Kinetic Study of Biodiesel Synthesis from Palm Oil by Using Low-Cost Calcium Oxide Catalyst

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ABSTRACT

The biodiesel production from palm oil by using the low-cost calcium oxide catalysts, prepared from eggshells, cockle shells and crab shell, calcined at 800 ^{O}C for 3h was investigated. The results showed that the use of the catalyst preparation from eggshells exhibited the highest conversion of palm oil to biodiesel following by cockle shells and crab shell. With the speed of mixing 800 rpm, the catalysts particle size 90-106 µm, molar ratio of methanol to palm oil of 12:1, the biodiesel conversion can reach 57%. For the transesterification kinetics, the pseudo-first-order was in good agreement with the experimental results. The reaction rate constant (k) and activation energy were determined as 0.0046 (min)$^{-1}$ at 65^{O}C and 58.47 kJ/mol, respectively.

***Keywords**: Biodiesel, Calcium oxide, Pseudo-first order, Transesterification.*

1 INTRODUCTION

Biodiesel, an alternative to fossil diesel fuel, which is produced by transesterification of vegetable oil or esterification of fatty acid with methanol, can be used as a renewable and environmentally benign fuel. The conventional catalysts for transesterification reaction are homogeneous strong alkaline bases such as sodium hydroxide and potassium hydroxide. However, alkaline catalysts are corrosive to process equipment and require a number of purification steps in order to comply with the fuel quality standard and treat the pollutions. These problems can be overcome by the use of heterogeneous catalysts. Calcium oxide (CaO) has been proved as a promising heterogeneous catalyst for transesterification reaction of vegetable oil due to its high basicity, low solubility in biodiesel, and easy handling [1] - [2]. Recently, the utilization of calcium carbonate solid wastes, such as eggshell [3] - [4], clamshell [5] - [6], crab shell [7] to produce low-cost calcium oxide catalyst has been attractive because of the catalysts derived from wastes will fulfill the environmental and economical issues.

The reaction mechanism of calcium oxide-catalyzed transesterification is involved in the formation of strong base specie, methoxide anion (CH_3O^-), from the reaction of oxygen ion on calcium oxide surface and methanol [7]. Eventually, three methoxide ion attacks the carbonyl carbon of triglyceride molecule to produce three methyl ester molecules and a glycerine molecule. Although several researchers reported the kinetics of homogeneous transesterification, the kinetics of heterogeneous transesterification has been rarely investigated.

In this research, the catalytic activity of catalyst from eggshell, cockle shell and crab shell was investigated. The influences of temperature, methanol to oil molar ratio, rotational speed, and catalyst particle size were evaluated to determine the optimal conditions. Finally, a kinetic study was also performed and the reaction rate constant (k) and activation energy (E_a) at various temperatures were studied.

2 RESEARCH METHODOLOGY

2.1 Catalysts Preparation

The waste shells were collected from the local restaurants. To remove impurity, the waste shells were washed several times with tap water. The waste shells were then dried at 100°C for 24 h in oven and calcined in the muffle furnace at 800°C for 3 h. After calcinations, CaO catalysts were cooled in desiccator. Prior to activation, the catalysts were ground and sieved to obtain the desired particle sizes. The catalyst activation in static air conditions at 800°C for 1 h preceding the reaction is required for the formation of strong basic sites.

2.2 Catalyst Characterization

X-ray diffraction (XRD) patterns were recorded on a X-ray diffractometer (JDX-3530, JEOL, Japan); using a CuK_α radiation (λ=0.1541 nm) at 40 kV and 30 mA. The detection range was 25-80° with the step size of 0.02°/0.5s. The basicity and basic strength of the catalyst was tested using various Hammett indicators and titration method [8] - [9]. The following Hammett indicators were used: bromthymol blue ($H\_$=7.2), phenolphthalein ($H\_$ = 8.2), 2,4-dinitroaniline ($H\_$ = 15) and 4-nitroaniline ($H\_$ = 18.4).

