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Egg Shell Waste-Catalyzed Transesterification of Mustard Oil: Optimization Using Response Surface Methodology (RSM)

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Abstract. The suitability of mustard oil (low grade edible oil with high production rate in India) for biodiesel production using waste of egg shell as a cost-effective and environmental friendly process was investigated. Response Surface Methodology (RSM) in combination with Central Composite Design (CCD) was used to optimize the biodiesel production parameters. A quadratic polynomial equation was obtained for mustard oil methyl ester yield by multiple regression analysis. Interactions between the variables were validated statistically. The optimum conditions of the independent variables in the present work were 9:1 molar ratio of methanol to oil, 3 wt% eggshell catalyst (calcined at 900˚C, 2 hr), 60˚C reaction temperatures at reaction time of 3 h. The predicted mustard oil methyl ester yield was 94.89% under the optimal conditions. Verification experiment (95%) confirmed the validity of the predicted model. Reusability and effect of calcination temperature on activity of eggshell catalysts were also investigated.

Keywords: Biodiesel, Mustard oil, Eggshell waste, Heterogeneous catalysis, CCD, RSM.

1. Introduction

Biodiesel, a biodegradable and renewable form of energy, emitting less carbon monoxide, sulfur compounds, particulate matter and unburned hydrocarbons than traditional diesel [1], is usually composed of fatty acid methyl esters formed by transesterification of renewable triglycerides such as vegetable oils and animal fats with methanol. Edible vegetable oils such as palm oil, sunflower oil, rapeseed oil and soybean oil are generally suitable feedstocks for biodiesel production [2]. However, non-edible oils such as Karanja oil, Polanga oil and Jatropha oil have attracted great attention as they do not face the 'food vs fuel' dilemma when used as feedstocks in fuel industry [3]. Mustard oil contains 60% mono unsaturated fatty acids of which 42% erucic acid and 12% oleic acid. In western countries mustard oil is used for external use and it is non-edible oil so it can be used as sustainable raw materials for biodiesel production. Successful ventures were reported on utilization of wastes viz. chicken egg shell [4], oyster shell [5], as cheap resources of CaO for application as low cost heterogeneous catalyst for biodiesel Synthesis. Calcium carbonate constitutes 85-95% of the dry Chicken eggshells [6]. The main objective of the present work is to investigate the suitability of low grade edible oil (high production rate in India) for biodiesel production using egg shell waste as a cost-effective and environmental friendly process. The obtained experimental data have been used to generate a historical design and to identify the optimum conditions by means of a response surface methodology (RSM) approach. Reusability of the catalysts was also tested.

2. Experimental

2.1. Materials

Commercial mustard oil was used in the present study. Waste Chicken egg shell was collected from local restaurant in Varanasi, UP, India. To remove the edible portion attached to the eggshells and other impurities,

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eggshells were rinsed thoroughly with tap water until the organic matter, which adheres on the inner surface of the eggshells, was removed, followed by double rinsing with distilled water. The washed eggshells were dried at 378 K for 24 h in a hot air oven. Before calcination, the dried eggshells were ground until they became a powder form. Calcination was performed in the muffle furnace at different temperatures (200˚C–1000˚C) for 2 h under static air. All other chemicals used were analytical reagents.

2.2. Catalyst Characterizations

The crystalline phases of calcined samples were analyzed by X-ray diffraction (XRD). The samples were characterized by N_2 adsorption-desorption (Micromertics, ASAP 2020) for their BET surface area, Pore volume and Pore size. FTIR spectra were obtained with FTIR (Thermo-Nicolet 5700 model). The spectra were obtained in the 500–4000 cm^{-1} region, with a resolution of 4 cm^{-1}. Averages of 32 scans were recorded.

2.3. Experimental setup

The transesterification reaction was carried out in a batch reactor. A 500 mL three necked round bottom glass flask was used. It had provisions for a water-cooled condenser, thermometer, and mechanical stirrer. The flask was kept inside a water bath with thermostat which maintained the temperature at the desired level. The reaction mixture was stirred at 600 rpm for all test runs.

2.4. Transesterification reaction

The oils were heated at 378 K for 1 h in N_2-purge to evaporate water and other volatile impurities. Heated oils were allowed to cool to room temperature. Subsequently, a mixture of methanol and catalyst at a designated amount was added to the oil. Each experiment was allowed to continue for a set period of time. The reaction mixture was allowed to cool down and equilibrate which resulted in separation of two layers. The upper layer consisted of methyl esters and unconverted triglycerides. The lower layer contained glycerol, excess methanol, catalyst and any soap formed during the reaction and possibly some entrained methyl esters. After separation of the two layers by sedimentation, the catalyst was separated from biodiesel product by centrifugation, and then excessive amount of methanol was evaporated before analysis of biodiesel yield.

