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Study on Solid Base Calcium Oxide as a Heterogeneous Catalyst for the Production of Biodiesel

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ABSTRACT

Biodiesel is the monoalkyl esters of long chain fatty acids are derived from vegetable oils and animal fats. The waste chicken eggshell was applied as raw material for the preparation of heterogeneous catalyst in biodiesel production. Prior to use, the waste chicken egg shell was converted into calcium oxide (CaO) by calcining at 900 °C for 4 h. The selected reaction conditions were optimized using response surface methodology (RSM). The catalytic activity of the catalyst in transesterification of waste frying palm oil with methanol was evaluated, and the experimental results was found that the maximum yield of fatty acid methyl esters was 94% at the following reaction conditions: reaction temperature of 60 °C, a reaction period of 4 h, a ratio of methanol to oil at 9:1, and amount of catalyst at 9% wt of oil. The base catalyst CaO can be successfully utilized for the production of biodiesel.

1. Introduction

Biodiesel is a nonpetroleum-based fuel defined as fatty acid methyl or ethyl esters derived from vegetable oils or animal fats and it is used in diesel engines and heating systems. Biodiesel could be regarded as mineral diesel alternative with the advantage of reducing greenhouse emissions [1]. It is produced by transesterification of vegetable oils or animal fats with methanol and can be catalyzed by an acid, base, enzymes to produce fatty acid methyl ester (FAME) and glycerol as a by-product [2,3]. Biodiesel is one of the attractive alternative fuels which can be produced from renewable sources [4]. The conventional procedure of biodiesel production proceeds in transesterification of oils or fats using homogeneous catalysts. On the other hand, the homogeneous catalytic process has some drawbacks; namely, production of wastewater from washing process of catalyst, catalyst separation process and non-reusability of the catalysts [5].

The heterogeneous catalytic process overcomes the homogeneous one because the solid catalysts, separation of catalyst is easy and reused for some extent, and no wastewater production [6]. Several heterogeneous catalysts have been employed in the biodiesel production, for example MgO, CaO, and hydrotalcites [7-9]. CaO is closely resembled to an environmental-friendly material. In general, $Ca(NO_3)_2$ or $Ca(OH)_2$ is the raw material to produce CaO. Besides, there are several natural calcium sources from wastes, such as eggshell, mollusk shell, and bone. By using this wastes as raw materials for catalyst production could reduce the wastes and at the same time produced the catalysts with high cost effectiveness.

The mechanism of transesterification of triglycerides to biodiesel in the presence of methanol using calcium oxide as a catalyst was explained as follows. Calcium oxide is a major active phase of the waste chicken egg shell. Calcium oxide reacts with methanol to form calcium methoxide and the methoxide anion attached to the carbonyl carbon atom of the triglyceride molecule to form a tetrahedral intermediate. Then, the unstable tetrahedral intermediate breaks down to diglycerides and fatty acid ester. Next, the rearrangement of the tetrahedral intermediate results in the formation of fatty acid ester and glycerol. The above steps are repeated finally three fatty acid esters and a glycerol as a by-product are formed [10]. Nakatani et al [11] found that combusted oyster shell at 700 °C is active for biodiesel production by transesterification of soybean oil. Wei et al [12] examined that calcination of eggshell above 700 °C could produce CaO catalyst for biodiesel production. However, the catalytic behaviour during the reaction as well as the catalyst characteristics were not clearly demonstrated. Boey et al [13] projected a waste mud crab shell as a catalyst for biodiesel production is used efficiently. The study of varying waste shells, such as mollusk shells and eggshell, were reported previously [14].

Boey et al [10] and Wei et al [12] examined that eggshells and mud crab shell could be used as a catalyst for biodiesel production. Further study on the characteristics of the catalysts and the catalytic activity together with the optimization of the catalyst preparation and the reaction conditions would be essentially useful for realizing this approach. All these works exposed that the waste shell-derived catalyst showed high potential to be used as a low-cost biodiesel production catalyst. Recently, the function of normal calcium sources from waste materials has been considered as a new trend for biodiesel production [15]. In this work, we have carried out transesterification using the chicken eggshell wastes as economical and environment-friendly catalyst. Biodiesel conversion was measured by the measurement of viscosity. The objective was to optimize the process for biodiesel production from waste frying Palm oil using CaO catalyst. The effects of reaction time, reaction temperature, methanol to oil molar ratio, and amount of catalyst were investigated.

