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Article

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Research paper

Biodiesel production from *Terminalia bellerica* using eggshell-based green catalyst: An optimization study with response surface methodology

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ABSTRACT

The main aim of this study was to find the possibility of biodiesel production from *Terminalia bellerica* and evaluation of optimal input reaction parameters (molar ratio, reaction temperature and catalyst amount) for maximizing the methyl ester yield with Box–Behnken design. Calcium oxide catalyst synthesized from waste chicken eggshells was used for conversion of *Terminalia bellerica* oil. Highest yield of 97.98% was achieved with optimized parameters: 62.5 °C temperature, 2.25 wt. % catalyst amount and 9:1 molar ratio where the agitation speed of the stirrer during reaction was kept constant at 600 rpm. The fuel properties of *Terminalia bellerica* methyl ester such as acid value 0.030 mg KOH/g, kinematic viscosity 4.722 cSt, flash point 160 °C, pour point 0 °C, cetane number 52 and oxidative stability 2.2h were within the limits of ASTM 6751 and EN14214 specifications.

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1. Introduction

The modern world is currently experiencing a continuous clash among various alternative energy technologies to overcome the much-exploited use of fossils. However, such zero carbon or low carbon energy sources are bound to succeed in the global market commercially only when their cost is lower to presently used fossil fuels (Covert et al., 2016). The use of renewable energy has had a lower impact on overall development than expected. Out of the top 38 renewable energy-consuming nations, only 57% had a positive effect on their respective economic output (Bhattacharya et al., 2016). Among various possible alternatives, biofuel industry has been seeing tremendous growth from a long time ago. Government policies have supported various biofuel-related schemes in order to promote low emission fuels. Biofuel programme in India, for instance, includes ethanol (derived from molasses) blended gasoline. But sugarcane farming has led to excess greenhouse gases GHG) emissions (Soam et al., 2015). The potential of biofuel industry has not been fully tapped in an effective manner (Luthra et al., 2015).

Mono alkyl esters of fatty acids (vegetable oil or animal fats), better known as, biodiesel is a well-known and commonly used

biofuel. It can be used either in pure form, that is B100 or in various blends of petrodiesel. The major advantage of using biodiesel is lower amount of emissions in the form of un-burnt carbons; carbon monoxide and particulate matter (Ranalli, 2007). Non-edible seeds derived oil have been claimed as suitable feedstock for biodiesel production. As these seeds do not affect the food demand and edible crops and also do not require fertile land with maintenance, it is expected to see a growth and demand of non-edible fruit bearing crops (Kumar and Sharma, 2011). Some of the reported literature on rarely used but promising non-edible seeds include Brucejavanicaseeds (Hasni et al., 2017), Simarouba glauca (Sivamani et al., 2018), Manilkara zapota (Kumar et al., 2015), rubber seed oil (Onoji et al., 2016), tobacco seed oil (Usta et al., 2011), Pangium edule (Atabani et al., 2015), Acrocomiaaculeata (macaúba) (César et al., 2015), Balanites aegyptiaca (Nitiema-Yefanova et al., 2016), Silybum marianum (Takase et al., 2014) and Annona diversifolia (Reyes-Trejo et al., 2014). *Terminalia bellerica* (baheda) oil is one of the possible alternatives in non-edible oil category for low-cost biodiesel production.

The most common and effective method of converting triglycerides to methyl ester is with transesterification method. This method involves a short alkyl group alcohol, like methanol reacting with a long fatty acid chain (triglycerides) and carried by alkoxide anion (R'O⁻), which is generated by base catalyst

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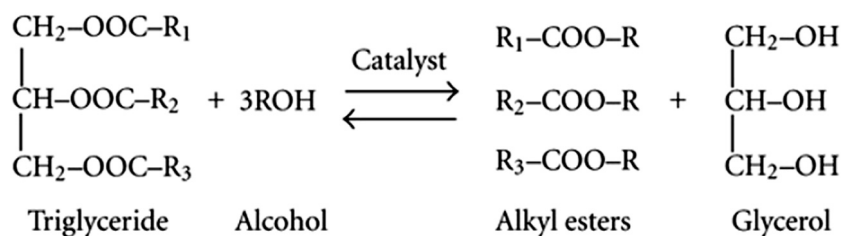


Fig. 1. Transesterification reaction mechanism.

Abbreviations

RSM	Response Surface Methodology
ASTM	American Society for Testing and Materials
EN	European Standards
PID	Proportional–Integral–Derivative
ANOVA	Analysis of Variance
CN	Cetane Number



Fig. 2. Terminalia bellerica tree.



Fig. 3. Terminalia bellerica dried seeds.

(Pullen and Saeed, 2015). The whole reaction mechanism is explained in Fig. 1.