2.5. Testing of biodiesel (methyl esters)

In the present work, mustard oil methyl esters (biodiesel) were analyzed by FTIR (Thermo-Nicolet 5700 model). The spectra were obtained in the 500–4000 cm^{-1} region, with a resolution of 4 cm^{-1}. Averages of 32 scans were recorded using a multi bounce ATR. The method developed by Giuliano et al. [7] was used for quantitative analysis. The height of absorbance band at wave number 1741 cm^{-1} was used to calculate the concentration of ester in the biodiesel layer. A calibration plot was obtained by measuring the height of the 1741 cm^{-1} bands for samples of ester and oil of known compositions. For the calibration purpose, methyl ester and triolien where taken as representative ester and oil respectively. The yield of biodiesel was calculated using the following formula:

$$\text{Yield} = \frac{E_l}{W_o} \times E_c \quad (1)$$

Where: El, Ec , Wo are the biodiesel layer volume in (mL), ester concentration in ($g.mL^{-1}$), and weight of mustard oil used in (g) respectively.

2.6. Statistical analysis

The biodiesel production yield was optimized using response surface methodology (RSM) provided by STATISTICA 8 software. A standard RSM design tool known as Central Composite Design (CCD) was applied to study the transesterification reaction parameters. The central composite experimental design (CCD) is a suitable design for sequential experiments to obtain appropriate information for testing lack of fit without a large number of design points [8]. A two-level, three-factor central composite experimental design was used to optimize the independent variables to achieve maximum fatty acid methyl ester (FAME) yield. A total of twenty experiments, including six replications at the centre point, were conducted.

3. Results and discussion

3.1. XRD analysis

XRD spectra of calcined eggshell samples were obtained with Cu radiation (λ=0.154178 nm) at 40 kV, 30 mA, a scan speed of 0.1 ˚/ s, and a scan range of 10-80˚. Indexing of the diffraction peaks was done using a Joint Committee on Powder Diffraction Standards (JCPDS) file. Fig. 1 shows the XRD of egg shell calcined at 800, 900 and 1000˚C, respectively. For the uncalcined catalyst, the main peak at 2θ=29.478˚and other peaks were at 2θ=48.601˚,51.825˚, 57.579˚,and 65.158˚. These peaks were characteristics of calcium carbonate. The peaks for the calcined catalyst appeared at 2θ=32.318˚, 37.455˚, and 53.930˚, which were characteristics of calcium oxide. Calcium hydroxide was also observed at 2θ = 14.772˚ and 17.8690˚ (Fig. 1). XRD patterns of the egg shell-derived catalyst showed clear and sharp peaks identically. The crystalline size of egg shell wastes catalyst was also calculated from the XRD data using Scherrer's formula given by Qin et al [9] after correction for instrumental broadening (Eq.(2)):

$$D \approx 0.9\lambda/\beta \cos 2\theta \quad (2)$$

The crystallite size of 800, 900 and 1000˚C calcined catalysts were calculated and the results were shown in Table 2. Whereas the crystallite size of the catalyst upon calcinations at 900˚C reduced to 25 nm. This shows that crystallinity of the eggshell decreased on calcination. Yoosuk et al. [10] also observed that calcination of CaO decreased its crystallinity.

3.2. FTIR Analysis

The FTIR patterns of egg shell with respect to calcinations at 800, 900 and 1000 ˚C are presented in Fig. 2. A study on FTIR spectra of eggshell is reported by Engin et al.[11] where in the uncalcined catalyst the major absorption bands occurred at 1415, 879, and 700 cm^{-1} ,which are attributed to asymmetric stretch, out-of plane bend and in-plane bend vibration modes, respectively, for CO_3^{-2} molecules. Upon calcination, eggshell starts to lose carbonate and absorption bands of CO_3^{-2} molecules shift to higher energy (i.e., 1470, 1040, and 820 cm^{-1}). This has been attributed to the decrease of the reduced mass of the functional group attached to the CO_3^{-2} ions.

3.3. BET Surface area

As shown in Table 2, the BET surface area of catalysts synthesized from eggshell at 900˚C was high as 59.0717$m2g^{-1}$. The BET studies confirmed that the particle size decreased as the calcination temperature increased leading to an increase in surface area. Whereas the catalysts calcined at 800˚C and 1000˚C had a lower surface area (Table 1). The egg shell catalysts calcined at 800˚C and 1000˚C were considered to be less-porous materials due to their trace pore volume. While catalyst calcined at 900˚C exhibit better porous structure. This result suggested that the decomposition of carbonates is accomplished at 900˚C. The surface fraction was reflected by a significant decrease in the average pore volume and pore size (Table 2). Boynton reported the sintering effect related to the calcination of limestones at high temperatures, which results in a dense and unreactive lime [12].

