The Kinetic Study of Transesterification Reaction for Biodiesel Production Catalyzed by CaO Derived from Eggshells

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Abstract

The kinetic study of transesterification reaction for biodiesel production catalyzed by CaO derived from eggshells as a solid heterogeneous catalyst compared with NaOH as a homogeneous catalyst was investigated. The results showed that CaO derived from eggshells displayed highly active catalyst for biodiesel production. Nevertheless, the rate constant of the reaction (k) catalyzed by CaO obtained from eggshells (1.22×10^{-2} min^{-1}) was lower than k value of NaOH catalyst (2.65×10^{-1} min^{-1}) approximately 22 times. Although, CaO of eggshells demonstrated lower catalytic performance than NaOH, they were also advantages than NaOH catalyst such green, low-cost, non-toxicity and reused several times. Furthermore, the comparison catalytic activity of CaO catalyst derived from natural waste materials namely river snail shells, cockel shells and golden apple snail shells versus eggshells derived CaO catalyst was also investigated in this study. All of the results was not only usage as database to develop biodiesel production, but it also illustrated the benefits of waste eggshells and natural waste sources as a material precursor for preparing green catalyst to produce biodiesel product.

KEYWORDS: Kinetics; Biodiesel production; Transesterification reaction; eggshells; CaO catalyst

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Introduction

Biodiesel is known to be clean renewable energy as a long-chain fatty acid alkyl ester for using instead petroleum diesel fuel due to the physicochemical properties are similarly with diesel fuel and it can be directly applied in a diesel-engine especially an agricultural engine without the need modification of the cylinder of engine or injection system and fuel line. Furthermore, biodiesel is lower gaseous pollutant emission (e.g. SO_x, NO_x, CO and HC) and particulate matter or soot [1 – 4]. Generally, biodiesel is synthesized via transesterification reaction using both the homogeneous and heterogeneous catalyst. Many types of homogeneous catalyst such as NaOH, KOH, $NaOCH_3$ (base catalyst), H_2SO_4 and H_2PO_4 (acid catalyst) are wildly used in biodiesel production because they are very high catalytic activity under mild reaction conditions but these catalyst have some disadvantages, such as, difficult to remove the catalyst from biodiesel product, requires large amount of water to eliminate the catalyst, easily to produce soap formation and corrosive the reactor. These disadvantages mean the expanding cost of biodiesel production which directly affected to price of biodiesel product [2, 5, 6].

Heterogeneous catalyst are widely employed to solve the problems of homogeneous catalyst since they are not required the water to wash biodiesel product, easily to separate from the reaction mixture and can be reused several times, very cheap and non-toxicity [7, 8]. Among the heterogeneous base catalysts, alkali earth oxides such as CaO, MgO, SrO and BaO have been

greatly researched because they are have high activity under mild reaction condition. Particularly, calcium oxide (CaO) is one of the most promising in the study though it has lower activity than BaO and SrO but less solubility in methanol, lower price, low toxicity and environmentally friendly than BaO and SrO [7, 9]. Moreover, there are several natural calcium sources for preparing CaO catalyst such eggshells [10 – 12], Golden apple snail shells and mollusk shells [4].

The kinetics of transesterification reaction for biodiesel production is one of the topic which several authors have reported due to this data can be used to design, optimize, control and scaled up conditions in the biodiesel production process to industrial scale. Therefore, in this present research work focus on the kinetics study of transesterification reaction for biodiesel production catalyzed by CaO derived from eggshells. Furthermore, the comparison of the catalytic activity between eggshells-derived CaO catalysts versus CaO derived from natural waste materials namely river snail shells, cockel shells and golden apple snail shells, and NaOH as a homogeneous catalyst were also investigated. The physicochemical properties of all the CaO catalyst that derived from those natural material sources were studied. All of the results in this work are expected to useful in actual application for planning the biodiesel production in the industrial scale.

Materials and Methods

Palm olein oil as starting material was obtained from Morakot Industries PCL., which contained free fatty acid (FFAs) of 0.31 mg KOH g^{-1} of oil (0.16 wt.%) and water content of 0.11 wt.%, respectively. Methanol (CH_3OH) analytical grade with purity 99.8% was purchased from RCI Labscan Ltd. to be used as a reagent. Eggshells, river snail shells, cockel shells and golden apple snail shells obtained from local restaurants were transformed to CaO as heterogeneous catalysts by thermal decomposition process. The raw materials (natural waste shells) were washed with water, dried, grinded, sifted and then calcined at designated temperature of 800 °C in air for 3 h (rate of 10 °C min^{-1}) in a furnace following the reports method of Roschat et al., [2, 10, 11] and N. Viriya-empikul et al., [4]. The obtained CaO catalysts were collected in glass bottles and sealed with paraffin film. The all CaO sample was analyzed by using X-ray diffraction with XRD-6100 Shimadzu, Japan. Additionally, BET surface area and basic site properties were determined by Bel-sorp-mini II, Bel-Japan and chemisorption Analyzed, Belcat B, respectively.

