Biodiesel Production from Crude Palm Oil off-grade Over a ZnO Catalyst Presipitant Zinc Carbonate

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ABSTRACT

Crude Palm Oil off-grade (CPO off-grade), a CPO product contains high free fatty acid's content (FFA > 5%). This oil is produced from Palm fruit off-grade which have categorized includes abnormal size, immature, pass to mature, and decay. In the refinery industries, this oil is rejected because it can be generate a low quality of cooking oil. Generally, this oil has been used to produce a biodiesel or fatty acid methyl ester (FAME) over a catalysts. In this research, this oil is converted to a crude biodiesel over Zinc oxide (ZnO) as a heterogeneous catalyst. This catalyst was prepared from zinc carbonate precipitant by a hydrothermal method. The ZnO catalyst can be made easily and the raw materials is cheap. The goal of this research is to increase CPO off-grade added value and determine the catalytic activity of the ZnO catalyst. The activity catalytic of ZnO is evaluated by regenerating the spent catalyst and it is reused several times in the transesterification reaction cycles. Results, yield of crude biodiesel is obtained maximally 96%. The catalytic activity of ZnO catalyst is high, and it cam be re-used determined by regenerating the spent catalyst, then it was regenerated and r-used four times in the transesterification reaction cycles. The catalytic activity of ZnO catalyst till retain in the 4$^{th.}$ reaction cycle giving the yield of crude biodiesel in the range of 96 – 71%. Overall, conversion CPO off-grade to crude biodiesel over ZnO catalyst was significant high. This ZnO catalyst is potential as a catalyst in the biodisel production.

Key words: *biodiesel; CPO off-grade; regeneration; Yield; ZnO catalyst*

INTRODUCTION

Crude palm oil off-grade (CPO off-grade), an oil contains high free fatty acid's content over 5% (FFA > 5%). CPO off-grade is produced from Palm fruit off-grade. This fruit is categorized includes abnormal size, immature, pass to mature, and decay. In the CPO refenery industries, this oil is rejected because it generate a low quality of cooking oil. In Indonesia, the need for fuel for diesel engines is increasing every year. Along with the number of industrial machinery and the number of diesel-engined vehicles. However, oil reserves dwindling, therefore it is necessary to find an alternative source of energy.

Research on edible oil as alternative energy sources are being developed, such as the oil into biodiesel [1, 2 & 3]. The use of biodiesel in diesel engines can reduce emissions imperfect burning of hydrocarbons, such as carbon monoxide, sulfates, polycyclic aromatic hydrocarbons, nitrate polycyclic aromatic hydrocarbons and solid particles

CPO off-grade can be processed to become biodiesel [1, 2 & 3]. Biodiesel, a fuel oil has calorie value 128.000 Btu [4] almost many as a petroleum of diesel 130.000 Btu [5], So, it can produce a torque engine and horse power as same as a petroleum of diese [6]. In room temperatures, biodiesel more safe to kept and used to be than petroleum of diesel, because is not condense and releases dangerous gas emission CO and SO_X . Biodiesel contains oxygen molecules, so it's flash point higher than petroleum, also it is not flammable easily [7], .

In general, the production biodiesel of edible oil conducted by esterification and transesterification reactions using methanol as reactant over acid catalyst (H_2SO_4) and of base catalyst (NaOH), biodiesel yield found ± 85% [1]. In the homogeneous systems, the separation product from by-product and catalysts require the expense of costly, and generate a bad impact of environment [8, 9 & 10].

The goal of this research is to increase CPO off-grade added value and determine the catalytic activity of the ZnO catalyst. In this research, the conversion CPO off-grade to crude biodiesel has been done over a ZnO catalyst. This catalyst was prepared from precipitan zinc carbonate.. The ZnO catalyst can be made easily and the raw materials is cheap. The activity catalytic of ZnO is evaluated by regenerating the spent catalyst and it is reused several times in the transesterification reaction cycles.

