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Production of Methyl ester from Coconut Oil using Heterogeneous K/γ-Al_2O_3 under Microwave Irradiation

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Key Words **:** *Methyl ester, Coconut oil, Trans-esterification, K/γ-Al2O3 catalyst, Microwave*

Abstract

Methyl esters derived from coconut oil are very interesting to study because they contain free fatty acids with a medium carbon chain structure (C12-C14), so most methyl esters (70%) can be bio-kerosene and the rest can be biodiesel. The process of preparing methyl ester by reaction of Trans-esterification triglyceride generally using a homogeneous KOH catalyst but this process requires a long catalyst separation process through washing and drying process. The use of heterogeneous catalysts in the production of methyl esters can remove the washing and drying processes, but trans-esterification reactions with heterogeneous catalysts require severe conditions (high pressure and high temperature), whereas at low temperatures and atmospheric conditions, the methyl ester yield is relatively low. Using microwave-irradiated trans-esterification reactions with heterogeneous catalysts, it is expected to be much faster and can obtained higher yields. Therefore, in this study we prepare a heterogeneous catalyst K/γ-Al2O3 using solution KOH that impregnated in catalyst support γ-Al2O3, and catalyst obtained are characterized by XRD, BET dan SEM. Our objective was to compare the yield of methyl esters obtained through the trans-esterification process of coconut oil assisted by microwave using a heterogeneous K/γ-Al2O3 catalyst with yield obtained using a homogeneous KOH catalyst. Experimental equipment consists of a batch reactor placed in a microwave oven equipped with a condenser, agitator and temperature controller. The batch process was carried out at atmospheric pressure with variation of K/γ-Al2O3 catalyst concentration (0.5, 1.0, 1.5, 2.0, 2.5%) and microwave power (100, 264 and 400 W). In general, the process of producing methyl esters by heterogeneous catalysts will get three layers, wherein the first layer is the product of methyl ester, the second layer is glycerol and the third layer is the catalyst. The experimental results show that the methyl ester yield increases with increasing of microwave power, catalyst concentration and reaction time. The results obtained with K/γ-Al2O3 catalysts are generally slightly lower than those obtained using a homogeneous KOH catalyst. However, the yield of methyl esters obtained by the K/γ-Al2O3 heterogeneous catalyst process are relatively easy to separate rather than using a homogeneous KOH catalyst.

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INTRODUCTION

The use of fossil fuel still dominates energy consumption in Indonesia, especially transportation sector and has been increase significantly in the last twenty years. Indonesia has changed from net oil exporter to net oil importer in recent years and faces major challenges since the international oil prices continue to increase. An alternative energy such as biodiesel is very necessary because of the use of fossil fuel always increasing [1]. One of alternative energy that is being to developed is methyl ester fatty acid (FAME) or known as biodiesel.. Generally, vegetable oils are preferred and have beneficials compare to animal fats because vegetable oils are very abundant and renewable natural resource. Vegetable oils does not require the complex purification for fuel requirements and does not need much pretreatment energy [2].

Biodiesel production in Indonesia currently uses palm oils, coconut oils and palm oil acid refining (PFAD). In particular, Indonesia is one of the biggest coconut producer countries in the world. The area of coconut crops in Indonesia reached 3,76 million hectares with a total production of around 14 billion and around 2,5 million as a source of income for farm families. Transesterification process is widely used to produce biodiesel because of simple and can produce a high purity of FAME. Transesterification process is a reaction between triglyceride and alcohol with the presence of a catalyst to produce alkyl ester as the main product and glycerol as the by-product [3]. Transesterification reaction can be fastened by an addition of catalyst [4].

Recently, the rapid increase in the rate of chemical reactions using irradiated microwaves has attracted the attention and interest of researchers in almost all fields of research, especially in biodiesel production. Several researchers have studed the use of microwave for biodiesel production from different materials and catalysts, such as [5] evaluated the preparation of Ti-SO3H/ICG in esterification of palm fatty acid distillate to methyl ester and the catalysts showed an effective result in reducing the catalyst separation problem and high percentage yield of biodiesel. [6] tested Chlorella Sp in biodiesel production using base catalyst under microwave irradiation and their study showed an increasing yield and shorter reaction time. Patil et al, 2011 also demonstrated biodiesel production from waste cooking oil using BaO and KOH with microwave as heating and repoted that microwave heating method consumes less than 10% of the energy to achieve the same yield as the conventional heating method. Researchers and industrialists are interested in the application of microwave irradiation, not only because of the high reaction rate, but also because of their ability to increase the yield and quality of the biodiesel produced. Apart from these, there are several advantages of microwave use such as fast heating, relatively low energy consumption, environmentally friendly, higher production yields, easy control and shorter processing times.

