

Development of Heterogeneous Alumina Supported Base Catalyst for Biodiesel Production

Nyoman Puspa Asri^{1,2+}, Santi Diyah Savitri¹, Suprpto¹, Kusno Budikarjono¹ and Achmad Roesyadi¹

¹Chemical Engineering Department, Industrial Technology Faculty, Sepuluh Nopember Institute of Technology, Surabaya 60111, Indonesia

²Chemical Engineering Department, Faculty of Engineering, WR. Supratman University, Surabaya 60111, Indonesia

Abstract. Double promoted γ -alumina heterogeneous base catalyst (CaO/KI/ γ -alumina) was firstly developed for the production of biodiesel from palm oil in refluxed methanol. This study have been conducted in order to improve the activity of single promoted catalyst (CaO/ γ -alumina) and to enhance the efficiency of biodiesel production that have been done in the previous work. The CaO/KI/ γ -alumina catalyst was prepared by precipitation and impregnation methods. Engineering catalyst done with some parameters that effect on the activity of a catalyst among other: % CaO loading (wt. % against alumina), temperature and time of calcinations. The catalyst was characterized by mean of XRD, and BET methods. The activity of catalyst has been tested by introduced to the transesterification reaction of palm oil. The reaction was carried out in the batch type of reactor (three-neck glass flask with 500 ml capacity) equipped with reflux condenser, thermometer and magnetic stirrer. The result showed that the optimum condition of preparation catalyst (% of CaO loading, temperature and time of calcinations) were 30%, 650°C and 4.5 h, respectively. Under the optimum condition of catalyst, reaction temperature 65°C, reaction time 5 h and oil to methanol molar ratio of 1:42 the biodiesel yield was almost 95%. Therefore, it can be proved that the activity of double promoted catalyst (CaO/KI/ γ -alumina) much higher than that the single promoted (CaO/ γ -alumina) catalyst.

Keywords: Biodiesel, Heterogeneous base catalyst, Palm oil, Refluxed methanol, Transesterification

1. Introduction.

Recently, depleting fossil oil reserves due to its usage continues to increase, as well as the rise of world crude oil price triggered energy crisis all over the world [1-3]. In order to overcome those problems and to further enhance the awareness of the environment, then the biomass has become the world's attention as one of a very promising alternative energy, which is sourced from renewable materials [2-5]. Biodiesel, fatty acid methyl ester (FAMES) derived from renewable resources such as vegetable oils or animal fats is expected to be one of the biomass-base alternative fuel to substitute the diesel oil due to its advantages include: renewability, lack of aromatic compounds, high biodegradability, and low SO_x particulate matter content [3,6-8].

Typically, biodiesel is produced by transesterification of vegetable oil in which one mole of triglyceride reacts with three moles of a short chain alcohol, preferably methanol, to produce three moles of methyl ester as the main product and one mole of glycerol, which is the most important by-product [3, 7, 9]. Homogeneous base catalyst such as KOH [10], NaOH [11], sodium methoxide and potassium methoxide [12] are the most conventional catalyst being used in the production of biodiesel. However, it should be noted that this conventional process has several drawbacks such as: need extra neutralization by mineral acid, produces

⁺ Corresponding author. Tel.: + 6285659774825; fax: +62315923815.
E-mail address: nyoman_puspaasri@yahoo.com

side product (soap), a large amount of waste water was produced to separate and clean the catalyst and the product [13]. In addition, the removal of the catalyst technically difficult and the catalyst can't reutilize [3, 6, 9, 13]. Furthermore, the total cost of the biodiesel fuel based on this process is not sufficiently competitive as compared to the cost of production of diesel oil from fossil fuel.

Based on those issues, a lot of studies have been conducted by researchers in order to find out an appropriate methods or an efficient process of technology. Transesterification with heterogeneous catalysts is one of a very promising alternative to produce biodiesel from vegetable oil, for being able to overcome the weaknesses of homogeneous catalysts. The process of heterogeneous catalyst is expected to be a process that is effectively and to provide minimal impact on the environment.

