologically derived. Alcohol to oil molar ratio, amount of catalyst, process time, process temperature, moisture content of raw materials, quality of ingredients, stirring speed, alcohol type, and catalyst type are some of the transesterification process parameters affecting the yield of the biodiesel. Out of which alcohol to oil molar ratio, amount of catalyst, process temperature and process timing are identified as most influencing process parameters (Morshed et al., 2011; Rashid et al., 2008; Nakpong and Wootthikanokkhan, 2010; Sánchez et al., 2013; Schinas et al., 2009; Eevera et al., 2009).

Arachis Hypogaea well known as groundnut and peanut is one of the nature gifted food stock. It contains 44%–50% oil, 22%–30% protein and good amount of minerals and vitamins. It is consumed in many forms such as oil, raw peanut, fried or roasted peanut, or as peanut butter. According to the Food and Agricultural Organisation of United Nations, the world total peanut production in the year 2016 was 44 million tonnes. China

leads with 38% contribution to the global total and followed by India with 16% contribution. The average annual peanut production in India is approximately 7 million tonnes. 80% of the peanut produced in India is utilized for oil extraction. The oil serves many purposes such as cooking oil, medicine, soap production, cosmetic production. It is best suitable for biodiesel production because of its high oleic acid content.

From the extensive review of literature, it was found that very few attempts were made to use ethanol for biodiesel production. Even though ethanol is less reactive than methanol with fatty acids, it has very good merits such as less toxic to the nature, biodegradable, produced from bio based products. Hence in this research work easily cultivatable, non-tree born edible oil resource Arachis Hypogaea oil was used to produce biodiesel with ethanol and optimization of highly influencing transesterification process parameters was carried out and reported.

2. Materials and method

2.1. Materials and experimental setup

Seeds of Arachis Hypogaea were obtained from the local market, 85% pure laboratory grade potassium hydroxide in pellet form and ethanol with 99% purity were (procured from Pentagon chemicals manufacturer, Chennai, India) used in this experimental study. The experimental setup used for esterification process consists of a three neck borosilicate glass spherical reactor of 5 litre capacity, speed controllable mechanical stirrer and temperature controllable heating mantle. A water cooled reflexive condenser is used for avoid the evaporation of ethanol during the process. For conducting optimization of transesterification processes, a 500 ml spherical borosilicate glass reactor is used in the same experimental setup instead of 5 litre reactor. In order to monitor the fixed process temperature, a thermometer is fixed in one of the necks in reactor. Fig. 1 shows the experimental setup used for two-stage transesterification process of Arachis Hypogaea oil.

2.2. Extraction of Arachis Hypogaea oil and its characterization

Well matured and dried Arachis Hypogaea seeds were collected from RKM seed supplier located in Chennai India was further dried in the sunlight for three days in order to remove moisture. Dried seeds were crushed in a screw expeller and neat raw oil was collected. The content of oil present was found to be approximately 40%–50% of the mass of the Hypogaea seeds. After extraction, oil was filtered using fine mesh filter and characterized for various physicochemical properties. Pour point and cloud point was measured as per ASTM D97 and ASTM D2500 standard respectively. Flash point was estimated using ABEL closed cup flash point apparatus. Kinematic viscosity was found out using redwood viscometer at 40 °C as per ASTM D445 standard. Density at 15 °C was measured using Rudolph apparatus. Heating value was calculated using bomb calorimeter. The acid value of Arachis Hypogaea seed oil was calculated by titration against potassium hydroxide solution. As per ASTM standard iodine and cetane number was determined.

Fatty acid compositions were measured using a Perkin-Elmer Clarus 500 XL Gas Chromatograph equipped with capillary column of dimension 30 m x 0.25 mm x 1 μm. The initial temperature of the oven was set to 100 °C for 10 min, later increased to 200 °C at the rate of 10 °C/min and then held for 10 min. The injector, source and the transfer line temperatures were 220 °C, 200 °C and 200 °C respectively. Helium was used as carrier gas at a flow rate of 1 ml/min. The equipment has a mass spectrometer of Turbo EI Ionization source of 70 eV electron