In this work, biodiesel was produced using heterogeneous catalyst and microwave irradiation as heating source to reduce reaction time [3]; [7]; [8], [9] and catalyst requirement [10], [11]. Some of the advantages of e catalysts are catalyst can be regenerated and easy to separate, therefore production cost and waste formation can be decreased. Heterogeneous catalysts also is an environmentally friendly catalyst to produce high quality of ester and glycerol. Transesterification reaction from coconut oils using heterogeneous catalyst and microwave irradiation expected can produce higher quality of biodiesel. The use of K/γ-Al2O3 as catalyst and microwave as a heating source was studied in this work to improve the quality of biodiesel production from coconut oil.

MATERIALS AND METHODS

Materials

Coconut oil obtained from the commercial coconut oil (Barco Co). Methanol (96% of purity), KOH and Al_2O_3 from MERCK were used and purchased from a local chemical supplier (O. V. Chemicals, Co Ltd).

Catalyst Preparation

K/γ-Al2O3 catalyst was prepared by dry impregnation method with the following procedure: 20% of potassium hydroxide (KOH) was added with 100 ml of aquadest in a beaker glass . The mixture was then added with 10 grams of γ-Al2O3 followed by stirring for 3 hours using a magnetic strirer. The slurry formed was heated at 120 oC in an oven for 12 hours to remove the water content and calcined in the muffle furnace at the temperature of 650 ^oC with nitrogen gas flow for 2 hours, followed by hydrogen gas flow for 3 hours.

Experimental procedures

Transesterification reaction carried out under microwave heating to investigate the effect of microwave power and K/γ-Al2O3 atalyst on the reaction time. Variable process are K/γ-Al2O3 catalyst concentration (1.0; 1.5; 2.0; 2.5; and 3.0 % wt%) and microwave powers (100, 264,400 and 600 W). The research conducted with dissolve catalyst into methanol solution and stirred using a magnetic stirrer. The mixture of methanol, catalyst and coconut oil are put in the reactor and inserted into microwave and turn on as the variable setting. After reaction completed, the product was kept into a separation funnel for 3 to 6 hours to separate methyl ester and glycerol. The washing of methyl ester conducted by 30% of water addition and then the methyl ester was dried for 1 hour at 110^0C. The product was analyzed and the characterization of product was compared with the characteristic of commercial fuel oil.

RESULTS AND DISCUSSION

The fatty acid composition of the coconut oil was obtained by gas chromatography (Table 1). The fatty acid content of coconut oil used in the present research contains approximately 70% of fatty acid for chain C8-C14 while for the chain C16-C18 of about 30%. This indicates that coconut oil is rich with saturated fatty acids which are stable at high temperatures and it is great to use as raw material for the production of alternative fuels, especially biodiesel.

Characterization of catalyst

K/γ-Al2O3 catalyst was characterized by XRD, BET and SEM analysis. The analysis were used to determine catalyst crystallinity, surface area, pore volume, average pore diameter, morphology and the average size of particle. Figure 2 shows the diffractogram pattern of ɣ-A2O3 and K/γ-Al2O3 catalyst and it can be seen that K compound is well dispersed at γ-Al2O3 support, therefore it can stated that K promoter attaches at γ-Al2O3 support and the active core of the catalyst has a wide diffraction peak. The width of diffraction peak provides information about how much the crystallinity produced. The high crystallinity of catalyst indicates the high catalytic properties and stable at high temperatures.