Kouzu et al. [14] using some kind of catalyst (CaO , $\text{Ca}(\text{OH})_2$ and CaCO_3) as a solid catalyst in the manufacture of biodiesel from soybean oil with yield biodiesel 93, 12 and 0%, respectively. Alumina supported CaO base catalyst has also been used by Zabeti et al. for the transesterification of palm oil [7]. They did the optimization with free variable molar ratio oil to methanol, the amount of catalyst and temperature reaction, while the response variable was yield of biodiesel (%). Reaction was done in batch type reactor at 5 h of reaction time. Optimal condition was obtained on molar ratio of oil to methanol 1: 12, amount of catalyst 6 % (w %) and temperature reaction 65°C . Asri et al. had conducted transesterification of palm oil with CaO catalyst in a batch reactor with refluxed methanol, at 75°C and time of reaction 7 h with a mount of catalyst various from 4, 6 and 8% (w% to oil), yield biodiesel obtained still relatively low [3]. The highest yield of 64, 95 % was obtained at 6% amount of catalyst. It has also been reported that the conversion of soybean oil reaches 87% with 35% potassium loaded alumina catalyst at molar ratio soybean oil to methanol 1:15, 6 h of reaction time and methanol reflux temperature [4]. However, the catalytic activities for most of them are not as great as that the homogeneous catalyst. Furthermore there is very little information regarding double promoted alkali metal alumina catalyst.

Therefore, in this work we intended to examine heterogeneous alumina supported base catalyst $\text{CaO/KI}/\gamma\text{-Al}_2\text{O}_3$ in order to develop an effective biodiesel's catalyst with high activity. $\text{CaO/KI}/\gamma\text{-Al}_2\text{O}_3$ was firstly adopted for the production of biodiesel from palm oil in refluxed methanol. The effect of loading amount of CaO (wt %), calcinations temperature and calcinations time on the yield of biodiesel were investigated

2. Experimental

2.1. Materials.

Analytical grade γ -alumina (anhydrous, surface area according to BET method $120\text{-}190\text{ m}^2/\text{g}$), analytical grade potassium iodide and other standard for GC analyses were purchased from Merck. Commercial grade of calcium oxide and commercial grade of methanol were provided by local supplier (BratacochemTM). While commercial grade BimoliTM refined palm oil were purchased from the local market. Fatty acid compositions of refine palm oil are lauric 0.26%, miristic 1.01%, palmitic 38.2%, stearic 3.64%, oleic 45.96% and linoleic 11% (wt.%)

2.2. Catalyst Preparation.

Double promoted alumina-supported ($\text{CaO/KI}/\gamma\text{-alumina}$) catalyst was prepared via the impregnation and precipitation procedure. The procedure as described below: pour 40 grams of $\gamma\text{-Al}_2\text{O}_3$ into 50 ml of distilled water, add calcium acetate with varied amount of CaO loading (w% to $\gamma\text{-Al}_2\text{O}_3$), and then stirred for 3-4 hours at room temperature. Calcium acetate was synthesized by reacting as a stoichiometrically calcium oxide with acetic acid. The formed suspension was impregnated by 35 ml of 35% KI solution (35 % weight to alumina). The performed slurry was heated up at $100\text{-}120^\circ\text{C}$ in an oven over night in order to remove the water content.

The synthesized catalyst was milled into powder, and then calcinated at varied temperature from 500 to 700°C with 50°C of interval in a muffle furnace with flowing air for varied time of calcinations. The catalyst was kept in a desiccator in the presence of silica gel in order to avoid water and CO_2 contact with the catalyst. The catalysts were characterized by means of XRD, BET. X-Ray Powder Diffraction (XRD) gives information of the structure information on crystallization. Powder XRD pattern were collected in order to

investigate diversification peaks after promoted by double promoter. The specific surface area, pore volume and pore diameter of the prepared catalysts were measured using the Brunauer-Emmet-Telle^f (BET) method.

2.3. Transesterification Reaction

Commercial grade BimoliTM refined palm oil was obtained from surrounding market. Methanol was obtained from BratacochemTM. Tranesterification process carried out in three-neck flask equipped with reflux condenser, thermometer and magnetic stirrer. Oil and methanol with a molar ratio of 1:42 was filled into a three neck flask, added with 6% amount of catalyst (wt % to oil). The mixture was refluxed at 65° C and 5 h of reaction time under stirring at a constant speed with a magnetic stirrer. After the reaction was completed, the solid catalyst was separated by filtration. The liquid were placed in a separator funnel, leave it for 24 hours at room temperature, until it split in three layers, top layer was methanol, the middle was FAMES and the bottom layer is glycerin. Biodiesel product was analyzed with GC, using a GC HP 5890 with HP's first column flow 28 ml/min, initial temperature of 125°C, and the temperature increment of 15° C per minute and the final temperature of 275°C.

