Chicken Eggshell Waste as a Suitable Catalyst for Transesterification of Palm Oil: Optimization for Biodiesel Production

Thi Thi Win, and May Myat Khine

***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 microscopy (SEM) to get optimal eggshell derived catalyst in the production of biodiesel from palm oil. Response surface methodology (RSM) was used to optimize the biodiesel production parameters. A quadratic polynomial equation was obtained for FAME yield by multiple regression analysis. Interactions between the variables were validated statistically. The optimum conditions of the independent variables in the present work were 8:1 molar ratio of methanol to oil, 25 wt% calcined eggshell catalyst (calcined at 900°C, 3hr), 65°C reaction temperature at reaction time of 3hr. The predicted FAME yield was 92 % under the optimal conditions. Reusability of catalyst was investigated.**

***Keywords*— Biodiesel, Palm oil, Eggshell wastes, Heterogeneous catalyst, Response Surface Methodology**

I. 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].

Recently, the application of natural calcium sources from waste has been considered as a new trend for biodiesel production [11]. In the present investigation, various egg shells such as chicken, duck and quail were used as raw materials for catalyst synthesis and characterization to get optimal egg shell derived catalyst in the production of biodiesel from palm oil. The parameters effecting on the transesterification such as catalyst loading, molar ratio of methanol/ oil, reaction time 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. Reusability of the catalyst was also tested.

II. Experimental

A. Materials

Palm oil was purchased from Local market. The density and molecular weight of oil were measured to be 0.808 g/ml and 847.816 g/mol, respectively [12]. The chicken, duck and quail egg shells were collected as wastes from Manthazin Hostel, Patheingyi Township, Mandalay. 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. All other chemicals used were analytical reagents.

(Paper submission date: Nov. 4, 2016).

Thi Thi Win is with Department of Chemical Engineering, Mandalay Technological University, the Union of the Republic of Myanmar.

May Myat Khine is with Department of Chemical Engineering, Mandalay Technological University, the Union of the Republic of Myanmar.

B. Preparation and Characterization of Eggshell Waste-Derived Catalysts

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. Fig. 1: illustrated the preparation process of egg shell waste derived catalysts.

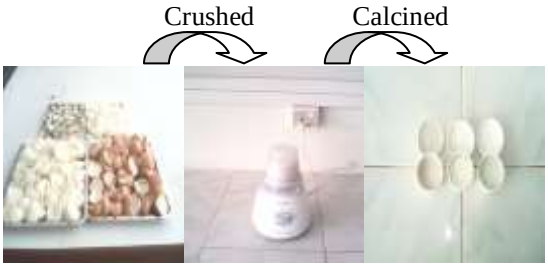

Fig. 1. Preparation Process of Egg Shell Waste Derived Catalysts

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).

C. Transesterification Reaction Procedure

The transesterification was 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 mixture was filtered to remove catalyst absolutely. After that, the 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 analysis of FAME %.

D. 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 %.

E. Statistical Analysis

The biodiesel production yield was optimized using response surface methodology (RSM). A standard RSM design tool known as Box- Behnken Design (BBD) was applied to study the transesterification reaction parameters. 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 [13]. A three-level, three- factor box- behnken experimental design was used to optimize the independent variables to achieve maximum FAME yield.

III. Results and Discussions

A. XRD Analysis

The thermal treatment I was done to remove CO_2 from the starting material. These results were shown as XRD patterns in Fig. 2. Indexing of the diffraction peaks was done using a Joint Committee on Powder Diffraction Standards (JCPDS) file. Upon calcination, the egg shells 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 $CaCO_3$, while samples calcined at temperatures > 800° C exhibited diffraction reflections 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 waste at 900ºC for 3 hr was CaO species. The result reveals sharp XRD reflections with (111), (200), (220), (311) and (222) orientations, implying 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 et al [14] after correction for instrumental broadening ("equation (1)") :

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

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 catalysts 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 8.852 nm. This shows that crystallinity of the eggshells decreased on calcination. Among eggshell wastes, chicken eggshell waste showed the smallest crystallite size.

TABLE I: Crystallite size of the various eggshell catalysts

Catalyst Type	Chicken eggshell			Duck eggshell			Quail eggshell		
Temp: (ºC)	700	800	900	700	800	900	700	800	900
Crystallite size (nm)	21.692	19.718	8.852	16.710	12.046	9.793	14.361	13.843	9.974

