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Biodiesel production from rubber seed oil using calcium oxide derived from eggshell as catalyst – optimization and modeling studies

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Abstract: In the present study, Calcium oxide (CaO) obtained from eggshells has been used as a heterogeneous catalyst for biodiesel production from highly viscous non-edible rubber seed oil (RSO). Characterization of synthesized catalyst was done with the help of scanning electron microscope equipped with Energy dispersive spectrometry (SEM-EDS), X-ray diffraction (XRD) and Fourier transform Infrared spectroscopy (FTIR). Response surface methodology (RSM) with central composite design (CCD) was used to optimize the process parameters and ^{1}H-NMR (Nuclear Magnetic Resonance) spectroscopy analysis was performed to find the conversion of RSO to biodiesel. A conversion of 99.7% of RSO to biodiesel was obtained at 12:1 methanol to oil molar ratio, 4 (wt%) of catalyst, and 3 hour reaction time with a quadratic regression model of R^2 of value 0.9566 was obtained. The composition of prepared biodiesel is estimated with the help of Gas Chromatogram-Mass Spectroscopy (GC-MS) analysis. Artificial Neural Network (ANN) with Levenberg-Marquardt algorithm was also trained to predict biodiesel conversion and the value of R^2 obtained was 0.9976. It was observed that predicted conversion values from ANN were better when compared to prediction using RSM.

Keywords: biodiesel; eggshells; calcium oxide (CaO); RSM; ANN

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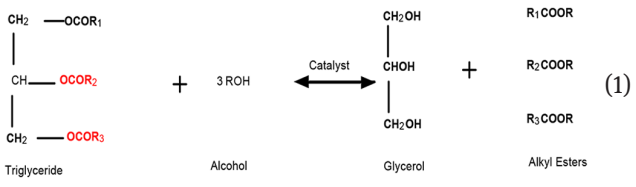
1 Introduction

The selection of feedstocks for biodiesel production is a critical factor in making biodiesel a viable alternative to the existing petroleum-based diesel. Plenty of oils obtained from seeds of plants and trees have been commonly used as feedstocks for the production of biodiesel, and among them, edible oils such as sunflower oil [1,2], palm oil [3-5], soyabean oil [6,7], peanut oil [8], corn oil [9] etc. have been used extensively in the production of biodiesel. The use of edible oils in biodiesel production is not advisable inview of its demand in processing of food. Non-edible oils which do not have many commercial applications and are also cost effective and excellent alternatives to overcome this issue [10-13]. Transesterification is one of the most widely used methods for producing biodiesel from vegetable oils, catalytically. In this process, as per stoichiometry, one mole of triglyceride reacts with three moles of alcohol in the presence of a catalyst to form methyl ester. The mechanism of transesterification is shown in Eq. 1 [14]. Transesterification using either the acidic catalysts or the basic catalysts are the two different types of transesterification processes which are used extensively. Carboxylic acids can be esterified by alcohols in the presence of a suitable acid catalyst in water-free conditions and the process is called acid esterification. Acid catalysts generally employed for transesterification processes are HCl, H_2SO_4, BF_3, and sulfonic acids [15-17]. Use of solid heterogeneous catalyst is more advantageous since it involves a single step process and the separation of the catalyst is also easy [16]. Esters in the presence of a base such as an alcoholate anion forms an anionic intermediate which can subsequently dissociate back to the original ester or form the new ester in the base catalyzed transesterification [15,16]. The only disadvantage of acid catalyzed transesterification is that the reaction rate is less when compared with the base-catalyzed transesterification, and hence it requires a temperature above 100°C [16]. As far as the homogeneous base catalysts are concerned, the commonly used ones are potassium hydroxide [17], and sodium hydroxide [15,18]. While using the homogeneous

base catalyst, the major disadvantage is the separation of catalyst from the transesterification products [14,16]. Recent research works state that a heterogeneous catalyst derived from alkali and alkaline earth metal oxides, transition metal oxides, mixed metal oxides, ion exchange resins, derivatives prepared from impregnation of sulfur, boron, and carbon can be used in biodiesel preparation [19-21]. Impregnation of potassium and sodium salts on metal oxide catalysts increases the basicity of catalysts and this approach can also be used in producing biodiesel from triglycerides with a high conversion [20]. Most of the solid waste materials and biomass resources can also be used as heterogeneous catalysts in biodiesel production [16]. The major advantages of using this catalyst are the reusability, low cost, solid waste management etc. All the catalysts mentioned above are solid-base heterogeneous catalysts which give a high conversion of oil feedstock to biodiesel when compared to homogenous catalyst [21,22].

Recent studies proposed that calcium oxide (CaO) derived from various wastes and the impregnation of CaO with different compounds as one of the best heterogeneous catalysts which can be effectively used for producing biodiesel [23-25] from waste frying oil and pongamia oil. Catalyst activity, reusability, loading, low cost are the major advantages of using calcium oxide as the catalyst [16]. A high yield of 98% was observed while using KOH impregnated with lime/carbon (CaO/C) synthesized by wet impregnation method as the catalyst in the transesterification of soyabean oil [26]. Heterogeneous catalyst CaO-La_2O_3 was used in the transesterification of soyabean oil which gave a biodiesel yield of 94.3% [27]. The use of CaO loaded with 3.7 wt% in $Ca(OH)_2$/CaO as the catalyst in soyabean oil transesterification with ethanol produced biodiesel with a conversion of 96.3% [28]. Mixed oxide catalysts CaO/ZnO prepared from calcium and zinc were used in biodiesel preparation from palm kernel oil [29]. An overall biodiesel yield of 88.06% was obtained while using waste cockles shells, having 93.98% of calcium oxide (CaO), as a heterogeneous catalyst in the transesterification of rubber seed oil (RSO) [30]. Calcium oxide prepared from bivalve clam shells produced biodiesel with a high yield of 95.84% from the waste cooking oil [23]. The catalytic activity of CaO supported on mesoporous silica was tested in the transesterification of ethyl butyrate with methanol [31]. Clinker, a by-product from cement industry, was also used as a catalyst in biodiesel production from RSO and a high conversion of 96.80% was achieved [33]. Microcapsules loaded with CaO and activated carbon were used as a heterogeneous catalyst in biodiesel production from rapeseed oil [34]. A review of literature also indicates that not much research has been done on the use of RSO as feedstock for biodiesel production, and also on the use of CaO from natural sources as catalysts in biodiesel production from non-edible oils. Hence, in the present study, a highly viscous non-edible RSO which is cheap and does not have much commercial application and mostly available in southern part of India in huge amount has been selected for biodiesel synthesis [35,36]. The main novelty of present work is the optimization of experimental parameters and determination of the best model in RSO conversion to biodiesel using calcium oxide derived from green renewable eggshell as a catalyst. The use of CaO derived from eggshells as a catalyst in biodiesel production from RSO is also not found till date in literature. Earlier, studies were carried out on the preparation of biodiesel from RSO using different homogeneous base catalysts [35] and also by using lime derived catalysts [30]. A maximum conversion of 90-95% was achieved on working with these catalysts. Eggshells a kitchen waste which is found mostly at bakeries, hotels can be used as a source of catalyst in biodiesel production. A large amount of calcium oxide obtained from eggshells has been used as a heterogeneous base catalyst in recent times [23]. Catalysts were characterized using X-ray diffraction (XRD), Scanning electron microscope (SEM), Energy Dispersive Spectroscopy (EDS) and Fourier Transform Infrared (FTIR) spectrometry. Characterization of Biodiesel was done by using Fourier Transform Infrared (FTIR) spectrometry analysis. The conversion of RSO to biodiesel was estimated using ^{1}H-Nuclear Magnetic Resonance (NMR) analysis. Optimization of process parameters such as molar ratio (methanol: oil), catalyst (wt%), reaction time (hours) was done by using design expert software 10 employed with Response Surface Methodology (RSM) [37]. Generally, Artificial Neural Networks (ANN) is used to solve problematic complex mathematical functions easily with accurate result [38]. In this study, ANN is also used to verify the agreement between the experimental and the predicted values. Also, an effort is made to identify whether RSM or ANN has better prediction capability.