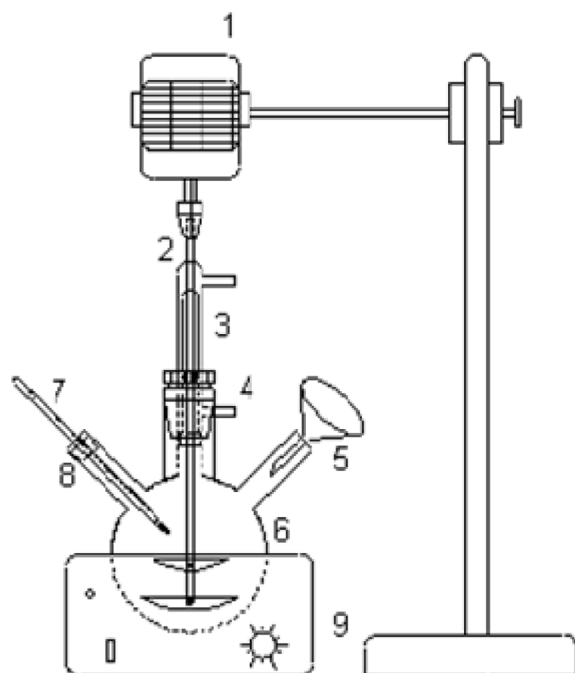


Fig. 1. Experimental setup for the batch type transesterification process.

Part no	Part name
1	Stirrer motor with chuck and stand
2	Glass rod with Teflon stirrer
3	Condenser
4	Stuffing box
5	Funnel
6	Four neck round bottom flask
7	Thermometer
8	Stopper box
9	Heating mantle

energy and ion energy of 1.5 V. The samples were injected in split mode as 10:1. Mass spectral scan range was set at 45–450 (m/z). FAME identification was carried out using NIST Ver.2.1 MS data library (Sathish Kumar and Sureshkumar, 2016).

2.3. *Arachis Hypogaea* biodiesel preparation procedure

The FFA value of *Arachis Hypogaea* oil was found to be 4.85%, so two step transesterification process was adapted in this research work. Based on the trial experiments conducted, 6:1 molar ratio of ethanol to oil, 1% (w/w) concentrated sulphuric acid, 50 °C process temperature, stirring speed of 600 rpm and two hours of process time were adopted for the first step esterification process. In this step 3000 (±0.1) g of neat oil was taken in reactor and heated up to 60 °C, meanwhile the 30 g of concentrated sulphuric acid was mixed with ethanol and prepared ethanol acid solution was poured in to the reactor. After two hours of process time was over the sample of the product was taken and tested for FFA value and found to be 0.86%. The product was poured into settling flask and kept undisturbed for 24 h for the settlement. The unreacted acid and other contaminations were removed by washing the products with deionized water and dried in an incubator.

100 (±0.1) g of esterified oil was taken in a small reactor for transesterification process and heated up to required temperature in heating mantle. The ethoxide solution was made by completely dissolving the carefully weighed potassium hydroxide pellets in required amount of ethanol. The prepared solution was slowly transferred into the esterified oil after reaching the required temperature. The end of the pouring time was considered as start of process time. The amount of potassium hydroxide (0.5–1.5 wt%), amount of ethanol (3:1 to 9:1 molar ratio), process temperature (50 to 70 °C) and process time (1 to 2 h) will vary depending upon the various experimental conditions designed for optimization study. Once the transesterification process was finished, the products were transferred to the 500 ml conical settling beaker and settled for 24 h. The produced biodiesel was separated from heavy glycerol settlement and washed with deionized water at 40 °C in order to nullify the effects of unreacted ethanol and catalyst and remove the impurities. The step by step biodiesel

production process is shown in Fig. 2. The yield of biodiesel obtained was calculated using Eq. (1).

$$\% \text{ Yield of biodiesel} = \frac{\text{mass of fatty acid ethyl ester obtained}}{\text{mass of oil used}} \times 100 \quad (1)$$

The mass of the clean biodiesel was measured using a well calibrated weighing machine of 0.01 g accuracy and the ratio between the mass of biodiesel and mass of raw oil taken for process (100 g) was calculated in percentage for each experimental trial.

2.4. Experimental matrix design using L_9 orthogonal array

The key feature of the orthogonal array based experimental design is the capacity of estimate several influencing input parameters in a minimum set of experiments. This method is much effective and most efficient because of more information can be obtained from a fewer number of trails. The step by step procedure followed in this method is described below.

