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Acid value optimization of calcined eggshells catalyzed biodiesel produced from rubber seed oil – A response surface methodology (RSM) approach

Sai Bharadwaj A V S L[1], Niju Subramaniapillai[2], Khadhar Mohamed Meera Sheriffa Begum[1]
& Anantharaman Narayanan*,[1]

[1]Department of Chemical Engineering, National Institute of Technology-Tiruchirappalli, India
[2]Department of Biotechnology, PSG College of Technology, Coimbatore, Tamilnadu, India.
Corresponding Author: [1*]Department of Chemical Engineering, National Institute of Technology-Tiruchirappalli, Tamilnadu 620 015, India

E-mail: naraman@nitt.edu

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Optimization of acid value in biodiesel production from high viscous rubber seed oil (RSO) using solid waste eggshells has been studied. A gradual reduction in acid value from 67.6 (mg KOH/ g oil) to 0.26 (mg KOH/ g oil) was observed in the synthesized biodiesel at the optimum process conditions of 12:1 methanol: oil molar ratio, 4 (wt %) catalyst concentration and 3hours of reaction time. Process parameter optimization was performed using a well organized optimization tool namely response surface methodology (RSM). It is also observed that molar ratio (mol/mol) and reaction time (h) are the more significant process parameters on the final product. Coefficient of determination R^2 value of 0.9335 observed from RSM analysis, signifies a minimum error between experimental and predicted responses.

Keywords: Acid value, Rubber Seed Oil (RSO), Response Surface Methodology (RSM), Biodiesel

Demand for eco-friendly alternate fuels is growing day by day because of depletion of not only fossil fuels, but also due to environmental degradation caused by fossil fuels[1]. Coal, crude oil and natural gas are the three main sources of fossil fuels which take care of most of our energy requirements. Due to rise in energy demand by 2040 globally, there is likely to be a depreciation in coal reserves by 2112 and depreciation of crude oil reserves by 2042[2]. Hence, there is a need to look beyond fossil fuels to meet our energy requirements. A Renewable, biodegradable, non-toxic and clean fuel for the global environment called biofuels are among the best substitutes for fossil fuels[3,4]. Energy security and socio-economic issues related to rural sector are some of the advantages of using biofuels over conventional fuels[5]. Three different generations of biofuels namely first, second and third generations are well explained in many research works[4]. These three generations of biofuels are classified based on the feedstock used for biofuel preparation. The biofuels which are prepared from food crops developed in cultivable lands are called first-generation biofuels. Sugar, starch, vegetable oils obtained from these crop fields are the main feedstocks used for the production of first generation biofuels. Transesterification is the process proposed by many scientists for preparing these first generation fuels (biodiesel). The first generation feedstock which also comprises various edible oils, have been used extensively for biodiesel production[6,7]. Most commonly used edible oils are sunflower oil[8,9], soyabean oil[10,11], canola oil[12,13], cotton oil[14], pumpkin oil[15], peanut oil[16], rapeseed oil[17], palm oil[18], and corn oil[19]. Focus towards increasing agricultural land, biodiversity loss, leaching of nutrients, applications towards food and food products results in greater demand for first generation feedstock which also includes edible oils. This is a major drawback in using the first generation feedstocks in biofuels production[4,20]. Agricultural residue, forest residue, aquatic biomass etc are the feedstock used for the second generation biofuels. Physical conversion, thermo chemical conversion and hydrotreating of oils are the proposed technologies for the preparation of second generation biofuels[4,21]. Biohydrogen, Biomethanol, dimethylfuran, Fischer-Tropsch diesel, and mixed alcohols are the other second generation fuels which are still under development[20]. Biofuels prepared from microalgae using anaerobic digestion process are called as third generation biofuels which are not expected to go commercial till 2050[4,20,22]. Due to more commercial applications of first generation feedstocks like edible oils for human life, their usage in biodiesel preparation is not advisable[23]. Utilization of second generation feedstocks i.e., non-edible oils derived from biomass seeds over edible oils is more significant now a days for the production of biodiesel by transesterification[2]. The most commonly used non-edible oils are Jatropha[23], pongamia pinnata[24], rubber seed oil[25,26] and waste frying oil[27,28]. Many research works reported on how much amount of respective feedstock converted to biodiesel in presence of a catalyst, only bounded amount of research work was conducted on minimization of acid value in biodiesel production[29]. Hence, the present study mainly focused on minimization of acid value in biodiesel production from second generation feedstock, rubber seed oil (RSO), in presence of solid waste eggshells as catalyst using transesterification procedure. Process parameters optimization such as methanol: oil molar ratio (mol/mol), catalyst concentration (wt %) and reaction time (h) is also studied using a well renowned optimization tool namely response surface methodology (RSM).

