

Biodiesel Production from Palm Oil using Heterogeneous Base catalyst

Sirichai Chantara-arpornchai, Apanee Luengnaruemitchai, and Samai Jai-In

Abstract—In this study, the transesterification of palm oil with methanol for biodiesel production was studied by using CaO–ZnO as a heterogeneous base catalyst prepared by incipient-wetness impregnation (IWI) and co-precipitation (CP) methods. The reaction parameters considered were molar ratio of methanol to oil, amount of catalyst, reaction temperature, and reaction time. The optimum conditions—15:1 molar ratio of methanol to oil, a catalyst amount of 6 wt%, reaction temperature of 60 °C, and reaction time of 8 h—were observed. The effects of Ca loading, calcination temperature, and catalyst preparation on the catalytic performance were studied. The fresh and spent catalysts were characterized by several techniques, including XRD, TPR, and XRF.

Keywords—CaO, ZnO, Biodiesel, Heterogeneous catalyst, Transesterification

I. INTRODUCTION

IN the recent years, the world's energy demand, derived from petroleum, mineral coal, and natural gas, is increasing at an exponential rate. The main reason that caused the fast diminishing of energy resources is due to a rapidly increasing of population and a growth of industrialization. In order to solve these problems, researchers are trying to find new alternative energy sources to substitute the fossil fuel. Therefore, biomass is increasingly gaining international attention as a source of renewable energy.

Biodiesel, a mixture of fatty acid methyl esters (FAMES), has been developed as one of the most promising alternative fuel for fossil fuel regarding to the limited resources of fossil fuels and the environmental concerns [1]. It has high biodegradability, low CO, SO_x, NO_x, and particulate matter (PM) contents, renewability, and lack of aromatic compounds as compared to conventional diesel fuel [2]-[5]. On the other hand, biodiesel can be used in diesel engines without engine modification because its characteristics are similar to those of petroleum-based diesel fuels. The production of biodiesel is performed by transesterification reaction of triglycerides using alcohol in the presence of a catalyst [6].

Transesterification or alcoholysis, is a reaction of a fat or oil reacts with an alcohol by using a catalyst to form esters and glycerol [7]. Many types of alcohol can be used such as

methanol, ethanol, propanol, and butanol. The most common used is methanol because it gives a proper viscosity and boiling point and a high cetane number. In the transesterification of vegetable oils, triglyceride reacts with methanol producing glycerol and a mixture of fatty acid methyl esters (biodiesel).

In the transesterification process, biodiesel is usually prepared in the presence of homogeneous base or acid catalysts. The acid-catalyzed process often uses hydrochloric acid or sulfuric acid as a catalyst [8],[9]; however, a high molar ratio of methanol to oil is needed, and the reaction time is very long [10]. So, the base catalysts are preferred to be used instead of the acid catalysts because the catalytic activity of a base is higher than that of an acid and acid catalysts are more corrosive [11].

However, in this conventional homogeneous method, the removal of these catalysts is very difficult, and a large amount of wastewater is produced to separate and clean the catalyst and the products. Therefore, conventional homogeneous catalysts are expected to be replaced by environmentally friendly heterogeneous catalysts. The replacement of homogeneous catalysts by heterogeneous catalysts would have various advantages such as the easy catalyst separation from the reaction mixture, product purification, and the reduction of environment pollutants [12]-[17].

In this work, transesterification was carried out using CaO–ZnO as heterogeneous basic catalyst. The effects of reaction parameters, such as molar ratio of methanol to oil, reaction time, amount of catalyst, and reaction temperature, were optimized for the production of biodiesel. The optimum condition at 15:1 molar ratio of methanol to oil, reaction time of 8 h, catalyst amount of 6 wt%, and reaction temperature of 60 °C. In addition, effects of %loading of Ca on ZnO support, calcination temperature, and catalyst preparation on the biodiesel yield were also studied.