- Step 1: Set the objective and determine the dependent variable. In the present study maximizing the ethyl ester yield from *Arachis Hypogaea* oil is the objective and the dependent variable is percentage yield of biodiesel.
- Step 2: Identification key parameters and their levels. In this present study the chosen parameters and their levels are given in Table 1.
- Step 3: Selection of suitable orthogonal array and identification of minimum number of experiments to be conducted based on the number of parameters and their levels. In the current research work the number of parameters chosen were four ($P = 4$) and their varying levels were three ($L = 3$), hence L_9 orthogonal array was selected using OA selector and given in Table 2. The minimum number of experiments to be tested was calculated as 9 using the relation $N = P(L-1) + 1$.

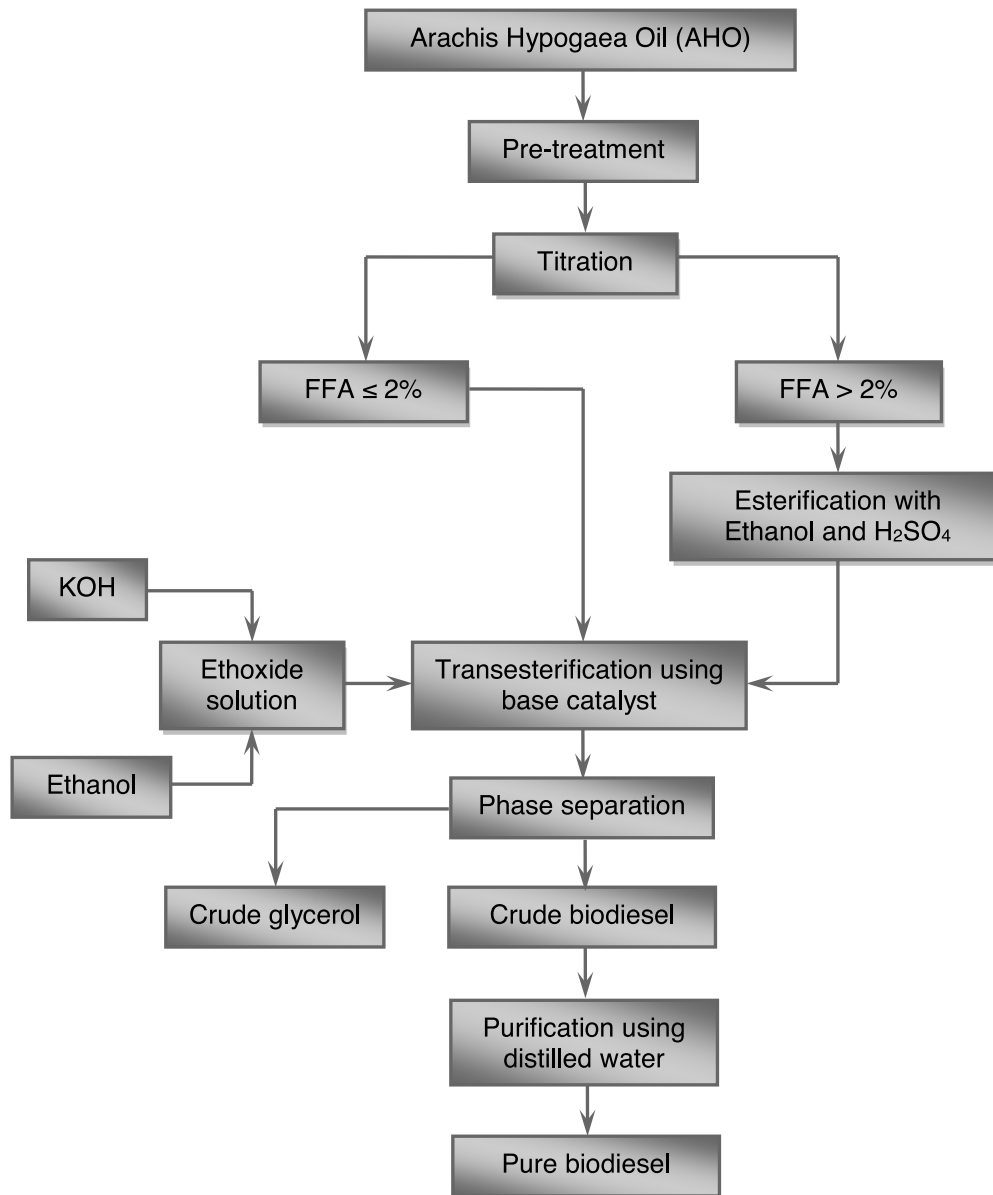


Fig. 2. Process flow chart of biodiesel production from Arachis Hypogaea oil.