3.4. Optimization of parameters

The response surface methodology was used for the optimization of parameters. The quadratic model was selected as it is the best model due to its highest order polynomial with significance of additional terms. The model equation based on the coded values (X_1, X_2 and X_3 as catalyst concentration, methanol/oil molar ratio and reaction temperature, respectively) for the biodiesel yield was expressed by Eq. (3).

$$Y = 94.89 + 1.089X_1 - 9.15X_1^2 + 2.64X_2 - 9.87X_2^2 - 0.63X_3 - 8.9X_3^2 + 0.81X_{\ 1}X_2 + 2.07X_1X_3 + 3.2X_2X_3 \quad (3)$$

The result of statistical analysis of variance (ANOVA) was carried out to determine the significance and fitness of the quadratic model as well as the effect of significant individual terms and their interaction on the chosen responses. The p-value (probability of error value) is used as a tool to check the significance of each regression coeffiecient, which also indicate the interaction effect of each cross product. It was found that the model is significant with a very low probability value (<0.0001). Furthermore, the value of pure error (0.063) is low which indicates good reproducibility of the data and a satisfactory coefficient of determination (R^2=0.93709). The coefficient of determination also revealed that there are excellent correlations between the independent variables. The lack of fit test with p-value of 0.0521, which is not significant (p-value>0.05 is not significant) showed that the model satisfactorily fitted to experimental data. It was found that all the

terms in the model with significant influence on biodiesel yield response. The relationship between predicted and experimental fatty acid methyl ester yields is shown in **Fig.3**. It can be seen that there is a high correlation (R^2=0.97351) between the predicted and experimental FAME yields indicated that the predicted values and experimental values were in reasonable agreement. It means that the data fit well with the model and give a convincingly good estimate of response for the system in the range studied.

3.5. Interaction between independent variables

The elliptical shape of the curves indicated a strong interaction between the variables. **Fig. 4** represents the effects of varying alcohol/oil molar ratio and catalyst amount on FAME yield. From the figure, it is obvious that an increase in FAME yield was observed with the increase of alcohol/oil molar ratio and catalyst amount at first, and then the trend was reversed when the alcohol/oil molar ratio and catalyst amount reached a certain values (9:1 molar ratio and 3 wt% catalyst respectively). **Fig. 4** shows the significant interaction between methanol-to-oil molar ratio and catalyst amount. The convex profile of the response surface shows a well defined optimum condition for the independent variables. Increasing the catalyst amount up to 3% increased the mustard oil methyl ester yield, whereas addition of more catalyst (>3%) resulted in poor mixing of the reaction mixture comprising solid (catalyst), non-polar (mustard oil and mustard oil methyl ester yield) and polar (methanol) phases. Hence, aggregation of catalysts and poor mass transfer between phases reduced mustard oil methyl ester yield. Similarly, excess methanol will shift the equilibrium to the right and improve FAME yield, but beyond a certain value the excess methanol causes dilution. Catalyst concentration with respect to the volume of reaction mixture decreased with an increase in methanol concentration which then caused a drop in FAME yield. In **fig. 5,** it was observed, when the reaction temperature is increased, two opposite effects are possible. First, an increase in the temperature will increase the rate of reaction due to a higher energy input and a reduced mass transfer resistance. Second, availability of methanol in the liquid phase may decrease due to a higher amount of methanol in the vapor phase at higher temperature.

3.6. Validation of the model

Optimum conditions of the independent variables for the egg shell catalyzed transesterification of mustard oil were determined as; catalyst concentration 3 % by weight; reaction temperature, 60˚C; and methanol-to-oil molar ratio of 9:1. To confirm accuracy of the model, egg shell catalyzed transesterification of mustard oil was carried out under the optimum conditions. Experimental FAME yield was found as 95%. Also predicted FAME yield was calculated as 94.89% from the model. According to the results, verification experiments confirmed the validity of the predicted model.

3.7. Effect of calcination temperature

Eggshell catalysts sample calcined at 900˚C was the most active catalyst. A yield of 95% was obtained in the presence of eggshell catalyst calcined at 900˚C. The calcination at higher temperatures led to desorption of carbon dioxide from the egg shell catalysts, producing basic sites that catalyzed transesterification of vegetable oil with methanol. However, further increasing the temperature to 1000˚C decreased the biodiesel yield to 90%.

3.8. Reusability of waste catalysts

Fig.6 shows yields after reuse of the catalyst. The results indicated that the catalyst can be repeated use for 14 times with no apparent loss of activity. After the 14^{th} cycle of transesterification, the yield was still 88%. The catalyst was completely deactivated after being used more than 18 times. The deactivation of catalyst may be ascribed to its structure change. The XRD patterns of the eggshell-derived catalyst used more than 18 times were characteristic of $Ca(OH)_2$. The structure change of catalyst could result from the reaction between H_2O and CaO, because the reactants (vegetable oils and methanol) contain a little amount of water.