II. EXPERIMENTAL

A. Preparation of CaO–ZnO Catalyst by Incipient-Wetness Impregnation (IWI) method

A Zinc oxide was dried in an oven at 110 °C for 2 h to remove the absorbed water on the surface. This unmodified ZnO was stored in a silica gel desiccator prior to use. To prepare modified ZnO with different Ca loadings, the ZnO was impregnated with an aqueous solution of Ca(NO₃)₂·4H₂O. Samples with various Ca loadings, given in weight percentage, were impregnated for 24 h to ensure that the Ca diffused and dispersed thoroughly on the surface of ZnO. The loading

S. C., A. L. The Petroleum and Petrochemical College, Chulalongkorn University, Soi Chula 12, Phayathai Road, Pathumwan, Bangkok 10330, Thailand (e-mail: benz_playboy@hotmail.com)

A. L. Center for Petroleum, Petrochemical, and Advanced Materials, Chulalongkorn University, Bangkok 10330, Thailand (Phone: +66-2-218-4139; fax: +66-2-218-4139; e-mail: apanee.l@chula.ac.th)

S. J. The Royal Thai Navy, Bangkok, Thailand

amounts of Ca were calculated on the basis of the amounts of the starting materials. The pretreated samples were dried in an oven at 110 °C for overnight and then calcined at different temperatures before being used for the reaction.

B. Preparation of CaO–ZnO Catalyst by Co-Precipitation (CP) method

Calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) and Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) were weighed for a desired amount, and then dissolved in deionized water under continuous stirring and heating at 80 °C. The pH of solution (~8) was adjusted by adding 0.1 M Na_2CO_3 then the mixture was aged for 1 h. The suspension was washed by warm deionized water to eliminate the residue ions. Deionized precipitate was dried at 110 °C overnight and calcined in air at various temperatures for 6 h. After calcination, the sample was stored in silica gel desiccator prior to use.

C. Transesterification of Vegetable Oil

The vegetable oil was weighed and heated to 60 °C in a 500 ml three-necked flask. Then, the catalyst and methanol were added to a three-necked flask. A magnetic stirrer was used for mixing oil, methanol, and catalyst. The reaction was carried out until it reaches the desired reaction time. After that the reaction was stopped by cool down the reactor to room temperature. The catalysts were separated out from the product by using a suction flask. The products were placed in a separatory funnel overnight to ensure that the phase of methyl esters and phase of glycerol are separated completely. The 25 wt% of sodium sulfate based on weight of methyl ester product was added into methyl esters to remove water.

III. RESULT AND DISCUSSION

A. X-ray fluorescence (XRF) spectroscopy

The chemical compositions of the whole samples were summarized in Table I. The synthesized catalysts have the values of metal concentrations closely to those of expected values.

TABLE I
CHEMICAL COMPOSITION BY USING XRF MEASUREMENT

Catalysts	Calcination Temperature (°C)	Synthesized Ca:Zn	Expected Ca:Zn
CaO-ZnO (1:5)(CP)	800 (6 h)	0.25	0.20
CaO-ZnO (1:3)(CP)	800 (6 h)	0.39	0.33
CaO-ZnO (1:1)(CP)	800 (6 h)	1.02	1.00
CaO-ZnO (3:1)(CP)	800 (6 h)	4.30	3.00
CaO-ZnO (1:3)(CP)	600 (6 h)	0.35	0.33
CaO-ZnO (1:3)(CP)	900 (6 h)	0.34	0.33
CaO-ZnO (1:5)(IWI)	800 (6 h)	0.24	0.20
CaO-ZnO (1:3)(IWI)	800 (6 h)	0.59	0.33
CaO-ZnO (1:1)(IWI)	800 (6 h)	1.07	1.00
CaO-ZnO (3:1)(IWI)	800 (6 h)	4.10	3.00
CaO-ZnO (1:3)(IWI)	600 (6 h)	0.48	0.33
CaO-ZnO (1:3)(IWI)	900 (6 h)	0.55	0.33

B. X-ray Diffraction (XRD)

The XRD patterns of ZnO and Ca–Zn mixed oxides catalysts with the various Ca:Zn atomic ratios are shown in Fig. 1a) (CP) and 1b) (IWI). The high intensities of diffraction peaks at 31.76°, 34.42°, 36.25°, 47.50°, 56.50°, 62.76°, 66.33°, 67.83°, 68.99°, 72.50°, and 76.91° represented the characteristic crystallinity of ZnO substance, which was similar to previous work [18]. Along with the same trends of CaO–ZnO mixed oxides catalysts in both preparation techniques, the intensities of CaO diffraction peaks, detected at 32.37°, 37.62°, 53.99°, 64.37°, and 67.49° [19], became more pronounced when adding the high amounts of Ca contents. This could be implied that the CaO particles started to be generated as a functional of Ca:Zn atomic ratio. In the case of ZnO diffraction peaks, the decrease in intensities was clearly observed with the addition of Ca, attributing to the new CaO phase generating in Ca–Zn binary system.