Transesterification reaction is given as follows:



(1)

2 Materials and methods

2.1 Materials required

RSO was purchased from virudhunagar Tamilnadu, and methanol used in this process is supplied by CDH suppliers, New Delhi, India, and sulphuric Acid (98% concentration, EMPARTA) used was procurred from Merck life sciences private limited, Mumbai. Eggshells were collected from a local bakery in Trichy, Tamilnadu.

2.2 Experimental methods

2.2.1 Catalyst preparation

Raw egg shells collected were washed thoroughly to remove dirt from them, followed by drying at 105°C in an oven. The dried shells were then ground into fine particles by using a grinder. Finely powdered shells were subjected to calcination in a muffle furnace at 900°C for 4 h to calcine calcium carbonate present in the shells to calcium oxide (CaO). The final product obtained after calcination is used as a catalyst in the transesterification process.

2.2.2 Catalyst characterization

X-ray diffraction (XRD) (Model: Ultima IV, Rigaku, Japan) using Cu kα radiation has been used to check the formation of calcium oxide (CaO) in eggshells after calcination. Scanning Electron Microscope-Energy Dispersive Spectroscopy (SEM-EDS) (Model: S3000H, Hitachi, Japan) equipped with EDS analysis was used to find the surface morphology and composition of the catalyst. Presence of functional groups in the catalyst were found by using Fourier transform infrared spectroscopy (FTIR, Model: Perkin Elmer, Spectrum 2) analysis.

2.2.3 Esterification procedure

A pretreatment process used to reduce the acid value of selected feedstock to the required level is called esterification. Whenever biodiesel is produced by transesterification process through base catalysis, and if the feedstock has free fatty acids (FFA) content more than 2, esterification is necessary to avoid soap formation. In this study the chosen feedstock RSO is having an acid value of 67.6, and hence treated with methanol in the presence of sulphuric acid (98% concentrated) as catalyst to reduce the FFA content. In this process, initially 50 ml of feedstock was preheated to 60°C, and this is followed by esterification reaction at a temperature of 65°C as cited in literature [24]. After the reaction is completed, the treated oil is separated from excess methanol-catalyst mixture in a separating funnel. Process conditions were optimized and the esterified oil was prepared at the optimized conditions of methanol to oil molar ratio of 15:1, catalyst 3% (v/v H_2SO_4), and 2 h reaction time. The esterified oil thus prepared was used for all the transesterification studies.

2.2.4 Biodiesel preparation (transesterifcation) procedure

For transesterification reaction, a 3-neck round bottomed flask with one end connected to a condenser, another end to a thermometer and the middle one to a mechanical stirrer was used. The round bottomed flask was kept in a constant temperature water bath. Esterified RSO was heated at methanol boiling point temperature for some time to make sure that excess methanol present in the oil has been evaporated. The catalyst prepared was mixed with methanol to form methoxide by stirring and then the formed methoxide was poured into the heated oil. The methoxide-treated RSO mixture was stirred well and the rotation of stirrer was controlled by a regulator. The formed product was transferred to a separating funnel through Whatmann No 1 filter paper to separate the catalyst from the transesterification products, and the solution was set aside for 48 h to separate. After perfect separation, the two layers are visible in the separating funnel, of which the bottom layer is glycerol which is drawn out and the top layer is the fatty acid methyl ester (FAME) which is called biodiesel. Excess methanol present in the top layer is subsequently evaporated using a rotary evaporator and the final sample was analyzed with 1^H-NMR (Model: Bruker 500 MHz) analyzer to estimate the conversion by using $CDCl_3$ as solvent [23].

3 Statistical analysis and modeling of formed biodiesel

3.1 Statistical analysis – Response Surface Methodology (RSM)

RSM is a statistical tool to not only optimize the process parameters but also identify the significant process

parameters that affect the process. It also predicts the desired parameter as a function of process parameters. In this study, RSM is employed with central composite design (CCD) for optimizing the process parameters like molar ratio (mol/mol), catalyst (vol %), and reaction time (hours). After performing several trails initially, the maximum and the minimum value of process parameters are fixed as molar ratio 18 (mol/mol) and 6 (mol/mol), catalyst (wt%) as 6 and 2, and reaction time (hours) as 5 and 1 respectively. Analysis of variance (ANOVA) and the effect of influencing factors on percent conversion are designed by using RSM. The process parameters and the range of coded values are presented in Table 1.

3.2 Artificial Neural Network (ANN)

In this study, a feed-forward back propagation ANN model has been developed for the conversion of RSO to biodiesel with input parameters as Methanol-oil ratio, catalyst weight% and reaction time in MATLAB R2018a software. The network consists of an input layer with 3 nodes, an output layer of 1 node and a hidden layer of 10 neurons. The neurons are based on the TANSIG transfer function. The network was trained using the TRAINLM (Lavenberg– Marquardt) algorithm and the Mean Squared Error (MSE) was used as the performance function which was to be minimized to 1×10^{-5} (default). 20 data points were used for modeling out of which 70% was used for training, 15% for validation and 15% for testing. The epoch was set at 1000. The ANN performance was evaluated using mean square error and the coefficient of determination R^2 for RSO conversion to biodiesel, and is calculated using Eq. 2 [38].

