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Synthesis and Characterization of CaO and KF Doped CaO (KF/CaO) Derived from Chicken Eggshell Waste as Heterogeneous Catalyst in Biodiesel Production

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Abstract

Chicken, duck and quail eggshell wastes were applied as raw materials for the preparation of heterogeneous catalyst. Prior to use, the calcium carbonate ($CaCO_3$) content in the waste shell was converted to calcium oxide (CaO) by calcining at 700-900°C for 3hr. The physicochemical properties of the solid oxide catalyst were characterized by X- ray diffraction (XRD), energy dispersive X- ray fluorescence (EDXRF) and scanning electron microscope (SEM). Response surface methodology (RSM) was used to optimize the biodiesel production parameters. The optimum conditions of the independent variables in the present work were 8:1 molar ratio of methanol to oil, 25 wt% of calcined eggshell catalyst (calcined at 900°C, 3hr), 65°C of reaction temperature at reaction time of 3hr. The predicted FAME yield was 92 % under the optimal conditions. Reusability of (CaO) catalyst was investigated. The KF doped CaO (KF/CaO) derived from chicken eggshell waste was prepared by reducing KF/CaO molar ratio from 0.45 to 0.003, synthesized by a wet impregnation method under microwave irradiation and used as heterogeneous catalyst in the transesterification of refined palm oil to get optimum FAME yield. The catalyst with the KF/CaO molar ratio of 0.006 and catalyst amount of 5 wt% exhibits the best performance under the optimum reaction conditions of preparation of biodiesel with the CaO catalyst using RSM. The doped catalyst could be reused at least four times with slight drop in activity which was attributed to the loss of active sites. The optimum reaction condition obtained for achieving maximum FAME yield of 95% were – 8:1 of methanol to oil molar ratio, 2.5 hr of reaction time, 5 wt% of catalyst amount and 65°C of reaction temperature.

Keywords: Biodiesel; Eggshell Wastes; Heterogeneous Catalyst (CaO); Response Surface Methodology (RSM); KF/CaO; Impregnation Method.

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1. Introduction

Because of the energy and global warming crisis, development of renewable energy has been focused worldwide [1]. Biodiesel is one of the most potential alternative energy since it is renewable and environmental friendly. Biodiesel is produced by transesterification of vegetable oils or animal fats with methanol to produce fatty acid methyl ester (FAME) and glycerol as a byproduct [2]. 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 [3]. Currently, homogeneous process catalyzed by sodium or potassium hydroxide is a common and efficient method for biodiesel production though the removal of these catalysts is costly, time consuming and generates large amount of waste water. Purifying the crude glycerol by means of filtration, chemical addition, 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 [4].

The use of a heterogeneous catalyst is a key technology to overcome such problems. Transesterification can be catalyzed by an acid, base or enzymes [5]. Heterogeneous catalysts have the advantage the separation and regeneration of the catalyst is easy and cheap [6]. Heterogeneous basic catalysts include alkaline earth metal oxides such as calcium oxide (CaO), magnesium oxide (MgO) and hydrotalcites [7,8]. Eggshells are comprised of a network of protein fibers, associated with crystals of calcium carbonate ($CaCO_3$), magnesium carbonate ($MgCO_3$), calcium phosphate ($Ca_3(PO_4)_2$) and organic substances and water. $CaCO_3$, the major constituent of the egg shell (96%), is an amorphous crystal that occurs naturally in the form of calcite (hexagonal crystal) [9]. Other components include 1.4 % magnesium carbonate, 0.76 % phosphate, 4 % organic matter and trace amounts of sodium, potassium, zinc, manganese, iron and copper [10].

Calcium compounds, although of lower basic strength than Sr and Ba, are less toxic, widely available, cheaper, ease to handle, making them promising catalyst and/or catalyst support in the biodiesel industry [11,12]. The catalytic activity of CaO can be accelerated with an initial pretreatment with methanol at room temperature [13], activation at high temperature [14] and /or surface modification to the catalyst support with potassium halides to generate strong active basic sites [15-17]. The last approach is of current interest to improve the catalytic activity of the supported catalyst [15-17]. In contrast to the conventional heating techniques, the use of microwave irradiation on chemical syntheses offers several advantages- cleaner and faster reactions by introducing remotely the energy consumed, instantaneous energy input on-off system, lower thermal inertia, delivery of energy through the mass of the products not at surface, and scaling-up of the reaction. For this reason, microwave- heating technique is expected to be more efficient for the synthesis, enhancing the safety conditions and eliminating the waste generation [18].

Catalysts derived from waste shells of egg, golden apple snail, Meretrixvenus, oyster shells were proposed for biodiesel production and it was concluded that these catalysts were environmental friendly as they are mainly prepared from natural sources. In addition to their eco friendly nature, these catalysts were also reported to exhibit high catalytic activity under optimum reaction conditions [19-22]. The aim of this investigation is to prepare CaO catalyst and KF doped CaO derived from chicken eggshell waste and used it as a heterogeneous base catalyst in the transesterification of refined palm oil. The catalyst (KF/CaO) was also prepared by wet

impregnation method followed by calcinations with various molar ratios of KF/CaO. The effect of reaction parameters such as KF loading, catalyst amount and catalyst reusability was also studied to achieve maximum FAME conversion of KF/CaO than that of CaO.