2.3 Reaction Procedure

The transesterification reaction was carried out in a batch reactor. The palm olein oil in a three-neck glass flat-bottom flask fitted with a reflux condenser and a thermometer. Agitation was performed with an adjustable speed magnetic stirrer. A mixture of catalyst and methanol (RCI Labscan, AR.Grade) preheated and stirred at 50°C was added to the oil and then temperature was raised to the desired reaction temperature. The experiments were carried out in a constant temperature water bath. Different methanol to oil molar ratios (9:1, 12:1, 15:1, and 18:1), temperatures (50°C, 55°C, 60°C and 65°C), rotational speeds (200 rpm, 400 rpm, 600 rpm and 800 rpm), catalyst particle sizes (90-106 µm, 106-125 µm, 125-150 µm, and 150-180 µm), and catalyst loading of 10 %w/w (based on the oil weight) were used to investigate their effects on the palm oil conversion. After the reaction, the catalyst was removed from reaction mixture by filtration, and then the glycerol was separated in a separating funnel to settle overnight, finally methanol was evaporated before determination palm oil conversion. The compositions of biodiesel were determined by a gas chromatograph (GC-8A, Shimadzu) equipped with Innovax capillary column and a flame ionization detector.

Palm olein oil was purchased from Lam Soon PCL., Thailand. in which the acid value (A.O.C.S Official Method Ca 5a-40) is 0.06 mg KOH/g oil and saponification value (A.O.C.S Official Method Cd 3-25) is 193.55 mg KOH/g oil. The average molecular weight (M) of oil is calculated by

$$M = \frac{5.61 \times 1000 \times 3}{(SV - AV)} \tag{1}$$

where AV is the acid value and SV is the saponification value. Hence, the average molecular weight of oil was calculated to be 870 g/mol.

2.4 Kinetics of Transesterification

In order to explore the kinetics of CaO-catalyzed transesterification of palm oil and methanol, reaction has been studied under optimal conditions.

The rate law of the transesterification reaction can be expressed as

$$-r_a = \frac{-d[TG]}{dt} = k' \cdot [TG] \cdot [ROH]^3 \tag{2}$$

where - r_a is rate of transesterification reaction, [TG] is the concentration of triglycerides and [ROH] that of methanol, k' is the reaction rate constant and t is the time. This rate law follows a forth order kinetic model. However, the high methanol to oil molar ratios was applied to drive the reaction equilibrium, and then the methanol concentration is considered constant during reaction. Therefore, the reaction kinetics was assumed to be pseudo-first order reaction [9] - [10]. Finally, the reaction rate expression can be written as:

$$-r_a = \frac{-d[TG]}{dt} = k \cdot [TG] \tag{3}$$

Integration and rearrangement of equation (3) results in:

$$-\ln(1 - X_{ME}) = k \cdot t \tag{4}$$

where X_{ME} is conversion of palm oil to biodiesel, and k is modified rate constant and $k = k' \cdot [ROH]^3$.

3 RESULTS AND DISCUSSION

3.1 Characterization of catalysts

According to the significant parameters of the catalysts derived from calcium-based solid for transesterification were active specie (CaO) content and basic properties on catalysts surface. Therefore, XRD and Hammett indicator method are applied in this research to measure the catalytic properties.

The powder XRD patterns of the waste shells-derived catalysts are demonstrated in Fig. 1. As can be seen, all XRD patterns reveal sharp CaO crystalline peaks indicating that the waste shells was calcined at 800°C for 3h providing a high purity CaO catalysts. The characteristic peaks are observed at 2θ of 32.2°, 37.4°, 53.9°, 64.1° and 67.3° that are consistent with previous results reported in the literature [5]. The minor peaks of $Ca(OH)_2$ crystalline phase were also observed at 2θ of 28.6°, 34.2°, 47.7° and 50.8° for all catalysts. This resulted from fact that CaO powder for XRD measurement was exposed to moisture and hydrated during storage for testing, which rapidly formed $Ca(OH)_2$ on the surface of CaO.

