

Effect of Catalyst Preparation on the Performance of CaO-ZnO Catalysts for Transesterification

Pathravut Klinklom, Apanee Luengnaruemitchai, and Samai Jai-In

Abstract—In this research, CaO-ZnO catalysts (with various Ca:Zn atomic ratios of 1:5, 1:3, 1:1, and 3:1) prepared by incipient-wetness impregnation (IWI) and co-precipitation (CP) methods were used as a catalyst in the transesterification of palm oil with methanol for biodiesel production. The catalysts were characterized by several techniques, including BET method, CO₂-TPD, and Hemmett Indicator. The effects of precursor concentration, and calcination temperature on the catalytic performance were studied under reaction conditions of a 15:1 methanol to oil molar ratio, 6 wt% catalyst, reaction temperature of 60°C, and reaction time of 8 h. At Ca:Zn atomic ratio of 1:3 gave the highest FAME value owing to a basic properties and surface area of the prepared catalyst.

Keywords—CaO, ZnO, Biodiesel, Impregnation, Co-precipitation.

I. INTRODUCTION

NOWADAYS, the demand in petroleum, mineral coal, and natural gas are increasing while the amounts of petroleum resources are largely decreasing because of a rapidly increasing of population and a growth of industrial. In addition, the impact of environmental pollution of exhaust gases from petroleum fuels is important [1]. Therefore, alternative energy resources, especially biodiesel, have received much attention.

Biodiesel is biodegradable renewable fuel derived from vegetable oils, animal fats, or used cooking oils. Biodiesel has similar combustion properties to fossil diesel but it is non-toxic and clean-burning which can decrease the exhaust emissions of CO₂, SO_x and unburned hydrocarbon. On the other hand, biodiesel has good properties; for example, low volatility, flammability, and high cetane number as well as good transport and storage properties, [2-5].

Biodiesel is produced by transesterification reaction in which triglyceride molecules present in vegetable oils or animal fats react with an alcohol in the presence of a catalyst to form ester (biodiesel) and glycerol [6]. Different types of alcohols such as methanol, ethanol, propanol, and butanol can be used in order to produce biodiesel. However, methanol is

the most widely used due to its low cost and industrial availability.

Catalysts mainly used for biodiesel production can be classified due to its chemical presence in the reaction into homogeneous catalysts and heterogeneous catalysts. Homogeneous basic catalysts are the most widely used for biodiesel production for example NaOH and KOH. The reaction using homogeneous basic catalysts obtain very high yields under mild conditions and that reaction generally takes short time for completion [7]. However, homogeneous basic catalysts show many disadvantages: need a high purity feedstock in order to prevent undesirable saponification reaction, production costs are high as the processes involve washing and purification steps in order to meet the stipulated biodiesel quality, it is quite difficult to remove traces amounts of catalyst remaining in biodiesel product, high amounts of water are needed in washing and consequent waste water treatment of the effluent adds to the overall process cost. Therefore, they have motivated intense research on heterogeneous catalysts because of the easy catalyst separation from product, the reduction of environment pollutants and its reusability [8-13].

In this work, the effects of precursor used in catalyst preparation, ZnO support morphology (shape and size), % loading of Ca on ZnO support, and calcination temperature on the catalytic activity of CaO-ZnO as a heterogeneous catalyst for the transesterification reaction of vegetable oil with methanol under mild reaction conditions were studied. Also, the catalyst reusability of each CaO-ZnO catalysts in biodiesel production was compared.

II. EXPERIMENTAL

A. Catalyst Preparation

Preparation of CaO-ZnO Catalyst by Incipient-Wetness Impregnation (IWI) Method

1. Preparation of ZnO Support by Precipitation

Zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) was 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 Na₂CO₃ or NaOH at various concentrations, 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

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overnight and calcined in air at various temperatures for 6 h.

2. Preparation of CaO-ZnO Catalyst

A Zinc oxide was dried in an oven at 110 °C for 2 h to remove the absorbed water on the surface. To prepare modified ZnO with different Ca loadings, the ZnO was impregnated with an aqueous solution of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. 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 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.

3. 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 Na_2CO_3 or NaOH at various concentrations 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.