Materials and Methods

RSO used was purchased from Virudhunagar, Tamilnadu, and Methanol was supplied by CDH suppliers, New Delhi, India.Eggshells were collected from a nearby restaurant in Trichy, Tamilnadu.

Catalystpreparationand characterization

Preparation and characterization of calcium oxide derived from raw eggshells was well explained in our previous studies cited in literature[29].

Physico-chemical characteristics of raw rubber Seed Oil (RSO)

As reported in our earlier works[29] acid value (mg KOH/g oil), specific gravity, kinematic viscosity (mm^2/sec) are the measured physico-chemical characteristics of raw RSO and the data is reported in Table 1, which signifies that the acid value and viscosity of raw RSO are slightly higher. Carbon deposition, engine fouling and partial combustion are the three main disadvantages of using high viscous and acid value feedstocks directly into diesel engine[30].

Biodiesel production

The acid value of raw RSO was observed to be 67.6 mg KOH/g oil (shown in Table 1), which leads to soap formation while working on transesterification process. Acid pretreatment process has been adopted to reduce the acid value content of raw RSO to the required limit for biodiesel production. This process is performed at 65°C, maintained with the help of constant temperature water bath in the presence of sulphuric acid (98% concentrated) as the acid catalyst to minimize the acid value of feedstock. Acid value of pre-treated oil reduced to 2.97 (mg KOH/ g of oil) which was observed at optimized esterification reaction conditions of 15:1 methanol: oil molar ratio, 3 (vol %) acid catalyst, and 2 h of reaction time. The treated oil is prepared at these operating conditions for all further transesterification experiments[29].

Table 1 — Physico-chemical properties of raw rubber seed Oil (RSO)

Property	Raw oil (Present work)
Acid number (mg KOH/g oil)	67.6
Viscosity (mm^2/s)	65.98
Specific gravity	0.91

Biodiesel preparation by transesterification of treated oil is carried out in the presence of CaO derived from raw eggshells, operated at a temperature close to methanol boiling point temperature in a constant temperature water bath. The formed product after the complete reaction was transferred to a separating funnel and kept aside for the separation of fatty acid methyl ester (FAME) and by-product glycerol. From the FAME obtained excess methanol was removed using rotary evaporator[27]. Titration method with 0.1N KOH solution is used to measure the acid value of the synthesized biodiesel and is calculated by using Equation (1)[27].

$$\text{Acid Value} = \frac{0.1\text{N}_{\text{KOH solution}} \times \text{Molecular Weight}_{\text{KOH}} \times (\text{V}_\text{i} - \text{V}_\text{f})}{\text{Weight of Oil}} \quad \dots (1)$$

where V_f = final burette volume, V_i = Initial Burette volume, N = Normality of potassium hydroxide solution

Optimization of process parameters

Process parameter optimization is the most important aspect to be considered in biodiesel production. Response Surface Methodology (RSM) is a well defined optimization tool is used to work on optimization process in a simple manner.The main factors that affect the feedstock (oil) conversion to biodiesel are:

- Methanol: Oil (molar Ratio) (mol/mol).
- Catalyst Concentration (wt %).

- Reaction Time (h)
- Reaction Temperature (°C).

Optimization of methanol: oil (molar ratio) (mol/mol)

Molar ratio is one of the most important factors that affect the feedstock (oil) conversion to biodiesel. As per the stoichiometry of transesterification reaction 1 mole of oil reacts with 3 moles of alcohol to produce biodiesel. Use of excess alcohol is well preferred in biodiesel preparation by many researchers to ensure maximum conversion of oil to biodiesel[29]. Increase in biodiesel conversion can be observed with increase in molar ratio and it reaches the optimum value. Beyond the optimum molar ratio, the product formed may remain stable or it may decrease which is due to reverse action of transesterification reaction mechanism. Optimum value of molar ratio depends on type of catalyst used for experiment. For homogeneous catalysts the range of methanol: oil ratio obtained will be in the range of 6:1 to 9:1[30], whereas for heterogeneous catalysts molar ratio range can be in the range of 9:1 to 18:1[27] respectively.