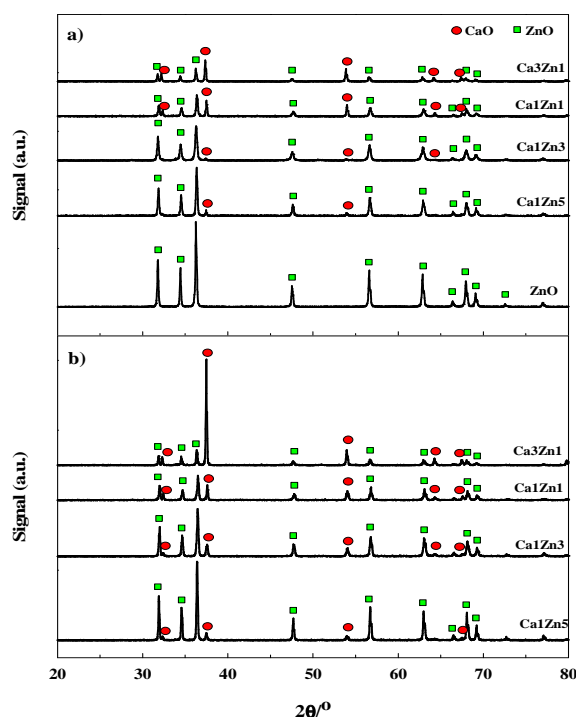


Fig. 1 XRD patterns of ZnO and Ca–Zn mixed oxides catalysts with the various Ca:Zn atomic ratios: a) CP and b) IWI techniques

As varying the calcination temperature, presented in Fig. 2a) (CP) and 2b) (IWI), the intense of ZnO and CaO became detectable after rising the calcination temperature up to 900 °C for both preparation techniques. Additionally, the crystallite structure of CaO and ZnO were definitely improved to the higher values. These results revealed that two possible mechanisms could be occurred in the highest calcination temperature in ordering; (i) CaO started to separate from the binary mixed oxides system, and (ii) the segregated CaO particles became sintering together to form larger particle sizes. That was reasonable to explain the generating of

uninteracted ZnO (high intensities). Thus, the activities of these catalysts were diminished by this sintering effect. Similar observation and explanation have been reported by Ngamcharussrivichai and coworker (2008) [19].

Interestingly, the very weak peak of CaCO_3 ($2\theta = 29.56^\circ$) could be detected at the lowest thermal treatment (600°C) for only CP technique, corresponding to the remaining carbonate group depositing on the surface of the catalyst. In the other words, an incompletely changed form of $\text{CaCO}_3 \rightarrow \text{CaO}$ could not be efficiently happened when performing with low calcination temperature [19]. However, no peaks of CaCO_3 existed with applying high treating temperature ($>600^\circ\text{C}$). Thanks to the decomposition of carbonate modeling in Ca–Zn mixed precipitate at high calcination temperature, the CaCO_3 was decomposed to CaO particle and CO_2 gas, and this product gas then diffused out of the pore of the catalyst where the CO_2 film was still surrounding [19]. The high catalytic performance could be achieved in 800°C . This kind of phenomenon has already been reported over MgCO_3 [20]. That was the reason why the catalytic performance was improved at 800°C thermal treating.

activity was then recovered when compared with the pure support.

