EGG SHELL AS ECO-FRIENDLY CATALYST FOR TRANSESTERIFICATION OF RAPESEED OIL: OPTIMIZATION FOR BIODIESEL PRODUCTION

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Abstract- Calcined eggshell was investigated in rapeseed oil transesterification with a view to determine its viability as a solid catalyst for use in biodiesel synthesis. Response Surface Methodology (RSM) was used to optimize the biodiesel production parameters. A quadratic polynomial equation was obtained for biodiesel 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% calcined eggshell catalyst (calcined at 900˚C, 2 hr), 60˚C reaction temperatures at reaction time of 3 h. The predicted biodiesel yield was 96 % under the optimal conditions. Reusability and effect of calcination temperature on activity of eggshell catalysts were also investigated. The catalyst was characterized by X-ray diffraction (XRD), N_2 adsorption-desorption and Fourier transform infrared spectrometry (FTIR).

Index Terms*- Biodiesel, Rapeseed oil, Eggshell, Heterogeneous catalysis, Response Surface Methodology.*

I. INTRODUCTION

Due to the depletion and increasing price of petroleum together with environment concerns caused by the combustion of fossil fuels, the search for alternative fuels has gained much attention [1]. Biodiesel (fatty acids methyl, FAME) can be derived from the transesterification of triglycerides (the main component of vegetable oils or animal fats) with a short chain alcohol (mainly methanol). It has become popular as a possible alternative to fossil fuels. The main advantages of this fuel are that its properties and performance are similar to conventional diesel fuels [2]. Currently, homogeneous process catalyzed by sodium or potassium hydroxide is a common and efficient method for biodiesel production [3] though the removal of these catalysts is costly, time consuming and generates large amounts of waste water. In addition, crude glycerol by-products have very low value due to high impurities such as other catalysts, soap, methanol and water. Purifying the crude glycerol by means of filtration, chemical additions, fractional vacuum distillation, bleaching, deodoring, and ion exchange yields various commercial and technical grades, however, it is costly, especially for medium and small biodiesel producers. Therefore, there is a need for a milder, environmentally friendly and integrated process producing cost-efficient biodiesel and high-quality glycerol. The use of a heterogeneous catalyst [4] is a key technology to overcome such problems. Direct utilization of analytical reagent grade chemicals has been attempted [5] for catalyst preparation invoking high cost. Successful ventures were reported on utilization of wastes viz. chicken egg shell [6,7], oyster shell [8], mud crab shell [9], golden apple snail and meretrix venus [10] and mollusk shell [11] as cheap resources of CaO for application as low cost heterogeneous catalyst for biodiesel Synthesis. Chicken eggshells typically weigh 5-6 g, approximately 10% of the total egg mass, with calcium carbonate constituting 85-95% of the dry eggshell. Other components include 1.4% magnesium carbonate, 0.76% phosphate, 4% organic matter, and trace amounts of sodium, potassium, zinc, manganese, iron, and copper [12]. As a part of the process, desirable feedstock characteristics include adaptability to local growing conditions, regional availability, high oil content, favorable FA composition, compatibility with existing farm practices, low agricultural inputs, definable growing season, uniform seed maturation rates, markets for byproducts, compatibility with fallow lands, and rotational adaptability with commodity crops [13]. Biodiesel prepared from rapeseed oil meet all or most of these criteria. Rapeseed is now second largest oilseed crop after soybean and the third largest vegetable oil and characterized by high level of erucic acid which may cause serious damage to heart and lever [14]. Using waste of egg shell as raw materials for catalyst synthesis could eliminate the wastes and produce the biodiesel from rapeseed oil with high cost effectiveness. In the present investigation, eggshell was characterized and utilized in the production of biodiesel using rapeseed oil. The parameters effecting on the transesterification such as catalyst concentration, molar ratio of methanol/oil, reaction temperature, reaction time and calcination temperature were optimized. 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. The fuel properties of biodiesel produced were compared with ASTM standards for biodiesel. Reusability of the catalysts was also tested.

II. EXPERIMENTAL

A. Materials.

Commercial rapeseed 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, 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.

B. 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.

C. 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.

D. 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.

E. Testing of Biodiesel

In the present work, vegetable oil and 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. [15] 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.

F. 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 [16,17]. A two-level, three-factor central composite experimental design was used to optimize the independent variables to achieve maximum biodiesel yield. A total of twenty experiments, including six replications at the centre point, were conducted.