As the homogeneous catalysts are susceptible to water, soaps are formed easily during the reaction resulting into emulsified solution mixture. This means that the recovery of catalyst becomes impractical making it unsuitable for economical alcoholysis of oils (Lam et al., 2010). On the other hand, heterogeneous catalysis involves easy separation of glycerol products from the methyl esters, thus permitting reuse of recovered catalyst for further reaction runs. These catalysts are fairly tolerant to high FFA and moisture content (Endalew et al., 2011). Solid base catalysts can further be classified into several types: metal oxides, metal hydroxides, mixed metal oxides and alkaline earth metal oxides (Marwaha et al., 2018a). Among the various heterogeneous catalysts, calcium oxide is one of the most promising solid base catalysts possessing high basicity and activity (Kawashima et al., 2009). Also, due to availability of large number of pores on its surface area, calcium oxide is a favorable catalyst support. In order to decrease the costs associated with catalysts involved in the reaction, various alternative sources of catalysts have been proposed in the recent past. The overall cost of production process is directly dependent on the recyclability, cost and life of the specific catalyst used (Semwal et al., 2011).

Several waste materials available across different industrial sectors have proved to be of immense value as heterogeneous

catalysts. Further, some of the biological occurring materials have been upgraded to effective and functional heterogeneous catalysts, as validated in some of the recent studies. Calcium oxide catalyst has been found to be in significant amount in industrial waste products (lime mud, red mud, slag, and boiler, and fly ash) and biological wastes (mussel shell, chicken eggshell, cockle shell, snail shell, oyster shell, fish scales, animal bones and plant ash) (Marwaha et al., 2018b).

The researchers have been using various experimental techniques to obtain optimized values for maximizing the biodiesel yield. Design of experiment (DOE) is a systematic approach used to establish a cause-and-effect relationship between a number of independent and dependent variables of interest. Various techniques could be employed within the DOE network to obtain optimized results and also reduce the associated process costs (Khang et al., 2018). Methods such as Taguchi approach (Adeyemi et al., 2017), Full factorial composite design (CCD) (Kılıç et al., 2013), and Box–Behnken design (Dwivedi and Sharma, 2015) have been widely used in recent past for optimization purposes. Response Surface Methodology (RSM) is one of these statistical tools used to predict the results, thus reducing time, cost and effort in the process. This is achieved by creating a mathematical model made by collecting the experimental data. Box–Behnken design can consider three to nine quantitative factors at three levels each, that is, high, low and center point level. This design is not practical to run with all factors set at their highest levels. RSM has been used in various studies for optimization of biodiesel produced from different feedstocks (Hasni et al., 2017). Dwivedi and Sharma (2015) used Box–Behnken design to achieve Pongamia biodiesel yield of 98.4% with optimized molar ratio of 11.06:1, 1.43 wt.% KOH catalyst, reaction temperature of 56.6 °C and 81.43 min time. Whereas, Dharma et al. (2016) optimized Jatropha curcas biodiesel to obtain 93.33% yield with three factors: 30% molar ratio, 0.5 wt.% KOH amount and 1300 rpm agitation speed. Thirugnanasambandham et al. (2016) used RSM coupled with 4

Table 1
Comparison of *Terminalia bellerica* oil properties.

Properties	Method	Diesel	<i>Terminalia bellerica</i> oil	Jatropha Curcas oil	Pongamia pinnata oil	Madhuca indica oil
Density at 15 °C (kg/m ³)	ASTM D287	852	922	940	936.5	960
Kinematic Viscosity at 40 °C (mm ² /s)	ASTM D445	2.78	32.2	33.9	43.61	24.58
Calorific value (MJ/kg)	ASTM D	45.01	39	38.65	40.51	36
Flash point (°C)	ASTM D93	49	102	225	230	232
Pour point (°C)	ASTM D97	0	3	–2	0	15
Oxidative stability (h)	EN 14112	–	7.9	2.56	–	–
Cetane number	ASTM D613	40	–	38.9	36.9	43.5

factor, 3-level Box–Behnken response surface design to optimize castor oil based biodiesel production with various conditions such as catalyst concentration (KOH), treatment time, ethanol to oil ratio and microwave power. Thirugnanasambandham et al. (2017) achieved biodiesel production yield of 97% from waste frying oil using microwave assisted transesterification with optimized parameters: microwave power of 325 W, catalyst dose of 1 g/g, irradiation time of 200 s and 70 °C temperature. Latchubugata et al. (2018) achieved a maximum biodiesel (from palm oil) yield of 93.5% with 6 wt.% calcium oxide (CaO) catalyst and molar ratio of 15:1 at reaction temperature of 65 °C in 4 h of reaction time using RSM based on 3-level, 3-factor Box–Behnken Design.

Terminalia bellerica is one of the many potential non-edible feedstocks on which some studies have been performed in the recent years. The study by Sarin et al. (2010) concluded *Terminalia bellerica* methyl ester as a suitable blend for diesel up to 20% concentration. Omkaresh et al. (2017) carried out RSM based optimization to obtain maximum biodiesel yield from *Terminalia bellerica* at 1.40% catalyst concentration, 60 min reaction time, 50 °C reaction temperature and 7.5:1 methanol to oil molar ratio using KOH catalyst.