B. Transesterification of Vegetable Oil Using CaO-ZnO Catalyst

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 methyl ester (top phase) was washed with distilled water (50 °C) until the washed water is clear. The glycerol phase (bottom phase) was removed and left in a separated container.

respectively. The shape of the isotherm and the presence of a hysteresis loop at high relative pressure for CP catalyst at 1:3 Ca:Zn atomic ratio (Fig. 1) suggest that the CaO-ZnO framework prepared by co-precipitation method can be ascribed to type IV of the IUPAC classification (Sing et al., 1985) [14]. It is essentially mesoporous with some macropores. Moreover, the hysteresis loop has characteristics of H1 types, indicating that the CaO-ZnO framework prepared by CP method consist of agglomerates or compacts of approximately uniform spheres in fairly regular array, and hence to have narrow distributions of pore with 18.22 nm of a pore size.

For IWI catalyst, when Ca:Zn atomic ratio of catalyst was increased from 1:5 to 1:3, the specific surface area increases from 1.118 to 2.598 m^2/g . However, when Ca:Zn atomic ratio of catalyst increase over 1:3, the specific surface area decreases. This was consistent with the appearance of CaO agglomeration, which has been reported elsewhere [15]. For the hysteresis loop of the IWI catalyst at 1:3 Ca:Zn atomic ratio shown in Fig. 2, it is essentially mesoporous with some macropores like CP catalysts. The hysteresis loop has characteristics of H1 types, indicating that the CaO-ZnO prepared by IWI method framework is the same with the CaO-ZnO framework prepared by CP method. An average pore size of CaO-ZnO prepared by IWI method is 17.69 nm.

TABLE I
TEXTURAL PROPERTIES OF CAO-ZNO CATALYSTS

Sample	Calcination Temperature (°C)	Surface Area (m^2/g)	Pore Volume (cc/g)	Pore Diameter (nm)
<i>Incipient wetness impregnation (IWI)</i>				
CaO-ZnO (1:5)	900	1.12	0.0042	15.20
CaO-ZnO (1:3)	900	2.60	0.0115	17.69
CaO-ZnO (1:1)	900	1.36	0.0038	11.20
CaO-ZnO (3:1)	900	0.91	0.0031	13.54
CaO-ZnO (1:3)	800	2.68	0.0084	12.53
CaO-ZnO (1:3)	1,000	1.08	0.0045	16.70
<i>Co-precipitation (CP)</i>				
CaO-ZnO (1:5)	800	6.16	0.0266	17.32
CaO-ZnO (1:3)	800	7.33	0.0334	18.22
CaO-ZnO (1:1)	800	8.09	0.0421	20.82
CaO-ZnO (3:1)	800	10.65	0.0640	24.03
CaO-ZnO (1:3)	900	5.63	0.0244	17.34
CaO-ZnO (1:3)	1,000	3.10	0.0112	14.52

III. RESULT AND DISCUSSION

A. Textural Properties

The textural properties of the CaO-ZnO catalysts with various Ca:Zn atomic ratios and calcination temperatures were characterized by Brunauer-Emmett-Teller (BET) method and the results are given in Table I. For CP catalysts, an increasing of Ca loading can cause an increasing of the specific surface area, pore size, and pore volume. The highest specific surface area of the CaO-ZnO prepared by CP method was 10.65 m^2/g at a 3:1 Ca:Zn atomic ratio and calcination temperature of 800 °C. However, an increase of calcination temperature of catalyst brings to a decrease in the specific surface area from 7.333 m^2/g at calcination temperature of 800 °C to 5.631 and 3.101 m^2/g at calcination temperature of 900, and 1,000 °C,

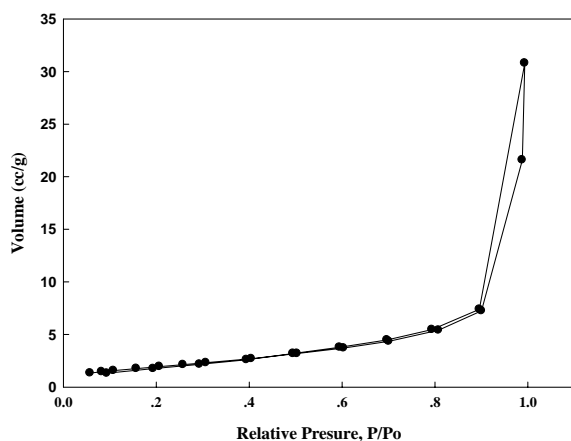


Fig. 1 N_2 adsorption-desorption isotherms of CaO-ZnO prepared by CP method

B. Hammett Indicator

The basic strength (H_-) and total basicity of the CaO-ZnO catalysts was measured by the method of Hammett indicator-benzene carboxylic acid (0.02 mol/l anhydrous methanol solution) titration [16] and the results are shown in Table II. In term of basic strength (H_-), all of the catalysts in both preparation techniques achieved high basic strength in the range of 11.0–15.0.