MSE-(Mean Square Error):

$$\frac{1}{n}\left(\sum_{i=1}^{n}\left(X-Y\right)^2\right) \tag{2}$$

where, X → Experimental Output, Y → Predicted Output, n → total number of training data

Table 1: Coded values of process parameters.

Factor	Name	Units	Minimum	Maximum	Coded Values	
A	Molar Ratio	mol/mol	6	18	−1.000=9	1.000=15
B	Catalyst	wt%	2	6	−1.000=3	1.000=5
C	Time	hours	1	5	−1.000=2	1.000=4

4 Results and discussion

4.1 Characterization of calcined egg shells

4.1.1 X-Ray Diffraction (XRD)

The formation of calcium oxide (CaO) in the prepared catalyst is found by using XRD technique. Results of this analysis are shown in Figure 1. The CaO formation peaks observed at respective 2θ values of 32.44, 37.58, 54.07, 64.35, 67.56, 79.82 and 88.65 were compared with the standard reference patterns in XPERT High Score Plus and found to match well. Similar results were observed by Niju et al., for calcium oxide (CaO) derived from egg shells [23].

4.1.2 Scanning Electron Microscope-Energy Dispersive Spectrometry (SEM-EDS)

SEM image of calcined eggshells at different magnifications is shown in Figures 2a-c. On calcination of raw eggshells at 900ºC for 4h the surface morphology of the calcined

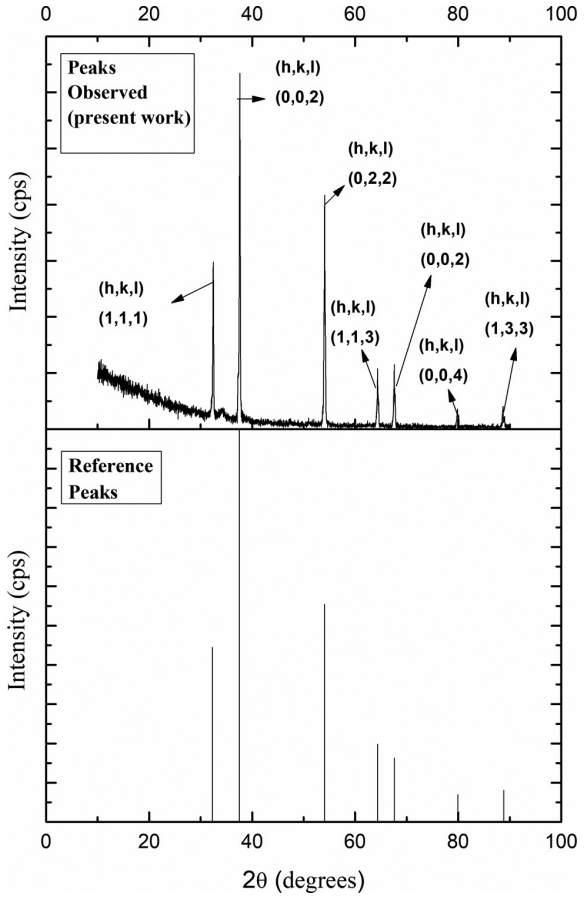


Figure 1: X-Ray Diffraction (XRD) analysis of calcined eggshells.

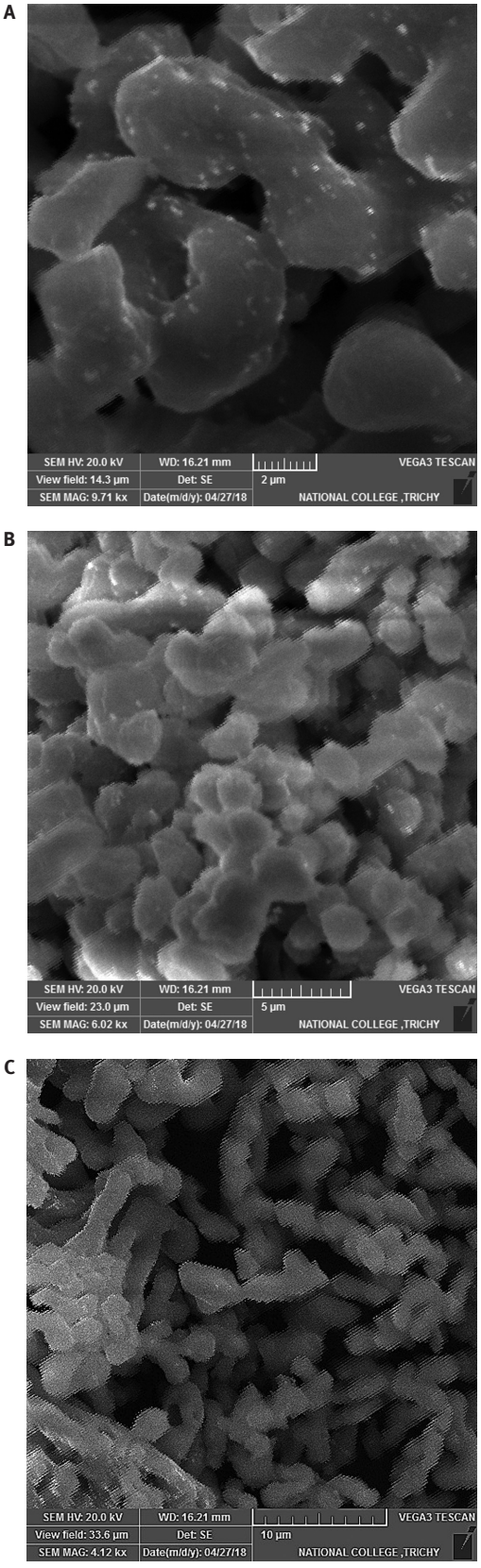


Figure 2: SEM images of calcined eggshells.
(a) 9.71kx magnification, (b) 6.02kx magnification, (c) 4.12kx magnification

catalyst appears to be in cane shape particles of size range between 2 µm-10 µm. Similar results are reported in literature by Niju et al. [23].