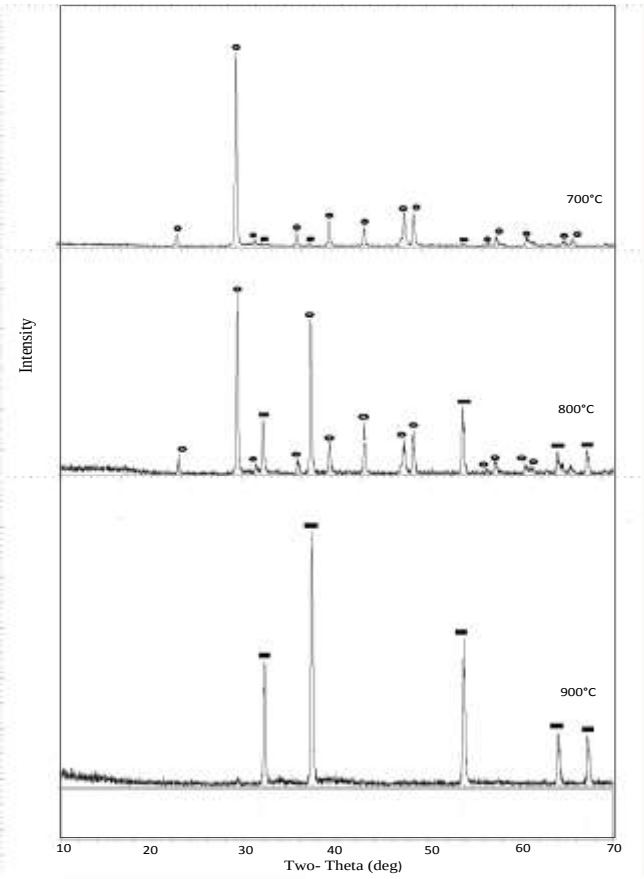

Fig. 2 XRD patterns of the materials obtained by calcining chicken eggshell waste in the range of 700- 900° C for 3 hr (Symbols: ○ $CaCO_3$ and ■ CaO)

B. EDXRF Analysis

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 II: ELEMENTAL CHEMICAL COMPOSITIONS (ATOMIC PERCENTAGE) OF THE WASTE SHELL-DERIVED CATALYSTS AT 900°C FOR 3 HR

Source of catalysts	Compositions (wt %)			
	CaO	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

C. SEM Analysis

The morphology of various eggshell waste derived catalysts at 900°C for about 3 hr was resulted by SEM as shown in Fig. 3. The calcined chicken eggshell was rod- like particles and some of them were bonded together as aggregates. The smaller size of the grains and aggregates could provide higher specific surface area. Since all samples are considered to be less- porous or even non- porous, the size of the particle should directly respond to the surface area. The calcined duck eggshell showed similar particle morphology, but larger size of aggregates. The largest size of aggregated particles was observed in the calcined quail eggshell.

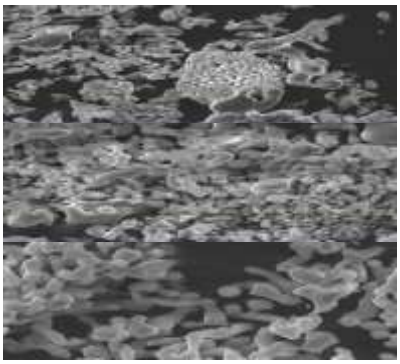

Fig.3 SEM images of the materials obtained by calcining (a) chicken, (b) duck and (c) quail eggshell wastes at 900ºC for about 3 hr

The chicken eggshell waste – derived catalyst was chosen to use in the production of biodiesel by seeing the result of XRD, XRF and SEM. From XRD and SEM results, the crystallite size of chicken eggshell was smallest. The particle size should directly respond to the surface area. The smaller size of the grains and aggregates could provide higher specific areas. The highest specific surface area might obtain the highest FAME%. From EDXRF result, the maximum content of CaO was obtained in the chicken egg shell waste. CaO content was mainly important to be a good reaction in the production of biodiesel from heterogeneous catalyst (CaO). Therefore, the chicken eggshell waste was chosen as a suitable eggshell to produce biodiesel according to above reasons.

D. 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 methanol to oil molar ratio, catalyst concentration and reaction time, respectively) for the yield of FAME from palm oil was expressed by "equation (2)".

$$Y = 27.3464 + 2.2517\,X_1 + 1.8014\,X_2 + 7.6686\,X_3 - 0.253\,X_1^2 - 0.142\,X_2^2 - 13.841\,X_3^2 + 0.0528\,X_1X_2 + 0.2641\,X_1X_3 + 0.2113\,X_2X_3 \quad (2)$$

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 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.

E. Interaction between Independent Variables

Fig. 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. The maximum FAME content of 91.930% 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. 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.