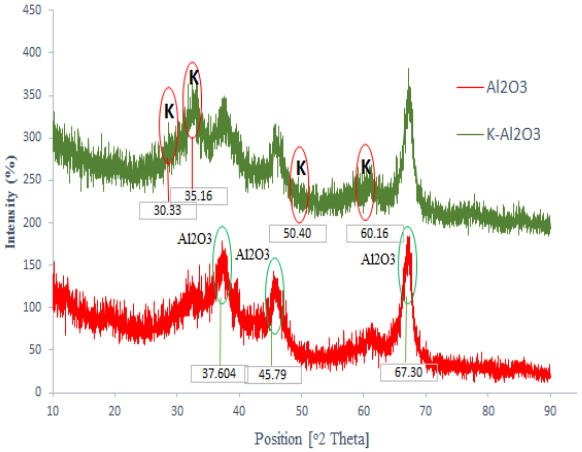


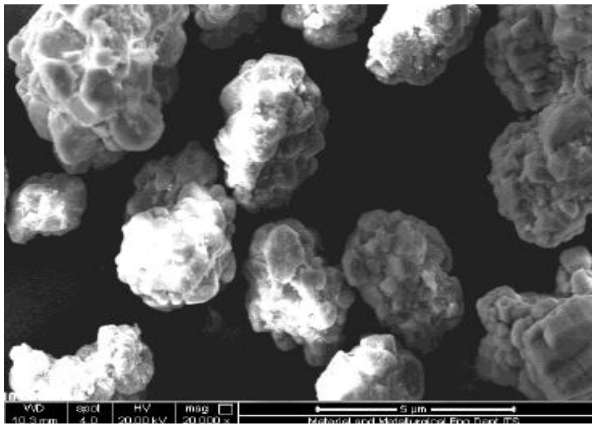
Figure. 1 X-Ray Diffraction Analysis (a) γ-Al_2O_3 dan (b) K/γ-Al_2O_3

Analysis of surface area, pore volume and average pore diameter of catalyst were carried out using the BET method. The complete K / ɣ-Al2O3 catalyst test results are shown in Table 1. The surface area of K / ɣ-Al2O3 catalyst is smaller compared to the surface area of ɣ-Al2O3 which shows that potassium hydroxide is well dispersed in alumina pores so that it partially covers the alumina surface.

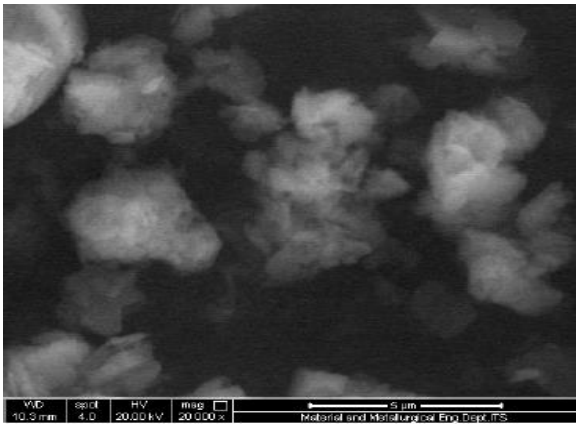
Table 1: .Characteristic of K/ɣ-Al_2O_3 catalyst

Catalyst	Surface Area (m^2/g)	Pore diameter	Pore Volume (cm^3/g)
K/ɣ-Al_2O_3	34,031	66,12	0,102
Ca/ɣ-Al_2O_3	83,77	35,218	0,145

The characterization with SEM aims to discover the morphology and size of catalyst. From the figure 3 can be seen that the morphology of ɣ-Al2O3 shows clumps, coarse and hard grains while K/ɣ-Al2O3 catalyst seen fine grains and soft catalyst. This shows that potassium oxide adheres well to the surface of ɣ-Al2O3. The particle size produced was mesoporous with around 2,764 μm.



(a)



(b)

Figure 2. Scanning Electron Microscopy, SEM of Catalyst (a) ɣ-Al_2O_3 and (b) K/ɣ-Al_2O_3

Effect of K/γ-Al2O3 Catalyst on Yield and Conversion of Methyl Ester

The use of heterogeneous acid catalysts did not show good results on changes in the physical properties of coconut oil used as reactants so it was stated that the reaction conversion was still very small. The K / γ-Al2O3 catalyst test in the transesterification reaction can be seen in the following Figure 3.

Figure 5 shows the use of K / γ-Al2O3 with catalyst concentration of 0.5; 1; 1.5; 2 and 2.5% (b/b) at the reaction time of 2 and 3 minutes. It can be seen that the effect of catalyst concentration on reaction conversion and yield increased significantly. However, at concentrations of 0.5 and 1% (b / b) yield was still low at around 2.47% and increased slowly after the number of catalysts increased to 2.5% (b/b) with 26.54% of yield.

