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Biodiesel from Avocado Seed Oil with ZnO/CaO Nanocatalyst

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ABSTRACT

The efficiency of biodiesel production from vegetable oil needs to be developed. The transesterification process using heterogeneous catalysts has been widely studied to replace the role of homogeneous catalysts. Zinc oxide (ZnO) doping into metal oxides can increase the activity of the heterogeneous catalyst in the transesterification reaction. This study was conducted to provide information on the effect of ZnO concentration doped into calcium oxide (CaO) to the transesterification reaction of avocado seed oil with high free fatty acid (ALB) to methyl ester, at 65ºC, methanol ratio: oil = 10:1, for 1.5 hours, using a reactor. Research variable is ZnO concentration doped into CaO, that is: 0%, 1%, 2%, and 3%. The test parameters are methyl ester content obtained from the results of transesterification reaction with gas chromatography analysis. In this study, ZnO/CaO nanocatalysts were synthesized and doped with sol-gel method and calcined at 450ºC in the air for about 60 minutes. The synthesized ZnO/CaO nanoparticles were characterized by X-ray powder diffraction (XRD). From the experiment, the highest yield of methyl ester was obtained on ZnO/CaO 1% catalyst with a yield of 90, 8820%.

Keywords: Biodiesel, Avocado, Transesterification, Nanocatalyst, ZnO-CaO

1. INTRODUCTION

Biodiesel is a bioenergy made from vegetable oils, both new oils and frying oils through transesterification, esterification, or esterification processes - transesterification as an environmentally friendly alternative petroleum replacement petrodiesel. In terms of price, biodiesel will not produce cheaper price compared to petroleum diesel, but as an alternative material that is environmentally friendly and renewable, it can be a solution to the problem of resilience of national energy reserves that are dwindling so that efforts to build national resilience in the energy field of biodiesel is feasible to be implemented.

The catalyst is a substance that can affect the speed of the transesterification reaction but the substance does not undergo chemical changes at the end of the reaction. The catalyst works specifically for a particular reaction and can decrease the magnitude of the activation energy of a reaction. This decrease in activation energy is due to the activity of a catalyst that seeks another reaction pathway which has lower activation energy.

The ideal heterogeneous catalyst (not activated by water, stable, active at low temperatures, and have high selectivity) can be active in the transesterification process and esterification of free fatty acids. The heterogeneous catalyst forms that have been used are alkali metal oxides, transition metal oxides, and mixed metal oxides.

From the results of [(1)], biodiesel yield using CaO/ZnO catalyst size of about 40.58 ~ 46.44 nm is highly effective on variations of Ca:Zn atom ratio. The use of ZnO/CaO nanoparticle catalysts can

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increase the methyl ester formation reaction of Palm Fatty Acid Distillate (PFAD) with ALB 0.896%. The highest formation of methyl esters was obtained on the use of CaO catalyst with ZnO doping of 1% is 90.882%. The experiments were also carried out in a pressurized reactor, with a methanol molar ratio with PFAD of 12:1 for 3.5 hours.

Based on previous research, the use of alkali catalysts in the transesterification reaction causes easy saponification reaction to form soap. The use of CaO catalyst has a high activity, durable, low cost, and high base strength. The use of ZnO catalysts can be used repeatedly and it is very easy to do separation process. The use of ZnO/CaO nanoparticle catalysts can increase the methyl ester formation reaction of PFAD.

So, in this study, the formulation of the problem can be expressed as 1) How the transesterification process of making biodiesel from avocado seed oil using nanocatalyst ZnO/CaO, and 2) How the effect of ZnO/CaO nanocatalyst in transesterification process of making biodiesel from avocado seed oil.

This study aims to explore the process of transesterification of biodiesel production from avocado seed oil by using ZnO/CaO nanocatalyst, investigate the effect of nanocatalyst concentration of ZnO/CaO on transesterification process of making biodiesel from avocado seed oil.