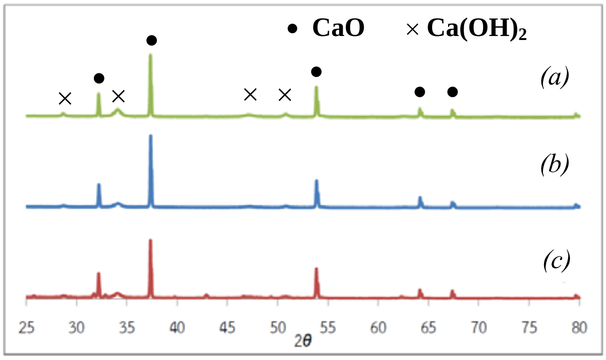

***Fig. 1** XRD patterns of (a) eggshell, (b) cockle shell and (c) crab shell calcined at 800 ℃ for 3h.*

The basic strength and basicity of CaO catalysts are the most important properties regarding their utilization as catalysts for transesterification reaction [11] - [12] - [13]. The basic strength and basicity of the developed catalysts is listed in Table 1.

Table 1 Basic strength and basicity of the CaO catalysts.

Catalyst source	Basic strength	Basicity (mmol/g)
Eggshell	7.2 <H_<9.3 9.3 <H_<15.0	0.040 0.040
Cockle shell	7.2 <H_<9.3 9.3 <H_<15.0	0.013 0.023
Crab shell	7.2 <H_<9.3 9.3 <H_<15.0	0.010 0.016

The catalysts changed the color of bromthymol blue and phenolphthalein, but failed to change the color of 2, 4-dinitroaniline and 4-nitroaniline. It was found that the catalysts basic strength was within 7.2<H_<15.0 and is considered as a strong base for transesterification reaction. Based on the indicator and titration test results, CaO catalysts derived from eggshell exhibits the highest basicity following by cockle shell and crab shell, respectively. However, the basic strength of CaO catalysts derived from eggshell was slightly lower than CaO prepared from snail shell [9] and limestone [12] where the basic strength of 15<H_<18.4. In addition, as others have reported [3]-[4]-[5], the CaO catalysts derived from eggshell, a low surface area solid (≈ 1 m^2/g) with strong basic active site, obtained the best biodiesel yield when calcination at 800°C for 2-4 h.

3.2 Effect of catalyst source and rotational speed

The effect of catalyst sources and rotational speeds on catalytic activity are shown in Fig.2.

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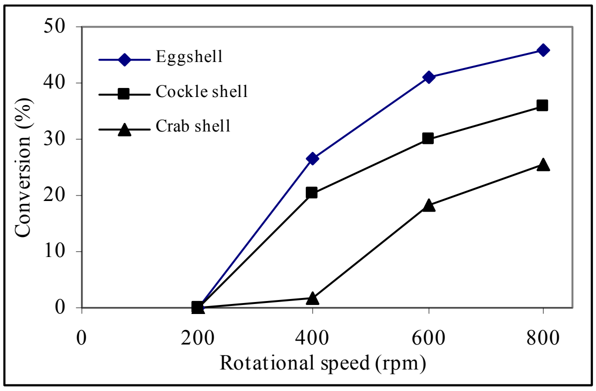

***Fig. 2** Effect of catalyst source and rotational speed with methanol to oil molar ratio of 12:1, catalyst loading of 10%, temperature of 65 ℃, catalyst particle size of 90-106 µm, and reaction time 90 min.*

As demonstrated in Fig. 2, the ascending order of the catalytic activity in term of conversion (%) over the waste shell derived catalysts was as follows: crab shell cockle shell, and eggshell. As mentioned previously, the strength and quantity of basic site on solid-base catalyst surface are the important factors relating to the yield of transesterification. The results implied that the amount of strong basic sites on catalyst surface directly influenced to the catalytic activity and the conversion of palm oil. Consequently, the catalyst derived from eggshell was chosen to investigate in the following experiments. Furthermore, this result showed the similar tendency that the catalyst derived from eggshell showed the higher yield of biodiesel than that of golden apple snail and meretrix venus in accordance with the catalyst derived from eggshell contains the higher amount of strong basic sites [5]. It cloud be deduced that a calcination temperature of 800°C for 3 h was sufficient to produce the active catalysts.