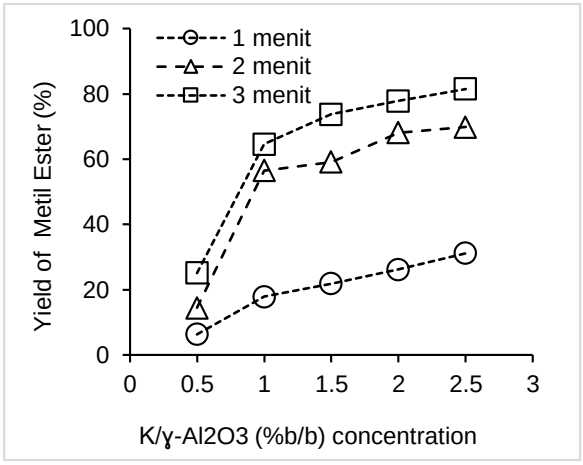


Figure 3 Yield of methyl ester at 1:9 of molar ratio; 400W of microwave power; K/γ-Al2O3 concentration

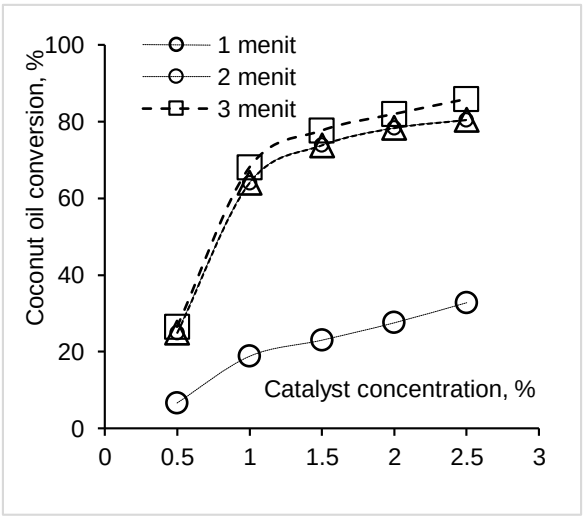


Figure 4. Conversion of ME at 1:9 of molar ratio; 400 W of microwave power; catalyst concentration0,5; 1;1,5; 2 dan 2,5 % (b/b).

As shown from figure 3 and 4, the effect of heterogeneous catalysts use on yield and conversion at concentration of 0.5; 1; 1.5; 2 and 2.5% (b / b) showed a significant increase with the increase in reaction time. At concentrations of 0.5 and 1% (b/b), yield was still low at 2.47% and slowly rose after the number of catalysts increased to 2.5% (b / b) with yields of 26.54%. This shows that heterogeneous catalysts with low concentrations and short periods of time have not been able to produce large methyl ester so that greater concentration is required, which was above 1% (b/b).

But in general it is seen that the transesterification reaction process has begun to occur even though it produces a small product. From Figure 3 and 4, it can be seen a significant increase of methyl ester at the higher concentration of catalyst which shows that the catalyst activity will be better if the amount of catalyst used is in accordance with the need to initiate the transeterification reaction.

From this experiment reported that the use of microwaves in the transesterification process of coconut oil can reduce the reaction time. The previous researchers reported that heterogeneous catalysts produced yields above 90% with reaction time more than 4 hours.

Effect of time and Power on Yield of Methyl Ester

Figure 4 shows the increase in K/γ-Al_2O_3 catalyst concentration followed by the increase in yield of methyl ester in transesteriofication reaction using microwave. The use of K/γ-Al_2O_3 catalyst to produce methyl ester requires longer periods of time, while microwave irradiation can reduce reaction time. The reaction was increased slowly at the beginning of the reaction due to the problem of mixing and dispersion of methanol into oil [12]. As shown in Fig. 6, the use of microwave can achieve yield of 81.5% only with reaction time of 3 min.