Focusing on the Ca–Zn mixed oxides prepared by CP technique, the decrease in hydrogen consumption (area under peak of ZnO) in the Ca:Zn ratio of 1:5 was observed since some parts of Zn might be incorporated with Ca to form Ca–Zn binary system. Then, the remaining ZnO to be reduced was lower than that of pure ZnO support. After increasing the Ca:Zn ratio to 1:3, the shifting reduction peak to lower temperature (600°C)—representing the change in interaction and upgrading of CaO–ZnO reducibility—was observed, while the hydrogen consumption became much higher. This could be implied that some of CaO registration could possibly help promote the ZnO reduction sites during the preparation step. Nevertheless, in the presence of high Ca loading (Ca:Zn = 1:1 and 3:1), the slight shifting in peaks toward higher temperature were discovered (608 and 619°C), indicating that the separation of ZnO from Ca–Zn binary system became favored. On the other hand, the strength of Ca–Zn interaction could be disturbed when registering an excess Ca concentration (Ca:Zn $> 1:3$). Interestingly, the lowest hydrogen consumption was observed for the high Ca contents (Ca:Zn = 1:1 and 3:1), indicating that the agglomeration or sintering of CaO particles might inhibit or block the surface area of reduction sites, then the number of hydrogen adsorbed was low. As mentioned previously, the Ca–Zn interaction at the suitable Ca:Zn ratio of 1:3 could play an important role for enhancing the catalytic activity. Likewise, the lowest catalytic performance of CaO–ZnO catalysts was found in very high Ca:Zn ratio of 4 since the CaO became separating to form the film coating on the ZnO surface, which could be evidenced by SEM technique [19].

In the case of IWI catalysts, the shifting reduction peaks toward lower temperature appeared for all Ca loadings, compared to pure ZnO. This kind of behavior also confirmed the combination of homogeneous Ca–Zn interaction, resulting in increasing the reducibility of ZnO (reduced much easier). Interestingly, no significant differences among the reduction peaks of high Ca:Zn ratios (1:3–3:1) were observed, even the width of the reduction peaks. In some cases, it has been proposed that the width of the reduction peak could relate the dispersion of metal briefly. In our results, we interpreted that there was no change in dispersion of CaO particles in the presence of high Ca contents. Linking with the catalytic activity, the unchanged dispersion of CaO could be the main factor which exhibited similarity in 80% biodiesel yield in the Ca:Zn range of 1:3–3:1. In addition, the hydrogen consumption in all reduction peaks of high Ca loading (Ca:Zn = 1:3, 1:1, and 3:1) were also the same. This could be related with the unchanged in CaO particle sizes during the Ca variation. Consequently, the similarity activity could be provided with the unchanged particle size. We suggested that the size of CaO particle might be one of the main factors to control the catalytic activity.

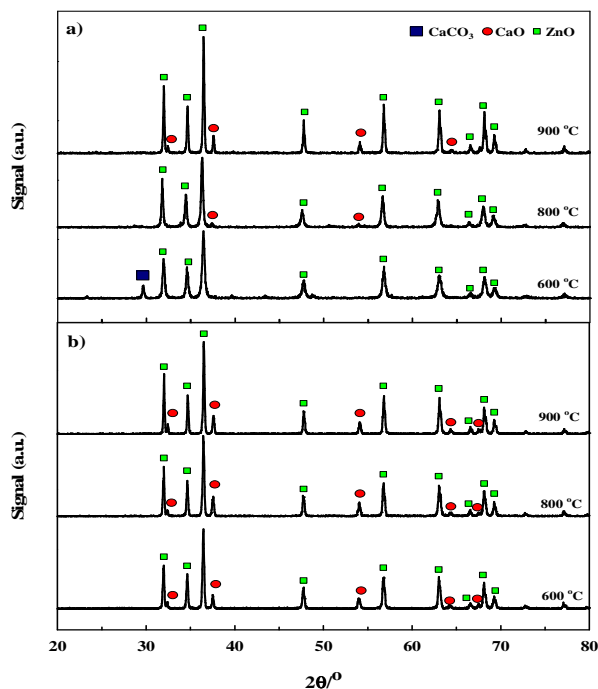


Fig. 2 XRD patterns of Ca_1Zn_3 catalysts at different calcinations temperatures: a) CP and b) IWI techniques.