The effect of the rotational speed on palm oil conversion is also depicted in Fig. 2. The variation of palm oil conversion at different rotational speed ranging from 200-800 rpm was investigated. It is obvious from

Fig. 2 that the conversion of palm oil to biodiesel is greatly affected by rotational speed. Due to the high shearing rates, the boundary layer of liquid on the catalyst surface was decreased, which reduced the external mass transfer resistance [14]. This revealed that the immiscible phases of methanol and oil, and the solid catalyst, require a certain rotational speed in order to gain homogenized. If the external mass transfer exists; diffusion of the reactants from bulk liquid phase to the outermost surface controls the reaction rate. As illustrated in Fig. 2, in case of the catalyst derived from eggshell, the conversion of palm oil was rapidly increased to 40% for the rotational speed of 600 rpm, and then slightly raised to 46% for the rotational speed of 800 rpm. This also supports the previous findings that the minimum rotational speed to eliminate the external mass transfer limitation should be more than 900 rpm for the catalyst loading of 10% [15].

3.3 Effect of catalyst particle size

The evaluation of internal mass transfer limitation can be studied by examining the effect of the catalyst particle size on palm oil conversion.

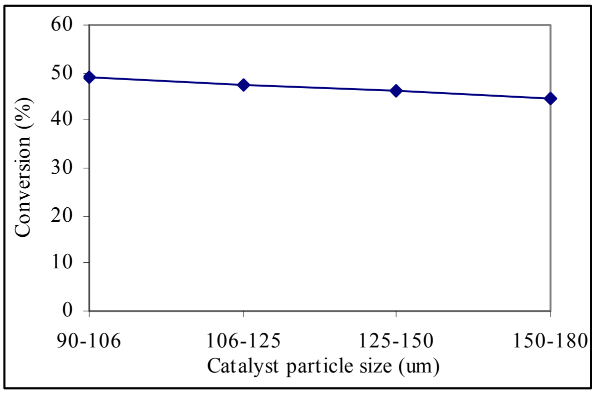

Fig. 3 *Effect of catalyst particle size with methanol to oil molar ratio of 12:1, catalyst loading of 10%, rotational speed of 800 rpm, temperature of 65 ℃, reaction time 90 min and the catalyst derived from eggshell.*

Fig. 3, where the palm oil conversion is plotted as a function of the catalyst particle size, indicates that the palm oil conversion was slightly influenced by the catalyst particle size. Thus, the external mass transfer plays an important role on the reaction rate of transesterification. However, the suggestion to get rid of the internal mass transfer limitation, the largest catalyst particle size was 15.3 µm [15]. To examine the effect of methanol to oil molar ratio, reaction temperature and time on the palm oil conversion, the investigation was conducted under the catalyst loading of 10%, rotational speed of 800 rpm, particle size of 90-106 µm with CaO derived from eggshell as catalyst.

3.4 Effect of methanol to oil molar ratio

The methanol to oil molar ratio is one of the important factors affecting the palm oil conversion to biodiesel. Because the transesterification reaction was a reversible reaction, methanol was employed in large excess to shift the forward reaction for the formation of biodiesel based on Le Chatelier's Principle.

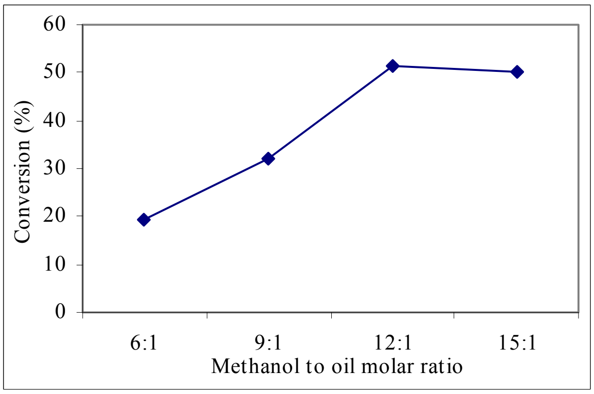

Fig. 4 *Effect of methanol to oil molar with catalyst loading of 10%, rotational speed of 800 rpm, temperature of 65℃, particle size of 90-106 µm, and reaction time 90 min.*

As can be seen from Fig. 4, the palm oil conversion increased with increasing of the methanol to oil molar ratio over the range from 6:1 to 12:1. With further the increase of methanol, little effect on the palm oil conversion can be observed. This effect could be attributed to that the vast excess of methanol dilute the concentration of oil in the reaction system, hence reducing the possibility of collision of palm oil and catalyst. It was found that the highest conversion was obtained at the optimum methanol to oil molar ratio of 12:1. Moreover, the high amount of methanol retards the separation of the glycerin and oil phase. In contrast, the low amount of methanol diminishes the biodiesel yield as a consequence of the limitation of methoxide ions formation on CaO surface, resulting in the low reaction rate and palm oil conversion [3].