RSM is an effective statistical technique which requires few experimental trials to calculate the complex interaction between the independent variables. The purpose of this work was to produce methyl ester from baheda oil using calcined eggshell as an economical catalyst. To best of the author's knowledge, no research was noticed on the calcium based economical catalyst assisted production of *Terminalia bellerica* biodiesel along with optimization using Box–Behnken design. The novelty of the work is the green catalyst (eggshell) based Box–Behnken optimization of *Terminalia bellerica* methyl ester. This study accomplishes the optimization of biodiesel yield performed with Response Surface Methodology (RSM) technique, with three independent variables, that is, molar ratio, catalyst amount and reaction temperature. Baheda tree is a large deciduous tree whose height could be much as 30 m. Inside the hard cover of baheda fruit, sweet kernels are found which can be narcotic. Its fruit resembles to haritaki fruit but without ridges (Anon, 0000).

Fig. 2 shows the structure of *Terminalia bellerica* tree bearing seeds with long leaves. Fig. 3 displays the seeds dried for a few hours in oven at 100 °C.

2. Materials and methods

2.1. Material–oil extraction and characterization

The seeds of *Terminalia bellerica* were supplied by Herbs N Spices, Neemuch, Madhya Pradesh. All the chemicals and materials used for the work such as methanol (99.9% purity), and filter paper were of analytical grade. Waste chicken eggshells were collected from the local market.

Biodiesel reactor of 1 L capacity was used to carry out the multiple trials of transesterification reaction.

The kernels of the baheda fruit were obtained by manually breaking the outer shell followed by cleaning and subsequent drying in oven at 100 °C for 6h to remove the moisture. The dried

kernels were then put in mechanical press to obtain raw baheda oil. The mechanical extraction of baheda seed yielded 33% oil. The formula used to calculate the yield of oil is given below (Hasni et al., 2017; Leung and Guo, 2006):

$$\text{Extracted oil yield} = \frac{\text{Weight of oil extracted}}{\text{Weight of seed sample used}} \times 100 \quad (1)$$

The fatty acid composition of *Terminalia bellerica* oil was determined by gas chromatography technique, where nitrogen was used as a carrier gas as according to the ASTM D-1983 test method. Various other properties of oil such as flash point, kinematic viscosity, pour point, density, oxidation stability and calorific value were tested and evaluated with standard apparatus as per the ASTM standards as shown in Table 1 drawing a comparison with the properties of diesel and other feedstocks.

2.2. Catalyst preparation

Calcium oxide catalyst was synthesized from raw waste chicken eggshells collected from local market. Initially, the collected chicken eggshells were rinsed with distilled water to remove impurities and dirt, followed by oven drying at 100 °C for 24 h. The clean and dried shells were then crushed to fine powder with pestle and mortar. Following this, the eggshells were calcined in muffle furnace at 900 °C for 4 h. This was done to ensure complete conversion of calcium carbonate present in the eggshells to calcium oxide phase. Lastly, the obtained powdered catalyst was stored in a desiccator to avoid the exposure of moisture present in air. Fig. 4 presents the flow chart for catalyst preparation.

2.3. Catalyst characterization

The basicity of the CaO catalyst was determined by using Hammett indicator method. This method utilizes the value of acidity function (H_-) to estimate the basic strength of catalyst (Leung and Guo, 2006; Mootabadi et al., 2010) The following Hammett indicators were used for evaluation of basicity: phenolphthalein ($H_- = 9.3$), 2,4-dinitroaniline ($H_- = 15.0$) and 4-nitroaniline ($H_- = 18.4$). In a 5 ml solution of Hammett indicator diluted in methanol, around 25 mg of catalyst was mixed and was left to equilibrate for 2 h. Following the attained equilibrium state, the color change is observed. Color change could be observed only when the basic strength of catalyst was identified to be stronger than the other weak indicator. Otherwise, no change in color is noticeable when strength is weaker than the strongest indicator. The calcium oxide catalyst was identified as a strong base catalyst as per the results obtained by the Hammett indicator method. The CaO catalyst was able to change the colorless indicator, phenolphthalein ($H_- = 8.2$) to pink color, and yellow colored indicator, 2,4-dinitroaniline ($H_- = 15.0$) to pale purple. As the catalyst was not able to change the color of 4-nitroaniline ($H_- = 18.4$) indicator, the basicity range of catalyst was identified as $15 < H_- < 18.4$.