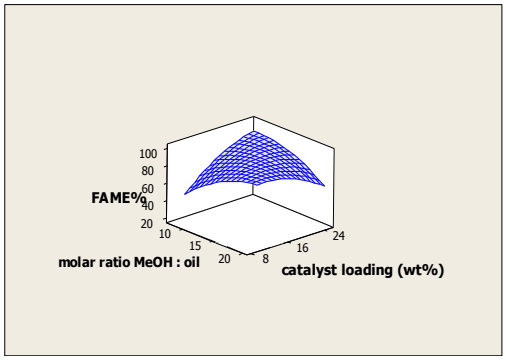

Fig.4 Response surface curve plot showing effect of methanol to oil molar ratio and catalyst concentration on FAME yield.

Fig. 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 91.930% was obtained in 2.5hr 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 8.840% 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 91.930 % for chicken eggshell waste. However, further increases 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 [15].

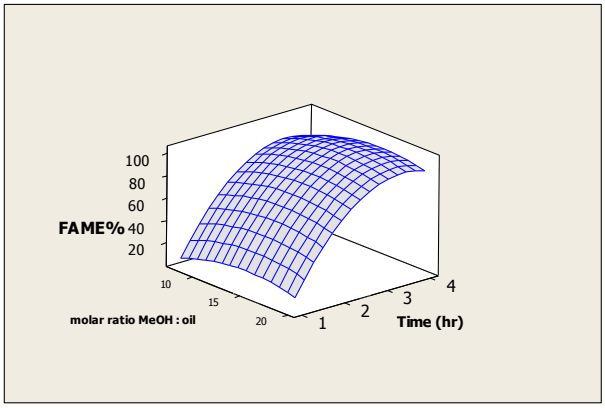

Fig. 5 Response surface curve plot showing effect of methanol to oil molar ratio and reaction time on FAME yield.

Fig. 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 91.930% 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 highest in about 2.5 hr. The lowest FAME yield of 7.880% 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.

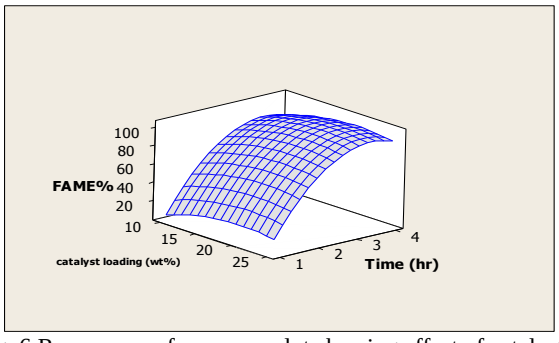

Fig. 6 Response surface curve plot showing effect of catalyst concentration and reaction time on FAME yield.

F. Validation of the Model

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.

G. Reusability of Waste Catalyst

Fig. 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^- [16].

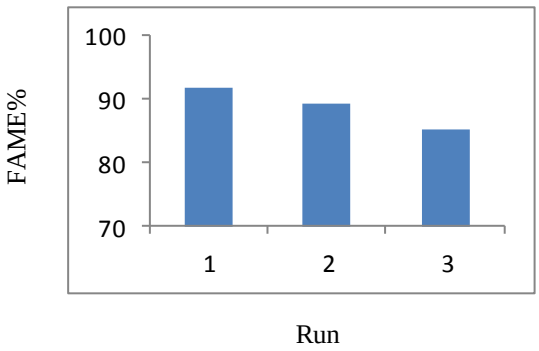

Fig.7 Effect of reusability of catalyst on % yield of FAME

IV. Conclusion

The catalyst derived from chicken eggshell had excellent activity in heterogeneous 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 method of reusing chicken eggshell wastes to prepare catalyst could recycle the waste, minimizing contaminants, reducing the cost of catalyst, and making the catalyst environmentally friendly. Hence, chicken eggshell heterogeneous catalyst showed high activity, 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 FAME were almost similar to that of homogeneous catalytic system. The results indicated that the chicken egg shell can be repeated use for 3 times with no apparent loss of activity.

Acknowledgment

The author would like to express her thanks to Dr. Myint Thein, Rector, Mandalay Technological University, for his kindness, help, permission and suggestion for completion of this paper. The author also expresses his gratitude to Dr. Khaing Zaw Naing, Associate Professor and Head, Department of Chemical Engineering, Mandalay Technological University, for his kindness, help and suggestion. Finally, I especially acknowledge my great special thanks to my family.