2. Experimental Methods

2.1 Materials

Waste frying palm oil was purchased from local restaurants in Chidambaram, Cuddalore district, Tamil Nadu. The density of the oil was measured to be 845 kg/m^3. The chicken eggshell was collected as wastes from restaurants in Chidambaram, Cuddalore district, Tamil Nadu. The eggshell was rinsed with running water to remove dust and impurities, and then dried in an oven. All chemicals were analytical-grade reagents (Merck, >99% purity) and were used as received.

2.2 Preparation of Eggshell Waste-Derived Catalyst

CaO catalyst was prepared from waste chicken eggshell by calcination method. The waste eggshell was cleaned thoroughly with running water for removal of organic matter and dried for whole night at 102 °C, and then the waste eggshell (100-200 mesh) was calcined at 900 °C in air atmosphere with a heating rate of 10 °C/min for 4 h [15]. The product was obtained as white powder. All calcined samples were kept in the close

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vessel to avoid the reaction with humidity in air and carbon dioxide (CO_2) before used. Because the CaO catalyst will be reacted with CO_2 and converted into $CaCO_3$, thus reducing its activity as a catalyst. Catalyst separation, catalyst reusability, production purification, less energy and water consumption is the special advantages of using heterogeneous catalyst [13]. Among the alkaline earth metal oxides, calcium oxide (CaO) is the promising heterogeneous catalyst for biodiesel production [16].

2.3 Calibration Curve for Determining Conversion of Biodiesel by Viscosity Method

Biodiesel conversion can be measured by different methods. The biodiesel conversion measured by HPLC method [17] and the biodiesel conversion measured by GC analysis [18]. Here biodiesel yield measurement by viscosity measurement method [19] at the start certain amount of waste frying oil undergoes CaO catalyzed transesterification reaction, and produced biodiesel [20]. This produced biodiesel were separates and again undergoes CaO catalyzed transesterification and the produced biodiesel was assumed 100% biodiesel and viscosity was measured. Then different proportion of raw waste frying oil was blended with produced biodiesel and the viscosity of each blend was measured. From the viscosity the percentage conversion of biodiesel was calculated. Viscosity versus percentage conversion plot was illustrated in Fig. 1 which used for the determination of biodiesel conversion.

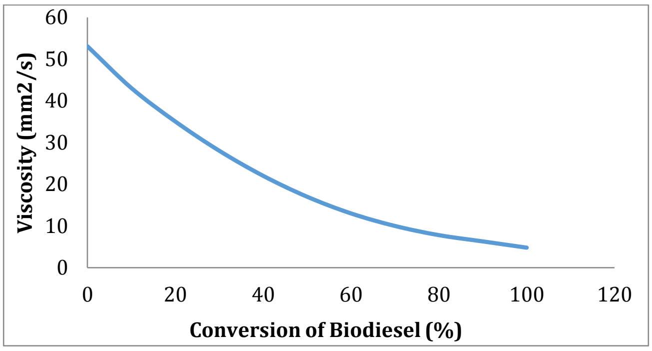


Fig. 1 Viscosity Vs Conversion of biodiesel. (Viscosity measured at 40 °C, Reaction temp. 60 °C, Methanol/oil ratio 9:1, Catalyst (CaO) concentration 9% wt of oil, under reflux)

2.4 Transesterification Process

Transesterification reactions were performed in a 500 mL 3-necked round bottom flask. One of side neck was fitted with a water-cooled condenser, the middle neck was used to insert magnetic stirrer and other raw materials in it, and the third neck was fitted with a temperature indicating thermometer. The speed of the magnetic stirrer was monitored. The transesterification process parameters such as amount of catalyst, methanol to oil ratio, reaction temperature and reaction time were varied to attain maximum methyl ester conversion. By inserting methanol into a flask with a variable ratio of 7:1, 9:1, 11:1 mol ratio of methanol to oil. Secondly, adding CaO catalyst as many as 8% of the mass of the oil. After a homogeneous mixture, Waste frying oil is inserted into a flask and heated at a variable temperature 55, 60, 65 °C in 3, 4, and 5 hours of stirring. After the reaction is completed, the catalyst was screened by using a filter paper (0.7 μm) and the transesterification products were allowed to settle overnight for the clear separation of biodiesel and glycerol. The upper layer fatty acid methyl esters, formed by the conversion of fatty acids to their respective esters are termed as biodiesel and the lower dense layer is termed as glycerol.