2. Experimental

2.1. Materials

The chicken, duck and quail egg shells were collected as wastes from Manthazin Hostel, Patheingyi Township, Mandalay. Palm oil was purchased from Local market. Potassium Fluoride and methanol (95% assay) were purchased from Mandalay, Able, Hospital Equipment and General Trading, Co., Ltd. A microwave oven was ME711k Samsung household microwave with an operating power output from 100-800 W (IEC-705), 7 power levels, and 35 min dual speed timer.

The egg shells were rinsed with water to remove dust, impurities and the organic matter which adheres on the inner surface of the egg shells. The washed eggshells were dried at 105° C for 24 hr in a hot air oven. Before calcination, the dried egg shells were crushed until they became a powder form.

2.2. Preparation and Characterization of Eggshell Waste- Derived Catalysts

The CaO catalysts were prepared by calcination method. The dried egg shell wastes (~150 µm) were calcined at 700-900° C in a muffle furnace for 3 hr. All calcined samples were kept in the closed vessel to avoid humidity in air before used. Figure 1: illustrated the preparation process of egg shell waste derived catalysts.

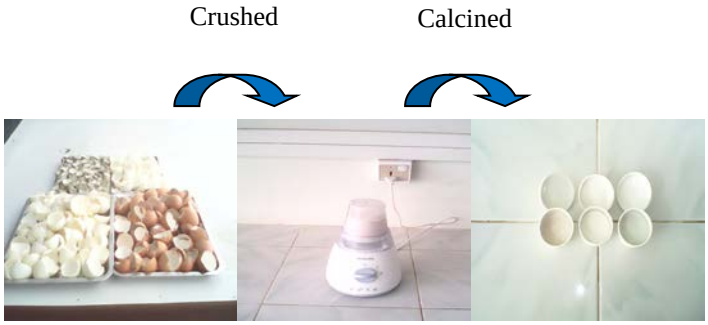

Figure 1: Preparation Process of Egg Shell Waste Derived Catalysts

The X- ray diffraction (XRD) characterization of the CaO catalyst was performed on a Rigaku (Miniflex II Japan). The elemental composition of the samples was analyzed by energy dispersive X- ray fluorescence spectroscopy (EDXRF) (XTF- pioneer, Bruga, Japan). The calcined samples were characterized by scanning electron microscope (SEM) (EVO- 60, Jermany).

2.3. Transesterification Reaction Procedure of Chicken Eggshell Waste- Derived Catalyst (CaO)

The transesterificationwas carried out in a batch reactor. A 100 ml of palm oil in a 500 ml two necked flat bottom flask equipped with a reflux condenser was stirred at 600 rpm for all test runs. The oils were heated at 105°C for 5 min in a heating mental to evaporate water and other volatile impurities. A mixture of oils and

catalyst were stirred with a magnetic stirrer at about 600 rpm. A designated amount of methanol was added into the reactor. Each experiment was allowed to continue at 65°C. After finishing the reaction, the mixture was allowed to cool down and centrifuged to separate catalyst. The resulted catalyst was treated with methanol to reuse or regenerate. The decanted mixture was filtered to remove catalyst absolutely. After that, the filtrate mixture was settled in a separating funnel for 10 min to separate layers clearly. The upper layer consisted of methyl esters and unconverted triglyceride. The lower layer contained glycerol, excess methanol and any soap formed during the reaction and possibly some entrained methyl esters. The excessive amount of methanol was recovered by distillation before the analysis of Fatty Acid Methyl Esters (FAME) %.

2.4. Determination of Biodiesel Purity

The compositions of biodiesel were determined by a gas chromatograph mass spectrometer (GCMS- QP2010, Shimadzu) equipped with capillary column and a flame ionization detector. Methyl-heptadecanoate was used as internal standard for quantification, according to EN14103. The biodiesel purity was characterized in term of FAME %.

$$FAME\ (\%) = (\sum A - A_{EI})/ A_{EI} \times (C_{EI} \times V_{EI})/W \times 100\% \quad (1)$$

Where, FAME is Fatty Acid Methyl Esters, $\sum A$ is Sum of area under the curve from C_{14} – C_{24}, A_{EI} is Area under the curve of Internal Standard, C_{EI} is Concentration of Internal Standard (mg/ml), V_{EI} is volume of Internal Standard used (ml) and W is Weight of product (mg).

2.5. Statistical Analysis of Biodiesel Preparation using CaO Catalyst

The biodiesel production yield was optimized using response surface methodology (RSM). A standard RSM design tool known as a three- level, three- factor Box- Behnken experimental design was applied to get the optimum reaction parameters of transesterification which provide maximum FAME yield. The Box- Behnken Experimental Design (BBD) is a suitable design for sequential experiments to obtain appropriate information for testing lack of fit without a large number of design points [23].