Both IWI and CP catalysts, when increasing the Ca:Zn atomic ratio or Ca amount, total basicity of these catalysts increased. For IWI catalysts, CaO-ZnO calcined at 900 °C exhibited the highest total basicity compared with 800 and 1,000 °C. For CP catalysts, CaO-ZnO calcined at 800 °C exhibited the highest total basicity.

Especially, the basicity of catalysts prepared by IWI method exhibited higher values than those of CP method in all of Ca:Zn ratios. However, basic strength and basicity of the catalysts are not the only one factor that affects to the reaction yield since the FAME yield of IWI catalysts did not show higher values than those of CP catalysts. The specific BET surface area should be discussed as one of factors that affected to transesterification.

C. Temperature Programmed Desorption of CO_2 (TPD- CO_2)

The total basicity and basic site distributions were evaluated by using temperature programmed desorption of CO_2 . The CO_2 -TPD profiles of the CaO-ZnO catalysts prepared by both CP and IWI methods are displayed in Figs. 3 and 4. The TPD patterns of the CaO-ZnO catalysts prepared by CP method (Fig. 3) showed CO_2 desorption peaks at the temperature ranging from 400 to 600 °C and 600 to 850 °C. Di Serio et al. explained that a very broad desorption band extending from 400 to 600 °C could be assigned as interaction of CO_2 with sites of weak and medium basic strengths. The narrower band at higher temperature between 600 and 850 °C can be attributed to the presence of much stronger basic site [17].

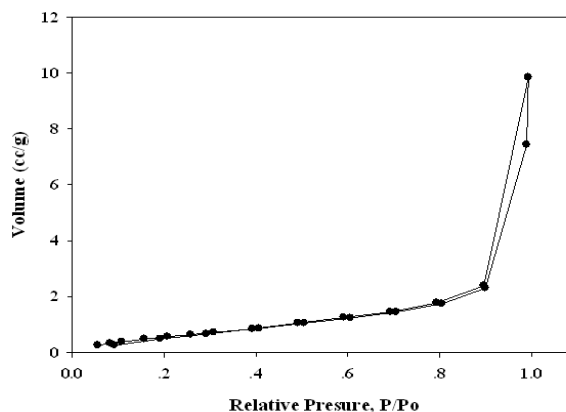


Fig. 2 N_2 adsorption-desorption isotherms of CaO-ZnO prepared by IWI method

When the Ca amounts or Ca:Zn atomic ratio increased from 1:5 to 3:1, the CO_2 desorption peaks of both weak and strong basic strength become higher intensity. In addition, the weak desorption peak was shifted into lower temperature, while the strong desorption peak was shifted into higher temperature. This situation shows the interaction between Ca and Zn when increasing the Ca amount or Ca:Zn atomic ratio.