2.5 Statistical Analysis

The production of biodiesel yield was optimized using Response Surface Methodology (RSM). 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 [21,22]. A two-level, three-factor central composite experimental design was used to optimize the independent variables to achieve maximum biodiesel yield. A total of thirty one experiments were conducted.

Table 1 Central composite design (CCD) of factors in coded levels for determining the optimal conditions for biodiesel production process

Run	A	B	C	D	Biodiesel Conversion (%)	RSM-Predicted
1	-1	1	-1	-1	83	83
2	1	-1	1	1	86	85
3	0	0	2	0	85	85
4	-1	-1	1	-1	82	79
5	1	-1	-1	-1	81	82
6	2	0	0	0	80	75
7	0	0	0	-2	86	86
8	0	0	0	2	89	87
9	0	0	0	0	94	94
10	0	0	0	0	94	94
11	-1	1	1	-1	88	86
12	-1	-1	-1	-1	78	75
13	0	0	0	0	94	94
14	0	0	0	0	94	94
15	1	-1	-1	1	86	86
16	1	-1	1	-1	85	84
17	0	-2	0	0	79	79
18	-1	-1	1	1	80	80
19	0	0	0	0	94	94
20	0	0	-2	0	83	82
21	1	1	-1	-1	80	78
22	-1	-1	-1	1	81	79
23	1	1	-1	1	75	76
24	1	1	1	1	73	75
25	0	0	0	0	94	94
26	0	0	0	0	94	94
27	1	1	1	-1	78	79
28	-1	1	1	1	86	83
29	-1	1	-1	1	83	82
30	0	2	0	0	80	78
31	-2	0	0	0	69	75

The experimental data were analyzed via response surface regression procedure using a second-order polynomial design expert programme.

Table 2 Five level-four factor central composite design for transesterification process of waste frying palm oil

Variable	Symbol	Level				
		-2	-1	0	+1	+2
Reaction Time	Rt	2	3	4	5	6
Reaction Temperature	RT	50	55	60	65	70
Catalyst Size (%wt of oil)	C	5	7	9	11	13
Molar Ratio	M	7	8	9	10	11

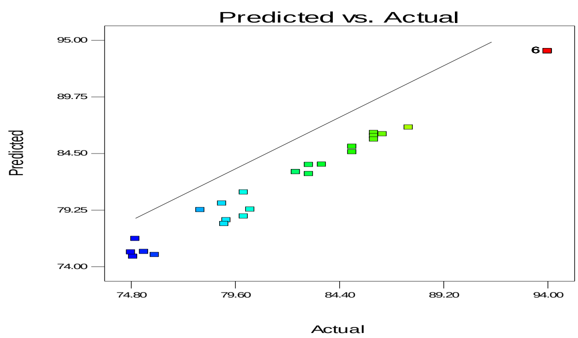


Fig. 2 Parity plot between the Predicted and Actual value

3. Results and Discussion

3.1 Optimization of Biodiesel Production

Response surface methodology (RSM) consists of a group of empirical techniques used for estimate of relationship between controlled experimental factors and measured response. The central composite design (CCD) was used to attain a quadratic model, consisting of factorial trials and star points to estimate quadratic effects and central points to estimate the pure process parameter with biodiesel production. The process parameters namely reaction time, reaction temperature, catalyst concentration, methanol to oil molar ratio were optimized using central composite design (CCD) for biodiesel production. The 31 runs design matrix of the variables with the experimental responses is represented in Table 1. The range of process parameters selected for its actual and coded values are given in Table 2. The results of the biodiesel conversion ANOVA fir Response Surface Quadratic Model Analysis of variance table from the CCD experiments are given in Table 3. This model can be used to predict the biodiesel production within the limits of the experimental factors. Fig. 2 shows that the actual response values agree well with the predicted response values.