2.6. Preparation of KF Doped CaO Catalyst

According to Figure 2 which illustrated the preparation of KF- doped CaO derived from chicken eggshell waste. KF/CaO catalyst was prepared using a wet impregnation method under microwave irradiation with some modifications of a reported method [24]. Typically, 6 g of CaO was slowly immersed into 60 ml of aqueous KF solution (0.006 mol of KF/mol of support, CaO) with 200 rpm and left the mixture for 2 hr at room temperature under continuous stirring. Thereafter, the white slurry mixture was heated up to 80˚C for additional 2 hr, and then irradiated it in a microwave oven operating to a power of 100 W for 10 min. Finally, the solid was calcined at 500˚C for 3 hr in air and the material was collected as KF/CaO catalyst.

Figure 2: Preparation of KF – doped CaO derived from Chicken Eggshell Waste

2.7. Transesterification Reaction Procedure of KF/CaO

The transesterification was also carried out in a batch reactor. A 100 ml of palm oil in a 500 ml two necked flat bottom flask equipped with a reflux condenser was stirred at 600 rpm for all test runs. The oils were heated at 105°C for 5 min in a heating mantle to evaporate water and other volatile impurities. A mixture of oils and catalyst were stirred with a magnetic stirrer at about 600 rpm. A designated amount of methanol was added into the reactor. Each experiment was allowed to continue at 65°C. After finishing the reaction, the mixture was allowed to cool down and centrifuged to separate catalyst. The resulted catalyst was treated with methanol to reuse or regenerate. The decanted mixture was filtered to remove catalyst absolutely. After that, the filtrate mixture was settled in a separating funnel for 10 min to separate layers clearly. The upper layer consisted of fatty acid methyl esters. The lower layer contained glycerol. The excessive amount of methanol was recovered by distillation before analysis of FAME %.

3. Results and Discussions

3.1. XRD Analysis of Various Eggshell Wastes

The thermal treatment was done to remove CO_2 from the starting material. Indexing of the diffraction peaks was done using a Joint Committee on Powder Diffraction Standards (JCPDS) file. Upon calcinations, the eggshells turned completely white in appearance, which indicates that the calcium carbonate escaped and the product constitutes only calcium oxide. The peaks were compared to the JCPDS file also. The diffraction patterns of the samples heated at temperatures < 800°C were characteristic of CaO. Samples calcined at 800° C contain $CaCO_3$ as the major phase and CaO as a minor phase. The major component of the calcined eggshells at 900ºC for 3 hr was CaO species. The result reveals sharp XRD reflections with (111), (200), (220), (311) and (222) orientations, which implied that the calcined material was well crystallized during the heat treatment process. The crystalline size of egg shell wastes catalyst was also calculated from the XRD data using Scherrer's formula given by Qin and his colleagues [25] after correction for instrumental broadening (Equation 2):

$$D = \frac{k\lambda}{\beta cos\theta} \qquad (2)$$

Where, D is the crystal size (nm), k is Scherrer constant (0.9 for oxide material), λ is the wavelength of X ray, β is the Full Width of Half Maximum (FWHM) and θ is the Bragg angle.

The crystalline size of 700°C, 800°C and 900°C calcined wastes were calculated and the those results were shown in Table 1. Whereas the crystalline size of the chicken eggshell catalyst upon calcination at 900 °C reduced to 9.793 nm. This shows that the crystalline size of the eggshells decreased on calcination. Among eggshell wastes, chicken eggshell waste showed the smallest crystalline size.

Table 1: Crystalline Size of the Various Eggshell Wastes

Catalyst Type	Temp: (˚C)	Crystalline Sizes (nm)
Chicken Eggshell	700	14.384
	800	10.282
	900	9.793
Duck Eggshell	700	16.710
	800	12.046
	900	9.974
Quail Eggshell	700	21.641
	800	14.752
	900	13.843

3.2. EDXRF Analysis of Various Eggshell Wastes

The elemental chemical compositions of the catalysts were presented in Table 2. According to the EDXRF, the carbon content of the various eggshell wastes (such as chicken, duck and quail) was slightly low due to the higher temperature whereas the calcium content was gradually high. The amount of calcium was the maximum at 900°C whereas the content of carbon was nearly empty.

This result suggested that the decomposition of carbonates was accomplished at 900°C for about 3 hr. Majority of all catalysts above 95% was from CaO species. The descending order of CaO content in the catalysts was ranked as follows: chicken eggshell (96.39%), quail eggshell (95.79%) and duck eggshell (95.65%).

Table 2: Elemental Chemical Compositions (Atomic Percentage) of the Eggshell Waste- Derived Catalysts at 900˚ C for 3 hr

Source of catalysts	Compositions (wt %)			
	Ca	Mg	S	C
Chicken eggshell	96.39	0.54	-	3.07
Duck eggshell	95.65	0.24	-	4.11
Quail eggshell	95.79	0.81	0.27	3.13

3.3. SEM Analysis of Various Eggshell Wastes

The SEM as shown in Figure 3 investigated the morphology of the chicken eggshell waste- derived catalyst. According to the SEM images, shapes of particles scattered. This result showed that the decomposition of carbonate was not found before calcined. At 700°C, the chicken eggshell waste typically comprises irregular shape of particles. In other words, there were various sizes and shapes of particles. The smaller size of the grains and aggregates could provide higher specific surface area at 900°C.