The transesterification reaction of palm oil was performed by following the conditions consist of 12:1 methanol to oil molar ratio, 5 wt.% of CaO catalyst and reaction temperature of 65 °C agreeable with report of Roschat et al., [3, 10]. While NaOH was used as a catalyst, the reaction conditions included methanol to oil molar ratio of 7.5:1, 0.3 wt.% of catalyst and 65 °C of reaction temperature. To monitor the progress of reaction, the reaction mixture was sampled every specific period time and then it was eliminated the excessive methanol with hot air oven. Overall of the biodiesel sample was evaluated yield of fatty acid methyl ester (%FAME) using ^{1}H-NMR technique followed the reports of Roschat et al., [2,3] and Niju et al., [13] as depicted in Fig. 2. The study of reaction kinetics in the present work used the method from the referring research of Rochat et al., [3] and Birla et al., [14].

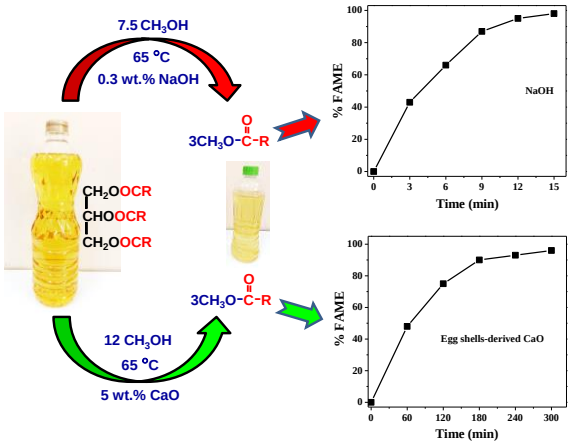

Fig. 1 The overview for the kinetics study of transesterification reaction to produce biodiesel catalyzed by CaO derived from eggshells.