References

[1] Viriya-empikul N., Krasae P., Nualpaeng W., Yoosuk B., Faungnawakij K., " Biodiesel production over Ca- based solid catalysts derived from industrial wastes", *Fuel*, 92, 239-244, 2012. https://doi.org/10.1016/j.fuel.2011.07.013

[2] Suryaputra W., Winata I., Indraswati N., Ismadji S., "Waste cap iz(Amusium cristatum) shell as a new heterogeneous catalyst for biodiesel production", *Renew. Energy*, 50, 795-799, 2013. https://doi.org/10.1016/j.renene.2012.08.060

[3] Dias JM, Alvim- Ferraz MCM, "Almeida MF," Mixtures of vegetable oils and animal fat for biodiesel production: influence on product composition and quality," *Energy Fuel 22* (2008) 3889–93. https://doi.org/10.1021/ef8005383

[4] Phan AN, Phan TM.," Biodiesel production from waste cooking oils," Fuel 87, (2008), 3490–6. https://doi.org/10.1016/j.fuel.2008.07.008

[5] Birla A., Singh B., Upadhyay S.N., Sharma Y.C., "Kinetics studies of synthesis of biodiesel from waste frying oil using a heterogeneous catalyst derived from snail shell", *Bioresour*. Technol., 106,95- 100, 2012. https://doi.org/10.1016/j.biortech.2011.11.065

[6] Sharma Y.C., Singh B., Upadhyay S.N., "Advancements in development and characterization of biodiesel: A review", *Fuel*, 87, 2355- 2373, 2008. https://doi.org/10.1016/j.fuel.2008.01.014

[7] Liu X., He H., Wang Y., Zhu S., Piao X.,"Transesterification of soybean oil to biodiesel using CaO as a solid base catalyst", *Fuel*, 87, 216- 221, 2008. https://doi.org/10.1016/j.fuel.2007.05.059

[8] Kouzu M., Kasuno T., Tajika M., Sugimoto Y., Yamanaka S., Hidaka J., "Calcium oxide as a solid base catalyst for transesterification of soybean oil and its application to biodiesel production",*Fuel*, 87, 2798- 2806, 2008. https://doi.org/10.1016/j.fuel.2007.10.019

[9] Oliveira D.A., Benelli P., Amante E.R.,"A literature review on adding value to solid residues: Egg shells", *J.Cleaner Production*, 46, 42-47, 2013. https://doi.org/10.1016/j.jclepro.2012.09.045

[10] Chojnacka K.," Biosorption of Cr(III) ions by eggshells," J.Hazard. Mater. 121 (2005), 167–173. https://doi.org/10.1016/j.jhazmat.2005.02.004

[11] Khemthong P., Luadthong C., Nualpaeng W., Changsuwan P., Tongprem P., Viriya-empikul N., Faungnawakij K.,"Industrial eggshell wastes as the heterogeneous catalysts for microwave-assisted biodiesel production", *Catal.Today*, 190, 112-116, 2012. https://doi.org/10.1016/j.cattod.2011.12.024

[12] WAI-LIN, SIEW and JOHARI MINAL, MPOB, OFI Middle East 2007. Palm oil and Fractions: *Properties and Characteristics*, www. Soci. Org/../ Siew Wai Lin .ashx.

[13] Myers RH, Montgomery DC. Response surface methodology: process and product optimization using designed experiments. 2nd ed. USA: John Wiley & Sons; 2000.

[14] Qin C., Li C., Hu Y., Shen J., Ye M.," Facile synthesis of magnetite iron oxide nanoparticles using 1-methyl-2-pyrrolidone as a functional solvent," *Colloids Surf*., A, 336 (2009), 130–134. https://doi.org/10.1016/j.colsurfa.2008.11.040

[15] Obadiah A., Swaroopa G.A., Kumar S.V., Jeganathan K.R., Ramasubbu A., "Biodiesel production from palm oil using calcined waste animal bone as catalyst",*Bioresour.Technol*., 116,512-516, 2012. https://doi.org/10.1016/j.biortech.2012.03.112

[16] Buasri A., Ksapabutr B., Panapoy M., Chaiyut N., "Biodiesel Production from waste cooking palm oil using calcium oxide supported on activated carbon as catalyst in a fixed bed reactor", *Korean J. Chem. Eng*., 29, 1708-1712, 2012. https://doi.org/10.1007/s11814-012-0047-7

First A. Author was born in Chanmyatharzi Township, Mandalay, Myanmar. Date of birth is Dec. 26, 1986. First A. Author studied in Technological University (Mandalay) in Chanayetharzan Township, Mandalay from 2003 to 2008 for holding a Bachelor of Engineering (BE) Degree and further studied in Mandalay Technological University (MTU) in Patheingyi Township, Mandalay from 2010 to 2012 for holding a Master of Engineering (ME) Degree. Major field of study is chemical engineering subjects.

She was a teacher and also a Chemical Engineer. Now, her job age is seven years and eight months. She taught her pupils about Food Technological Subject in Technological University (Mandalay) for about one year. After that, she taught her students about Thermodynamics and Chemical Reaction Engineering (Kinetics) in Tehnological University (Magway) for nearly two years. Now, she is a Ph.D. (ChE-3) candidate (10^{th} batch) from Chemical Engineering Department in MTU.

Ms. Thi Thi Win (Paper Title– Chicken eggshell as a Suitable Catalyst for Transesterification of Palm Oil: Optimization for Biodiesel Production).