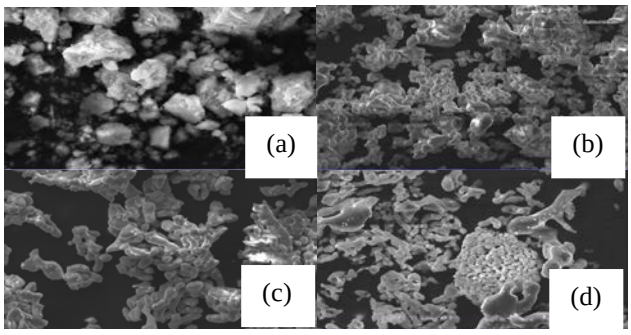

Figure 3: SEM images of chicken eggshell waste derived catalyst for (a) Raw, (b) 700˚C, (c) 800˚C and (d) 900˚C

The chicken eggshell waste – derived catalyst was chosen to use in the production of biodiesel according to the result of XRD, XRF and SEM. From XRD and SEM results, the crystallite size of chicken eggshell was smallest. The particle size directly responds to the surface area. The smaller size of the grains and aggregates could

provide higher specific areas. The highest specific surface area might give the highest FAME yield. From EDXRF result, the maximum amount of CaO was obtained in the chicken egg shell waste. The amount of CaO and purity was mainly important to be a good reaction in the production of biodiesel as a heterogeneous catalyst. Therefore, the catalyst, which was derived from the chicken eggshell waste, was chosen as a suitable catalyst in the preparation of biodiesel according to above reasons.

3.4. Statistical Optimization for Parameters of the Preparation of Biodiesel with CaO Catalyst

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 general form of the quadratic polynomial regression model was given by (Equation 3).

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i<j} \sum \beta_{ij} X_i X_j + \varepsilon \quad (3)$$

Where, Y is response variable (FAME yield %), β_0 is constant coefficient, β_i, β_1, β_2 and β_3 is coefficients for the linear effect, β_{ii}, β_{11}, β_{22} and β_{33} is coefficients for quadratic effect, β_{ij}, β_{12}, β_{13} and β_{23} is coefficients for interaction effect, X_i, X_j, X_1, X_2 and X_3 is independent variables and ε is error.

The model equation based on the coded values (X1, X2 and X3 as methanol to oil molar ratio, catalyst concentration and reaction time, respectively) for the yield of FAME from palm oil was expressed by (Equation 4).

$$Y = 27.3464 + 2.2517 X_1 + 1.8014 X_2 + 7.6686 X_3 - 0.253 X_1^2 - 0.142 X_2^2 - 13.841 X_3^2 + 0.0528 X_1 X_2 + 0.2641 X_1 X_3 + 0.2113 X_2 X_3 \quad (4)$$

Table 3: Analysis of Variance for FAME (%)

Source	Degree of Freedom	Seq SS	Adj MS	F Value	P Value	R^2	R^2 (adj)
Regression	9	17776.3	1975.15	87.42	0.000	99.37%	98.23%
Linear	3	12565.8	1358.52	60.13	0.000		
Square	3	3846.7	1282.23	56.75	0.000		
Interaction	3	1363.9	454.62	20.12	0.003		
Residual Error	5	113.0	22.59	-	-		
Lack of Fit	3	111.5	37.51	49.08	0.020		
Pure Error	2	1.5	0.76	-	-		

The result of statistical analysis of variance (ANOVA) for FAME (%) was shown in Table 3. The result of 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 coefficient, which also indicates the interaction effect cross product. It was found that the model is significant with a very low probability value (< 0.0001). Furthermore, the value of pure error (0.76) is low which indicates good reproducibility of the data and a satisfactory coefficient of determination (R^2 = 0.9823). The coefficient of determination also revealed that there are excellent correlations between the independent variables. There is a high correlation (R^2 = 0.9823) 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.

3.5. Interaction between Reaction Parameters of Biodiesel Preparation using CaO Catalyst

Figure 4 represents the effects of varying methanol to oil molar ratio and catalyst amount on the yield of FAME. From the figure, it is obvious that an increase in the yield of FAME was observed with the increase of methanol to oil molar ratio and catalyst amount with the reaction time of 2.5 hr.

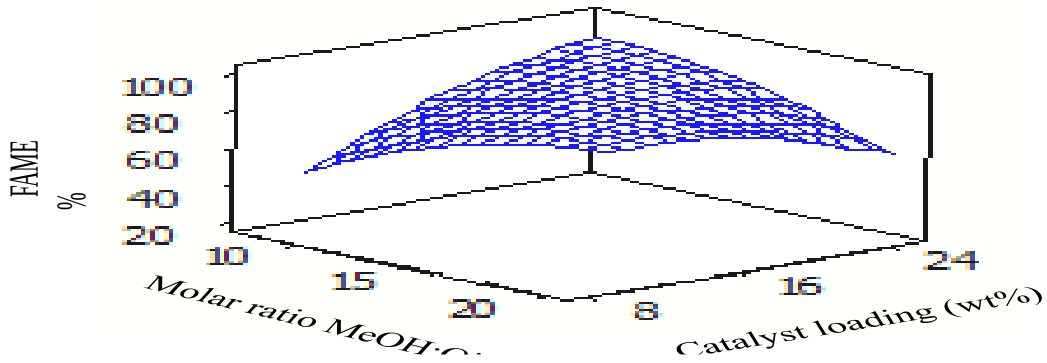

Figure 4: Response surface curve plot showing effect of methanol to oil molar ratio and catalyst concentration on FAME yield