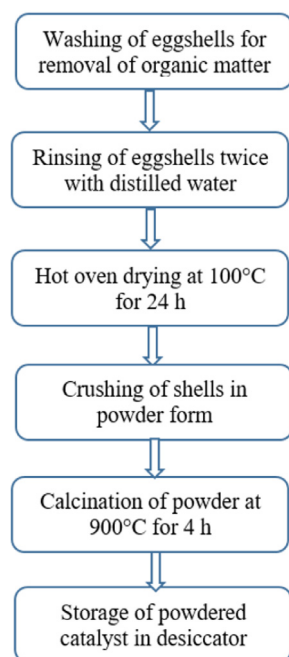


Fig. 4. Catalyst preparation procedure.

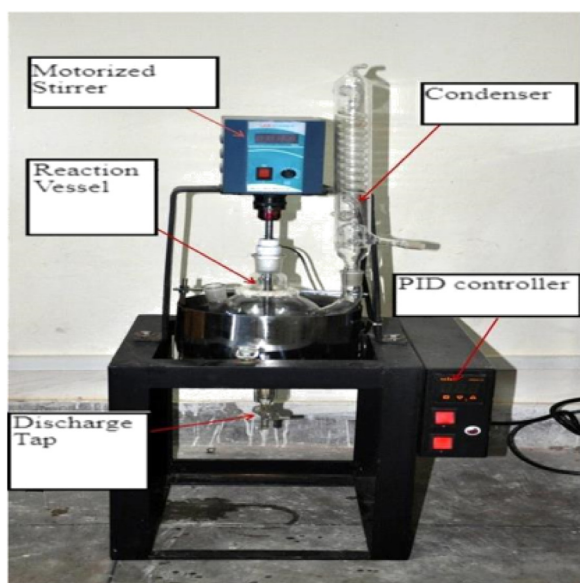


Fig. 5. Biodiesel reactor.

2.4. Experimental setup and transesterification reaction

The transesterification reaction of *Terminalia bellerica* oil was carried out in a 1 L capacity three-necked round bottom flask equipped with reflux condenser as shown in Fig. 5. The round flask was inserted in water bath where 15 experimental runs were carried out by taking 15–20 g oil in every run at atmospheric pressure conditions. Before each run, the oil was firstly preheated to 60 °C in oil bath. The solution mixture of methanol and calcined catalyst was then transferred to preheated oil, and the mixture was firmly agitated at constant speed of 600 rpm for 1.5 h.

The solution mixture was allowed to settle in the separating funnel for decantation to occur. After duration of 3 h, the

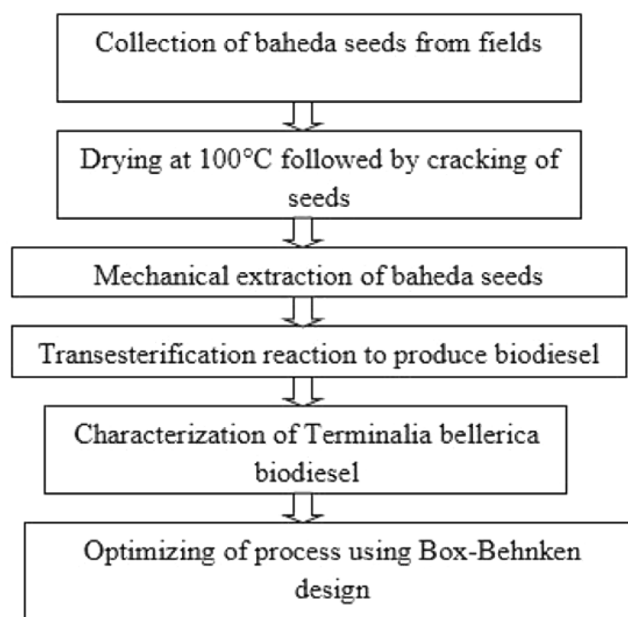


Fig. 6. Block diagram explaining entire process.

Table 2

Properties of extracted oil.

Properties of oil	Color (at room temperature)	Acid value (mg KOH/g)	Oil extraction (%)
	Pale yellow	3.52	33

Table 3

Fatty acid profile of *Terminalia bellerica* seed oil.

Fatty acid profile	Molecular formula	% by weight
Palmitic acid	C ₁₆ H ₃₂ O ₂	28.9
Palmitoleic acid	C ₁₆ H ₃₀ O ₂	0.5
Stearic acid	C ₁₈ H ₃₆ O ₂	4.8
Oleic acid	C ₁₈ H ₃₄ O ₂	48.2
Linoleic acid	C ₁₈ H ₃₂ O ₂	20.3
Arachidic acid	C ₂₀ H ₄₀ O ₂	0.2

process was expected to complete as visible clearly from the separate phases of biodiesel and methanol–water achieved through gravity separation. The impurities present in the upper phase, that is, biodiesel layer was separated by water washing with distilled water in three cycles. The required temperature was controlled using PID (Proportional–Integral–Derivative) controller. The whole approach of the experiment is described in Fig. 6.