Optimization of catalyst concentration

Catalyst concentration also plays an important role in biodiesel production. Favourable amount of catalyst concentration must be used in biodiesel production process. Complete conversion of feedstock (oil) to biodiesel may not take place by using low amount of catalyst concentration[29]. Many research works state that the optimum catalyst concentration range for homogeneous base catalysts can be observed in the range of 0.5 (wt %) to 1.5 (wt %)[30] and a slightly high catalyst concentration can be observed while working with heterogeneous catalysts in biodiesel preparation[31]. Beyond the optimum amount of catalyst concentration, the percentage conversion may reach the equilibrium point which is due to the presence of hindering active sites in catalyst selected[27]. Numerous research works have been performed by using homogeneous solid base catalysts in biodiesel production. Use of calcium derived from solid waste eggshells as heterogeneous catalyst is the latest attempt presented in this work.

Optimization of reaction time

Variation of reaction time in biodiesel preparation is yet another important factor to be optimized. Slow reaction between the oil and alcohol can be observed initially; upon increase in reaction time a gradual increase in feedstock (oil) conversion to biodiesel was observed and it reaches a maximum value[27,29]. Beyond this point of reaction time a gradual decrease in feedstock (oil) conversion to biodiesel can take place which is due to the hydrolysis of ester formed which would result in the formation of fatty acids further leading to soap formation[27]. Lesser reaction time can be observed while using homogeneous catalysts, whereas while using heterogeneous catalyst more reaction time is required for biodiesel formation[31,32].

Optimization of reaction temperature

Another important parameter to be considered in biodiesel preparation process is the reaction temperature. Literature also cites that the yield of biodiesel formed is maximum for different feed stocks at a temperature of 65°C while using methanol for transesterification process[27]. Hence, studies on optimization of reaction temperature are not carried out in this study, and it was preferred to run all the transesterification experiments at boiling point close to that of methanol. Rise in temperature beyond the boiling point of alcohol leads to vaporization of it and will end with no final product formation[33,34].

Design of Experiments (DOE)

DOE version 10 (software) has been used to design the acid value optimization experiments of biodiesel produced from RSO and is represented in Table 2.

Response surface methodology (RSM) optimization

Analysis of Variance (ANOVA) has been developed from RSM analysis to determine the most influencing parameter on the response and also to find the sensitivity of the suggested model, and the pictorial explanation of most affecting parameter on the response is shown by two dimensional contour plots and three dimensional surface plots obtained from ANOVA. A second order quadratic model as shown in Equation-2 can be used to predict the response of the complete design.

Table 2 — Range of coded factors 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

$$\text{Predicted Response} = H_0 + H_1[A] + H_2[B] + H_3[C] + H_{12}[AB] + H_{13}[AC] + H_{23}[BC] + H_{11}[A^2] + H_{22}[B^2] + H_{33}[C^2] \quad \ldots (2)$$

Where, $H_0 \rightarrow$ intercept; $H_1, H_2, H_3,\ H_{11}, H_{22}, H_{33} \rightarrow$ linear and quadratic constant coefficients; $H_{12}, H_{13}, H_{23} \rightarrow$ interaction constant coefficients

A, B and C are the process parameters shown in Table 3 with coded factors which are to be optimized.

Uncertainty Error Analysis

A characteristic parameter which is analogous to the deviations in experiments performed is called uncertainty error analysis[35]. Three different deviations of 5%, 10% and 15% are calculated for both upper bound and lower bound cases of the optimum conditions of process parameters.

Result and Discussion

Catalyst characterization

Entire results observed for characterization of synthesized catalyst are well explained in our previous studies cited in literature[29].

RSM optimization

Complete experimental design carried out is shown in Table 3. ANOVA analysis of the complete design is presented in Table 4, from which it is observed that the suggested quadratic model (shown in Equation 2) for overall design is significant with F-value of 15.60. It is also observed from the Table 4 that molar ratio is the most influencing process variable with F-value of 6.27. Coefficient of determination R^2 value of 0.9335 is observed to be in acceptable range. Predicted responses of the complete design are calculated by Equation 3.