The maximum FAME content of 92% was obtained in 2.5 hr at about 65°C with a catalyst amount of 25 wt% relative to methanol to oil molar ratio of 8:1. Figure 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. Figure 5 indicates a gradual increase in the yield of FAME with time from 1 to 4 hr with a catalyst amount of 17.5 wt%. The maximum FAME yield of 92% was obtained in 2.5 hr at about 65°C with methanol to oil molar ratio 8:1. In the initial stages of the transesterification reaction, production of methyl esters was very low, and then the rate was highest in about 2.5 hr. The lowest FAME yield of 9% was obtained in 1 hr at about 65°C with a catalyst amount of 17.5 wt% relative to methanol to oil molar ratio of 20:1. This can be explained by that transesterification reaction between oil and alcohol is incomplete, when the reaction time is very short. The FAME content increased significantly when the methanol to oil molar ratio was changed from 8 to 20. The high amount of methanol promoted the formation of methoxy species on

the CaO surface, leading to a shift in the equilibrium in the forward direction, thus increasing the rate of conversion up to 92 % for chicken eggshell waste. However, further increased methanol to oil molar ratio did not promote the reaction. It is understood that the glycerol would largely dissolve in excessive methanol and subsequently inhibit the reaction of methanol to the reactants and catalyst, thus interfering with the separation of glycerin, which in turn lowers the conversion by shifting the equilibrium in the reverse direction. Therefore, the optimum molar ratio of methanol to oil was 8, which is more than the practical methanol to oil molar ratio for homogeneous tranesterification of 6 [26].

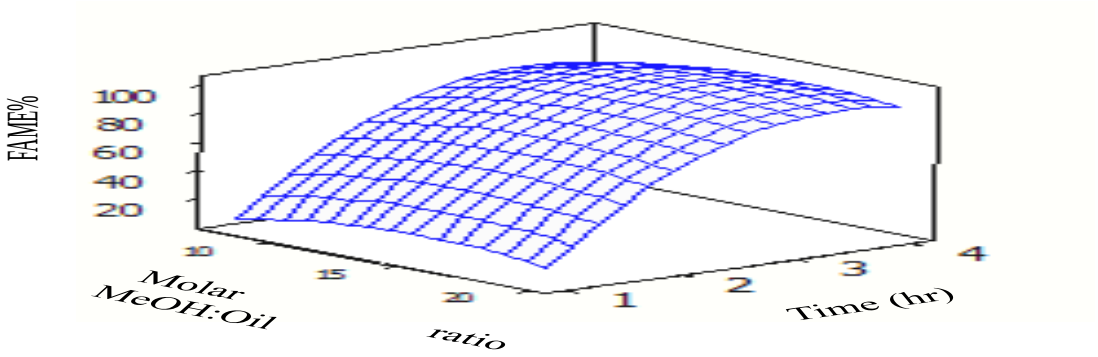

Figure 5: Response surface curve plot showing effect of methanol to oil molar ratio and reaction time on FAME yield

Figure 6 shows the effect of catalyst amount and reaction time on FAME yield obtained in transesterification over chicken eggshell waste. The maximum FAME yield of 92% was obtained in 2.5 hr at about 65°C with a catalyst amount of 25 wt%. In the initial stages of the transesterification reaction, production of methyl esters was very low, and then the rate was the highest in about 2.5 hr. The lowest FAME yield of 8% was obtained in 1 hr at about 65°C with a catalyst amount of 10 wt% relative to methanol to oil molar ratio of 14:1. This can be explained by that transesterification reaction between oil and alcohol is incomplete, when the reaction time is very short. Moreover, the rate of reaction increases with the mass of catalyst loading of 10 wt% and then reaches the maximum with higher loadings. This can be explained by that transesterification reaction was complete in a suitable condition which was catalyst amounts of 10, 17.5 and 25 wt%, methanol/ oil molar ratio of 8:1, reaction time of 2.5 hr and reaction temperature of 65°C.

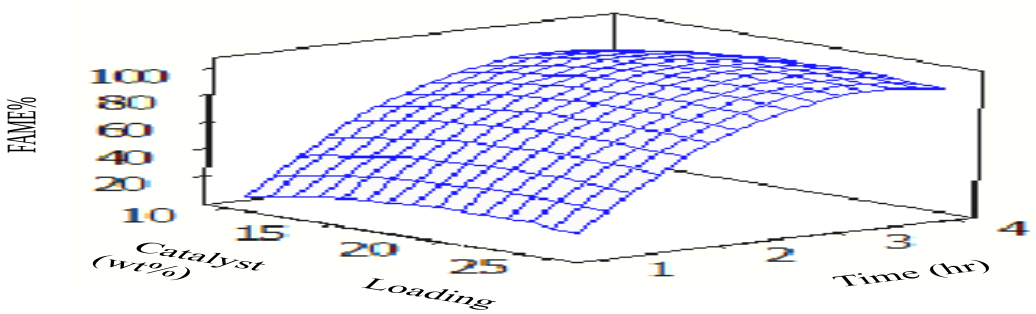

Figure 6: Response surface curve plot showing effect of catalyst concentration and reaction time on FAME yield