The three parameters selected for statistical analysis was methanol to oil molar ratio: A, catalyst amount: B, and reaction temperature: C. Lower molar ratios (alcohol/oil) directly have an impact on conversion tendency of fats to methyl esters, whereas excessive molar ratios may further decrease the yield. The effect of catalyst amount is also similar to the effect of molar ratio on FAME yield. High reaction temperatures are favorable to a certain extent, above which side reactions may occur apart from transesterification reaction, leading to lower biodiesel yield (Verma and Sharma, 2016). Thus, the mentioned three process parameters were crucial to study, as they have pronounced effect on methyl esters yield. A total of 15 experimental runs were conducted which developed a mathematical equation model. A statistical analysis was then carried out to fit the quadratic equation.

Response Surface Methodology (RSM) was used for statistically analyzing the results obtained with 15 experimental runs. A quadratic polynomial equation was produced in Minitab 17

software. Yield of baheda oil methyl ester was chosen as response variable against independent variables A (molar ratio), B (catalyst amount) and C (reaction temperature). The suitability of fit of the model was evaluated by using ANOVA test. The fitted polynomial equation is as follows:

$$y = b_0 + \sum_{i=1}^k b_i X_i + \sum_{i=1}^k b_{ii} X_i^2 + \sum_{i<j}^k b_{ij} X_i X_j + e \quad (2)$$

where, Y = response output (biodiesel yield);

b_0 = intercept value

b_i = first order model coefficient

b_{ii} = quadratic coefficients of X_i

b_{ij} = coefficient for effect of interaction between i and j

X_i = i th independent factor

X_j = j th independent factor

k = number of parameters studied

e = random error

3. Results and discussions

3.1. Oil content and properties

The quality of the oil extracted was evaluated by determining its properties. With 33 wt.% oil extracted from the baheda seed, properties such as acid value, oxidative stability have been shown in Table 2. As can be seen from the table, the acid value of raw baheda oil was not very high (1.85% FFA content), therefore, the esterification of oil was not required (Ong et al., 2014). The fatty acid profile of oil is crucial to study as it affects the biodiesel stability (Ramos et al., 2009). The structural features, or more generally, fatty acid profiles influence the fuel properties of biodiesel. The GC (Gas Chromatography) analysis as according to EN 14103 method was performed to find the ester content. The fatty acid profile of *Terminalia bellerica* is shown in Table 3. The presence of double bonds (more degree of unsaturation) in fatty acid chains leads to the autooxidation of fuels (Knothe, 2005). As can be seen from the table, the unsaturated fatty acids (palmitoleic acid, oleic acid and linoleic acid) cover a larger portion (69%) of the overall fatty acid profile. This leads to a conclusion that *Terminalia bellerica* biodiesel would be prone to oxidation effect. A high value of oxidative stability of *Terminalia bellerica* seed oil as 7.9 h was observed. This high oxidative nature of oil is affected by the fatty acid composition of a specific oil. This leads to rapid rate of oxidation of oils that are more unsaturated than the saturated oils.

3.2. Fuel properties

Table 4 includes the fuel properties of produced *Terminalia bellerica* methyl ester. The oxidative stability of biodiesel is influenced not only by the surrounding air, but with other factors such as high temperatures, presence of light, presence of metals in container and also with surface area between air and biodiesel (Knothe, 2007). An appropriate value of 2.2 h of oxidative stability was observed, which is well within the ranges of standard ASTM and EN specifications. Cetane number (CN) is indicative of ability of fuel to readily auto-ignite at given temperature and pressure. CN of produced methyl ester, that is 52, is comparable with results of CN 53 demonstrated by Chakraborty et al. (2009).

3.3. Optimization of methyl ester using Response Surface Methodology

The experiments were conducted for ANOVA analysis with RSM based on Box–Behnken design with three input variables to create quadratic equation model. The risk level of 0.1 and confidence level of 95% was optimal for highly significant model. Table 5 lists the properties of selected factors: molar ratio (A), catalyst amount (B) and reaction temperature (C) as defined to conduct the analysis through RSM technique. Table 6 includes 15 combinations of experimental runs achieved by varying the process parameters. The experimental and predicted response yield value achieved for different experimental runs is mentioned in the table.

The methyl ester yield is the response variable depending upon different variations in the given three parameters (molar ratio, catalyst amount and reaction temperature). This dependence defines the relationship between response output (yield) and input parameters by using mathematical equation developed. The validity of the significant model is verified on account of low p value ($p < 0.05$) obtained. In the model obtained, all the terms were significant except the term (A^*C), as shown in Table 7. The regression coefficient (R^2) or coefficient of determination indicates and measures the goodness of fit for regression models. A higher value of R^2 would mean that there is a smaller difference between the actual and fitted data. If the regression coefficient value is more than 80%, a good fit of the model can be expected.

In this study, R^2 value of 98.7% and R^2 (adjusted) value of 98.6% was obtained as shown in Table 7. The R^2 adjusted values indicate the goodness of empirical model developed. Fig. 7 depicts the plot between actual and predicted yield.

