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Palm biodiesel production using by heterogeneous catalyst based corn cobs

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Abstract. In this research, heterogeneous solid base catalysts were derived from corn cobs. the solid base catalyst was obtained which was then used for the production of palm oil biodiesel with a transesterification reaction. The catalyst prepared corn cobs with impregnation of NaOH then calcined temperature 400°C at 2 hours. The optimum conditions for the function of duration reaction time and catalyst amount obtained catalyst amount 3% at 60 minutes, temperature 65°C, ratio methanol to oil 12:1 obtained yield of biodiesel 93.10% while the function of reaction temperature and catalyst amount obtained catalyst amount 2.5%, ratio methanol to oil 12:1, at duration time is 60 minutes and temperature 60°C obtained yields 97.35%. The catalyst was easily separated from the reaction mixture by filtration and able to reuse for 2 times. The biodiesel product is specified with EN14214. Heterogeneous catalysts derived from corn cobs that show high-cost potential and produce easy ones as solid catalysts for the transesterification reaction of biodiesel production.

Keywords: Corn cobs, palm oil, solid base catalyst, transesterification

1. Introduction

In the past few decades, the problems that are of major concern to the world are energy and the environment, research on energy and alternative sustainability has received great attention. Biodiesel is one good candidate to replace alternative fuels because it can be used in diesel engines. In addition, biodiesel is also a renewable energy, clean, non-toxic, inexpensive and environmentally friendly [1,2].

Transesterification reaction is a general reaction to produce biodiesel. Triglyceride compounds found in raw materials such as vegetable oil, fat oil, and palm oil are reacted with an alcohol in the presence of catalyst [3,4]. Generally, as a homogeneous base catalyst is potassium hydroxide, sodium hydroxide, and sodium methylene because the catalyst has a high catalytic activity which can react in 1 hour at a temperature of 40-60°C [5].

However, the utilization of this homogeneous base catalyst still has many problems such as the separation of difficult catalysts at the end of the product, the formation of soap and reactor corrosion. In addition, large quantities of water are usually needed to wash biodiesel products to remove the homogeneous catalyst contained in biodiesel. This causes an increase in production costs and environmental problems [6].



On the other hand, the use of heterogeneous base catalysts as catalysts for the transesterification process is in great demand due to easy separation at the end of the product, the catalyst can also be reused, and can be recycled in several times and no neutralization or washing process is needed on the final biodiesel product. Therefore the use of heterogeneous base catalysts in the transesterification process for biodiesel production is very effective and efficient [7,8].

Many types of heterogeneous base catalysts are used for biodiesel production. One example of a heterogeneous base catalyst for the transesterification process is a catalyst derived from biomass which is from corn cobs where corn cobs are agricultural waste. Besides that the use of corn cobs waste can reduce environmental waste both physical waste that damages the scenery and air pollutant waste. The research is the production of biodiesel using heterogeneous catalysts from corn cobs which are waste management. Some parameters of concentration and reaction with variation in catalyst concentration and reusability. Biodiesel obtained through the purification process will be evaluated by the European standard method (EN14214).

2. Materials and Methods

2.1 Material

The raw material for palm oil is obtained commercially from Indonesia with 0.14% FFA content and 0.05% moisture content. Pro analyst methanol and corn cobs are obtained from one of the corn refineries that have undergone a deionized water washing process with the aim of removing impurities and then drying at 110°C overnight before use.

2.2 Preparation Catalyst form Corn Cobs

Corn cobs were calcined with a temperature of 700°C for 3 hours so that corn cobs were obtained, then corn cobs ash was dissolved with 2 M NaOH solids at 75°C for 3 hours. Then the solution was calcined at 400°C to obtain a solid base catalyst derived from corn cobs.

2.3 Transesterification of Palm Oil

The transesterification process used three flask reactor neck flasks with condenser reflux equipment, a magnetic stirrer with 300 rpm equipped with a thermometer. Heterogeneous catalysts derived from corn cobs were first reacted with methanol for 1 hour under room temperature conditions. After that, it is mixed with 25 grams of palm oil. Biodiesel obtained is then filtered to separate the catalyst. Then the washing process is done using water 80°C 300 ml up to neutral pH. After that, the heating process is carried out at a temperature of 105°C to remove the water content and the remaining methanol.

2.4 Product Analysis

Biodiesel product produced was analyzed for the content of methyl ester using by the GC-MS Shimadzu-2010 gas chromatograph. The refined biodiesel is tested according to the European standard method (EN14214) for fuels derived from vegetable oils [9]. The viscosity, density and ester content of biodiesel were analyzed standard using EN 14214 specifications. The catalyst leaching ion sodium for reuse was invistage with AAS.