Table 1 Chosen parameters and their levels.

Parameters		Levels		
		1	2	3
A	Molar ratio of ethanol to oil	3:1	6:1	9:1
B	Catalyst amount (Wt. %)	0.5	1	1.5
C	Process temperature (°C)	50	60	70
D	Process time (min)	60	90	120

Step 4: Conduction of the experiments according to the selected OA and record the output data. In the present study each experiment was repeated three times and mean value was taken as response variable.

2.5. Analysis of means and analysis of range

Analysis of means (ANOM) is one of the important analysis to find out the optimal level of each parameters and optimal level

Table 2 L₉ orthogonal array for four parameters at three levels (3⁴).

Experiment no.	Parameters and their levels			
	A	B	C	D
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	2	1	2	3
5	2	2	3	1
6	2	3	1	2
7	3	1	3	2
8	3	2	1	3
9	3	3	2	1

combination of parameters. Mean values of each parameter at different levels can be represented as \bar{Y}_{jk} . In this research work for L₉ orthogonal array of four parameters and three levels each, j represents parameters (j = A, B, C, D) and k represents levels (k = 1, 2, 3). Mean values of each parameter at different levels

Table 3
Fatty acid composition of Arachis Hypogaea oil.

Fatty acids	Molecular formula	Saturated/Unsaturated	Content (%)	Molecular weight (g/mol)
Capric acid	C ₁₀ H ₂₀ O ₂	Saturated	7.85	172.26
Lauric acid	C ₁₂ H ₂₄ O ₂	Saturated	7.80	178.14
Palmitic acid	C ₁₆ H ₃₂ O ₂	Saturated	6.35	256.40
Stearic acid	C ₁₈ H ₃₆ O ₂	Saturated	6.69	284.48
Oleic acid	C ₁₈ H ₃₄ O ₂	Monounsaturated	45.46	282.46
Linoleic acid	C ₁₈ H ₃₂ O ₂	Polyunsaturated	22.57	280.45
Arachidic acid	C ₂₀ H ₄₀ O ₂	Saturated	1.62	312.53
Behenic acid	C ₂₂ H ₄₄ O ₂	Saturated	1.48	340.58
Lignoceric acid	C ₂₄ H ₄₈ O ₂	Saturated	0.17	368.64

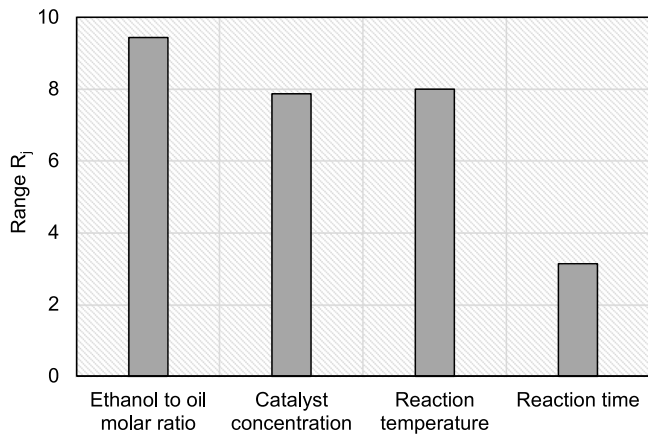


Fig. 4. Range value of each parameters.

can be calculated using the following relations.

$$\begin{aligned}
 Y_{A1} &= Y_1 + Y_2 + Y_3; & Y_{A2} &= Y_4 + Y_5 + Y_6; & Y_{A3} &= Y_7 + Y_8 + Y_9 \\
 Y_{B1} &= Y_1 + Y_4 + Y_7; & Y_{B2} &= Y_2 + Y_5 + Y_8; & Y_{B3} &= Y_3 + Y_6 + Y_9 \\
 Y_{C1} &= Y_1 + Y_6 + Y_8; & Y_{C2} &= Y_2 + Y_4 + Y_9; & Y_{C3} &= Y_3 + Y_5 + Y_7 \\
 Y_{D1} &= Y_1 + Y_5 + Y_9; & Y_{D2} &= Y_2 + Y_6 + Y_7; & Y_{D3} &= Y_3 + Y_4 + Y_8
 \end{aligned}$$

$$\bar{Y}_{jk} = \frac{Y_{jk}}{3} \quad (2)$$

where Y_1, Y_2, \dots, Y_9 are response dependent variable (% yield of biodiesel) of experiment numbers 1, 2, ..., 9 respectively. The maximum mean value of particular parameter at particular level indicates the best level of that parameter and the combination of highest mean values of each parameter will give the optimal parameter combination.