EXPERIMENT

All reagents were applied, such as methanol (impure), H_2SO_4(±98.99% purity, ethanol p.a, toluene p.a. kalium hydroxide pellet(±99.95% purity, Merck), phenolphtalein indicator. High FFA-crude palm oil is obtained from a CPO industry PTPN V Sei. Pagar Riau-Indonesia. There are several steps have been done in this research namely CPO sampling, CPO characterization, and the conversion CPO to crude biodiesel, determination of the crude biodiesel product, finally the activity catalytic of catalyst by regeration of the spent catalyst and re-used several times.

Several characterization over CPO off-grade has been determined of oil, such as pH (universal indicator, Merck), water content (British 1016 Part 104.1:1999**)**, bulk density (SNI 01-2891-1992**),** kinematic viscousity (ASTM D445**)** , and Free Fatty Acid (FFA) (RSB, 2008). Conversion oil to biodiesel has been carried out by two sreps, esterification and transesterification reactions**.**

The experiment was conducted using a necked boiling flask with the type blade--turbin-machine impeller (Heidolph). A thermometer was immersed in the boiling flask by using a metal stand, one neck of boiling flask use for input a certain amount reactans and catalysts. The capacity of boiling flask 1 litre, 18.5cm heigth, outside diametre 8.725cm and inside diametre 12.95cm dimensions. The reactor is combined with a water bath/hot plate.

The esterification reaction of oil with methanol was carried out over H_2SO_4 as a catalyst in batch reactor. Catalyst H_2SO_4 and methanolic 0.5% was mixed in a bulb glass of batch reactor. This mixture was agitated and heated until the reaction temperature reached 65^oC ± 2 ^oC , then it added oil and proceed for 30 minutes prior. Afterward, ZnO catalyst 0.5% was poured into te reaction mixture and heated at 65^oC ± 2 ^oC for 1 hour prior to

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complete. The transesterifcation reaction parameters are keeping identical condition under molar ratio variation between oil and methanol (1:6, 1:12 and 1:18), also variation the amount of catalyst (0.3, 0.4 & 0.5 wt.%).

The spent catalyst from the reaction mixtures was recovered by filtration and regenerated for further use. The recovered catalyst was washed thoroughly with methanol and dried in oven at 105 ^{o}C for 4 hours followed by activation at 200 ^{o}C C for 4 hours. Then, regenerated catalyst was used in the conversion of oil to biodiesel process. Oil Conversion to biodiesel over the catalyst re-used has been done. Each reaction was carried out at 65^{o}C ± 2 ^{o}C for 1 hor using molar ratio of methanol to oil of 1:18, and the amount of catalyst 0.5%.

All other reaction using the catalyst re-used are running for three times under this identical condition. Determination the activity catalytic of the regenerated catalyst has been investigated based on calculating the crude biodiesel yield and alkyl ester content. The product obtained was analyzed by density at 40^{o}C (ASTM D 1298**)**, kinematic viscousity at 40^{o}C (ASTM 1298), glycerole total (ASTM (ASTM D6584), and alkyl ester content (FBI-A03-03).

RESULTS AND DISCUSSION

The amount of FFA in CPO off-grade is high significantly around 14.5% (Table 1). Based on this result, the conversion oil to biodiesel has been done by two steps namely esterification and transesterification reactions.. Edible oil contains high FFA > 2% was convetrted to biodiesel by two steps processes reactions is applied by many researches [1, 2, 3, 11 & 12].

Table 1. Characterization resutlts of CPO off-grade

Properties	Results
Water content	3.19 % dry weight
pH	6.98
FFA content	14.5 %
Oil content	82.31 %

Results of conversion oil to biodesel as can be seen in Figure 1. Overall, the stochiometri reactions between oil and methanol and amount of catalyst are affected to yield of crude biodiesel production. Yield of crude biodiesel has been obtained maximally ± at mol ratio of reactan 1:18 and amount of ZnO catalyst 0,5%.