The elemental composition of calcined eggshells found by using Elemental Dispersive Spectroscopy (EDS) analysis is shown in Table 2. From these results, it is clear that huge amount of CaO is present in the prepared catalyst with 47.47 (w/w %) of oxygen and 48.70 (w/w %) of calcium, and small amounts of magnesium 0.65 (w/w %) and carbon 3.18 (w/w %) are also observed.

4.1.3 Fourier Transform Infrared Spectroscopy (FTIR)

The presence of different functional groups in calcined egg shells is identified by FTIR analysis and is presented in Figure 3. On calcination at 900°C, the calcium carbonate in the eggshells gets converted to calcium oxide. From the FTIR results, it is observed that for calcined egg shells, the major peaks were observed at wave numbers 3600 cm^{-1} which indicates the presence of hydroxyl groups with O-H stretch and the presence of C-O stretch at wavenumber 1100 cm^{-1} indicates the presence of alkoxy functional class. C≡C asymmetric stretch with the presence of alkenes functional groups was observed at wave number of 2000 cm^{-1}, peaks observed at wavenumbers 1800 cm^{-1}

Table 2: EDS analysis of the calcined eggshells.

Element	Weight %	Atomic %
C	3.18	5.91
O	47.47	66.33
Mg	0.65	0.60
Ca	48.70	27.16
Totals	100.00	

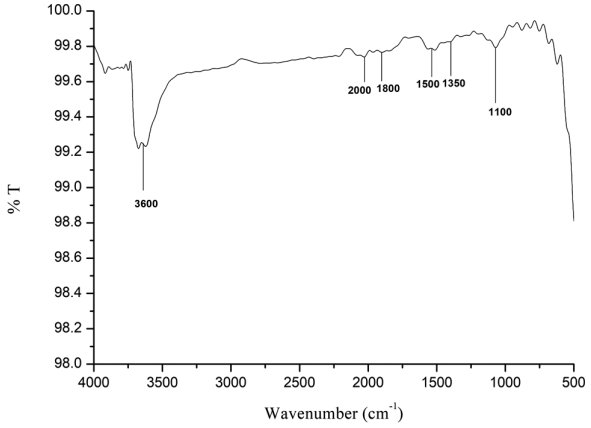


Figure 3: Fourier Transform Infrared Spectroscopy (FTIR) analysis of calcined eggshells.

and 1500 cm^{-1} indicate the presence of C=O stretch and C=O bands with carbonyl absorption respectively. C-F stretch with the presence of alkyl halides functional class is observed at wavenumber 1350 cm^{-1}.

5 Statistical analysis and modeling of formed biodiesel

5.1 Statistical analysis

Transesterification experiments were designed using Design Expert software 10.0 based on Central Composite Design (CCD) and are shown in Table 3. ANOVA analysis is reported in Table 4. From the ANOVA, it is clear that the molar ratio (mol/mol) is the most influencing factor when compared to catalyst quantity (wt%) and the reaction time (hours). It was also observed that with an increase in molar ratio beyond the optimized limit, conversion of biodiesel decreases gradually, and may lead to reversible reaction. The model terms are said to be significant if the p-value is less than 0.05, and from the Table 4 it is clear that the design model is significant, and also molar ratio is the significant variable when compared to other two variables. The consistency of model and the variance of output response can be explained by F-value of the model. If the value of F is more, the effect of that

Table 3: Design of transesterification experiment performed.

Run	A:Molar Ratio (mol/mol)	B:Catalyst (wt%)	C:Time (hours)	Experimental Response Conversion (%)	Predicted Response (RSM)	Predicted Response (ANN)
1	6	4	3	60	62.38	60
2	9	3	2	84.26	80.92	83.37
3	9	3	4	84.56	81.32	84.56
4	9	5	2	83.87	84.17	83.87
5	9	5	4	80.15	79.43	80.15
6	12	2	3	86.76	90.94	86.76
7	12	4	1	80.63	81.27	84.03
8	12	4	3	99.7	98.68	98.8
9	12	4	3	97	98.68	98.8
10	12	4	3	98	98.68	98.8
11	12	4	3	99.7	98.68	98.8
12	12	4	3	95.8	98.68	98.8
13	12	4	3	99.7	98.68	98.8
14	12	4	5	82.5	84.06	82.96
15	12	6	3	95	93.02	95
16	15	3	2	88.37	86.87	88.37
17	15	3	4	96.91	94.39	96.91
18	15	5	2	89.82	90.84	89.82
19	15	5	4	92.1	93.22	92.1
20	18	4	3	82.3	82.12	82.3

Table 4: ANOVA analysis for response (percentage conversion).

Source	Sum of Squares	DF	Mean Square	F Value	p-value Prob> F	
Model	1715.78	9	190.64	24.50	< 0.0001	significant
A-Molar Ratio	389.67	1	389.67	50.08	< 0.0001	
B-Catalyst	4.33	1	4.33	0.56	0.4730	
C-Time	7.76	1	7.76	1.00	0.3416	
AB	0.26	1	0.26	0.033	0.8588	
AC	25.35	1	25.35	3.26	0.1012	
BC	13.21	1	13.21	1.70	0.2218	
A^2	1097.68	1	1097.68	141.09	< 0.0001	
B^2	70.53	1	70.53	9.07	0.0131	
C^2	403.02	1	403.02	51.80	< 0.0001	
	R^2=0.9566					

particular variable on the output will be more. The Model F-value of 24.50 for the response implies that the model is significant, and it is also observed that the molar ratio is the most influencing factor on output response values with F-value of 389.67. The coefficient of determination R^2 value which shows positive predictive results with respect to output response is in the acceptable range of 0.9566. A complete design equation in terms of actual parameters is given in Eq. 3. This can be used to make predictions of the response for the given values of each factor. This is presented in Table 3.

$$\begin{aligned}\text{Conversion \%} = &-84.9526 + (17.2447 \times \text{Molar Ratio}) \\ &+ (17.0541 \times \text{Catalyst}) \\ &+ (22.7381 \times \text{Time}) \\ &+ (0.06 \times \text{Molar Ratio} \times \text{Catalyst}) \\ &+ (0.593333 \times \text{Molar Ratio} \times \text{Time}) \\ &- (1.285 \times \text{Catalyst} \times \text{Time}) \\ &- (0.734154 \times \text{Molar Ratio}^2) \\ &- (1.67489 \times \text{Catalyst}^2) \\ &- (4.00364 \times \text{Time}^2)\end{aligned} \tag{3}$$

5.1.1 Effect of influencing factor on conversion to biodiesel

Based on the above results, two-dimensional contour plots and three-dimensional response plots are obtained and shown in Figures 4a-c and Figures 5a-c respectively. From these plots, it was observed that for an increase in the molar ratio (mol/mol) beyond the optimized point, a decrease in percentage conversion is observed. As far as heterogeneous catalysts are concerned, more methanol: oil ratio is required when compared to homogeneous catalyst reactions in biodiesel production. Girish et al. utilized clam shells as heterogeneous catalysts for biodiesel production from waste cooking oil at a methanol: oil ratio of 18:1 [24]. Biodiesel production from RSO using waste cockles as heterogeneous catalyst is obtained at a higher molar ratio of 16:1 [30]. This indicates that the most influencing process parameter is the molar ratio (mol/mol) when compared to the other two variables. High conversion of 99.7% was observed at optimized values of molar ratio 12:1, catalyst 4 wt% and reaction time of 3 h.