3.6. Validation of the Model of Biodiesel Preparation with CaO Catalyst

Optimum conditions of the independent variables for the chicken eggshell catalyzed transesterification of vegetable oil were determined as; catalyst concentration of 25 wt% by weight; reaction time of 2.5 hr and methanol to oil molar ratio of 8:1. To confirm accuracy of the model, chicken eggshell catalyzed transesterification of vegetable oil was carried out under the optimum conditions. Experimental FAME yield was found as 91.930%. Also predicted FAME yield was calculated as 91.176% from the model. According to the results, verification experiments confirmed the validity of the predicted model. The value of pure error was 0.76.

3.7. Reusability of CaO Catalyst

Figure 7 shows reusability of CaO catalyst in the transesterification of palm oil under optimum condition. After each run, the used catalyst was taken out from the reactor and dried for utilization. The result indicated that the catalyst can be repeated use for 3 times with no apparent loss of activity. After the 3rd cycle of transesterification, the yield was still 85 %. The decay in catalyst activity could be due to the leaching of active sites to the reaction media. Leaching of the active phase to the alcoholic phase can be attributed to the bond breaking and formation of Ca^{2+} and CH_3O^- [27].

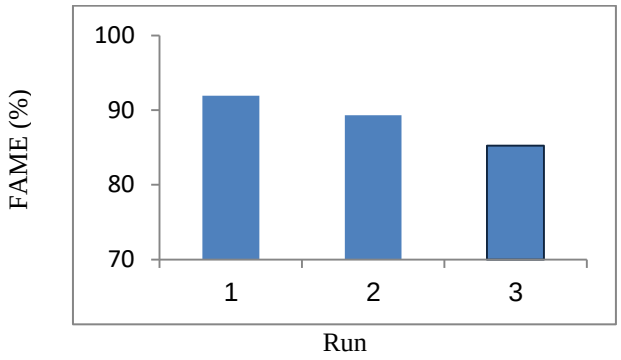

Figure 7: Effect of reusability of CaO catalyst on % yield of FAME

3.8. XRD Analysis of KF/CaO Catalyst

Fig. 8 represents the XRD patterns of KF doped CaO derived from chicken eggshell waste catalyst with various levels of KF- doping. For all samples, the diffraction peaks due to rock-salt CaO are clearly seen. No crystalline KF- containing phase was detected by XRD in these samples. For low KF content, the intensity of the diffraction peaks due to the CaO increases with a decrease in the KF/CaO molar ratio of 0.006, indicating the KF-doping enhances the crystallization of CaO. For the higher levels of KF-doping with the KF/CaO molar ratio from 0.18 to 0.45, the increase in intensity of the CaO peaks slows down. An incipient calcium hydroxide phase was observed in the samples of the KF/CaO molar ratio from 0.18 to 0.45. It is well known that the close ionic radius of K^+ (r_{K^+} = 2.4767° A) compared with that of Ca^{2+} ($r_{Ca^{2+}}$ = 1.39605°A) allows for easy substitution accommodation within the CaO lattice [28].

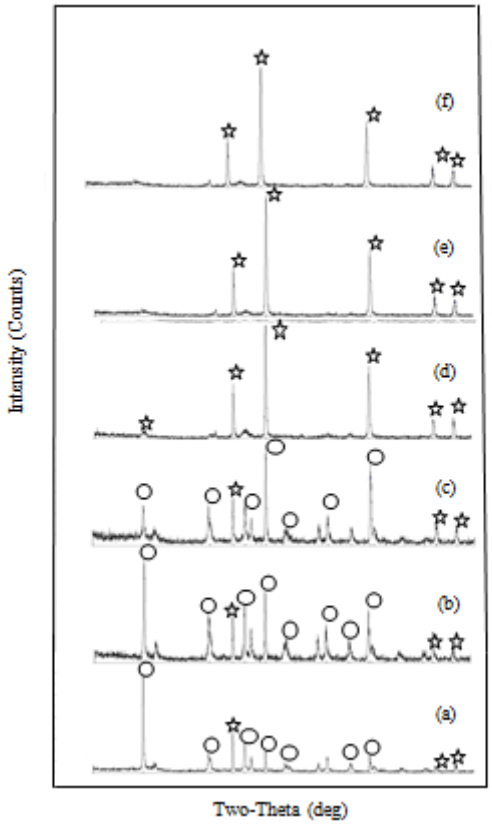

Figure 8: XRD patterns of KF doped CaO derived from chicken eggshell waste catalyst with molar ratio of KF/CaO (a) 0.45, (b) 0.36, (c) 0.27, (d) 0.009, (e) 0.006 and (f) 0.003. (Symbols: ☆ CaO and ○ $Ca(OH)_2$)

Diffusion of doping KF ions in/ on CaO, KF/CaO molar ratio more than 0.09 and excess KF ions form separated calcium hydroxide phase. This results suggested that amount of KF mainly affects the percentage of FAME yield. Therefore, the maximum yield of FAME was 95% with KF loading of molar ratio of 0.006 and catalyst amount of 5 wt%.