3.5 Effect of temperature and reaction time

Reaction temperature is another important variable that affecting the conversion of palm oil to biodiesel and the conversion increases with increasing of temperature as shown in Fig. 5. The results signified that higher temperature leads to higher yield, and the palm oil conversion reaches to 57% at 65°C.

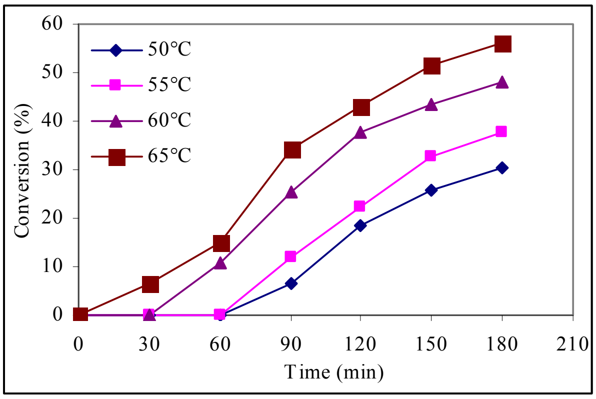

Fig. 5 *Effect of temperature and reaction time with methanol to oil molar ratio of 12:1, catalyst loading of 10%, rotational speed of 800 rpm, and particle size of 90-106 µm.*

The effect of reaction time on the palm oil conversion was also studied in Fig. 5. The reaction time was varied within the range from 0 min to 180 min. The palm oil conversion of the transesterification reaction usually increased with the reaction time. It can be seen that the palm oil conversion reached the maximum value at the reaction time of 180 min. Therefore, the optimum reaction conditions were methanol to oil molar ratio of 12:1, catalyst loading of 10%, temperature of 65 °C, rotational speed of 800 rpm, catalyst particle size of 90-106 µm, and reaction time 180 min, at which the highest palm oil conversion was 57%. However, the unexpectedly lower the palm oil conversion than as reported in literatures that the biodiesel yield exceeded 95% with methanol to oil molar ratio of 9:1, catalyst loading of 3%, temperature of 65 °C, and reaction time of 180 min [4], and the biodiesel yield of 87% with methanol to oil molar ratio of 15:1, catalyst loading of 10%, temperature of 60 °C, and reaction time of 180 min [5]. A possible explanation of the lower palm oil conversion might due to the catalysts used in this work has significantly lessen the strength and lower amount of basic sites as reported above. Future research should focus on the development of the basic properties of catalysts that would be improved to both palm oil conversion and reaction rate.

3.6 Kinetics of CaO catalyzed transesterification

Based on the proposed kinetic model, the reaction was described as a pseudo-first order reaction and the kinetic parameters were determined with the catalyst derived from eggshell. To minimize the influence of internal and external mass transfer limitations, the rotational speed of 800 rpm and catalyst particle size of 90-106 µm were chosen in this experimentation. By plotting $-\ln(1-X_{ME})$ versus reaction time as shown in Fig. 6, strong linear correlations were obtained which supported the assumption of pseudo-first order model. The rate constants (k) at different temperatures can be obtained from the linear slope through the origin.