5.2 ANN-model

A simple mathematical computation of human brain function with a well-trained neural network containing

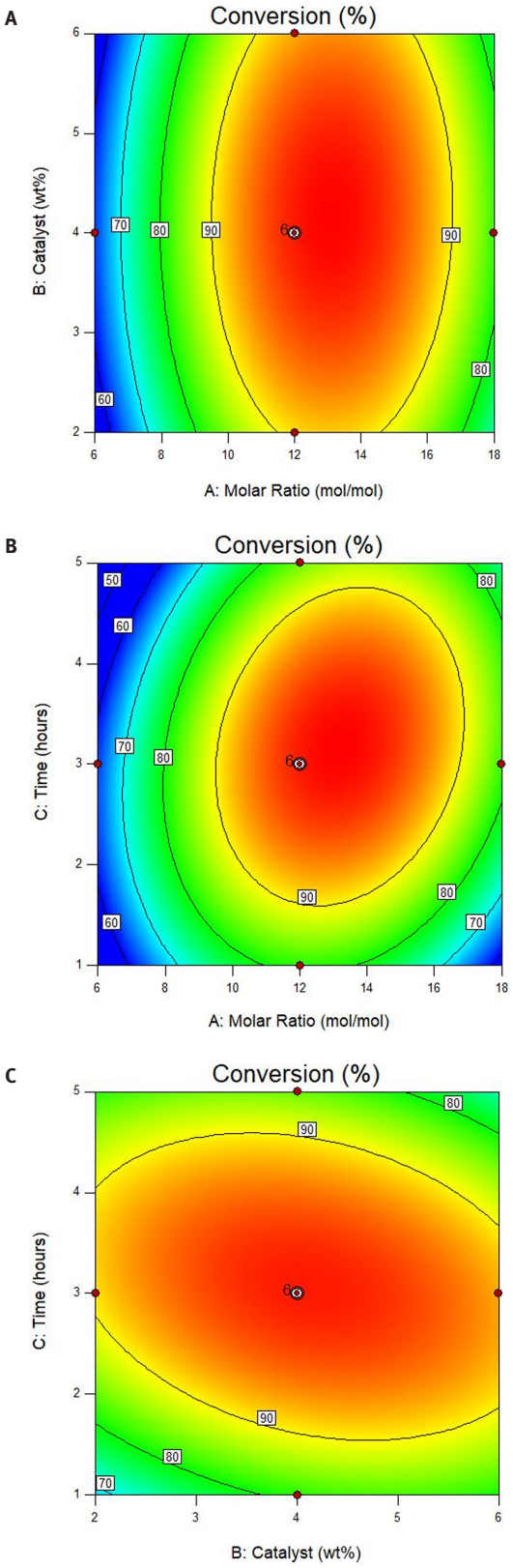


Figure 4: Contour plots of process parameters affecting Biodiesel Conversion%.
(a) Molar Ratio (mol/mol) vs Catalyst (wt%); (b) Catalyst (wt%) vs Time (hours); (c) Molar Ratio (mol/mol) vs Time (hours).

several neurons in it is called ANN. ANN is completely based on the input data given for network training [32]. Figure 6 shows the architecture of the ANN model with a single input layer, one hidden layer with 10 neurons which appear like biological neurons of human brain and an output layer. The main function of neurons in hidden layer of neural network is to build complicated relationship between input and output layers. From the Figure 6, it is observed that the input layer distributes all the three inputs to weights of the hidden layer. Neurons present in hidden layer of neural network receive information from the input layer linked to weight factor to form a desired output. At first, the output of the first hidden layer was computed which acts as input to the next hidden layer and continues consecutively to form a well desired output of complete network. In Figure 6, Methanol: Oil molar ratio, catalyst (wt%), and reaction time (hrs) are the three selected inputs. Minimum error is found from design table between the predicted and experimental outputs by training the network several times which is known as the transformation of weights in the network. Regression value, R, which is a measure of correlation between desired inputs and outputs, with value close to 1 concludes a good relationship, with value 0 as a random relationship. From Figure 7 it is

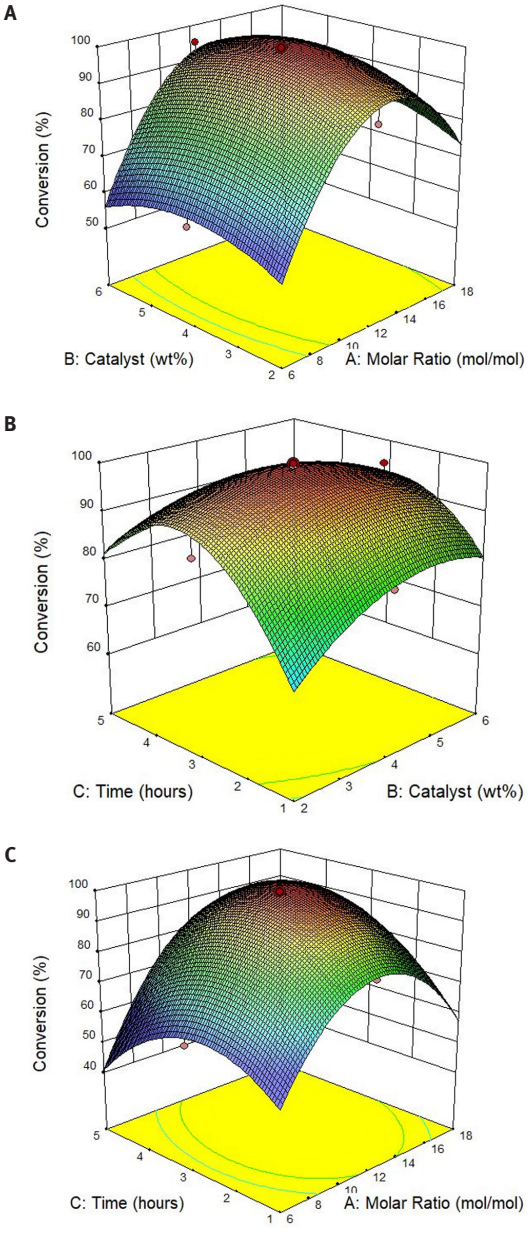


Figure 5: 3D-Surface Plots of process parameters affecting Biodiesel Conversion%.
(a) Molar Ratio (mol/mol) vs Catalyst (wt%); (b) Catalyst (wt%) vs Time (hours); (c) Molar Ratio (mol/mol) vs Time (hours).