4. Conclusion

We anticipate that the low-cost catalyst could be used in a large-scale industrial process of biodiesel, making the process cheap and ecologically benign. In addition to biodiesel production, such environmentally benign waste catalysts should find application in a wide range of other base-catalyzed important organic

reactions. The model from central composite design was considered to be accurate and reliable for predicting the FAME yield for egg shell catalyzed transesterification of mustard oil. The optimum conditions of egg shell catalyzed transesterification reaction were 9:1 molar ratio of methanol to oil, addition of 3 wt% eggshell catalyst (calcined at 900˚C, 2 hr), 60˚C reaction temperature at 3 h gave the best results. The predicted FAME yield was 94.89% under the optimal conditions and the subsequent verification experiment (95%) confirmed the validity of the predicted model. The results indicated that the egg shell can be repeated use for 14 times with no apparent loss of activity.

5. References

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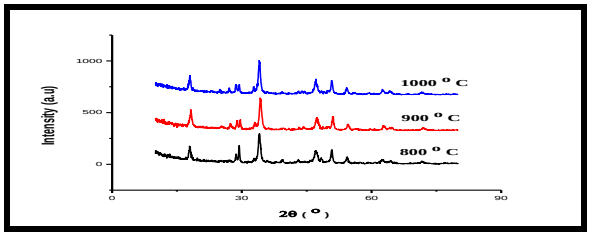

Figure1. XRD of the calcined egg shell catalyst calcined at different temperature.

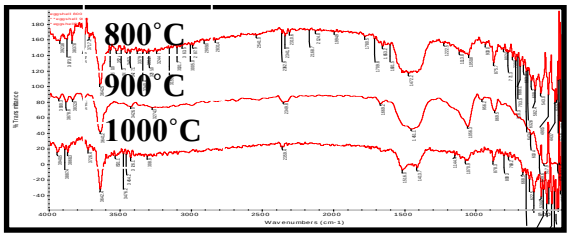

Figure2. FTIR spectra of eggshell catalyst calcined at different temperature.

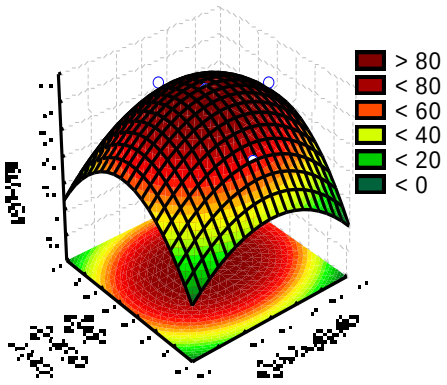

Figure4. Response surface curve plot showing effect of methanol-to-oil molar ratio and catalyst concentration on FAME yield.

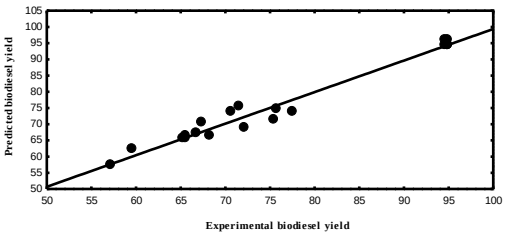

Figure3. Predicted FAME yield versus experimental FAME yield (R2:0.97351; Standard deviation of residual values: 2.29).

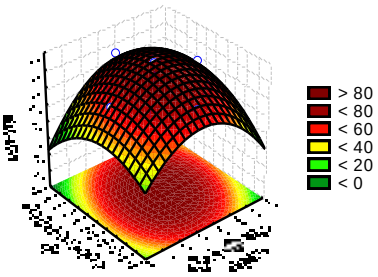

Figure5. Response surface curve plot showing effect of reaction temperature and methanol-to-oil molar ratio on FAME yield.

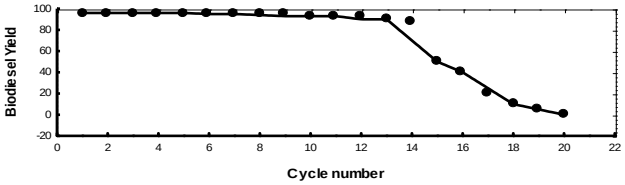

Figure6. Effect of reusability of the catalyst.

Table1. BET surface area (S_{BET}), total pore volume and crystallite size of the eggshell catalysts.

Cat. type	Temp. (˚C)	S_{BET} (m^2/g)	Total Pore Volume (cm^3/g)	Crystallites size (nm)
Eggshell	800	3.4056	0.015455	25.47022
Eggshell	900	59.0717	0.109827	25.39265
Eggshell	1000	4.7966	0.018494	29.42068