2. RESEARCH METHODOLOGY

Variable and process condition in this research is process fixed variables and variable changed process. Process fixed variables; the materials are volume of avocado seed oil 300 ml, ratio of mol avocado/methanol seed oil is 1:10, CaO mass is 10 gram with a temperature of calcinations at 450ºC, calcinations time is 1.5 hours, the reaction time is 1 hour, operating temperature is 60ºC and pressure is 1 bar. For condition, variable changed process are the composition of ZnO: 0%, 1%, 2%, and 3%.

Analysis of the raw material for density determination (ASTMD-1298) uses pignometer, and the determination of viscosity (ASTM 445) uses viscometer. From the determination of free fatty acid, the sample mixture was titrated with 0.1N KOH solution until a red color lasted for approximately 30 seconds.

Analysis for the catalyst preparation (ZnO/CaO) was done using the wet impregnation method. The impregnation method for this analysis is a mixture of CaO and ZnO heated and mixed by magnetic stirrer with 300 rpm for 2 hours. After that, the mixture was dried and calcinated at 450ºC temperature for 1.5 hours.

The production of biodiesel is started at esterification step and continued transesterification. At transesterification, all of the mixtures was heated for 1 hour at a constant temperature and the percent of methyl ester produced was analyzed.

Results analysis indicates that ZnO/CaO catalyst can be characterized using XRD analysis and Methyl Ester Analysis can be analyzed by gas chromatography.

3. RESULTS AND DISCUSSION

Table 1 Analyzed for the raw material

Analyzed	Result
Free fatty acid	0,73%
Viscosity	0,068 poise
Density	0,781 gram/ml

3.1 Analyzed ZnO/CaO

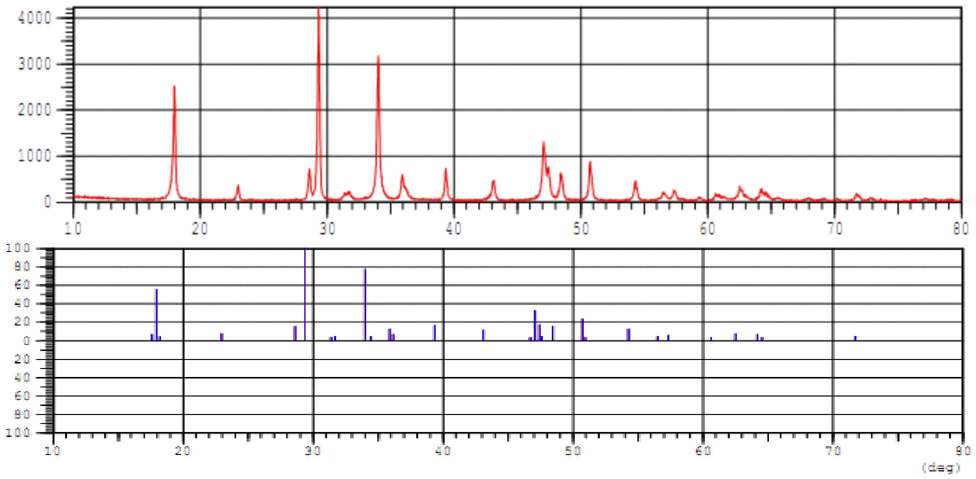

Figure 1. Identification of X-ray diffraction patterns (Sample ZnO/CaO).

Description:
X = Intensity
Y = 2Θ

Table 2 Results of calculation of crystal diameters of ZnO/CaO samples

K	Λ (A)	K*λ	θ (⁰)	Center 2θ (⁰)	COS θ	FWHM (B) (Rad)	D (nm)
0,9	1,54	1,386	14,6613	29,3225	0,9674	0,1763	8,1265
0,9	1,54	1,386	17,0103	34,0205	0,9563	0,2002	7,2394
0,9	1,54	1,386	8,9811	17,9621	0,9877	0,1976	7,1015

Table 3 Results of Methyl Esters Formation and Analyzes

Catalyze	% ZnO	Composition				
		TG	DG	MG	ME	G
CaO	0	67,5008	12,4552	1,1946	13,1264	0,5471
ZnO/CaO	1	0	0	0,2394	90,8820	0,8853
ZnO/CaO	2	0,056	0,0098	0,5849	90,1282	0,8972
ZnO/CaO	3	0,123	0,7628	0,8832	89,2834	0,9284

Description:
TG = Trigliserida
DG = Digliserida
MG = Monogliserida
ME = Metil Ester
G = Gliserol

Below is a chromatogram of one of the methyl esters produced from the research that has been done.