3.9. EDXRF Analysis of KF/CaO

The elemental chemical compositions of KF/CaO were presented in Table 4. According to the EDXRF result, the amount of Ca and KF mainly contains 80.305% and 19.381% in KF /CaO molar ratio of 0.45 in which contains a trace amount of Sr (0.204%), Fe (0.083%) and Cu (0.027%). When molar ratio of KF/CaO was slightly low, the amount of Ca was slightly high and the amount of KF was slightly low. It is an efficient condition for doping between KF and CaO.

The amount of Ca and KF was very important in KF/CaO to be a good catalytic activity and stability for the production of biodiesel. If the amount of KF was high, the only activity of KF would lead in the activity of KF/CaO. Because the only activity of KF cannot give the maximum FAME yield. Therefore, the maximum FAME yield was KF molar ratio of 0.006 in which contains 98.494% (Ca), 1.238% (KF), 0.184% (Sr), 0.046% (Fe) and 0.037% (Cu), respectively.

Table 4: Elemental Chemical Compositions of KF/CaO

KF/CaO molar ratio	Compositions (%)				
	Ca	KF	Sr	Fe	Cu
0.45	80.305	19.381	0.204	0.083	0.027
0.36	85.406	14.319	0.180	0.071	0.024
0.27	88.450	11.270	0.180	0.052	0.048
0.18	91.485	8.220	0.210	0.085	-
0.09	94.272	5.429	0.208	0.060	0.031
0.03	97.081	2.623	0.202	0.061	0.034
0.009	98.182	1.514	0.212	0.061	0.030
0.006	98.494	1.238	0.184	0.046	0.037
0.003	98.837	0.867	0.203	0.058	0.035

3.10. Effect of Reaction Parameters of Biodiesel Preparation using KF/CaO Catalyst

1. Effect of KF Loading

The effect of KF loading on FAME yield was studied by conducting transesterification of refined palm oil with methanol at 65˚C, catalyst amount of 3 wt%, methanol to oil molar ratio of 8:1 and reaction time of 2.5 hr. The percentage of FAME yield with the different loadings was presented in Figure 9. We have selected 2.5 hr of reaction time and 8:1 of methanol to oil molar ratio because in our study the best activity for the activity of the parent catalyst (CaO) was obtained for 2.5 hr and 8:1. It was observed that the optimum percentage of FAME yield was 93% with KF loading of 0.6 mol% and catalyst amount of 3 wt%. The percentage of FAME yield decreased slightly while KF loading increased slightly. This can be explained that KF loading directly respond to the yield of FAME. If the amount of KF was high, the only activity of KF would lead in the activity of KF/CaO. Therefore, the amount of KF loading is very important in KF/CaO for the production of biodiesel.

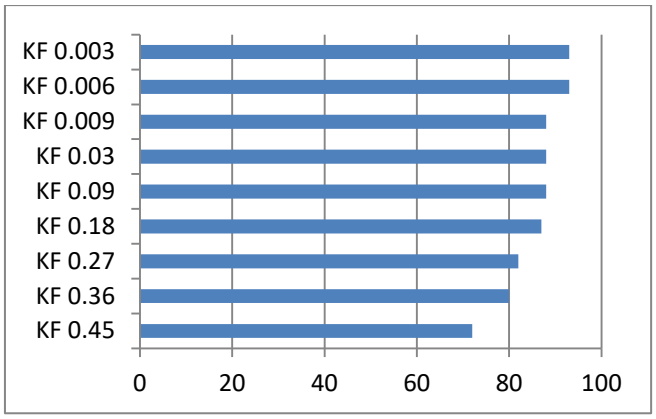

Figure 9: Effect of KF Loading

2. Effect of Catalyst Amount

Reactions were carried out with different amount of catalyst and the results are presented in Figure 10. The reaction was carried out at 65°C for 2.5 hr with a methanol to oil molar ratio of 8:1 and KF/ CaO of 0.6 mol%. It was observed that the percentage of FAME increased with KF loading of 0.6 mol% and complete conversion was obtained for 5 wt% of catalyst amount. The decrease in catalyst amount with 1 wt% decreases the percentage of FAME of 89% when the increase in catalyst amount with 5 wt% increases the yield of FAME of 95%. The highest FAME yield of 95% was obtained with 5 wt% catalyst amount which is attributed to the sufficient number of active sites available for the reaction.