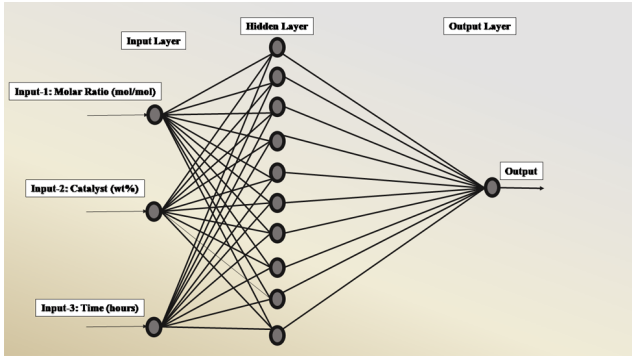


Figure 6: Architecture for ANN model.

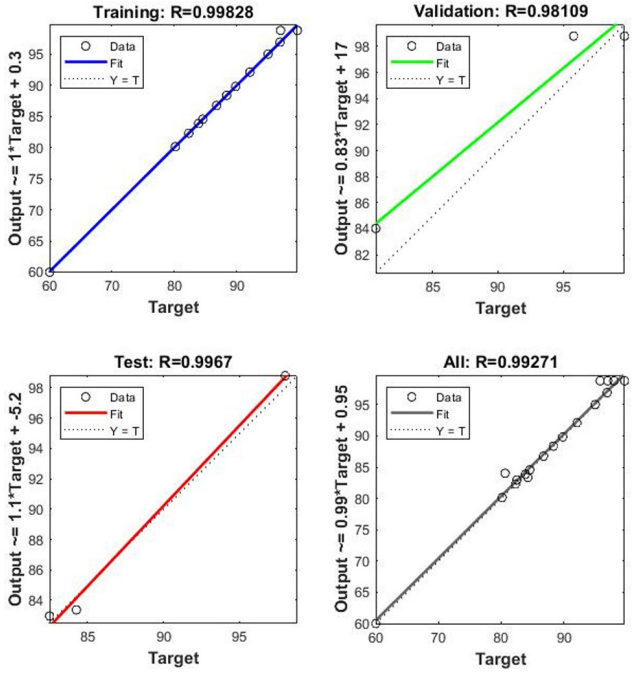


Figure 7: Regression plot for ANN model of Biodiesel Conversion%.

clear that R values of 0.99828, 0.98109, 0.9967, 0.99271 for training, validation, test and all respectively show a good relationship for the model. The mean square error (MSE) value of 1.3929 for the overall design is calculated as mentioned in Eq. 2. The summary of ANN Modeling is shown in Figure 8 along with performance plot in Figure 9.

5.3 Comparison of RSM and ANN

The efficiency of the model is explained by the coefficient of determination R^2 value, which is observed to be 0.9976 for ANN model and 0.9566 for RSM. Relationship between predicted and actual experimental values is shown in Figures 10 and 11 for RSM and ANN respectively. By comparing the above results, it is concluded that the ANN is a better model for finding the conversion of RSO to biodiesel when compared with RSM.

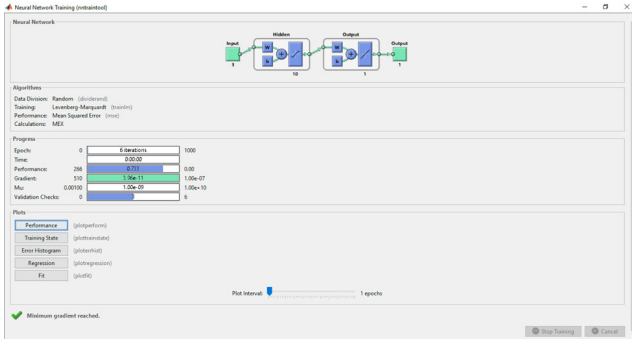


Figure 8: Summary of ANN modeling.

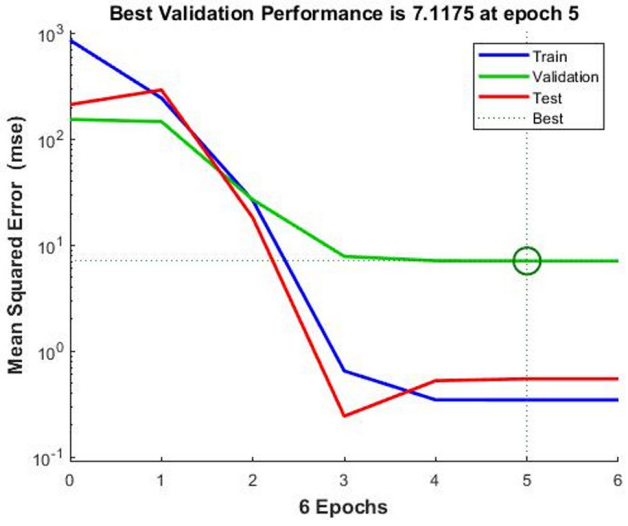


Figure 9: ANN performance plot of Biodiesel Conversion%.

6 Characterization of biodiesel formed

6.1 Physico-chemical properties of prepared biodiesel

The properties like acid number, density, viscosity, the flashpoint were calculated for the biodiesel prepared in this study, and compared with the literature values for biodiesel prepared from RSO using other catalysts and are presented in Table 5. The properties of biodiesel synthesized are found to agree well with the standard ASTM values.