Optimization of process parameters

Figure 1 (3D-surface plots) shows the graphical representation of the effect of process parameters on the final response. From these plots, it is observed that the most significant process variables on acid value optimization are methanol to oil molar ratio (mol/mol) and reaction time (hours). Beyond the optimized level on increasing the molar ratio and reaction time a gradual rise in acid value is observed which may be due to reverse reaction of transesterification process, and also longer reaction time drives to hydrolysis of esters and leads to soap formation. The acid value of 0.26 (mg KOH/ g oil) for synthesized biodiesel is observed at the optimized values of 12:1 methanol: oil molar ratio (mol/mol), 4 (wt %) catalyst and a reaction time of 3 hours. Acid value of prepared biodiesel is observed to be well within the limit of standard ASTM values as shown in Table 5. Figure 2 explains about the error between experimental and predicted acid values observed in the form of coefficient of determination R^2-value. In this study R^2-value was observed to be 0.9335, which signifies

Table 3 — Complete Design of Biodiesel Preparation experiments Performed

A:Molar ratio mol/mol	B:Catalyst wt%	C:Time hours	Acid value (Experimental response) mg KOH/g oil	Acid value (RSM)(Predicted response) mg KOH/g oil
12	2	3	0.4	0.36
15	5	2	0.55	0.48
9	5	2	0.4	0.34
12	4	3	0.22	0.26
15	3	2	0.53	0.49
15	5	4	0.49	0.45
9	3	2	0.54	0.55
15	3	4	0.26	0.28
12	6	3	0.26	0.32
12	4	3	0.25	0.26
12	4	3	0.26	0.26
12	4	3	0.28	0.26
12	4	3	0.33	0.26
6	4	3	0.8	0.78
9	3	4	0.53	0.56
12	4	3	0.22	0.26
9	5	4	0.53	0.53
12	4	1	0.49	0.54
18	4	3	0.6	0.64
12	4	5	0.56	0.52

Table 4 — ANOVA analysis for Acid value optimization

Source	Sum of squares	Degree(s) of freedom	Mean Square	F- Value	p-value Prob > F	
Model	0.46	9	0.051	15.60	< 0.0001	Significant
A-Molar ratio	0.020	1	0.020	6.27	0.0313	Significant
B-Catalyst	1.806E-003	1	1.806E-003	0.56	0.4725	
C-Time	3.062E-004	1	3.062E-004	0.094	0.7648	
AB	0.019	1	0.019	5.87	0.0359	
AC	0.025	1	0.025	7.81	0.0190	
BC	0.015	1	0.015	4.72	0.0548	
A^2	0.32	1	0.32	97.79	< 0.0001	Significant
B^2	9.830E-003	1	9.830E-003	3.03	0.1122	
C^2	0.12	1	0.12	36.43	0.0001	Significant
		R^2 =0.9335				

Table 5 — Physico-Chemical Properties of Synthesized Biodiesel

Properties	ASTM Standard values	Present work	A.S Ramadhas *et al*.	Junaid Ahmad *et al*.	Ahmad Hussain *et al*.
Acid value (mg KOH/g oil)	<0.6	0.26	0.114	0.42	0.07
Kinematic viscosity (mm^2/sec)	1.9-6.0	4.49	5.81	3.89	4.64
Specific gravity	0.86-0.90	0.88	0.874	0.885	0.87
Calorific value (MJ/kg)	-	33.94	36.50	-	39.37