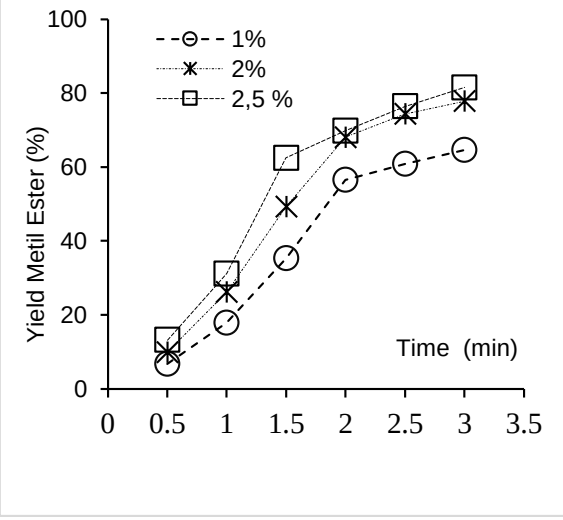


Figure. 5. Yield of methyl ester on different K/γ-Al_2O_3 concentration 1;2 and 2.5 (% b/b), 400 W, 1:9 of molar *ratio.*

Power input of microwave influences the amplitude. The rational speed of polar molecule has a linier relationship with the microwave amplitude. The experiment results at 2 and 2.5% of K/γ-Al_2O_3 concentration, 1:9 of oils-methanol molar ratio and reaction time (1.5;2;2.5)min are shown in fig. 7. Yield obtained at 100 W of power with 2.5% of K/γ-Al_2O_3 concentration, 2.5 min of reaction time was 80,68 %, whereas yield increased to 81.91% at 3 min. Yield produced can be increased with the increase in catalyst concentration or reaction time. The use of K/γ-Al_2O_3 catalyst on transesterification reaction shows the activity of catalyst even though it has not shown the optimal yield produced as describe in fig. 6. The increasing of power will increase in the rate of microwave radiation, so that the excitation of molecule compounds or materials will be great and heat effects also will be greater. The reaction process should be conducted on 60^0C of temperature and 264 W of microwave power. The reaction process using K/γ-Al_2O_3 catalyst using microwave as heating source can be carried out with reaction time shorter than 10 min.

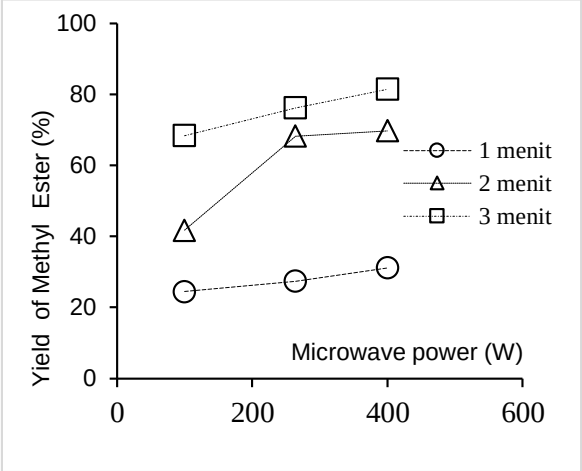


Figure 6. The effect of microwave power on yield of methyl ester (2.5% b/b of K/γ-Al_2O_3; reaction time 2,5 and 3min; 1:9 of molar ratio and 100, 264 and 400 W of microwave power.

The heating process by microwave is the heating process in the liquid or solid which electromagnetic wave changed to heat energy. Heat effect produced from the electric field of microwave which force dipoles to rotate and ions to move from slow response following the fast electric field. Energy from microwave transferred into materials by dipole polarization, ionic conduction and surface polarization that produce local heating. This experiment supported with the previous research that variables of power have

effect on yields. The use of heterogeneous catalyst needs higher of heat compare to homogeneous catalyst, so that the increasing of power will increase the temperature of reaction.

CONCLUSIONS

The application of microwave irradiation is a promising method compare to conventional method for biodiesel production as it can accelerate and shorten the transesterification process. Heterogeneous catalysts also is an environmentally friendly catalyst to produce high quality of ester with the characteristics are high activity stability, strength and surface area. In this study the use of microwave in the process of coconut oil transesterification reaction with heterogeneous catalysts can produce yields above 80% and reduce reaction time with only around 3 min. The methyl ester yield increases with the increasing of microwave power, catalyst concentration and reaction time**.** The highest yield of methyl esters was 81,5% obtained under operating conditions of microwave power of 400 W, concentration of K/γ-Al_2O_3 catalyst by 2.5%, reaction time of 3 min.

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