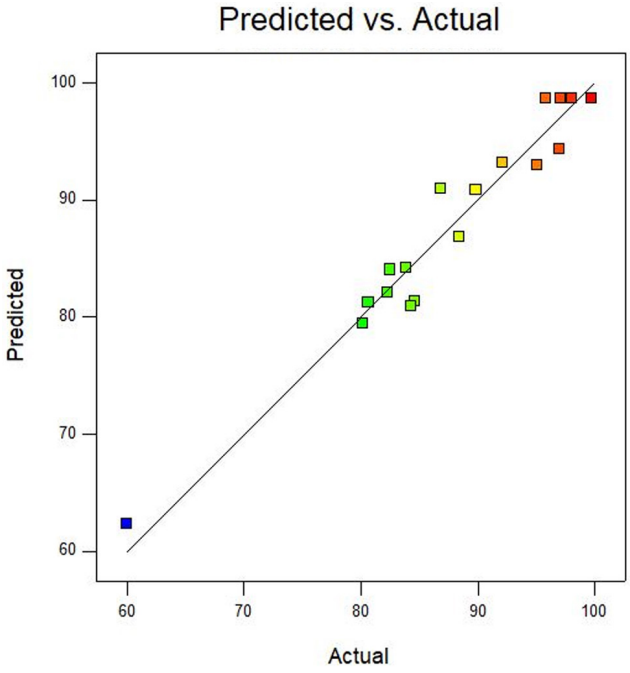


Figure 10: Actual Biodiesel Conversion% (X-Axis) vs Predicted Biodiesel Conversion% (Y-Axis) – RSM.

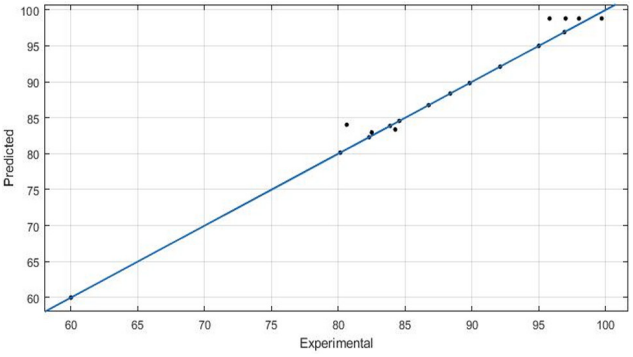


Figure 11: Actual Biodiesel Conversion% (X-Axis) vs Predicted Biodiesel Conversion% (Y-Axis) – ANN.

6.2 ^{1}H-Nuclear Magnetic Resonance (NMR) spectroscopic analysis

The conversion of fats to fatty acid methyl esters (biodiesel) was determined by using ^{1}H-NMR analysis. The ^{1}H-NMR spectrum of the biodiesel synthesized is shown in Figure 12. Formation of methoxy protons of methyl esters at 3.6 ppm and α-methylene protons of methyl esters at 2.3 ppm in NMR spectrum indicates the formation of biodiesel. Equation 4 was used for calculating the conversion of esterified oil to biodiesel [23]. From the Figure 12, the formation of methoxy protons of methyl esters at 3.6 ppm and α-methoxy protons of methyl esters at 2.3 ppm is observed. 99.7% of RSO was converted to biodiesel at optimum process conditions of 12:1 molar ratio (mol/mol), 4 (wt%) catalyst and reaction time of 3 h. A comparison of conversion achieved with RSO in the present work with the values reported in literature for RSO using other catalysts is shown in Table 6. From this table, it is clear that biodiesel produced from RSO using eggshells as catalyst gives a higher conversion when compared to the other works reported in literature.

$$\textbf{Conversion \%} = \frac{2 \times A_{ME}}{3 \times A_{\alpha-CH_2}} \quad (4)$$

$A_{ME} \rightarrow$ *Integration value of methoxy protons of formed methyl esters*

$A_{\alpha\text{-}CH_2} \rightarrow$ *Integration value of* α *– methylene protons*

6.3 Fourier Transform Infrared (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) analysis was performed to determine the various functional groups present in the biodiesel and is shown in Figure 13. Carboxylic acids and derivatives functional compounds with C-H stretch are detected at wavenumber 2923 cm^{-1}. Ester functional group with C=O stretch was observed at wave number 1717 cm^{-1}. O=C-O-C stretch at wave

Table 5: Comparison of physico-chemical of biodiesel in literature with the properties of biodiesel synthesized in the present study.

Properties	Acid value (mg KOH/g oil)	Specific gravity	Kinematic viscosity (30°C) (mm²/s)	Flash point (°C)
ASTM standard values	<0.6	0.86-0.90	1.9-6.0	100-170
A.S Ramadhas et al. (Feedstock- Rubber Seed Oil) [35]	0.118	0.874	5.81	130
Junaid Ahmad et al. (Feedstock- Rubber Seed Oil) [39]	0.42	0.885	3.89	152
Ahmad Hussain et al. (Feedstock- Rubber Seed Oil) [33]	0.07	0.87	4.64	154.6
Mahbub Morshed et al. (Feedstock- Rubber Seed Oil) [10]	0.12	0.85	4.5	120
Present Work	0.26	0.88	4.49	140

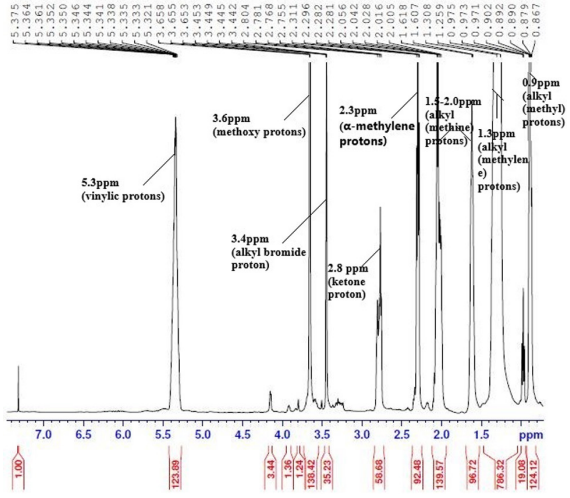


Figure 12: ^{1}H-NMR spectrum analysis of rubber seed oil biodiesel.

Table 6: Comparison of percentage conversion of formed biodiesel with various other catalysts using rubber seed oil.

Feedstock	Catalyst used	Conversion %	Reference
Rubber Seed Oil	Eggshells	99.6	Present Work
Rubber Seed Oil	NaOH	98	A.S Ramadhas et al. [35]
Rubber Seed Oil	Clinker	96.80	Ahmad Hussain et al. [33]
Rubber Seed Oil	KOH	96.8	Junaid Ahmad et al. [39]
Rubber Seed Oil	Waste Cockles shells	88.06	M. M. Zamberi et al. [30]
Rubber Seed Oil	H_2SO_4	98	Mahbub Morshed et al. [10]
Rubber Seed Oil	Activated cement clinker	96.9	Jolius Gimbun et al. [40]

number 1183 cm^{-1} indicates the presence of aliphatic esters in the synthesized biodiesel. S-OR esters functional group at a wavenumber of 704.86 cm^{-1} was also observed.