The models terms including B, C, AB, BD, CD, A^2, B^2, C^2, D^2 are significant model terms were found to have influence on biodiesel production. The minimum and maximum biodiesel production in the design ranges between 74.8% and 94% corresponds to Run No. 30 and Run No. 9, 12, 13, 19, 25 respectively. The ANOVA indicated the R^2 value of 0.9890, which ensured a satisfactory adjustment of the quadratic model to the experimental data and showed that these models could explain above 98% of the variability in response. The R^2 predicted value of 0.9368 was also in reasonable agreement with the R^2 adjusted value of 0.9788 which reflects the accuracy and applicability of CCD for optimization of process parameters.

The three dimensional surface plots predicting the biodiesel production for different levels of variables are shown in Fig. 3 (a-c) and 4 (a-c). The optimum values of the process parameters for biodiesel production are reaction time – 4 h, reaction temperature - 60 °C, catalyst concentration - 9% (wt of oil) and methanol to oil molar ratio - 9:1. Various other studies reported that the parameters namely, reaction time, reaction temperature, catalyst concentration, methanol to oil molar ratio [23, 24] and the results obtained in this study is also in reasonable agreement with that. Therefore, this study shows that base CaO heterogeneous catalyst is a potential catalyst for the production of biodiesel from waste frying palm oil via heterogeneous transesterification. The optimization result also tells the same result as the ANOVA output. The ANOVA output shows that the transesterification process is highly and significantly affected by the temperature, catalyst concentration and the interaction between the temperature and the catalyst.

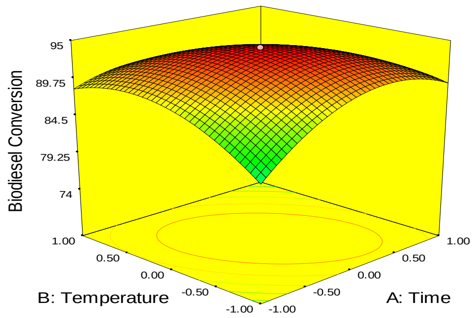
Table 3 Response 1 biodiesel conversion ANOVA fit response surface quadratic model analysis of variance table [Partial sum of squares – Type III]

Source	Sum of Squares	DF	Mean square	F-Value	P >F
Model significant	1166	14	83.3	96.6	<0.0001
A-Time	0.082	1	0.082	0.095	0.7625
B-Temperature	5.41	1	5.41	6.28	0.0242
C-Catalyst Size	9.63	1	9.63	11.2	0.0045
D-Molar Ratio	0.38	1	0.38	0.43	0.5196
AB	169	1	169	196	< 0.0001
AC	3.61	1	3.61	4.19	0.0587
AD	1.10	1	1.10	1.28	0.2760
BC	0.81	1	0.81	0.94	0.3479
BD	25.5	1	25.5	29.6	< 0.0001
CD	4.62	1	4.62	5.36	0.0352
A^2	605	1	605	701	< 0.0001
B^2	390	1	390	452	< 0.0001
C^2	176	1	176	204	< 0.0001
D^2	92.2	1	92.2	107	< 0.0001
Residual	12.9	15	0.86		
Lack of fit	12.9	10	1.29		
Pure Error	0.00	5	0.00		
Cor Total	1179	29			

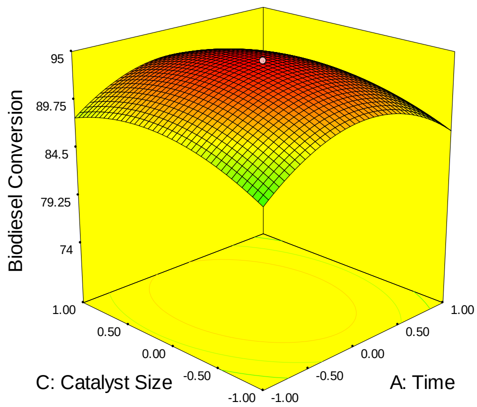
Values of "P > F" less than 0.0500 indicate model terms are significant. In this case B, C, AB, BD, CD, A^2, B^2, C^2, D^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

Std, Dev.	0.930	R-Squared	0.9890
Mean	83.73	Adj R-Squared	0.9788
C.V. %	1.110	Pred R-Squared	0.9368
PRESS	74.52	Adeq Precision	29.041

The "Pred R-Squared" of 0.9368 is in reasonable agreement with the "Adj R-Squared" of 0.9788. "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 29.041 indicates an adequate signal. This model can be used to navigate the design space.