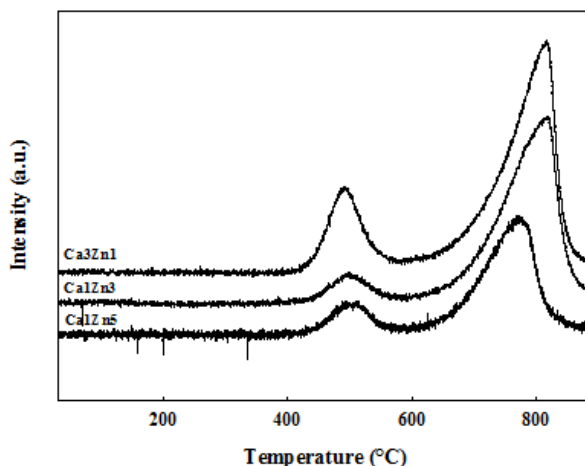
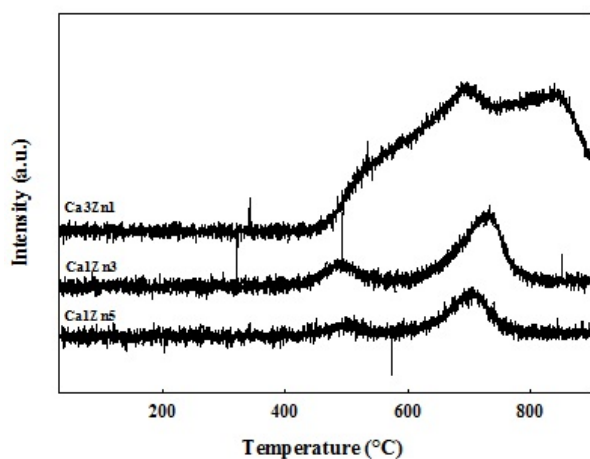
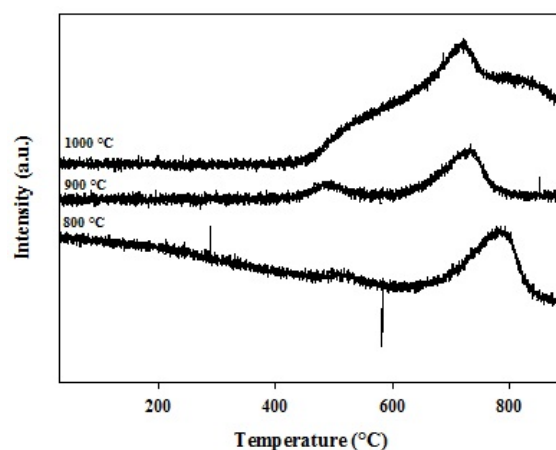
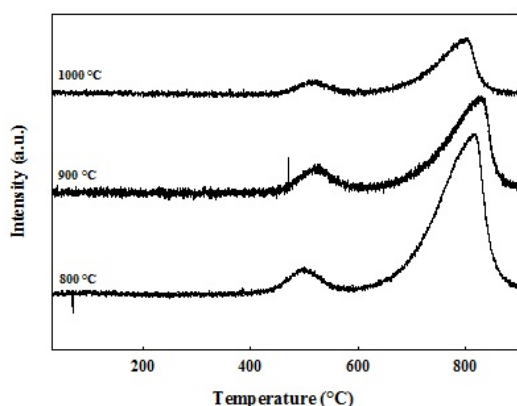


Fig. 3 CO_2 -Temperature programmed desorption profiles of CaO-ZnO catalysts prepared by CP method with varying Ca:Zn atomic ratio

TABLE II
 BASIC STRENGTH AND BASICITY OF CaO-ZNO CATALYSTS

Sample	Temperature (°C)	Basicity (mmol/g)				Total basicity (mmol/g)
		7.2<H<9.8	9.8<H<11	11<H<15	15<H<18.4	
Incipient wetness impregnation (IWI)						
CaO-ZnO (1:5)	900	0.4962	0.1527	5.2099	-	5.8588
CaO-ZnO (1:3)	900	0.4314	0.6667	7.7059	-	8.8040
CaO-ZnO (1:1)	900	0.2026	2.6151	16.1142	-	18.9319
CaO-ZnO (3:1)	900	0.5100	2.8051	26.2659	-	29.5774
CaO-ZnO (1:3)	800	0.2268	0.4128	6.7297	-	7.3653
CaO-ZnO (1:3)	1,000	0.2174	0.1661	5.2797	-	5.6632
Co-precipitation (CP)						
CaO-ZnO (1:5)	800	0.6744	0.2312	3.3911	-	4.2967
CaO-ZnO (1:3)	800	1.0476	0.2857	5.5286	-	6.8619
CaO-ZnO (1:1)	800	1.1176	0.6078	12.2157	-	13.9411
CaO-ZnO (3:1)	800	1.5926	1.5556	19.7222	-	22.8704
CaO-ZnO (1:3)	900	0.3669	0.2385	4.5298	-	5.1352
CaO-ZnO (1:3)	1,000	0.2385	0.1853	3.4495	-	3.8733


 Fig. 4 CO₂-Temperature programmed desorption profiles of CaO-ZnO catalysts prepared by IWI method with varying Ca:Zn atomic ratio

 Fig. 6 CO₂-Temperature programmed desorption profiles of CaO-ZnO catalysts prepared by IWI method with varying calcination temperature

 Fig. 5 CO₂-Temperature programmed desorption profiles of CaO-ZnO catalysts prepared by CP method with varying calcination temperature

For the CO₂-TPD profiles of the CaO-ZnO catalysts prepared by IWI method (Fig. 4), the CO₂ desorption peaks occurred at the temperature ranging from 420 to 600 °C for weak basic strength and 600 to 800 °C for strong basic strength. These IWI catalysts have the same situation with CP catalysts. When increasing Ca amount or Ca:Zn atomic ratio, the CO₂ desorption peaks of both weak and strong basic strength become higher intensity and the weak desorption peak was shifted into lower temperature, while the strong desorption peak was shifted into higher temperature.