Table 4
Properties of *Terminalia bellerica* methyl ester.

Fuel properties	Test method	<i>Terminalia bellerica</i> methyl ester	ASTM D6751	EN 14214	Diesel
Density at 15 °C (kg/m ³)	ASTM D287	896.55	–	860–900	852
Kinematic viscosity at 40 °C (mm ² /s)	ASTM D445	4.722	1.9–6.0	3.5–5.0	3.5–5.0
Acid value (mg KOH/g)	ASTM D664	0.030	<0.8	0.05	–
Flash point (°C)	ASTM D93	160	100–170	>120	60–80
Pour point (°C)	ASTM D97	0	–15 to 10	–	–15 to –35
Cetane number	ASTM D613	52	47	55	40
Oxidative stability (h) at 110 °C	EN 14112	2.2	3	6	–
Calorific value (MJ/kg)	ASTM D	40.51	–	–	45.01

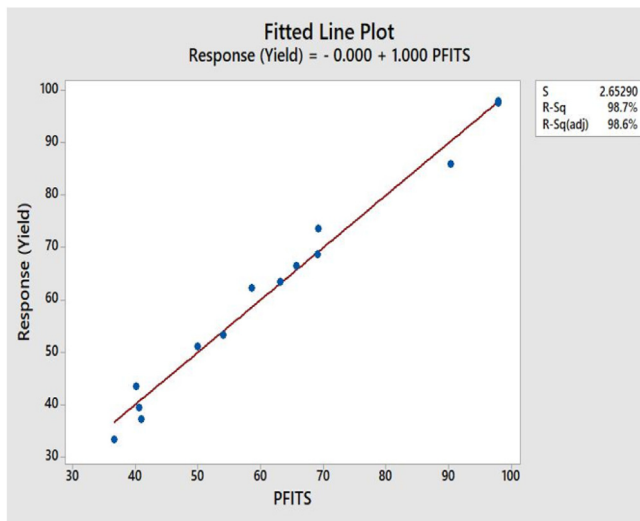
Table 5
Description of independent input parameters.

Abbreviation	Factor properties					
	Name	Units	Number of levels	Low level (–1)	Middle level (0)	High level (1)
A	Molar ratio	mol/mol	2	6:1	9:1	12:1
B	Catalyst amount	%	2	0.50	2.25	4.00
C	Temperature	°C	2	40	55	70

Table 6

Experimental yield of 15 runs using Box–Behnken design.

Run	Molar ratio (mol/mol)	Catalyst amount (wt.%)	Temperature (°C)	Experimental yield (%)	Predicted yield (%)
1	6	4.00	62.5	62.23	58.56
2	6	2.25	70.0	66.44	65.70
3	12	0.50	62.5	37.21	40.88
4	9	2.25	62.5	97.89	97.80
5	12	2.25	55.0	53.22	53.95
6	9	2.25	62.5	97.98	97.80
7	12	4.00	62.5	51.02	49.93
8	9	4.00	55.0	68.66	69.01
9	9	0.50	55.0	73.55	69.14
10	12	2.25	70.0	43.41	40.09
11	6	2.25	55.0	33.30	36.61
12	9	0.50	70.0	63.44	63.08
13	6	0.50	62.5	39.45	40.53
14	9	2.25	62.5	97.55	97.80
15	9	4.00	70.0	85.90	90.30

**Fig. 7.** Plot of experimental and predicted yield.

The catalyst amount parameter was found to be the most dominating of all the factors affecting methyl ester yield. As can be seen from Table 7, catalyst amount shows highest sum of squares (3677.4) than molar ratio (997.0) and reaction temperature (2547.9). Based on the model developed by software,

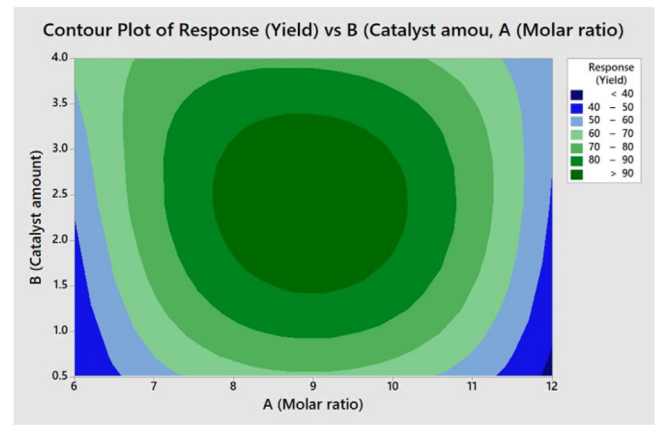
Table 7

Analysis of variance obtained from experimental results.