III. RESULTS AND DISCUSSION

G. 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. Figure 1 depicts the XRD of egg shell calcined at 800, 900 and 1000˚C, respectively. Upon calcination, the eggshells turned completely white in appearance, which indicates that the calcium carbonate escaped and the product constitutes only calcium oxide [18]. The peaks were compared to the JCPDS file also. 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 sample calcined at 900 ˚C for 2 h exhibited similar results to those by Wei et al. [6] and showed clear and sharp peaks identically. The peaks are subjected to a single crystalline phase of CaO. The crystalline size of egg shell wastes catalyst was also calculated from the XRD data using Scherrer's formula given by Qin et al [19] after correction for instrumental broadening (Eq.(1)):

$$D \approx 0.9\lambda/\beta \cos \qquad (1)$$

The crystallite size of 800, 900 and 1000˚C calcined catalysts were calculated and the results were shown in Table 1. 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. [20] also observed that calcination of CaO decreased its crystallinity.

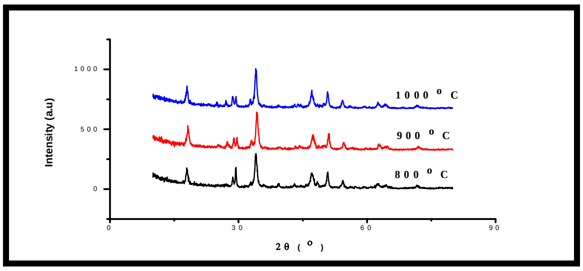

Fig.1 XRD of the calcined egg shell catalyst at (a) 800˚C, (b) 900˚C and (c) 1000˚C.

Table 1. BET surface area (SBET), total pore volume and crystallite size of the eggshell catalysts.

Catalyst type	Temperature (˚C)	Surface Area (m^2/g)	Total Pore Volume (cm^3/g)	Crystallite 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

H. FTIR Analysis.

The FTIR patterns of egg shell with respect to calcinations at 800, 900 and 1000 ˚C are presented in Fig. 2. A thorough study on FTIR spectra of eggshell is reported by Engin et al.[19] 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. A sharp OH^{-1} stretching band is observed at 3625 cm^{-1} at the catalyst calcined at 900˚C.

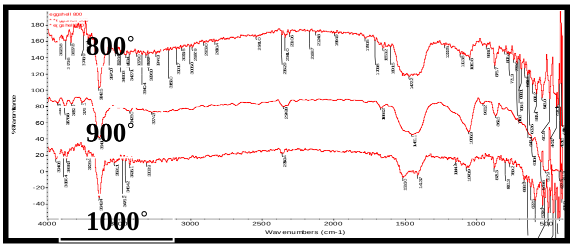

Fig.2 FTIR spectra of eggshell calcined at 800, 900 and 1000˚C.

I. BET Surface area.

As shown in Table 1, the BET surface area of catalysts synthesized from eggshell at 900˚C was high as $59.0717 m^2g^{-1}$. 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. It should be noted that, at the calcination temperature of 1000 °C, there were large fractures appearing on the surface. These should be due to a severe reduction of unit cell after the complete decarbonation [21]. The surface fraction was reflected by a significant decrease in the average pore volume and pore size (Table 1). Boynton reported the sintering effect related to the calcination of limestones at high temperatures, which results in a dense and unreactive lime [21].

J. 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 from rapeseed oil was expressed by Eq. (2).

$$Y = 95.89 + 1.089X_1 - 9.15X_1^2 + 2.64X_2 - 9.87X_2^2 - 0.63X_3 - 8.9X_3^2 + 0.81X_1X_2 + 2.07X_1X_3 + 3.2X_2X_3 \qquad (2)$$

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=0.97351). 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 fatty acid methyl ester 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.

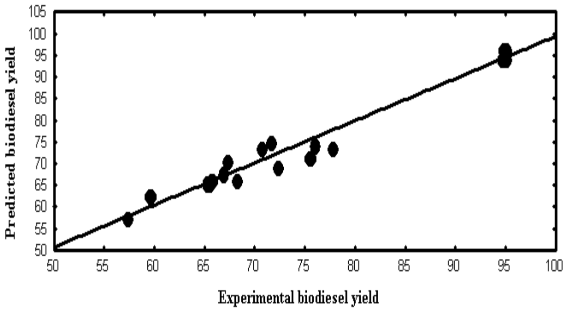

Fig .3 Predicted fatty acid methyl ester yield versus experimental fatty acid methyl ester yield.