3. Results and Discussion

3.1 Effect of duration Reaction Time and Catalyst amount

The transesterification process of palm oil with reaction methanol using a heterogeneous catalyst from corn cob ash 400°C temperature calcined for 2 hours, ratio methanol to oil 12:1, the reaction temperature of 65°C. Effect of duration reaction time and catalyst amount catalyst was variation the

reaction time 30-120 minutes and the catalyst amount 2% -3%. The relationship between reaction time to yield of biodiesel with various catalyst weight variations in this study is shown in Figure 1.

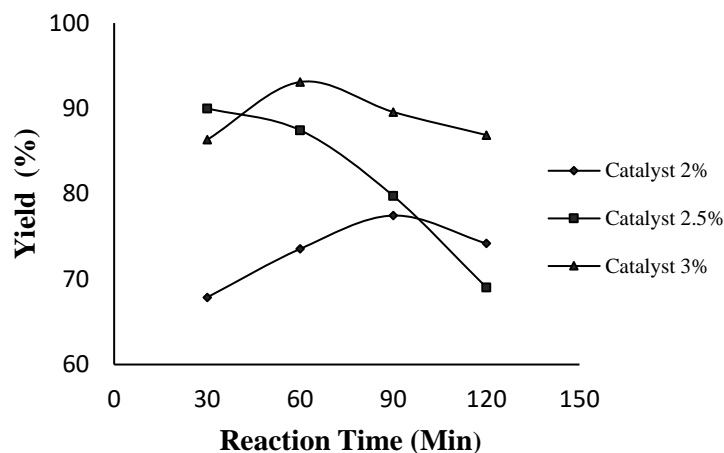


Figure 1. Effect reaction time and catalyst amount

The transesterification reaction of palm oil into biodiesel is a reversible reaction. From Figure 1. it can be seen that the tendency of using catalysts of 2% and 3% have similarities where the yield increases at 60 minutes and the yield decrease at the reaction time of 120 minutes. This is due to the concentration of the catalyst 2% at 30 and 60 minutes Na active site to catalyst is still small and in addition with a short time the equilibrium reaction has not been achieved so that the next low yield at 90 minutes with a concentration of 2% is close to equilibrium reaction thus yielding a yield of 77.45% while at 120 minutes the yield decreases because it is caused by the product of methyl ester which has been formed again to become monoglycerides or produce higher glycerol content.

At the use of the catalyst as much as 2.5%, the tendency is different, where at the 30 minute reaction time the highest yield is obtained which then decreases in yield with increasing reaction time. This is because Na active groups on the surface of the catalyst to catalyze sufficiently close to the equilibrium reaction which results in a 90% yield then the possibility of decreasing the number of products or yields at a longer reaction time is caused by a reverse reaction, ie methyl esters which are re-formed monoglycerides or products more and more glycerol too.

At the use of 3% catalyst the tendency is different where at the reaction time of 30 minutes the yield obtained by 86.33% has increased compared to the concentration of 2% where the yield obtained is 67.87 this is due to the active group Na content at 3% more so active site of Na to catalyze triglycerides in palm oil. Furthermore, at 60 minutes obtained 93.10% biodiesel yield because the reaction has approached the equilibrium of the next reaction at 90 and 120 minutes yield tends to decrease because the back reaction on the ester product becomes monoglyceride or glycerol products increase. From the above conditions, it can be concluded that the longer the reaction time does not guarantee to produce more ester products this is the same as in the amount of catalyst 2%, 2.5% and 3% which decreases at 120 minutes. While for reaction times that are too short, triglycerides have not yet been converted into methyl esters so that the yield produced is smaller [10].

3.2 Effect of Catalyst amount reaction and Temperature reaction

The transesterification process palm oil with reaction methanol using catalyst from corn cob ash 400°C temperature calcined for 2 hours, ratio methanol to oil 12: 1, a reaction time of 60 minutes. The effect of reaction temperature and catalyst amount was assessed variations the reaction temperature of 50-65°C and the weight of the catalyst 2% -3%. The relationship between the reaction temperature to the yield of biodiesel with various variations in the weight of the catalyst in this study is shown in Figure 2.