(a)



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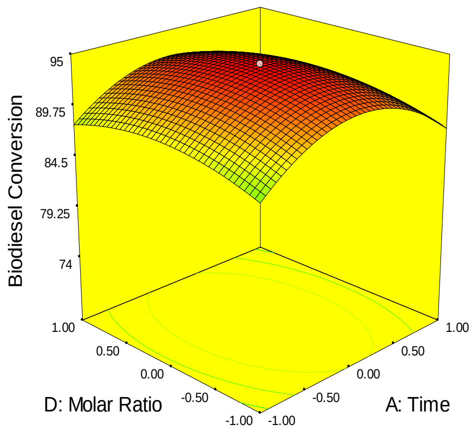
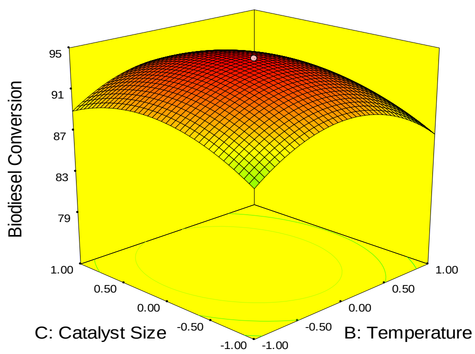
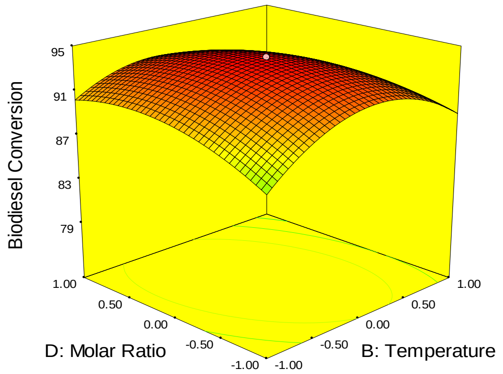


(c)

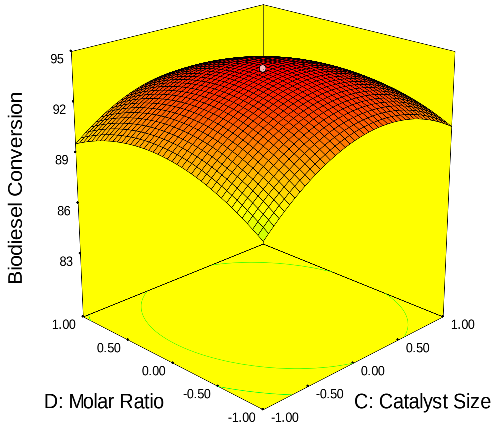
Fig. 3 Respond surface of a)Interaction effect of reaction temperature -reaction time versus biodiesel conversion, b) interaction effect of catalyst size- reaction time versus biodiesel conversion c) interaction effect of molar ratio-reaction time versus biodiesel conversion



(a)



(b)



(c)

Fig. 4 Respond surface of (a) interaction effect of catalyst size- reaction temperature versus biodiesel conversion (b) interaction effect of molar ratio-reaction temperature versus biodiesel conversion and (c) interaction effect of molar ratio of methanol to oil-catalyst size versus biodiesel conversion.

4. Conclusion

The waste chicken eggshells are used as the catalyst for the production of biodiesel process. This waste eggshell contains $CaCO_3$ which is converted to CaO after calcination at temperatures 900 °C for 4 h and CaO was acknowledged as an effective heterogeneous catalyst for the transesterification of waste frying palm oil and methanol. The effect of reaction conditions, which yielded a conversion of 94% biodiesel, were reaction time 4 h, reaction temperature 60 °C, methanol to oil molar ratio 9:1, and catalyst concentration 9% wt of oil. The experimental results show that CaO catalyst had excellent activity and stability during transesterification reaction, and it has potential for industrial application in the transesterification of waste frying palm oil to fame. As a heterogeneous catalyst, CaO can reduce the cost of biodiesel production.

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