For the effect of calcination temperature of CaO-ZnO catalysts prepared by CP method, the CO₂-TPD profiles (Fig. 5) shows that the CaO-ZnO catalyst calcined at 800 °C has high basicity in both weak and strong basic strength of catalyst. When the calcination temperature was increased from 800 °C to 900 °C, an area of the strong desorption peak decreases. After further increasing the calcination temperature

until reach 1,000 °C, area of both weak and strong desorption peak largely decreases. This result related with transesterification reaction activity of catalysts which the calcination temperature of 800 °C shows highest biodiesel yield compared with 900 and 1,000 °C.

For IWI catalysts shown in Fig. 6, the catalyst calcined at 900 °C gave the highest desorption peak areas for both weak and strong desorption peaks. While, at the calcination temperature of 800 °C shows lower desorption peak at weak basic strength position. For the calcination temperature of 1,000 °C, both weak and strong desorption peak were very low when compared with the others.

D. Effect of Calcination Temperature

The effect of calcination temperature on the biodiesel yield, as illustrated in Fig. 7, was tested over 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, amount of catalyst 6 wt%, and reaction time 8 h. From the calcination temperature range (800–1,000 °C), Fig. 7 indicates that the catalysts prepared by CP method gave the highest % FAME yield (81.73%) at calcination temperature of 800 °C and % FAME yield decreased after increasing calcination temperature above 900 °C. From Hemmett indicators and TPD-CO₂ results, the CaO–ZnO calcined at 800 °C gave the highest basicity compared with CaO–ZnO calcined at 900 and 1,000 °C. Moreover, BET surface area of CaO–ZnO calcined at 800 °C appeared the highest BET surface area compared with the catalyst calcined at 900 and 1,000 °C, respectively. For the catalysts prepared by IWI method, the calcination temperature of 800 °C showed lower catalytic activities compared to the CP catalysts. At the calcination temperature of 900 °C, the catalyst prepared by IWI method gave the highest biodiesel yield of 83.82 % FAME. However, at the calcination temperature of 1,000 °C shows the almost no catalytic activities for both CP and IWI catalysts. From BET surface area of IWI catalysts shows that increasing calcination temperature will decrease surface area of CaO–ZnO, the catalyst calcined at 800 °C gave the highest BET surface area of CaO–ZnO and slightly decreased when calcination temperature up to 900 °C. Ngamcharussrivichai and coworker [15] proposed that increasing calcination temperature up to high temperature could significantly decrease the methyl ester content since the sintering of CaO particles could be possibly affected. However, basic strength and basicity should be one of important factors that affected to biodiesel yield. From Hemmett indicator and TPD-CO₂ results, the CaO–ZnO calcined at 900 °C gave the highest basicity and basicity decreased at calcination temperature of 800 °C. However, the basicity at calcination temperature of 1,000 °C dramatically decreased, causing low of biodiesel yield.

According to the above results, it should be noted that the catalytic activities of the CaO–ZnO catalysts could be related with the type of catalyst preparation techniques. In summary, the suitable calcination temperature of the CaO–ZnO catalysts prepared by CP method was 800 °C, while the catalysts

prepared by IWI method exhibited high activity at calcination temperature of 900 °C.