C. Temperature–Program Reduction (TPR)

The TPR profiles of CaO–ZnO catalysts with various Ca:Zn atomic ratios were recorded in Fig. 3a) (CP) and 3b) (IWI). Three broaden reduction peaks of ZnO were observed at 351 , 458 , and 637°C . When adding Ca to form the Ca–Zn binary system for both CP and IWI techniques, the improvement in reducibility was observed noticing from the shifting peaks toward lower temperatures, compared to pure ZnO. The initial

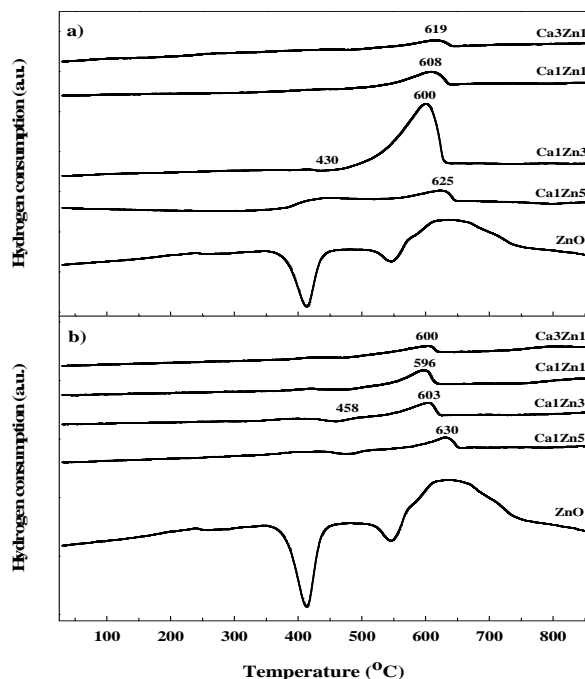


Fig. 3 TPR profiles of ZnO and Ca–Zn mixed oxides with the various Ca:Zn atomic ratios: a) CP and b) IWI techniques

From Fig. 4, the effect of calcination temperature on the catalytic activity was also tested for the catalysts prepared by CP (a) and IWI (b) techniques. For CP catalysts calcined at 600 °C, the reduction of mixed CaO–ZnO peak shifted toward higher temperature (close to ZnO region), compared to 800 °C. To explain this phenomenon using XRD technique, this low temperature might be not suitable for the creation of CaO–ZnO mixed phase due to the fact that the CaCO₃ could not decompose to CaO at this low temperature, so the probability of CaO formation, including interaction, might be not favored. As mentioned above, the difficult in mixing ZnO with CaO could happen. That was reasonable for the high area or hydrogen consumption in ZnO without containing CaO. At the highest thermal treatment (900 °C), the trend of shifting peak was similar to that of 600 °C. Moreover, the area of hydrogen consumed was the lowest since the CaO would undergo sintering at this condition. Similar to the previous explanation of Ca:Zn variation, the shift of reduction peak from T_{max} of 600 °C could be referred to the segregation of some CaO from the region of mixed oxides system to agglomerate with another CaO particle. This CaO segregation behavior also affected in ZnO crystallinity, which was successfully in line with the very high ZnO diffraction peaks—representing the uninteracted ZnO from binary system—, as confirmed by XRD. Finally, the catalytic activity was well-inhibited by the effect of inhomogeneous CaO–ZnO phase in the highest calcination temperature. In addition, the improvement in CaO diffraction peak can be also used as an indicator for proving the CaO sintering.

In the case of IWI samples (Figure 4(b)), the results agree well with the XRD results that the sintering of CaO particles was more pronounced with increasing calcination temperature

according to the minute amount of hydrogen consumption in the mixed CaO–ZnO reduction peak. Taking into account of the sintering effect, the lacking of significant chemical properties could be related with this phenomenon. Besides, there were the shifts in T_{max} reduction temperatures of the samples calcined at 600 °C and 900 °C, representing the change in mixed oxides interaction in the CaO–ZnO catalysts during varying the calcination temperature. This could be another main factor for providing inhomogeneous mixed oxides catalyst. Nevertheless, the reason why the T_{max} shifted to higher or lower reduction temperature after treating with unsuitable calcination temperatures (600 °C and 900 °C) for the catalysts prepared by both techniques was still unclear.