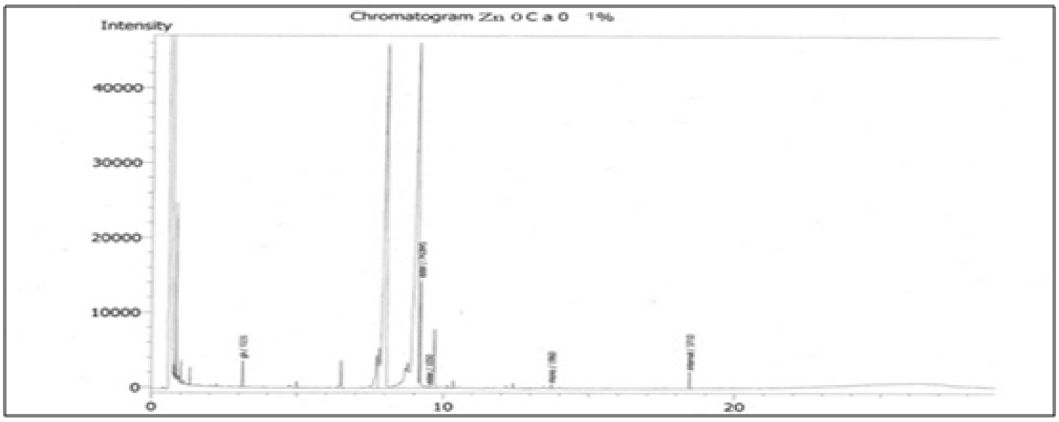

Figure 2. Chromatogram GC Analysis of Transesterification Result of Avocado Seed Oil with ZnO / CaO catalyst with ZnO loading 1%.

Table 4 Table Peak Area

Peak#	Ret.Time	Area	Height	Area%	Name
1	1.332	3035	2318	0.3708	
2	3.154	7321	3633	0.8835	Oli
3	4.992	2032	865	0.2483	
4	6.510	7714	3720	0.9424	
5	7.721	22150	4384	2.7061	
6	9.230	742845	14268	90.7537	Ester
7	9.505	1050	279	0.1283	
8	9.702	21994	7852	2.6810	
9	10.147	1012	385	0.1236	
10	10.341	2154	1006	0.2631	
11	12.400	1691	639	0.2066	
12	13.724	1960	524	0.2394	Mono
13	18.468	3710	2241	0.4532	Internal
Total	818528				

3.2 Effect of Doped ZnO Concentration into CaO on Methyl Ester Content

ZnO coupling into CaO catalyst aims to increase the reaction of methyl ester formation from avocado seed oil with the free fatty acid (FFA) level of 0.73%. In this research, transesterification reaction has been done using calcined CaO catalyst at 450ºC.