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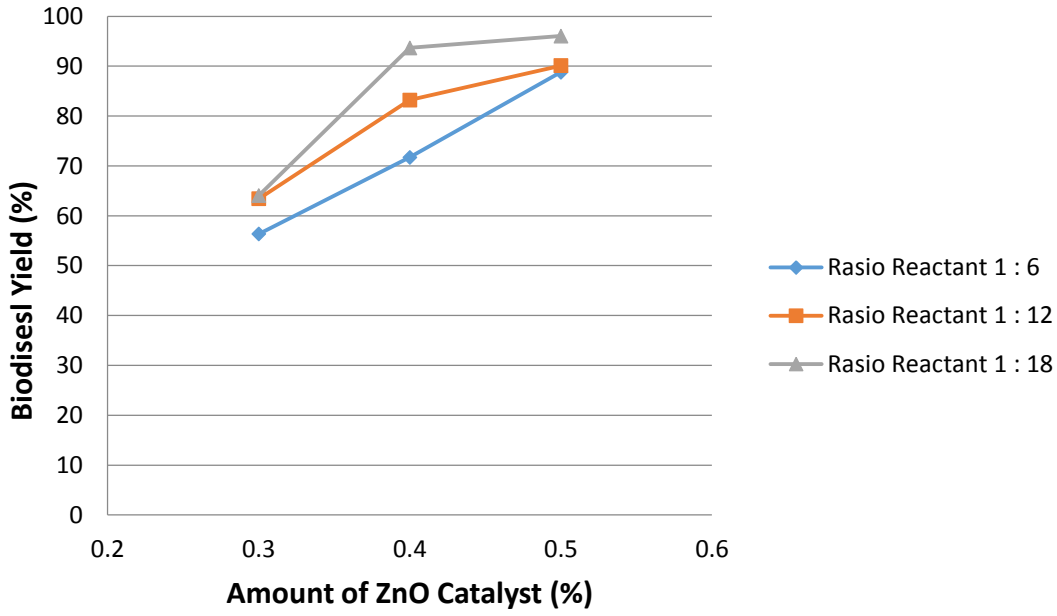

Figure 1. The influence of variation amount of ZnO catalyst and rasio reactant to biodiesel yield.

In the reaction using molar ratio of reactants 1: 6 is the lowest yield of crude biodiesel found than others. Also, this yield is not different significantly than the reaction using molar ratio of reactants 1: 12. Others found that the stochiometri reactions 1:6 is the best produced yield of biodiesel approximately 90 – 98% [1, 2, 13 &14]. The consideration for this cause CPO off-grade contains high Free Fatty Acid 14.5% (Table 1), so in the reaction FFA can contribute to produce high a glycerole content as a by product.

Molar ratio of alcohol to triglyceride present in oil is an important parameter to be considered while screening the catalyst performance and in maximizing the fatty acid alkyl ester/glycerol yield biodiesel [1, 2, 3 & 9]. Theoretically, the transesterfication of oil requires three moles of methanol per mole of triglyceride. Since transesterification of triglyceride is a reversible reaction, the excess of methanol shifts in the equilibrium towards the direction of methyl ester formation. In the presence of excess alcohol, the forward reaction is product formation. In addition, usage of excess alcohol is one of the better options to improve the rate of the transesterification reaction catalyzed by heterogeneous catalysts [1, 2, 3, 9 & 11]. In the present work, with pre-optimized reaction parameters, molar methanol to oil ratio was varied in the range of 6:1 , 12:1 and 18:1 and its influence on fatty acid alkyl ester yield.

The highest conversion of 96.03% was registered at molar ratio of 18:1. For molar ratio of reactants from 1:12 to 1:18, further increase in the methanol amount has not showed any significant improvement in the conversion. Probably, higher concentration of methanol interferes with the separation of glycerin because of its increased solubility. It is also possible that presence of glycerole in the solution might drive equilibrium to backward direction yielding lower contribution of glycerin in the product or may cause esterification of glycerol in

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presence of methanol. Thus, under the mentioned reactions conditions, methanol to oil molar ratio of 18:1 seems to be the most appropriate.