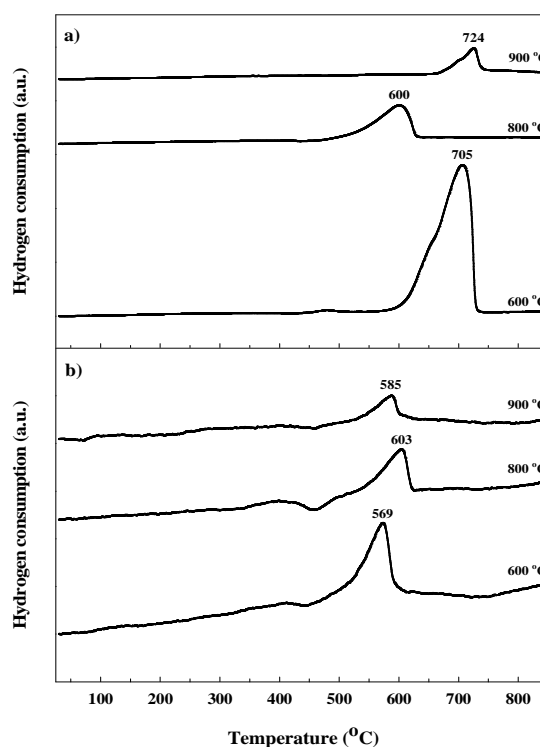


Fig. 4 TPR profiles of Ca1Zn3 catalysts at different calcination temperatures: a) CP and b) IWI techniques

D. Effect of reaction time

The effect of reaction time on the yield of biodiesel, illustrated in Figure 5, was tested by using the CaO–ZnO (atomic ratio Ca:Zn = 1:3) catalyst under the conditions of reaction temperature of 60 °C, 300 rpm of stirrer speed, 15:1 molar ratio of methanol to oil, and amount of catalyst 6 wt%. It is well-known that the transesterification of palm oil strongly depends on the reaction time [21]. As varying the reaction time range of 0–12 h, the biodiesel yield seemed to increase proportionally with the reaction time for both preparation techniques (CP and IWI). However, the yield became steadily—nearly equilibrium conversion—when the reaction time was higher than 8 h. According to the initial reaction time (<8 h), the large difference between the sample prepared by CP and IWI was observed. Interestingly, CP sample exhibited

the rate of reaction faster than that of IWI catalyst, while the reaction rate of IWI sample was favorable at higher reaction time than 8 h. To summarize, the reaction time of 8 h was suggested for being the suitable condition since the reaction time was not too high and also gave the 80% yield of biodiesel production for both preparation techniques.

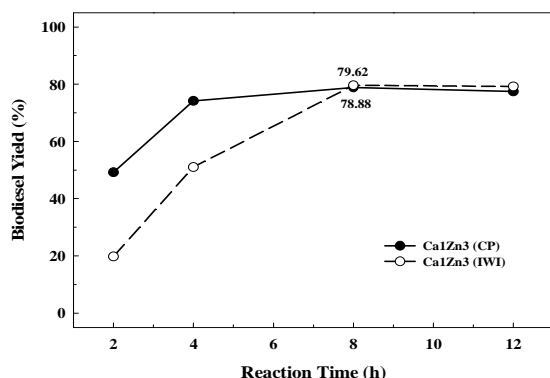


Fig. 5 Effect of reaction time on biodiesel yield. Reaction condition: 60 °C of reaction temperature, 1:3 atomic ratio of Ca:Zn, 15:1 molar ratio of methanol to oil, amount of catalyst 6wt%, and 300 rpm of stirrer speed

E. Effect of Calcination Temperature

The effect of calcination temperature (600–900 °C) was investigated on the reaction time of 8 h, while the remaining parameters were constantly fixed. Figure 6 indicates that both activities of CP and IWI catalysts were improved when calcination temperature was upgraded from 600 °C to 800 °C. However, the highest calcination temperature of 900 °C gave the lowest catalytic activities for both catalysts. Ngamcharussrivichai and coworker (2008) [19] achieved the same trends and proposed that increasing calcination temperature up to 900 °C could significantly decrease the methyl ester content since the sintering of CaO particles could be possibly affected, as evidenced by XRD technique. However, our results suggested that the incomplete decomposition of carbonate species (CO_3^{2-}) at the low calcination temperature of 600 °C might be the main factor for lowering the catalytic activity, which could be confirmed by XRD pattern of CP sample. Even though, there was no carbonate detected in IWI sample, the authors would like to note that the suitable calcination temperature of 800 °C might perform the suitable Ca–Zn interaction in the binary system, when compared to other calcination temperature (600 °C and 900 °C). The evidence of this type of interaction could be attributed to the shift of T_{max} from 600 °C. However, the reasons why the shift of T_{max} less or higher than 600 °C when increasing or decreasing the calcination temperature from 800 °C, were still unclear. Furthermore, the sintering effect of CaO particles should be another factor for deactivating the CaO–ZnO catalyst at the highest calcination temperature, as evidences from many previous characterization techniques (TPR and XRD). According to the results, the thermal treatment condition of 800 °C should be suitable for the catalyst preparation's condition since it could provide the

highest biodiesel (~80%), which was efficient enough for this reaction.