6.4 Gas Chromatogram-Mass Spectroscopy (GC-MS) analysis

Composition of prepared biodiesel was found by using GC-MS (TIC) analysis. 436-GC Bruker and TQ Quadrupole Mass Spectrometer were used for analysis. The column used for GC programme was BR-5MS (5% Diphenyl / 95% Dimethyl poly siloxane), 30m x 0.25mm ID x 0.25µm df. Software which was used to analyze the sample is MS Work Station 8. NIST Version-2011 is the library used for MS programme. Table 7 shows the list of compounds in the prepared biodiesel, and Figure 14 shows the gas chromatogram of biodiesel produced from RSO. An effective comparison of formed biodiesel composition with various other feedstocks used in literature is reported in Table 8, and it is clear from the table that around 99% of biodiesel is formed in the present work.

7 Conclusion

Optimization and modeling of process parameters for biodiesel production from RSO using solid waste catalyst, eggshells, by transesterification was done both by RSM and ANN. 99.7% conversion of RSO to biodiesel was observed at process conditions of 12:1 methanol to Oil molar ratio (mol/mol), 4 (wt%) catalyst and 3 h of reaction time and for the quadratic model, the value of R^2 was equal to 0.9566 by RSM. With ANN model, on training the neural network several times, a regression value of R^2 equal to 0.9976 was obtained. On comparison of R^2 values achieved from both the models and the error between experimental and predicted outputs in overall design, it is concluded that ANN is a better model for predicting the conversion of RSO to biodiesel. It is also observed from the overall design; the molar ratio (methanol: oil) is the most influencing factor for the conversion of RSO to biodiesel.

Table 7: List of compounds identified in biodiesel prepared.

Retention time	Name of the compound	Molecular formula	Molecular weight
3.87	Octanoic acid, methyl ester	$C_9H_{18}O_2$	158
9.89	Dodecanoic acid, methyl ester	$C_{13}H_{26}O_2$	214
10.22	Nonanedioic acid, dimethyl ester	$C_{11}H_{20}O_4$	216
12.33	Methyl tetradecanoate	$C_{15}H_{30}O_2$	242
14.70	Hexadecanoic acid, methyl ester	$C_{17}H_{34}O_2$	270
16.95	9,12-Octadecadienoic acid (Z,Z)-, methyl ester	$C_{19}H_{34}O_2$	294
17.05	9-Octadecenoic acid (Z)-, methyl ester	$C_{19}H_{36}O_2$	296
17.39	Methyl stearate	$C_{19}H_{38}O_2$	298
19.88	Cyclopropanepentanoic acid, 2-undecyl-, methyl ester, trans-	$C_{20}H_{38}O_2$	310
20.28	Hexadecanoic acid, 14-methyl-, methyl ester	$C_{18}H_{36}O_2$	284

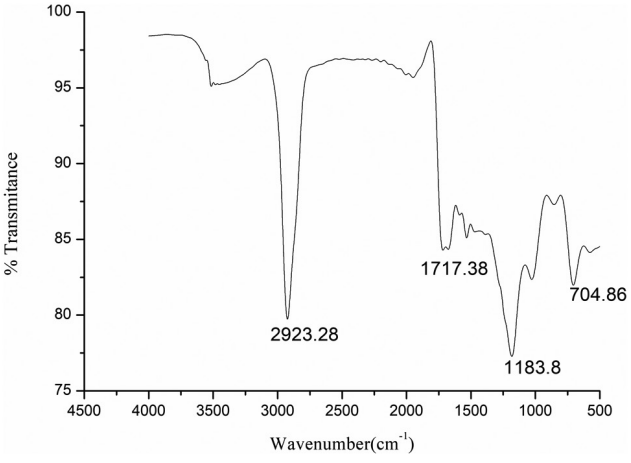


Figure 13: Fourier Transform Infrared Spectroscopy (FTIR) analysis of formed biodiesel.

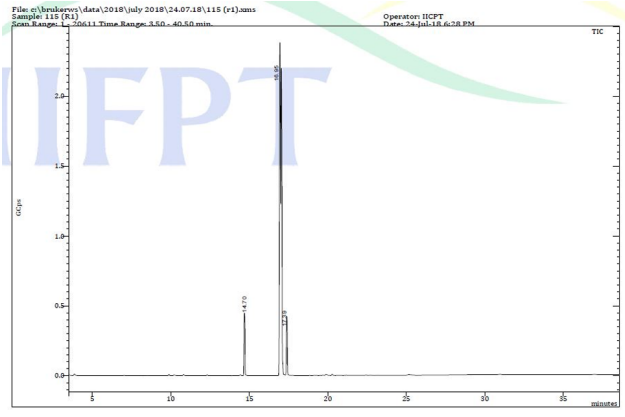


Figure 14: Gas Chromatogram- Mass Spectroscopy (GC-MS) analysis of formed biodiesel.

Table 8: Comparison of biodiesel composition with various other feed stocks in literature.

Compound name	Present work (rubber seed oil) (catalyst: waste eggshells) [%]	Sneha et al. (waste cooking oil) (catalyst: KBr/CaO) [%] [41]	Natarajan Girish et al. (waste frying oil) (catalyst: white bivalve clam shells) [%] [24]	Hanny Johanes Berchmans et al. (Jatropha curcas oil) (catalyst: NaOH) [%] [42]	Medy C. Nongbe et al. (palm oil) (catalyst: sulfonated graphene catalyst) [%] [43]
Octanoic acid, methyl ester	0.19	–	0.10	–	–
Dodecanoic acid, methyl ester	0.11	–	–	0.06	0.21
Nonanedioic acid, dimethyl ester	0.11	–	–	–	
Methyl tetradecanoate	0.08	–	0.14	0.10	0.56
Hexadecanoic acid, methyl ester	7.91	36.79	8.06	14.96	34.43
9,12-Octadecadienoic acid (Z,Z)-, methyl ester	45.36	5.03	0.22	47.43	7.03
9-Octadecenoic acid (Z)-, methyl ester	38.38	52.55	–	32.49	49.22
Methyl stearate	7.57	3.46	–	3.85	6.18
Cyclopropanepentanoic acid, 2-undecyl-, methyl ester, trans-	0.14	–	–	–	–
Hexadecanoic acid, 14-methyl-, methyl ester	0.15	0.34	–	–	–

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