Range analysis is used to identify which parameter will highly influence the dependent variable and assign rank accordingly. The range values of different parameters can be calculated using the following relation in Eq. (3)

$$R_j = \max \bar{Y}_{jk} - \min \bar{Y}_{jk} \quad (3)$$

The larger range value is the indication of higher influence of that parameter on dependent variable, hence assigned rank 1 and second larger will be assigned rank 2 and so on.

2.6. Analysis of variance

Range analysis will be helpful in ranking the individual parameters based on their influence on response variable, but it will not be helpful in quantifying the percentage contribution of each parameter on the dependent variable. This limitation will be overcome by performing Analysis of Variance (ANOVA) of the experimental data.

$$\% \text{ contribution of } j\text{th parameter} = \frac{SS_j}{SS_T} \times 100 \quad (4)$$

$$SS_j = \left(\frac{1}{n} \sum_{k=1}^n Y_{jk}^2 \right) - \frac{1}{N} \left(\sum_{i=1}^N Y_i \right)^2 \quad (5)$$

$$SS_T = \left(\sum_{i=1}^N Y_i^2 \right) - \frac{1}{N} \left(\sum_{i=1}^N Y_i \right)^2 \quad (6)$$

where

SS_T - Total sum of squares

SS_j - Sum of squares of j th parameter

$i = 1, 2, 3, \dots, N$

$k = 1, 2, 3, \dots, n$

$j = A, B, C, D$

N - Number of Experiments

n - Number of levels

3. Result and discussion

3.1. Properties of Arachis Hypogaea seed oil

Freshly crushed Arachis Hypogaea seed oil without any pre-processing is used for biodiesel production. Fatty acid composition, saturation type of each fatty acid and their molecular weight of Arachis Hypogaea seed oil is presented in Table 3. Oleic acid forms the major composition of fatty acid with 45.46% followed by linoleic acid with 22.57% and lignoceric acid with least content of 0.17%. Table 4 shows the physicochemical properties of AHO. The molecular weight of AHO was found to be 834.45 g/mol. As Arachis oil is a vegetable oil comprising of one glycerol and three fatty acids together known as triglyceride, its molecular weight can be calculated using the following relation given in Eq. (7).

$$MW = 3 \times (AMW_{FA}) + \text{Weight of the glycerol backbone} \quad (7)$$

The density of AHO is found to be 0.958 (g/cm³) which is approximately 11% higher than the commercial diesel. Higher density will possess higher energy content per volume and release higher heat energy during combustion. At the same time the kinematic viscosity of raw AHO is 18 times greater than the diesel which restricts the direct usage of raw AHO in diesel engines. The acid value of the raw oil is estimated by basic titration method as 9.7 (mg KOH/g) from this free fatty acid content is obtained as 4.85%. The calorific value of the oil is 38.6 (MJ/kg). The oil is acidic in nature since its pH value is 4.2.

3.2. Determination of optimal level and optimal combination of parameters

Table 5 shows the nine specific experiments designed based on L₉ OA, their experimental conditions and ethyl ester yield. The percentage yield values of ethyl ester shown in Table 5 is the mean value of three trails of each experiment. For four parameters and three levels each, full factorial experimental design requires 81 ($L^P = 3^4$) experiments to be conducted to find the optimal level and optimal combination of parameters. But OA based fractional factorial design requires only 9 specific experiments out of 81. Therefore direct tracing of optimal level and optimal combination of parameters is not possible. So it requires some statistical analysis such as analysis of means and analysis of range. The mean values of each parameter at different levels are calculated by the relations described in Section 2.5. The graphical representation of mean values are shown in Fig. 3. The highest mean value of each parameter is identified as the optimal level of that particular parameter since the problem is maximization kind of optimization problem. From Fig. 3 it is found that 9:1 molar ratio of ethanol to oil, 1% (w/w) catalyst concentration,