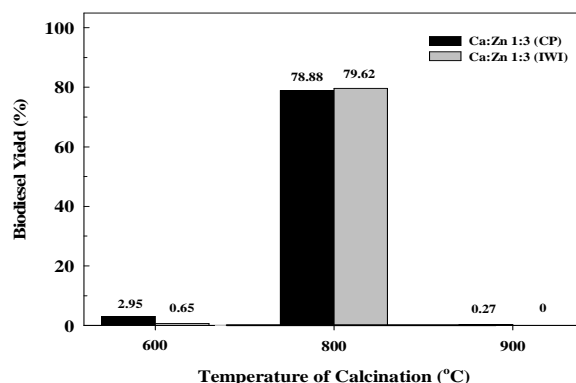


Fig. 6 Effect of calcination temperature on biodiesel yield. Reaction conditions: 60 °C of reaction temperature, 8 h of reaction time, 1:3 atomic ratio of Ca:Zn, 15:1 molar ratio of methanol to oil, amount of catalyst 6 wt%, and 300 rpm of stirrer speed

F. Effect of Ca:Zn atomic ratio

In order to study the effect of catalyst composition on biodiesel yield, the various Ca:Zn atomic ratios were studied at 1:5, 1:3, 1:1, and 3:1. From Fig. 7, the results revealed that the biodiesel yield was greatly effective on the variation of Ca:Zn atomic ratio. The highest biodiesel, approximately 78.88%, was observed in CP catalyst with Ca:Zn of 1:3, while the 80% biodiesel yield belonged to the IWI catalyst with the Ca:Zn range of 1:3–3:1. Focusing on the CP catalyst, the biodiesel yield was slightly decreased at high Ca concentrations. This was consistent with the appearance of CaO agglomeration, which has been reported in elsewhere [19]. The possible explanation might come from the combination of Ca–Zn mixed oxides, resulting in enhancing the surface area of the catalyst including the complete decomposition of carbonate species (or precursors), generating more active CaO sites, as confirmed by XRD characterization (Fig. 1). The mechanism of carbonate decomposition has also been proposed in MgCO_3 [20], but this work did not discuss in this part.

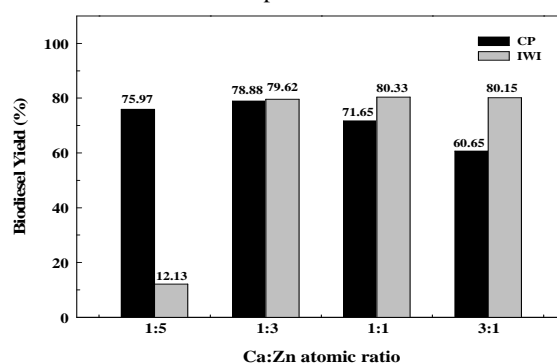


Fig. 7 Effect of Ca:Zn atomic ratio on biodiesel yield. Reaction conditions: 60 °C of reaction temperature, 8 h of reaction time, 15:1 molar ratio of methanol to oil, amount of catalyst 6 wt%, and 300 rpm of stirrer speed

IV. CONCLUSION

A heterogeneous catalyst CaO–ZnO can be used as a solid based catalyst for biodiesel production via transesterification of palm oil. The Ca:Zn atomic ratio 1:3 catalyst gave highest biodiesel yield of 78.88% and 79.62% for CP and IWI techniques, respectively, at reaction temperature of 60 °C, reaction time of 8 h, 1:15 molar ratio of palm oil to methanol, a catalyst amount of 6 wt%, and 300 rpm of stirrer speed.

ACKNOWLEDGMENTS

The authors would like to thank The Petroleum and Petrochemical College, and Center of Excellence on Petrochemical and Materials Technology, Chulalongkorn University, Thailand for providing support for this research work.