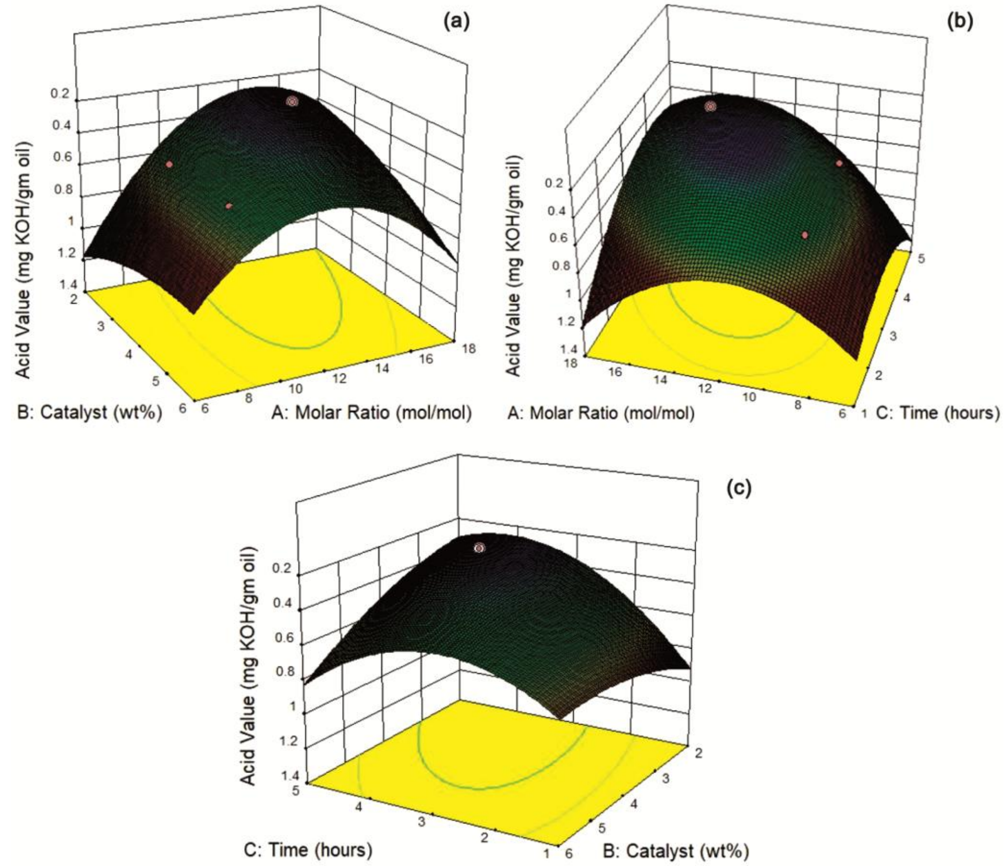

Fig. 1 — 3D plots of Acid Value Response [(a) Molar Ratio vs Catalyst (wt %); (b) Molar Ratio vs Time (hours) and (c) Catalyst (wt%) vs Time (hours)]

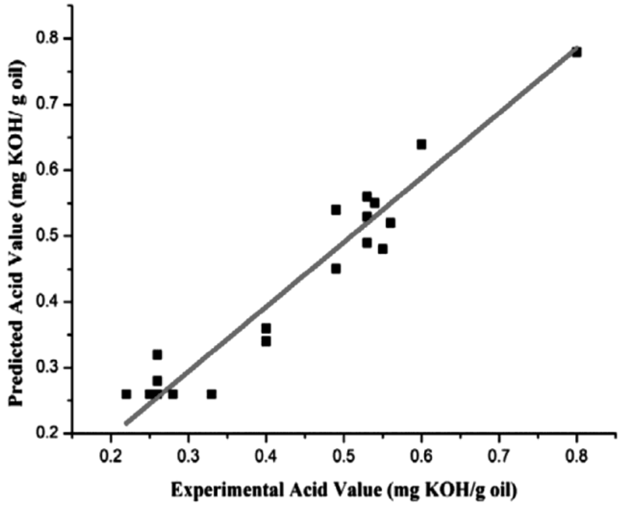

Fig. 2 — Experimental Acid Value (mg KOH/g Oil) (vs) Predicted Acid Value (mg KOH/g Oil) (RSM)

that a minimum error is present between the experimental and predicted responses.

$$\begin{aligned}\text{Acid Value} &= +3.82210 - (0.32002 \times \text{Molar ratio}) \\ &- (0.49506 \times \text{Catalyst}) - (0.36551 \times \text{Time}) \\ &+ (0.016250 \times \text{Molar ratio} \times \text{Catalyst}) \\ &- (0.018750 \times \text{Molar ratio} \times \text{Time}) \\ &+ (0.043750 \times \text{Catalyst} \times \text{Time}) \\ &+ (0.012475 \times \text{Molar ratio}^2) \\ &+ (0.19773 \times \text{Catalyst}^2) + (0.068523 \times \text{Time}^2) \qquad \ldots (3)\end{aligned}$$

Uncertainty Error Analysis

In this study the error analysis was performed for the optimum process conditions of 12:1 methanol: oil molar ratio, 4 (wt %) catalyst concentration and 3h of reaction time at 5%, 10% and 15% deviations respectively and the results were reported in Figure 3