K. 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 biodiesel yield. From the figure, it is obvious that an increase in biodiesel 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). 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 biodiesel yield, whereas addition of more catalyst (>3%) resulted in poor mixing of the reaction mixture comprising solid (catalyst), non-polar (vegetable oil and biodiesel yield) and polar (methanol) phases. Hence, aggregation of catalysts and poor mass transfer between phases reduced biodiesel yield. Similarly, excess methanol will shift the equilibrium to the right and improve biodiesel 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 biodiesel yield.

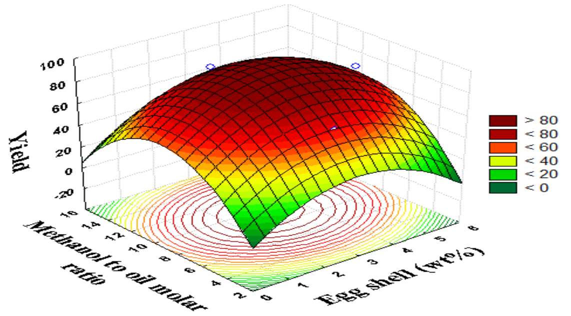

Figure4. Response surface curve plot showing effect of methanol-to-oil molar ratio and catalyst concentration on FAME yield.

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. Figures 5 and 6 show that the positive effect was more significant over the negative effect; hence the yield of biodiesel yield was increased with an increase in temperature of up to 60˚C. A further increase in temperature results in a significant negative effect due to increased evaporation rate of methanol.

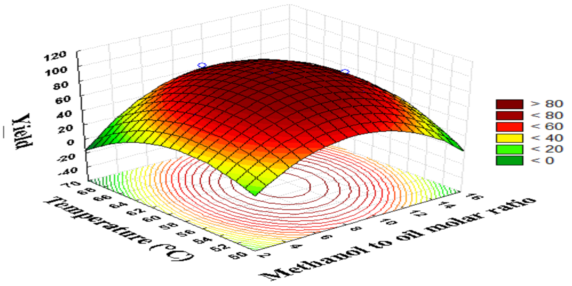

Figure5. Response surface curve plot showing effect of reaction temperature and methanol-to-oil molar ratio on FAME yield.

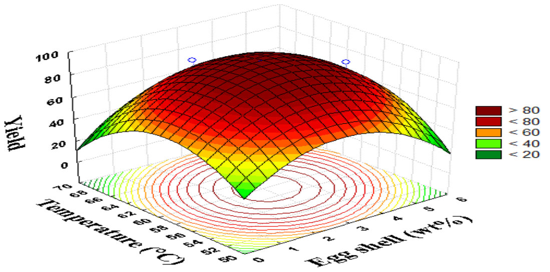

Fig.6. Response surface curve plot showing effect of catalyst concentration and temperature on FAME yield.

L. Validation of the model

Optimum conditions of the independent variables for the egg shell catalyzed transesterification of vegetable 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 vegetable oil was carried out under the optimum conditions. Experimental biodiesel yield was found as 96%. Also predicted biodiesel yield was calculated as 95.89% from the model. According to the results, verification experiments confirmed the validity of the predicted model.

M. Effect of calcination temperature

Eggshell catalysts sample calcined at 900˚C was the most active catalyst. A yield of 96% 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%.

N. Reusability of waste catalysts

Fig.7 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 14th cycle of transesterification, the yield was still 88%. After being used for more than 14 times, catalyst lost activity gradually. The catalyst was completely deactivated after being used more than 18 times. The deactivation of mixture 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.

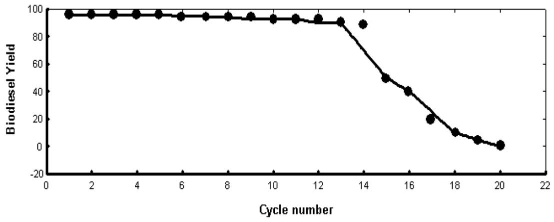

Fig.7 Effect of reusability of the catalyst.

IV. CONCLUSION

The catalyst derived from eggshell had excellent activity in heterogeneous transesterification of rapeseed oil for biodiesel production. Calcinations of the catalyst resulted in an increase in surface area, leading to better catalytic activity. Among the calcined catalysts, the catalyst calcined at 900 ˚C gives the highest biodiesel yield. The method of reusing eggshell wastes to prepare catalyst could recycle the waste, minimizing contaminants, reducing the cost of catalyst, and making the catalyst environmentally friendly. Hence, eggshell heterogeneous catalyst showed high activity, 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. The predicted value was in agreement with the experimental value. Both the reaction condition and yield of biodiesel were almost similar to that of homogeneous catalytic system. The results indicated that the egg shell can be repeated use for 14 times with no apparent loss of activity.

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