Source	Degrees of freedom	Adjusted sum of squares	Adjusted mean squares	F-value	P-value
Model	9	12231.1	1359.03	36.04	0.001
Linear	3	7222.3	2407.44	63.84	0.000
A (Molar ratio)	1	997.0	997.03	26.44	0.004
B (Catalyst amount)	1	3677.4	3677.39	97.52	0.000
C (Temperature)	1	2547.9	2547.91	67.57	0.000
Square	3	3422.8	1140.94	30.26	0.001
Molar ratio (A) * Molar ratio (A)	1	2874.0	2873.96	76.21	0.000
Catalyst amount (B) * Catalyst amount (B)	1	547.0	547.01	14.51	0.013
Temperature (C) * Temperature (C)	1	348.8	348.78	9.25	0.029
Interaction	3	1586.1	528.70	14.02	0.007
Molar ratio (A) * Catalyst amount (B)	1	262.6	262.60	6.96	0.046
Molar ratio (A) * Temperature (C)	1	23.5	23.52	0.62	0.465
Catalyst amount (B) * Temperature (C)	1	1300.00	1299.96	34.47	0.002
Lack of fit	3	188.2	62.72	334.65	0.003
Pure error	2	0.4	0.19	–	–

Model summary

S = 2.65290

R² = 98.7%R² (adjusted) = 98.6**Fig. 8.** Contour plot of effect of molar ratio and catalyst amount on FAME yield.

maximum methyl ester yield of 97.98% was predicted, which was quite close to the experimentally (actual) obtained results. The corresponding optimized reaction parameter conditions were observed as: molar ratio (methanol/oil) of 9:1, catalyst amount of 2.25 wt.% and reaction temperature of 62.5 °C. The developed equation is as given below:

$$\begin{aligned} \text{Response (Biodiesel yield)} = & -1305 + 104.22 A - 5.4 B \\ & + 29.52 C - 4.118 A * A - 4.332 B * B - 0.2071 C * C \\ & - 0.427 A * B - 0.4772 A * C + 0.521 B * C \end{aligned} \quad (3)$$

The three reaction parameter variables were varied to evaluate their interaction effects on the response yield variable. The contour plots were plotted to show the combined effects of two variables on methyl ester yield.

3.4. Effect of reaction parameters on methyl ester yield

In order to show the influence of independent variables on the dependent variable, contour plots have been produced. Various reaction parameters affect the percentage yield of biodiesel during transesterification reaction. Methanol to oil molar ratio, reaction time, reaction temperature and catalyst amount are some of the crucial variables studied for biodiesel optimization. Molar ratio (methanol: oil) is considered to be the most significant factor influencing the methyl ester yield (Meher et al., 2006). An appropriate methanol amount is required to break the fatty

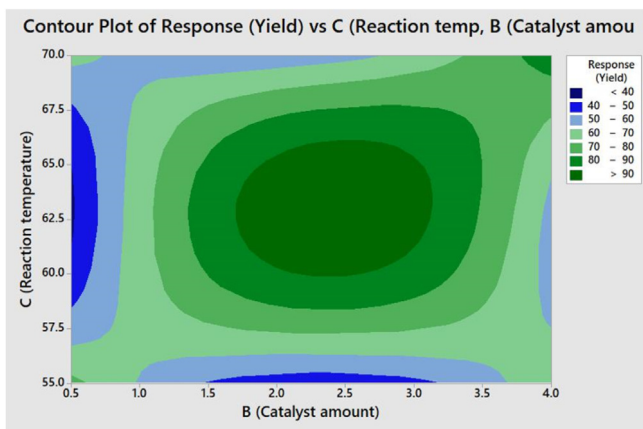


Fig. 9. Contour plot of effect of catalyst amount and reaction temperature on FAME yield.

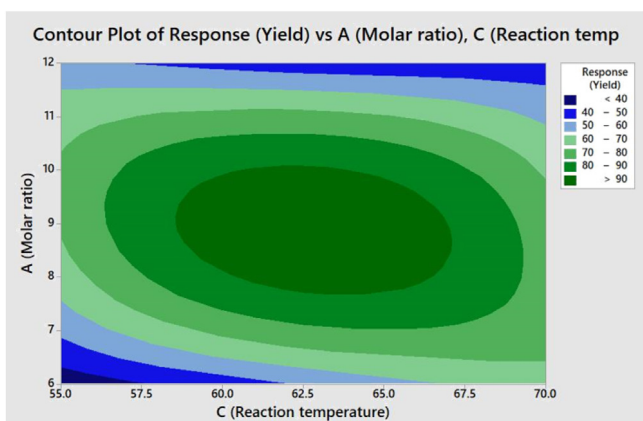


Fig. 10. Contour plot of effect of reaction temperature and molar ratio on FAME yield.