An arrangement reaction temperature is very important with an assumption that reactant particles for collosion has more potential of increasing each other, so the actiavation of energy for reaction will be reduced and the reaction accelaration will be rising. Reaction temperature in the conversion CPO off-grade to crude biodiesel is 65^{o}C. Generally, the limitation of temperature reaction usually which is used by several researches in biodisel production is around 50^{o}C - 65^{o}C [2, 3, 13 & 14]. If the reaction temperature higher than boiling point of methanol (68^{o}C), methanol tends more vapored easily, if conversion's temperature is under 50^{o}C, viscousity of biodiesel of biodiesel will increase [20 & 21].

In this research, H_2SO_4 1% is applied in order to minimaze formed of by product, then continue for 1 hours in the transesterification reaction over ZnO. Metal oxide catalyst ZnO is applied in the reaction because of it's reactivity higher than other acid catalyst, and reaction can be operated under medium temperature [15 & 16], also it is cheaper than other catalysts. Some studies believe that ZnO as a catalyst has high the activity and stability for application to an intensified method of biodiesel production [17]. Also it's surface contains high the acidity and basicity as a metal oxide [18], it can be generate high conversion CPO off-grade to biodiesel. In addition, in the other research found similar condition, because a certain amount of triglyceride turn to be monoglyceride and diglyceride compounds biodiesel [1, 3, 19, 20 & 21].

In order to understand the catalytic activity of ZnO, this catalyst was evaluated for optimizing the catalyst preparation method and reaction parameters, it is desired to check the reusability/recyclability of the catalyst. Results reaction using a catalyst re-used compare to transesterification reaction with a parent catalyst shown in Table 2.

Table 2. Comparison Crude Biodiesel product by using re-used catalysts

Reaction	Yield (%)
Reaction with a parent catalyst	96.03
Reaction with catalyst re-used (catalyst is regenerated in 1 st cycle)	90.78
Reaction with catalyst re-used (catalyst is regenerated in 2 nd cycle)	85.46
Reaction with catalyst re-used (catalyst is regenerated in 3 rd cycle)	75.68
Reaction with catalyst re-used (catalyst is regenerated in 4 th cycle)	70.98

Results shows, the catalytic activity of ZnO catalyst till 4 th rd reaction cycle giving the yield of crude biodiesel in the range of 96 – 71% (Table 5), which indicates that the sites of the catalyst are not deactivated in the regenerated catalyst. Overall, the conversion oil to crude biodiesel was observed to be reduced from 96.03% to 70.98%. This is indicate that the fresh catalyst gets little deactivated after used. The reduction in conversion could probably be

due to the deposition of reactants and/or products on the active sites, and/or loss of the active sites during the reaction. The yield decreased after four reaction cycles, which is attributed due to the deposition of carbonaceous material on the external surface of the used catalyst.

But, yield biodiesel of transesterification reaction over the spent catalyst regenerated were still high for two and three times cycles. Endelaw et.al (2014), found that activity catalytic of ZnO catalyst in the transesterification reaction is high significantly. The ZnO nanoparticles were reused 17 times without any activity loss in a batch stirred reactor an average yield of FAME was around 93.7% [1]. .It can be conluded that ZnO catalyst is potential as a catalyst in the biodisel production.

IN CONCLUSION

High-FFA CPO can be a potential material resources to produce crude biodiesel. Biodiesel yield of conversion oil to biodiesel found maximally approximately 96% under condition temperatures reaction 65^{o}C ± 2 ^{o}C, ratio moles of reactants oil : methanol 1:18 v/v and the amount of catalyst 0.5%. Yield conversion oil to biodiesel by using the spent catalyst has been obtained maximally ± 96%,. The catalyst ZnO was found highly active for transesterification of High-FFA CPO with methanol giving high yield of crude biodiesel (96%) after 2 hours. ZnO catalyst is potential as a catalyst in the biodisel production.

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