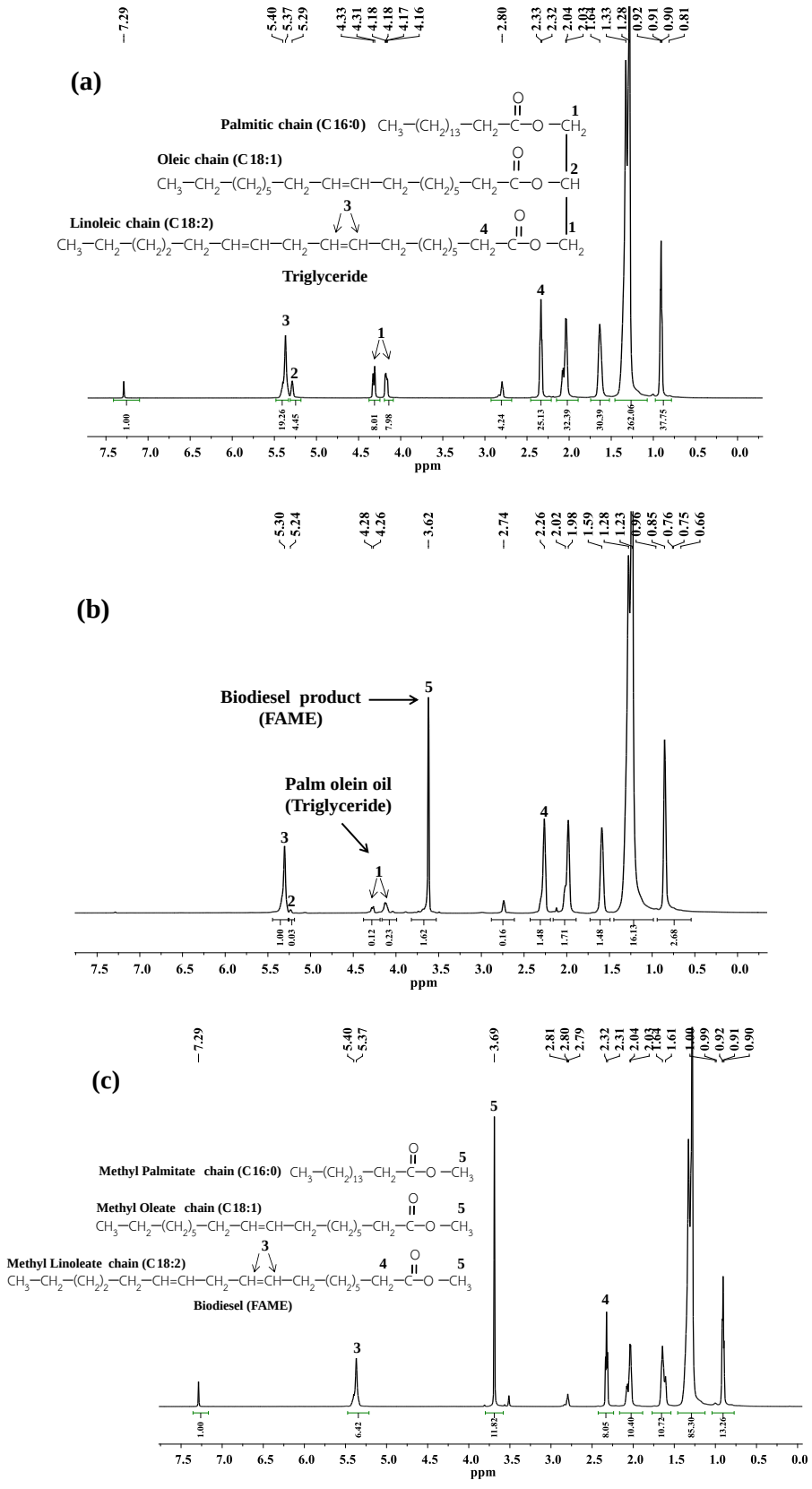

Fig. 2 ^{1}H-NMR spectrum of (a) palm olein oil (triglyceride) as starting material, (b) uncompleted transesterification reaction (triglyceride + FAME) and (c) Biodiesel product (FAME) when reaction completed.

Results and Discussion

The Catalyst characterization

Fig. 3 showed the XRD patterns of all CaO catalysts derived from natural waste shells material. The XRD results suggested that calcination of natural waste shells material at 800 °C for 3 h can completely transform $CaCO_3$ phase as the main component of the shells to CaO phase. Furthermore, the physicochemical properties of CaO_egg compared with CaO_gol, CaO_riv and CaO_coc were reported in the Table 1. The results found that BET surface area directly correlated with total basic sites due to the high BET surface area, which would generally enhance the strong total basic site meaning the greater catalytic activity of the catalyst. The similar results were found with the report of Viriya-empikul et al., [4], Maneerung et al., [8] and Roschat et al., [10].

Table 1 Physicochemical properties and catalytic activity of eggshells-derived catalysts (CaO_egg) compared with CaO_gol, CaO_riv and CaO_coc.

Catalyst material	BET surface area ($m^2\ g^{-1}$)[a]	Total basic sites ($\mu mol\ g^{-1}$)[b]	% FAME at reaction time of 3 h
CaO_egg	2.80	215.5	93.5
CaO_gol	2.63	188.9	92.2
CaO_riv	2.50	165.4	90.1
CaO_coc	3.0	220.2	94.2

[a] Evaluated by N_2 adsorption, [b] Evaluation by CO_2–TPD and [c] transesterification conditions of catalyst loading amount = 5 wt.%, methanol : oil molar ratio = 12 : 1 and reaction temperature = 65 °C.

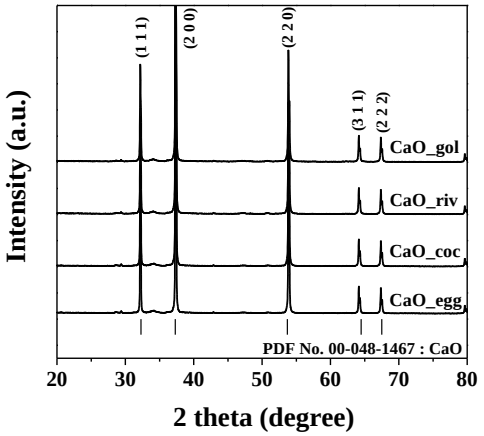

Fig. 3 XRD patterns of the obtained CaO catalyst derived from golden apple snail shells (CaO_gol), river snail shells (CaO_riv), cockel shells (CaO_coc) and eggshells (CaO_egg).