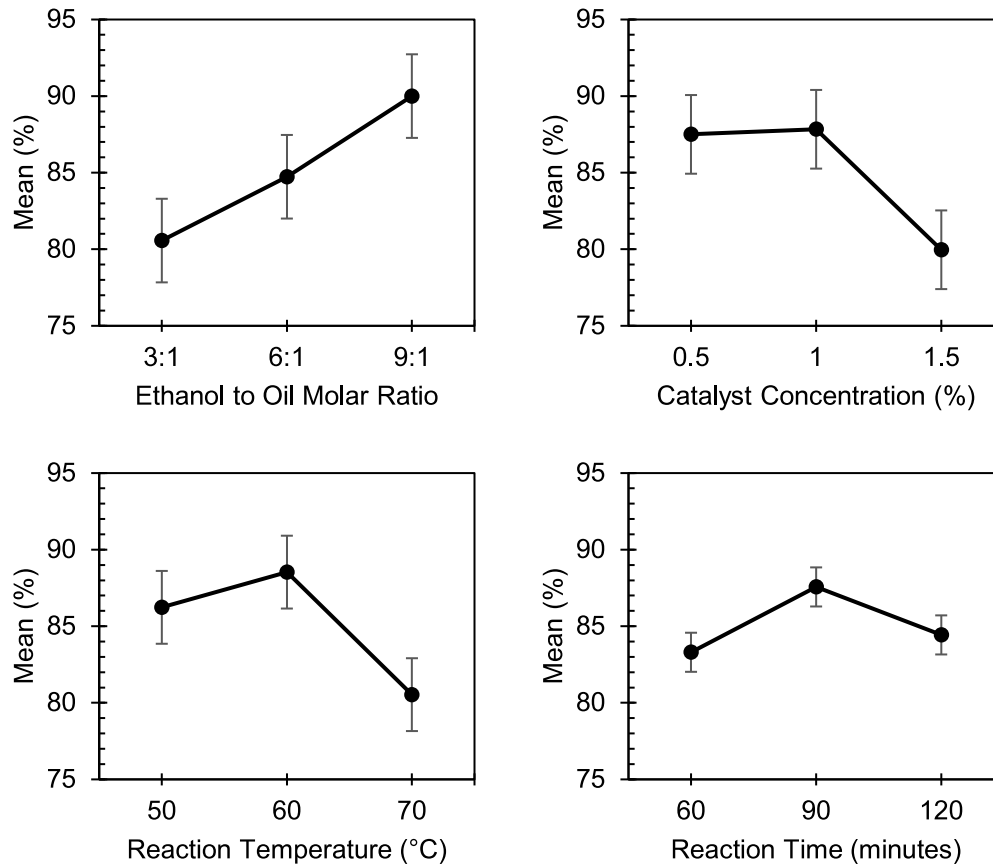


Fig. 3. Mean values of each parameters at different levels.

Table 4
Physicochemical properties of Arachis Hypogaea oil.

Parameters	Values
Density at 15 °C (g/cm ³)	0.958
Kinematic viscosity at 40 °C (mm ² /s)	53.14
Free Fatty Acid (% FFA as oleic acid)	4.85
Iodine value (g Iodine/100 g)	94
Acid value (mg KOH/g)	9.7
Colour	Yellowish Gold
Peroxide value (g/kg O ₂)	195.34
Molecular weight (g/mol)	834.45
Physical state at room temperature	Liquid
pH	4.2
Cloud point (°C)	4
Pour point (°C)	3
Flash point (°C)	232
Gross Heating value (MJ/kg)	38.6

60 °C of process temperature and 90 min of process time are identified as best levels and A₃B₂ C₂ D₂ is identified as the optimal combination of parameters. The range value of each parameters are calculated and shown in Fig. 4.

3.3. Analysis of variance (Anova)

Sum of squares of each parameters, total sum of squares and the percentage contribution of each parameter on the response variable are calculated using the relations described in Section 2.6 and given in Table 6. From Table 6, it is found out that ethanol to oil molar ratio is the most significant parameter with 34.93% followed by catalytic concentration and process temperature with 30.93% and 26.51%. The least contributing parameter is the time of reaction with 7.63%.

Table 5
Experimental conditions and ethyl ester yield.

Experiment no.	Molar ratio of ethanol to oil	Catalyst amount (Wt. %)	Process temperature (°C)	Process time (min)	Ethyl ester yield (mean of three trails) (Y _i) (%)
1	3:1	0.5	50	60	82.3
2	3:1	1.0	60	90	89.2
3	3:1	1.5	70	120	70.2
4	6:1	0.5	60	120	89.9
5	6:1	1.0	70	60	81.1
6	6:1	1.5	50	90	83.2
7	9:1	0.5	70	90	90.3
8	9:1	1.0	50	120	93.2
9	9:1	1.5	60	60	86.5
Mean (Y_m)					85.1

Table 6
Percentage contribution of process parameters.