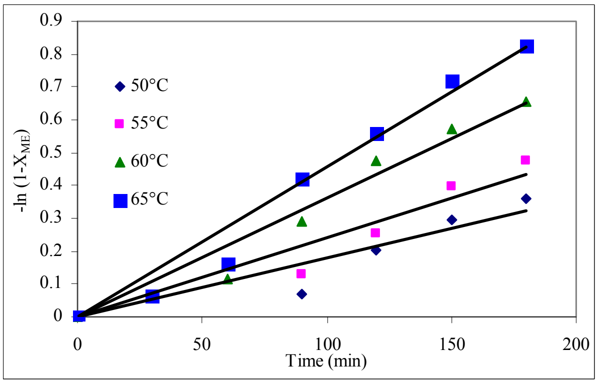

Fig. 6 *A plot of $-\ln(1-X_{ME})$ vs reaction time at different temperatures with methanol to oil molar ratio of 12:1, catalyst loading of 10%, rotational speed of 800 rpm, and particle size of 90-106 µm.*

Table 2 summarizes the rate constant values and the corresponding correlation coefficients (R^2) obtained from the linear fitting. High linearity of these plots supports that the proposed kinetic model describes the experimental results well.

Table 2 Rate constants (k) and correlation coefficients (R^2) for the transesterification of palm oil at different temperatures.

Temperature (°C)	k (min^{-1})	R^2
50	0.0018	0.8787
55	0.0024	0.9204
60	0.0036	0.9586
65	0.0046	0.9706

The activation energy and pre-exponential factor for the transesterification reaction can be calculated using the Arrhenius equation:

$$k = k_0 \cdot e^{\frac{-E_a}{RT}} \tag{5}$$

where E_a is the activation energy (kJ/mol), R is the gas constant (8.314 J/mol·K), T is the temperature (K), and k_o is the pre-exponential factor (min^{-1}).
By taking the natural logarithm of equation (5), equation (6) is obtained:

$$\ln k = -\frac{E_a}{R}\times\frac{1}{T} + \ln k_0 \tag{6}$$

where E_a and k_o can be determined from the slope and intercept, respectively.

Fig. 7 shows that strong linearity ($R^2 = 0.9923$) could be observed between lnk and 1/T. The activation energy (Ea) determined from the slope was 58.47 kJ/mol, while the k_o calculated from the intercept was 5.1×10^6 min^{-1}.

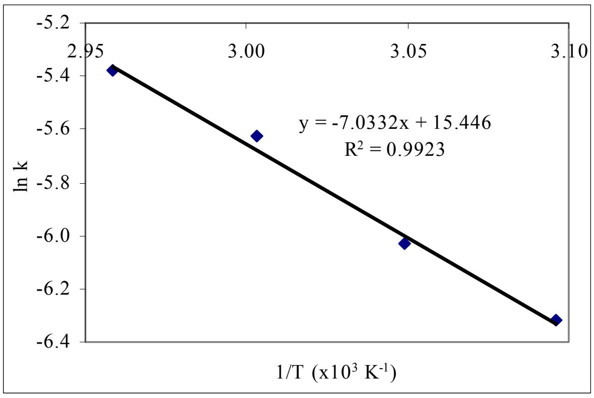

Fig. 7 *The Arrhenius plot for transesterification of palm oil in presence of the catalysts derived from eggshell.*

The activation energy for the transesterification of palm oil with the catalyst derived from eggshell was in the range of activation energy obtained for transesterification with calcium-based catalysts i.e. 42.56 [16] -79 kJ/mol [9]. With the selected conditions, the large activation energy of 58.47 kJ/mol exhibits that the mass transfer resistance is slightly affected.

4 CONCLUSION

The biodiesel production could be achieved by low-cost CaO catalysts derived from waste shells in the transesterification of palm olein oil. The ascending order of the catalytic activity as following: crab shell, cockle shell, and eggshell was attributed to the increase of the quantity of strong base sites. The catalyst derived from eggshell can achieve the palm oil conversion of 57% using methanol to oil molar ratio of 12:1, catalyst loading of 10%, temperature of 65°C, rotational speed of 800 rpm, catalyst particle size of 90-106 µm, and reaction time 180 min. The pseudo-first order kinetic model and values of the rate constant and activation energy were determined to be 0.0046 min^{-1} (65°C) and 58.47 kJ/mol, respectively. Overall, although further development is required to synthesize the stronger basic strength of CaO catalyst, the potential of this low-cost heterogeneous Ca-based catalyst has been proved for transesterification applications.

5. ACKNOWLEDGEMENTS

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