Study of reaction kinetics of palm oil to biodiesel product

The effect types of the catalyst on the rate of transesterification reaction are generally known that they reflected in the rates constants or reaction rate coefficient (*k*) which can be calculated from the increase of biodiesel product versus reaction time or the decrease of triglyceride (reactant) against reaction time [15]. The high k constant is meaning greater rate of reaction which would give high yield product under short reaction time. The homogeneous catalyst both base and acid shows higher catalytic activity than heterogeneous catalyst for synthesis biodiesel product. However, the kinetic study of both catalysts is also important in term of data base for applied in the real production such as the reactor design and reaction control. Thus, this study presented the comparison the kinetic reaction between using NaOH catalyst and CaO catalyst derived from eggshells.

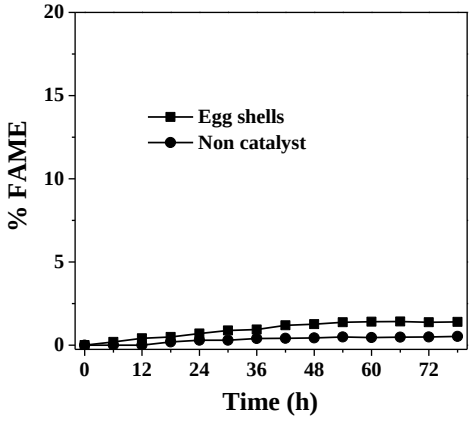

Fig. 4 The transesterification of palm olein oil without the catalyst and the use eggshells as a catalyst.

As demonstrated in Fig. 4, the transesterification of palm oil to be biodiesel product without the catalyst and the use eggshells as a catalyst presented that there is almost no biodiesel product (less than 1.5% of FAME). This phenomenon can be described that the transesterification reaction requires a catalyst to activate the reaction by reducing the activation energy (*Ea*), hence the reaction without a catalyst cannot generate biodiesel product and a reaction rate constant is nearly zero [15, 16]. Likewise, the use of eggshells as a catalyst is unable to catalyze the reaction because it is a $CaCO_3$ compound which non-catalytic activity. Hence, the calcination of eggshells to prepare CaO is very important for promoted the activity of the material [4, 9]. After calcination of eggshells at 800 °C for 3 h, CaO obtained from eggshells can be highly active to promote the transesterification reaction of palm olein oil to be biodiesel product completed between the reaction time of 180 – 240 min. The obtained *k* value of the use CaO synthesized from eggshells was displayed in Fig. 5 (b) which demonstrated linear graph of $-\ln[1-X_{ME}]$ versus reaction time and *k* constant of this reaction was 1.22×10^{-2} min^{-1}. These results can be discussed that CaO from eggshells was rather active according to the surface area and total basic sites as the physicochemical properties of catalyst. Similar results were also reported from Laca et al. [17] who reviewed the eggshells waste as catalyst and found that several reports indicated the completing biodiesel production around 3 – 5 h of reaction time.