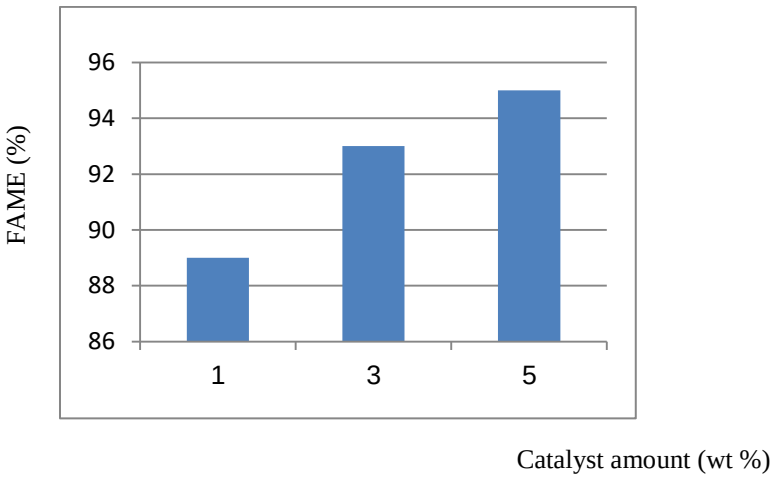

Figure 10: Effect of catalyst amount

3.11. Reusability Study of KF/CaO

An important aspect of heterogeneous catalyst is that it can be regenerated and reused for next reaction. Based on the best catalytic activity, the reusability study of 5 wt% KF doped CaO was investigated for consecutive four cycles under the optimum conditions obtained during the course of study as shown in Figure 11. After the reaction completed, the catalyst was recovered by washing with methanol. After methanol was washed, the catalyst was dried in a heating mantle at 100˚C and reused it in next cycle.

The catalyst showed slight drop in catalytic activity in consecutive cycles. For the fresh catalyst, FAME yield of 95% was achieved. As the catalyst was reused in the second, third and fourth cycle, the FAME yield decreased to 85%, 82%and 79%, respectively.

The decay in catalyst activity might be due to the leaching of active sites to the reaction media. Leaching of the active phase to the alcoholic phase can be attributed to the bond breaking and formation of Ca^{2+} and CH_3O^- [27].

Therefore, it can be concluded that the two unfavorable effects, i.e., leaching from the catalyst and the agglomeration of crystallites, give rise to the deactivation of the catalyst during the initial reaction cycles.

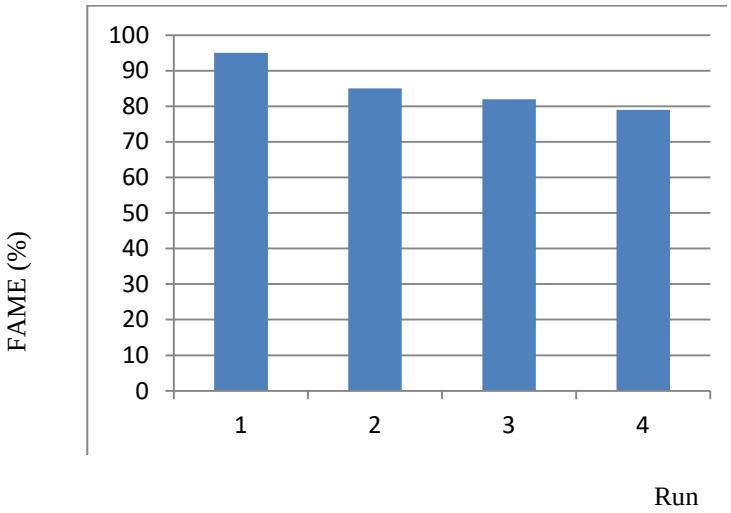

Figure 11: Effect of reusability of KF/CaO on % yield of FAME

4. Conclusion

The catalyst derived from chicken eggshell had excellent activity in transesterification of palm oil for biodiesel production. This catalyst contains $CaCO_3$ which is converted to CaO after calcination at temperatures 900°C for 3 hr. The optimum conditions, which yielded a conversion of palm oil of nearly 92% for chicken eggshell waste- derived catalyst, were reaction time of 2.5 hr, reaction temperature of 65°C, methanol to oil molar ratio of 8:1 and catalyst loading of 25 wt%. The predicted value was in agreement with the experimental value. The results indicated that chicken eggshell waste derived catalyst can be repeated use for three times with no apparent loss of activity. Transesterification of refined palm oil with methanol has also been studied in a heterogeneous system with the KF – doped CaO catalysts under the optimum condition of CaO. It has been found that the addition of KF enhances FAME yield. It is confirmed that the beneficial of KF doping is attributed to the promotion on the formation of strong active sites. The KF/CaO molar ratio of 0.006 exhibits the highest FAME yield of 95% at 65°C with methanol to oil molar ratio of 8:1 and the catalyst amount of 5 wt%. The percentage of FAME decreases with further increasing KF/CaO molar ratio above 0.006, which lead to the only activity of KF in the activity of KF/CaO. The FAME yield of KF/CaO of 95% with 5 wt% of catalyst amount was more than that of CaO of 92% with 25 wt% of catalyst amount. The KF doped CaO catalyst can be reused four times while CaO catalyst can be reused three times. This can be explained that the stability of KF/CaO was better than that of pure CaO catalyst. These results showed that the catalytic activity and resistance of KF/CaO catalyst with the lower amount of catalyst was more excellent than that of CaO in the production of biodiesel.

5. Recommendations

The followings are recommended to be done in the future.

(1) The chemical reaction kinetics of biodiesel should be studied by using heterogeneous catalyst (CaO).
(2) Large- scale biodiesel plants by using low cost heterogeneous catalyst (CaO) should be built in

Myanmar for energy conservation, preventing any negative impact on the environment, making the process cheap and ecologically benign.

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