3. Result and Discussion

3.1. Catalyst Characterization

The measured BET surface area, pore volume, and pore diameter are shown in Table 1. The BET surface area as well as pore volume decreased with loading CaO and KI. Surface area of analytical grade γ -Al₂O₃ from Merck was 120-198 m²/g. As shown in Table 1 when γ -Al₂O₃ was loaded with CaO or CaO and KI, total surface area of all catalyst were reduced due to covered of the alkaline compound on the porous surface of γ -Al₂O₃. The similar result was reported by Ilgen and Akin [15]. Moreover, basicity is much more important in the activity of the catalyst prepared for the transesterification of oil [4, 6, 9,15]. The crystal structure of CaO and K₂O seem to be form by the reaction Ca-acetate and KI with γ -Al₂O₃. The discussions of XR-D results have been describe deeply at the previous work [3].

Table 1: BET surface area, pore volume and pore diameter of the prepared catalyst

Catalyst properties	Technique	Unit	Value	
			CaO/ γ -Al ₂ O ₃	CaO/KI/ γ -Al ₂ O ₃ with 30% loading amount of CaO
Spesific surface area	BET	m ² /g	83,77	54,551
Pore volume	BET	cm ³ /g	0,135	0,083
Mean pore size	BET	A°	34,218	38,211

3.2. Effect of Loading Amount of CaO (wt.%)

In order to study the effect of CaO loading amount on the yield of biodiesel, a series of experiment with the loading amount of CaO ranging from 10 to 50% (wt.% to alumina) while loading amount of KI were kept constant 35% (wt.% to alumina), were synthesized and employed to catalyze the transesterification of palm oil. The result was presented in Figure 1. It seen, that the loading amount of CaO was raised from 10 to 25% the yield of biodiesel gradually increased from 80 to 83%. It could be possible because the loading amount of CaO has not sufficient yet result the reaction to be incomplete, eventually relatively low yield of biodiesel was obtained. In contrary at 30% of loading amount of CaO, the yield of biodiesel was sharply increased to almost 95%.

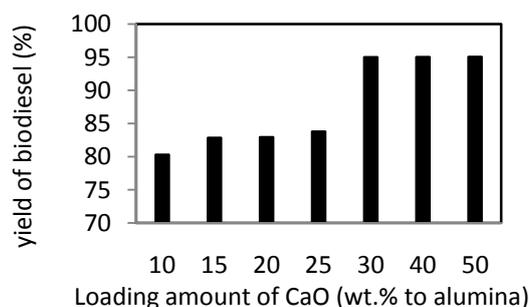


Fig. 1: Yield of biodiesel (%) versus loading amount of CaO (wt.%), at transesterification condition: 65°C, 5 h, molar ratio oil to methanol 1:42 and catalyst dosage 6%

Meanwhile, beyond 30% (40 and 50%) loading amount of CaO, the excessive addition of CaO loading had no significant effect on the biodiesel yield. It was happened due to the agglomeration of active site of CaO and K₂O or the covering of the basic site, hence a lowering of the surface area and eventually reducing the activity of the catalyst. These results agree well with the previous results of KNO₃/Al₂O₃ that was obtained by Xie and Li [4]. Therefore, it could be concluded that the optimum loading amount of CaO was taken to be 30%. Base on those result, 30% loading amount of CaO was selected for futher studies in order to determined the optimum calcinating condition, i.e. temperature and time of calcination.