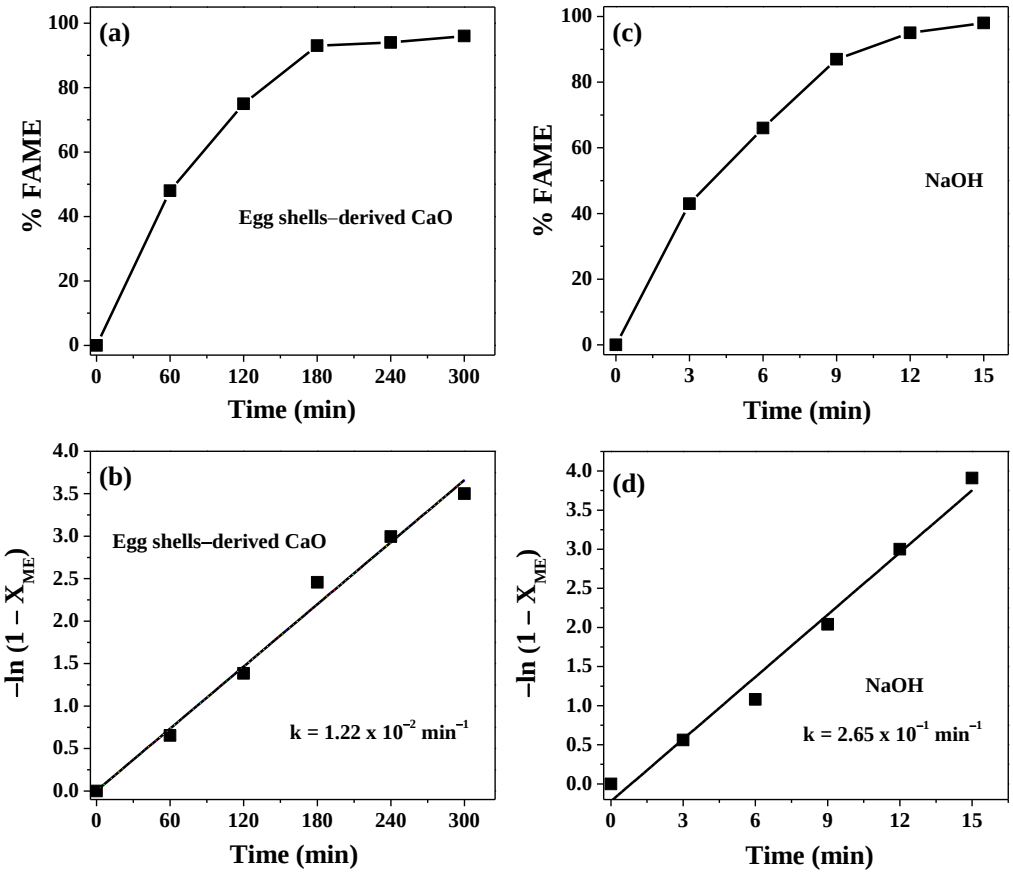

Fig. 5 The comparison of kinetics study of transesterification between (a)-(b) the use CaO-derived from eggshells as a catalyst versus with (c)-(d) the use NaOH as a catalyst.

Furthermore, the results of biodiesel production catalyzed by the employed NaOH catalyst were presented in Fig. 5 (c) and (d). In this case NaOH promoted very high active catalyst activity because it is homogeneous catalyst. This transesterification reaction is very short reaction time approximately 12 – 15 min which reaction completed and k constant as 2.65×10^{-1} min^{-1}. Additionally, when compared k constant of transesterification using the CaO catalyst obtained from eggshells and NaOH, NaOH have high catalytic performance more than CaO obtained from eggshells about 22 times. Though NaOH catalyst can produce biodiesel product under mild reaction condition and short reaction time than eggshells-derived CaO catalyst but the obtained biodiesel product required to wash with water several times for removing the leaching of catalyst [5, 6]. While CaO generated from eggshells are great in term of green and environmentally friendly with without cleaned the biodiesel product. Additionally, it is more tolerant to free fatty acid and water presence in raw material that cause soap formation than NaOH catalyst [13, 17, 18].

Comparison of catalytic performance of CaO derived from eggshells with natural waste shells.

The catalytic performance of CaO_egg was compared with CaO derived from natural waste shells namely CaO_gol, CaO_riv and CaO_coc as shown the data in Fig. 6 and Table 1. The results indicated that all of the CaO catalyst was close the catalytic performance due to similarity of their physicochemical properties.

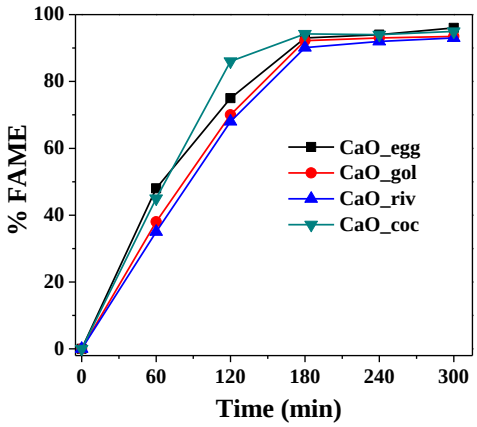

Fig. 6 Comparison of catalytic activity of CaO derived from natural waste shells material.

The data suggested that all transesterification reaction catalyzed by the CaO catalyst was completed to produce biodiesel in the range of reaction time 3 – 4 h with %FAME yield closely 94%. Therefore, in this point, we can be concluded that natural waste shells have high efficiency to use as raw material for generation CaO catalyst with low-cost and green for biodiesel production.

Conclusion

In summary, the kinetics study of transesterification reaction of palm olein oil to biodiesel product catalyzed both CaO derived from eggshells and NaOH catalyst have demonstrated important data for application in the real production process. All of the data reveal that NaOH has higher catalytic activity than CaO generated from eggshells approximately 22 times. Nevertheless, eggshells-derived CaO catalyst also has more advantages such low-cost and green material. In addition, this work also proves and presents the efficiency of natural waste shells material for synthesis CaO catalyst which gives similarly results with eggshells. Therefore, the assortment of suitable catalyst for biodiesel production not only considers the catalytic performance but also ponders regarding economically and ecologically friendly of production process.

Acknowledgements

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