REFERENCES

- [1] Serio, M., Tesser, R., Pengmei, L., and Santacesaria, E. "Heterogeneous Catalysts for Biodiesel Production". *Energy & Fuels* 2008;22:207-217.
- [2] Harrington KJ. "Chemical and physical properties of vegetable oil esters and their effect on diesel fuel performance". *Biomass and energy* 1986;9:1-17.
- [3] USEPA. "A comprehensive analysis of biodiesel impacts on exhaust emissions". Draft Technical Report. USEPA; 2002.
- [4] Fangrui, M. and Hanna, M.A. "Biodiesel production: a review". *Bioresource Technology* 1999;70(1):1-15.
- [5] Knothe, G., Sharp, C.A., and Ryan, T.W. "Exhaust Emissions of Biodiesel, Petrodiesel, Neat Methyl Esters, and Alkanes in a New Technology Engine". *Energy & Fuels* 2006;20:403-408.
- [6] Demirbas, A. "Biodiesel from vegetable oils via transesterification in supercritical methanol". *Energy Conversion & Management* 2002;43:2349-2356.
- [7] Fukuda, H., Kondo, A., and Noda, H. "Biodiesel fuel production by transesterification of oils". *Journal of Bioscience and Bioengineering* 2001;92:405-416.
- [8] J. Otera, "Trans-esterification". *Chem. Rev.* 1993;93:1449-1470.
- [9] E. Lotero, Y. Liu, D.E. Lopez, K. Suwannakarn, D.A. Bruce, J.G. Goodwin, "Synthesis of biodiesel via acid catalysis". *Ind. Eng. Chem. Res.* 2005;44:5353-5363.
- [10] Zhang, Y., Dube, M.A., Mclean, D.D., and Kates, M. "Biodiesel production from waste cooking oil: 2. Economic assessment and sensitivity analysis". *Bioresource Technology* 2003;90:229-240.
- [11] Dizge N, Aydinler C, Imer DY, Bayramoglu M, Tanriseven A, Keskinler B. "Biodiesel production from sunflower, soybean, and waste cooking oils by transesterification using lipase immobilized onto a novel microporous polymer". *Bioresource Technology* 2009;100:1983-91.
- [12] Liu X, He H, Wang Y, Zhu S, Piao X. "Transesterification of soybean oil to biodiesel using CaO as a solid base catalyst". *Fuel* 2008;87:216-21.
- [13] Shimada Y, Watanabe Y, Sugihara A, Tominaga Y. "Enzymatic alcoholysis for biodiesel fuel production and application of the reaction to oil processing". *J Mol Catal B: Enzym* 2002;17:133-42.
- [14] Kulkarni MG, Gopinath R, Meher LC, Dalai AK. "Solid acid catalyzed biodiesel production by simultaneous esterification and transesterification." *Green Chem* 2006;8:1056-62.
- [15] Qian WW, Yang L, Lu XP. "Preparation of biodiesel catalyzed by KF/CaO with ultrasonic". In: Zhuang X, editor. *International conference on biomass energy technologies*. Guangzhou, China; 2008.
- [16] Di Serio M, Cozzolino M, Tesser R, Patrono P, Pinzari F, Bonelli B, et al. "Vanadyl phosphate catalysts in biodiesel production". *Appl Catal A* 2007;320:1-7.
- [17] Kawashima A, Matsubara K, Honda K. "Acceleration of catalytic activity of calcium oxide for biodiesel production". *Bioresour Technol* 2009;100:696-700.
- [18] Taufiq-Yap Y, Lee H, Hussein M, Yunus R. "Calcium-based mixed oxide catalysts for methanolysis of *Jatropha curcas* oil to biodiesel". *Biomass and Bioenergy* 2011;35:827-834.
- [19] Ngamcharussrivichai C, Totarat P, Bunyakiat K. "Ca and Zn mixed oxide as a heterogeneous base catalyst for transesterification of palm kernel oil". *Appl Catal A* 2008;341:77-85.
- [20] El-Shoba G.A. ky, A.A. Mostafa, "Thermochim". *Acta* 2003;408:75-84.
- [21] Xie W, Huang X, Li H. "Soybean oil methyl esters preparation using NaX zeolites loaded with KOH as a heterogeneous catalyst". *Bioresource Technology* 2007;98(4):936-939.