Parameter	SS _j	% Contribution
Molar ratio of ethanol to oil	134.09	34.93
Catalyst amount (Wt. %)	118.75	30.93
Process temperature (°C)	101.78	26.51
Process time (min)	29.31	7.63
SS _T	383.92	100.00

3.4. Prediction of maximum yield and validation

The maximum theoretical yield of ethyl ester Y_o can be calculated using the following Eq. (8).

$$Y_o = Y_m + \{(Y_{A_{best}} \sim Y_m) + (Y_{B_{best}} \sim Y_m) + (Y_{C_{best}} \sim Y_m) + (Y_{D_{best}} \sim Y_m)\} \quad (8)$$

Table 7
Properties of Arachis Hypogaea ethyl ester (AHEE).

Properties	Units	EN 14214	AHEE	Diesel	Test method
Ester content	% (m/m)	Min 96.5	95.49	–	EN14103
Density at 15 °C	g/cm ³	0.86–0.90	0.893	0.861	ASTM D4052
Kinematic viscosity	mm ² /s	3.5–5	4.38	2.96	ASTM D445
Acid value	mg KOH/g	Max 0.50	0.18	0.18	ASTM D664
Iodine value	g iodine/100 g	Max 120	64.58	–	AOAC CD1–25
Pour point	°C	Max 0	–6	–12	ASTM D97
Flash point	°C	Min 120	159	48	ASTM D93
Heating value	MJ/kg	Min 35	36.5	44.8	ASTM D240
Cetane number	–	Min 51	51	51	ASTM D613
Sulphur content	mg/kg	Max 10	0	350	ASTM D5459

The predicted value is 98.63%. In order to validate the predicted ethyl ester yield, three trials of experiments with the optimized combination of parameter are conducted. The mean value of biodiesel yield of those trails is found as 95.49%. The 3.1% deviation between theoretically predicted value and confirmation test is due to the influence of the unaccounted extraneous experimental variable.

3.5. Properties of Arachis Hypogaea ethyl ester

Key physicochemical properties of AHEE were estimated using ASTM standards and reported in Table 7. The comparison between estimated properties and EN 14214 biodiesel standards were also reported in Table 7. The density of the AHEE (0.893 g/cm³) is reduced by 6.8% than that of raw oil due to the ethanolysis process. There is an appreciable reduction in the kinematic viscosity of AHEE due to the glycerine separation in transesterification process and the value is recorded as 4.38 (mm²/s). There is a slight drop in the calorific value of the ethyl ester than that of raw oil due to the lower calorific value of the ethanol. The cetane number of the AHEE is 51 which is at par with diesel. The great advantage of the AHEE than the diesel is the zero sulphur content. From the results it was confirmed that the requirements of EN14214 biodiesel standards were met by all the properties of AHEE and hence AHEE can be a suitable alternate to fossil diesel in diesel engine applications.

4. Conclusion

In this experimental analysis the oil extraction, physicochemical properties, fatty acid profile and optimization of Arachis Hypogaea ethyl ester production where investigated and reported. The FFA value of the Arachis Hypogaea oil was estimated as 4.85%, hence two step transesterification process was adapted. In the first step esterification was carried out with ethanol and concentrated sulphuric acid and its FFA value was reduced to 0.86%. In the second step, key transesterification process parameters such as molar ratio of ethanol to oil, amount of catalyst, process temperature and process time were optimized using OA based design of experiments and the following major conclusions were made.

- 9:1 molar ratio of ethanol to oil, 1% (w/w) amount of catalyst, 60 °C of process temperature and 90 min of process time were identified as best levels of parameters for production of Arachis Hypogaea ethyl ester.
- The theoretical predicted value of the AHEE yield was calculated as 98.63% and the maximum yield of the confirmation test was 95.49%. The deviation of 3.1% was due to the extraneous factors.
- Out of the four transesterification process parameters, ethanol to oil molar ratio was found to be the highly influenced process parameter with 34.93% contribution.
- The properties of Arachis Hypogaea ethyl ester was satisfactory with the EN 14214 biodiesel standard.

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