3.3. Effect of Temperature Calcination on the Yield of Biodiesel (%)

To determine the effect of calcination temperature on the yield of biodiesel, the synthesized catalyst was calcinated at varied temperature from 500 to 700°C with 50° interval. Figure 2 showed the yield of biodiesel versus calcinations temperature on transesterification of palm oil at 65°C, 5 h of reaction time, molar ratio of oil to methanol 1:42 and 6% dosage of CaO/KI/γ-alumina catalyst. It was clearly seen, that the activity of the catalyst strongly influenced by the calcinations temperature. Without calcinations, the CaO/KI/γ-Al₂O₃ catalyst did not showing any activity. From temperature 500 to 650°C the activity of catalyst start to appear, although not strong, proven to resulting yield of biodiesel was still relatively low and rise gradually from 1, 1.5 and 7 for 500, 550 and 600°C, respectively. It might be possible, due to lack of strong basic site on which transesterification reaction could occur [4]. After calcination at temperature 650°C the catalytic activity drastically increase which highest yield of biodiesel (95%) was obtained. Such a result represented that the high temperature calcination was indispensable for getting high activities of the CaO/KI/γ-Al₂O₃ catalyst. Moreover, to form high basic sites on calcium oxide, the adsorbed water and carbon dioxide must be removed, and at the same time Ca²⁺ and O²⁻ should be in a certain coordination state on the surface of calcium oxide [6]. Meanwhile, the highest soybean oil conversion of 87.4% was obtained at loading of 35 wt. % of KI on Al₂O₃ at calcination temperature 500°C [4]. It should be noted that the experiment used single promoted catalyst KI/Al₂O₃. However, in this work, when the calcinations temperature was higher than 650°C the biodiesel yield dropped considerably to 12% due to the catalytic activity sharply decreased resulting of the low basicity. The same performances were reported by Xie and Li and Huaping et al. [4, 6].

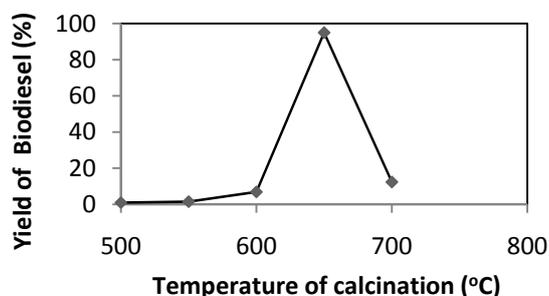


Fig. 2: Yield of biodiesel as a function of calcination temperature, at transesterification condition: 65°C, 5 h, molar ratio oil to methanol 1:42 and catalyst dosage 6%.

3.4. Effect of Calcination Time on the Yield of Biodiesel (%)

To study the effect of calcinations time in preparation of CaO/KI/ γ -Al₂O₃ catalyst on the yield of biodiesel, the catalyst was introduced on transesterification of palm oil with condition of reaction as the same as that the effect of temperature calcinations. The experiment was carried out at five type of calcination time from 3 to 5 h with 0.5 h interval at optimum calcinations temperature of 650°C. Figure 3 showed the effect of time calcinations on the yield of biodiesel. It can be seen that the biodiesel yield was increase along the increasing the time of calcination. The yield of biodiesel was sharply increased from 57 to 92% at 4 to 4.5 h of calcination time. Above 4.5 h, the extent of calcinations time does not give a significant impact on the yield of biodiesel. The maximum yield almost 95% was obtained at 5 h of calcinations time. The result agree with the previous results who conducted by Zabeti et al. and Ilgen and Akin [7,15]

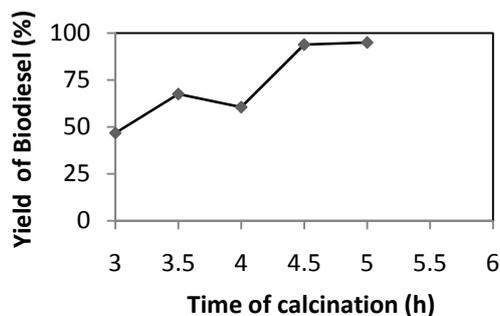


Fig. 3: Yield of biodiesel as a function of calcination time at calcination temperature of 650°C and transesterification condition: 65°C, 5h, molar ratio oil to methanol 1:42 and catalyst dosage 6%.

4. Conclusions

Being treated with double promoted catalyst to synthesized CaO/KI/ γ -alumina base catalyst, the activity of catalyst could sharply increase compared with the single promoted catalyst CaO/ γ -alumina. It can be proved from the result of the activity catalytic test by introducing the catalyst on the transesterification reaction of palm oil, the biodiesel yield was significantly increased from 65 to 95% for CaO/ γ -alumina and CaO/KI/ γ -alumina, respectively. The optimum conditions were obtained i.e. amount of CaO loading, calcination temperature and calcination time were 30% (wt. % to alumina), 650°C and 5 h, respectively. Therefore, it can be concluded that CaO/KI/ γ -alumina was a very promising heterogeneous base catalyst for producing biodiesel with a high activity.

5. Acknowledgements

The authors are grateful to financial support from Research institutions and community services of Sepuluh Nopember Institute of Technology (ITS) contained in the memorandum of agreement No: 1027.156/ITS.7/PN.01/2012.

6. References

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