acid–glycerol linkages formed during the reaction for easy removal of glycerol (Musa, 2016). A minimum of 3:1 methanol to oil molar ratio is necessary to complete the transesterification reaction process in biodiesel production. As transesterification reaction is reversible in nature, an excess of methanol is added to ensure complete formation of methyl ester. In the present study, methanol to oil molar ratio is varied from 6:1 to 12:1 to understand the effect of molar ratio on biodiesel yield. The contour plot as shown in Fig. 8 signify the combined effects of molar ratio and catalyst amount on *Terminalia bellerica* biodiesel yield. It was observed that excessive ratio of methanol led to emulsified solution mixture formation making it difficult to separate the biodiesel. Validating with the literature studies, excess methanol probably increased the polarity of solution, increasing glycerol solubility and thus making it difficult for it to separate from biodiesel formed (Dwivedi and Sharma, 2015; Dharma et al., 2016; Kafuku and Mbarawa, 2010). The contour plot shows that as the molar ratio increased above 9:1 approaching towards 12:1 molar ratio, the FAME yield started decreasing continuously. As can be seen from Table 6, the maximum *Terminalia bellerica* methyl ester yield was obtained at 9:1 molar ratio of methanol to oil, 2.25 wt.% and 62.5 °C reaction temperature, and it is evident that these were the optimal conditions required for transesterification reaction.

The effect of catalyst amount was studied by using the catalyst in varied concentrations from 0.5 wt.% to 4 wt.% of oil amount. Fig. 9 displays the contour plot of catalyst concentration and temperature having a combined effect on FAME yield. The variations

observed in methyl ester yield with respect to catalyst amount and reaction temperature were analyzed from the plot. As can be seen from the contour plot in Fig. 9, maximum response yield was obtainable at catalyst concentrations ranging from 2 to 3 wt.%. This statement was validated with optimal catalyst amount of 2.25 wt.% leading to maximum experimental yield obtained as 97.9%. As the concentration was increased above 3 wt.%, the yield response showed a continuous decreasing trend. This decreasing trend of yield after approaching the concentration above optimal value of 2.25 wt.% towards 4 wt.%, could be attributed to saponification phenomena and improper mixing of solution mixture with excess catalyst involved during the transesterification reaction (Xie and Li, 2006). The excessive amount of catalyst led to the formation of gel or slurry with increased viscosity of solution mixture (Chen et al., 2014). This effect is mostly responsible for irregular mixing of solution constituents leading to decreased yields with further addition of catalyst.

Fig. 10 shows the combined influence of reaction temperature and molar ratio on *Terminalia bellerica* methyl ester yield. During the experiment, reaction temperature in the range of 55–70 °C was varied to study its effect on biodiesel yield. For constant molar ratio parameter, the yield increased up to a certain value of reaction temperature after which it started decreasing again. As per the results obtained, highest yield would be obtained at optimal reaction temperature of 62.5 °C. Generally, the rise of reaction temperature in transesterification reaction implies higher biodiesel yield due to increased rate of constant in reaction. With the increase of temperature, viscous effect of fluid (solution) begin to decrease, thus leading to better mixing and rapid separation of glycerol (Ong et al., 2014). As seen from the results in Fig. 10, the influence of temperature led to increased yield, but as the temperature rose a much higher value, it had a negative impact on yield. As the boiling point of methanol is around 64.7 °C, considerable amount of methanol is lost as vapors during transesterification as the reaction temperature approaches 65 °C. This leads to reduction of methyl ester yield as the reaction temperatures are elevated. Also, low temperatures around 55 °C did not influence the increase of yield in considerable manner. Low temperature reaction would obviously consume more time to complete the process as compared to a high temperature reaction (Leung and Guo, 2006). According to the results shown in Table 6, maximum achievable experimental yield of 97.98% was obtainable at 62.5 °C reaction temperature. The transesterification reactions are mostly conducted at temperatures closer to boiling point of methanol (64.7 °C) that is in the range of 60–70 °C to achieve complete conversion of triglycerides (Leung and Guo, 2006). The study by Kafuku and Mbarawa had revealed similar results with conversion efficiency (%) following a decreasing trend above 60 °C temperature (Kafuku and Mbarawa, 2010). Generally, reaction temperatures above 65 °C are avoided, as it leads to boiling of methanol and results in stimulation of saponification effect of triglycerides in the solution (Dorado et al., 2004; Lin et al., 2009).

4. Conclusion

Box–Behnken design-based Response Surface Methodology method was implemented to optimize the biodiesel production process from *Terminalia bellerica* feedstock. Waste eggshell derived calcium oxide proved to be an effective catalyst for alcoholysis of *Terminalia bellerica* oil. The optimal reaction conditions of molar ratio of 9:1, 2.25 wt.% catalyst amount and reaction temperature of 62.5 °C gave a maximum yield of 97.98%. The developed empirical model successfully predicted response yield value with only minimal error percentage. The kinematic viscosity of *Terminalia bellerica* greatly reduced from 32.2 cSt to

about 4.72 cSt upon conversion to methyl ester, thus within the ASTM and EN limits for biodiesel. Degradation of biodiesel is a huge problem when storing it for future purposes. The optimization study was found constructive to make biodiesel production process economical.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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