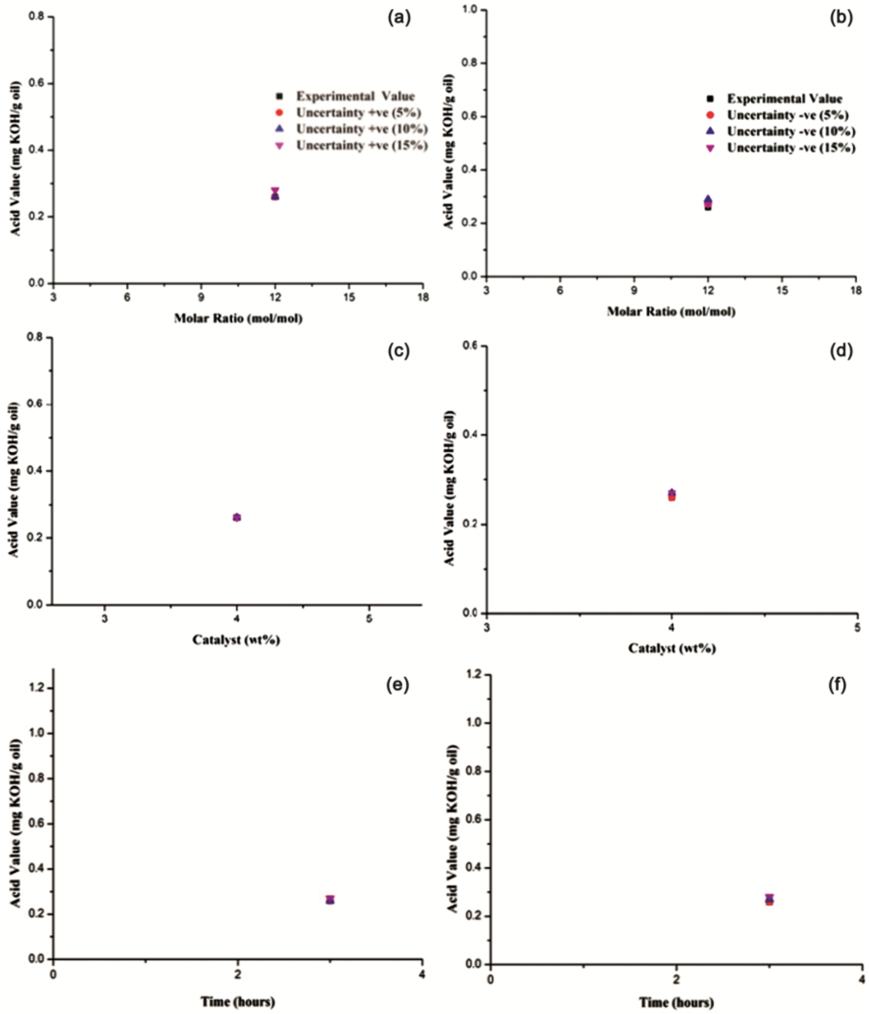

Fig. 3 — Uncertainty Error Analysis for Acid Value Optimization of Biodiesel Prepared using Calcined Eggshells as Catalyst [(a) Effect of Molar Ratio (+ve) uncertainty; (b) Effect of Molar Ratio (-ve) uncertainty; (c) Effect of Catalyst (+ve) uncertainty; (d) Effect of Catalyst (-ve) uncertainty; (e) Effect of Time (+ve) uncertainty and (f) Effect of Time (-ve) uncertainty]

(A-F). All the uncertainty runs are performed for both upper bound and lower bound cases. An error of almost equal to zero in all the process parameters cases is observed for both the upper and lower bound uncertainty runs.From the observed error analysis, it is concluded that there is no error for any small deviations in optimum process parameter conditions.

Conclusions

Acid value optimization in biodiesel production from high viscous rubber seed oil using solid waste eggshells as heterogeneous catalyst has been studied. A well defined optimization tool namely response surface methodology (RSM) was used for process parameter optimization in this study. It is concluded that the initial acid value of 67.6 (mg KOH/g oil) which was reduced to 2.97 (mg KOH/g oil) by pre-treatment with acid catalyst (at optimum process conditions 15:1 methanol: oil molar ratio, 3 (vol %) catalyst concentration and 2 hours of reaction time), which is further reduced to 0.26 (mg KOH/g oil) by using solid waste calcined eggshells as base catalyst at optimum process conditions 12:1 methanol: oil molar ratio, 4 (wt %) catalyst concentration and 3 hours of transesterification reaction time respectively. A significant quadratic model with molar ratio as the influencing process parameter is observed from RSM analysis. Coefficient of determination R^2 value observed from RSM, 0.9335, studies concluded that a minimum error exists between experimental and predicted responses for acid value optimization of RSO conversion to biodiesel. Uncertainty error analysis is performed for optimum process conditions at 5%, 10% and 15% deviations. From the uncertainty error analysis it is concluded that there is literally no error for any small deviations of optimum process conditions.

Conflicts of Interest: There are no potential conflicts of interest between authors.

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