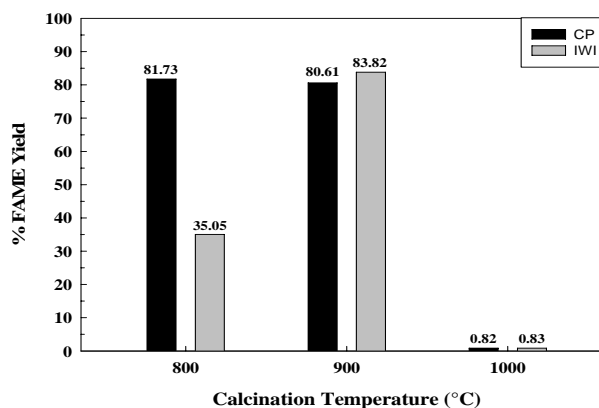


Fig. 7 Effect of calcination temperature on biodiesel yield. Reaction conditions: 60 °C of reaction temperature, 8 h of reaction time, 1:3 atomic ratio of Ca:Zn, 15:1 molar ratio of methanol to oil, amount of catalyst 6 wt%, and 300 rpm of stirrer speed

E. Effect of Ca:Zn Atomic Ratio

In order to study the effect of catalyst composition on biodiesel yield, the Ca:Zn atomic ratios were varied at 1:5, 1:3, 1:1, and 3:1, respectively. As shown Fig. 8, the results revealed that the FAME yield was significantly effective on the variation of Ca:Zn atomic ratio when the ratio was increased from 1:5 to 1:3. However, the FAME yield is slightly constant with increasing Ca concentration above 1:3. For the whole catalysts, the catalytic activity became increasing when higher amounts of CaO (more Ca:Zn) were presented and became steadily when Ca:Zn atomic ratio of catalyst was increased over than 1:3 for both methods. The biodiesel yield of catalysts prepared by IWI method is rather low at a 1:5 Ca:Zn atomic ratio of the CaO–ZnO catalyst. However, the highest biodiesel, approximately 83%, was obtained after adding the moderate amount of CaO (Ca:Zn = 0.33), while the average high value of biodiesel yield at 80% were observed on the Ca:Zn of 1:3–3:1 prepared by CP method. Regarding to the activity of catalyst prepared by IWI technique, the biodiesel yield was decreased slightly in the presence of the high CaO concentrations (Ca:Zn atomic ratio \geq 1:3). This was consistent with the appearance of CaO agglomeration which has been reported elsewhere [18]. The study reveals that an increment of CaO for high wt% does not lead to a better catalytic performance. From Hemmett indicator and TPD-CO₂ results show that increasing of Ca:Zn atomic ratio could increase the basicity of CaO–ZnO; however, BET surface area decreases when increasing Ca:Zn atomic ratio. At a 1:3 Ca:Zn atomic ratio should be optimum condition because both basicity and surface area are in the suitable value.

According to the results, it should be noted that the catalytic activities of the CaO–ZnO catalysts could be related with the Ca:Zn atomic ratio. For instance, the Ca:Zn atomic ratio of the

CaO–ZnO catalysts in both methods should be 1:3.

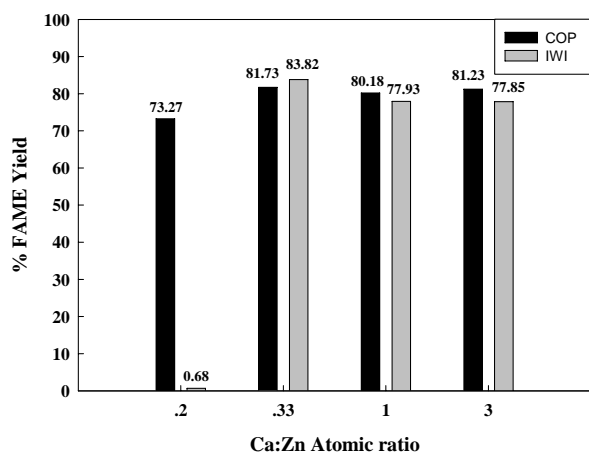


Fig. 8 Effect of Ca:Zn atomic ratio on biodiesel yield. Reaction conditions: 60 °C of reaction temperature, 8 h of reaction time, 15:1 molar ratio of methanol to oil, amount of catalyst 6 wt%, and 300 rpm of stirrer speed

IV. CONCLUSION

A CaO–ZnO is one of heterogeneous basic catalyst that can be used for biodiesel production via transesterification of palm oil. The Ca:Zn atomic ratio 1:3 catalyst gave the highest biodiesel yield for both CP and IWI methods. However, the optimum calcination temperature of CP catalyst is 800 °C while the calcination temperature of 900 °C is suitable temperature for IWI catalyst. 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 gave the biodiesel yield 81.73 and 83.82 % for CP and IWI catalyst, respectively.

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