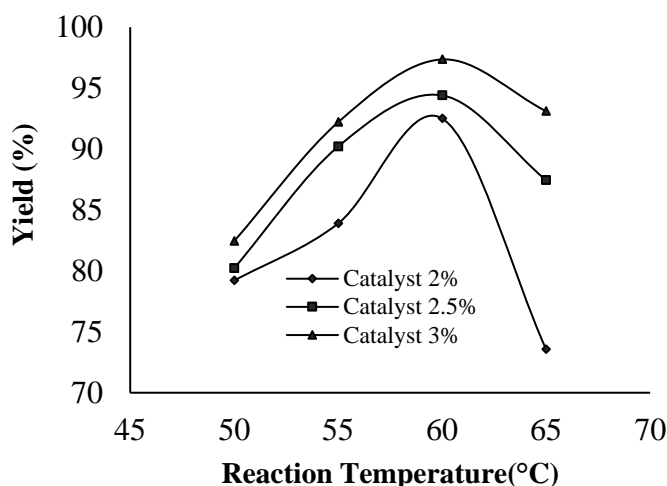


Figure 2. Effect amount catalyst and temperature reaction

From Figure 2., the tendency of the use of catalysts 2%, 2.5%, and 3% have similarities in which there is an increase in yield of 92.25%, 94.40% and 97.35% at a reaction temperature of 60°C. this is because with a concentration of 2%, 2.5% and 3% the transesterification reaction approaches the equilibrium of the reaction at a temperature of 60°C so that the biodiesel product produced is high. In addition, the higher the reaction temperature, the higher the reaction rate, but in the transesterification reaction, this is less valid because, at a temperature of 65°C, the boiling point of methanol is 64.7°C [11] so that it will cause the methanol to evaporate, it will reduce contact with oil due to the formation of bubbles between reactants. In addition, the use of catalysts with a concentration of 3% produces high yields due to the increasing number of methoxy (CH_3O^-) nucleophilic groups of methanol which react with the electrophilic of carbon carbonyl from triglycerides during the transesterification reaction compared to 2.5% amount and 2%. In Figure 2., the optimum conditions in this study were the reaction temperature 60 °C, the catalyst amount of 3%, the duration of the reaction time of 60 minutes, and ratio methanol to oil 1:12 which resulted in ester content of 99.60% and yield of 97.35%.

3.3 Reusability of catalyst based corn cobs

Reusability is one of the economic application factors in the use of solid catalysts for heterogeneous reactions. In this study, the use of reuse was done without the activation process. use of reuse of biodiesel yield with the optimum conditions is reaction temperature 60°C, reaction time 30 minutes, ratio methanol to oil 12: 1, catalyst amount 3%.

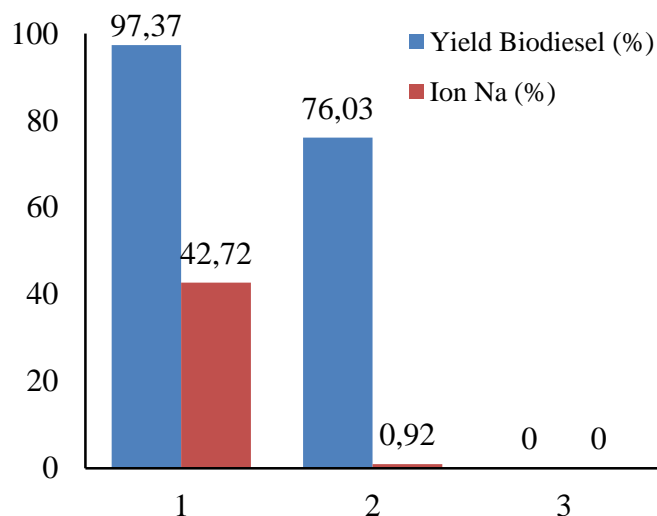


Figure 3. Effect of reuse of the catalyst on yield biodiesel and analysis amount of Na ion

From Figure 3 to show the second reuse time experienced a decrease in biodiesel yield by 76.03%. This is probably due to sodium silicate catalyst on the active side sodium (Na) of the catalyst leaching during the transesterification process [12]. In this study, AAS was used to analyze the content of Na (sodium) ions lost due to the transesterification process. In Figure 3. the use of the first catalyst contained in the Na ion was 42.72% and after the second use obtained Na content of 0.92%. this is because the Na ions on the catalyst have been mixed with biodiesel product and other components cover the surface area of the catalyst [13].

3.4 Characteristics of Methyl Esters

Characteristics of Methyl Esters obtained from the transesterification reaction of palm oil with methanol using calcined sodium silica catalyst derived from corn cobs after with purification process using water at 80°C to remove impurities in the form of methanol, remaining glycerol and ions remaining and heating process to remove residual water content in biodiesel. The biodiesel will be measured according to EN14214 standard.

Table 1. Physicochemical Properties of Palm Oil

Fuel Properties	Unit	Standard EN14214	This work
Ester Content	%	96,5	99,60
Density	Kg/m ³	860-900	879
Viscosity	cSt	3,5 - 5	4,26
Monoglycerides	%	Max 0,8	0,05
Diglycerides	%	Max 0,2	-
Glycerol	%	<0,24	0,225

The results of Table 2, biodiesel production in this study with 6 physicochemical parameters has a value corresponding to EN14214 standards, although there are still many other parameters needed to analyze biodiesel products as fuel. however, the 6 parameters above can serve as an early stage indicator with the aim of producing biodiesel as fuel

4. Conclusion

The use of heterogeneous catalysts derived from corn cobs synthesized with NaOH yields 93.10% with a catalyst concentration of 3%, 60 minutes temperature of 65°C and 97.35% with a catalyst concentration of 3% at 60 minutes at 60°C. Solid catalyst from corn cobs can be recovered for 2 x without catalyst regeneration process. the biodiesel product obtained is standardized with EN14214 that indicates that biodiesel products can be produced on an industrial scale.

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