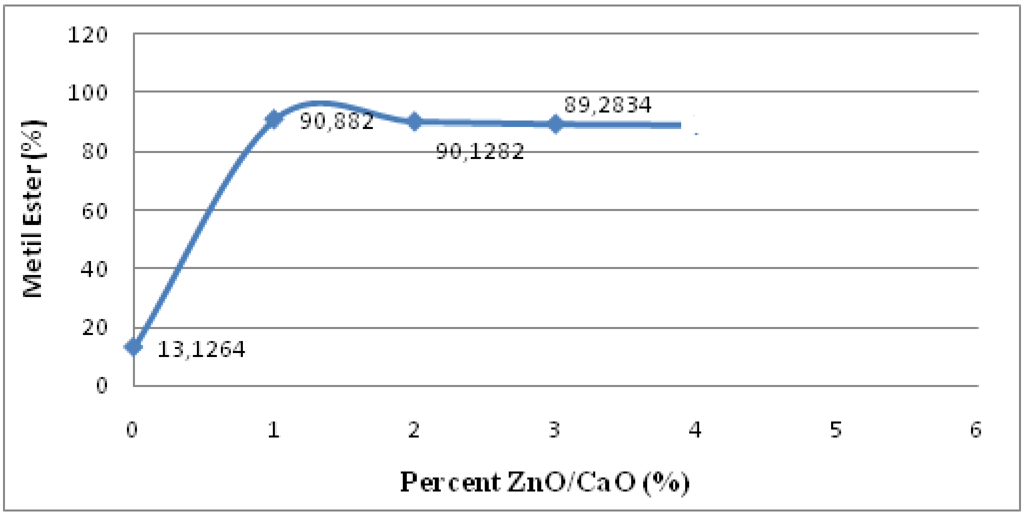

Figure 3. Percent ZnO/CaO (%) vs Metil Ester (%).

The content of methyl esters was formed by gas chromatography analysis. The increase of ester formation rise drastically from 0% loading to the use of CaO catalyst with ZnO doping of 1%, i.e. 13.624% to 90.87%. This is due to the reaction between CaO with fatty acid high free in avocado seed oil (2). The free fatty acid content can disturb the transesterification reaction [3]. The large amount of FFA in avocado seed oil greatly influences the reaction rate and the final concentration of methyl esters. The presence of water in the methyl ester will cause the concentration decrease at the beginning of the reaction which should be rapidly reacting, due to the hydrolysis reaction of the ester-forming the fatty acid back [4].

An increase in the amount of methyl ester when ZnO/CaO 1% is used due to the availability of a large catalyst surface area to react with the methanol and avocado seed oil. The catalyst can provide an alternative reaction path with a smaller activation energy (the minimum energy is required for the mixture to produce the product) through the formation of reactive intermediates on the surface of the catalyst, where many atomic or molecular reactions occur, then these active intermediates interact with each other to form the product. So, the catalyst is able to increase the likelihood of effective collision between reactant molecules (5). In line with Watkins (6), which is capable of producing methyl esters by transesterification reaction using a 1% ZnO/CaO catalyst.

When the use of a ZnO-doped catalyst of 2% to 3% of methyl ester, yield was decreased from 90.1282% to 89.234%, but slightly below the catalyst with ZnO doping of 1%. However, a decrease in methyl ester formation in the use of ZnO doped CaO catalysts is 2% to 3% compared to that of 1% approximated by measurement of other competing reactions (7). When compared with (8), transesterification results with a 1% to 3% catalyst of ZnO/CaO is higher>>10%. In general, the resulting methyl ester content should increase as ZnO increases in doping. This is due to the large content of free fatty acids contained in avocado seed oil. According to the theory, the catalytic activity in transesterification is proportional to the strength of the catalyst base. The higher the catalyst base level, the higher the conversion of the transesterification reaction (9).

3.3 Determination of the Best Use of Catalyst Doping

This study also obtained the composition data of glyceride transesterification process. Operating conditions used are Avocado Seed Oil: Methanol = 1:10, reaction temperature 65ºC, reaction time for 1 hour, and the amount of ZnO/CaO catalyst used varies. The determination of catalyst use is best approximated from the analysis of glyceride components of methyl ester products. Generally, transesterification reaction of avocado seed with methanol produces fatty acid esters, i.e. methyl esters and glycerol with monoglycerides and diglycerides as intermediate products. The transesterification reaction ideally runs consist of triglycerides being diglycerides, then diglycerides to monoglycerides and finally monoglycerides to esters [10]. The amount of glycerides obtained is doped CaO catalyst ZnO 0% shows a much higher glyceride composition compared to other concentrations of ZnO doping. The final concentration of the glyceride component on the use of 0% ZnO doping was triglycerides (67,5008%), diglycerides (12.4452%) and monoglycerides (1.1946%). The high content of glycerides in transesterification using ZnO/CaO 0% is thought to be due to high free fatty acids that can cause saponification reactions. Thus, the catalyst is unable to directly react toward the methyl ester product.

Based on the results of research conducted by [11], researcher in [11] stated that the use of raw materials with free fatty acid content above 1% leads to an increased yield of side reactions, i.e. saponification reaction in transesterification reaction due to the reaction of more reactive base catalyst with fatty acid free than glycerides.

Conducting a study of kinetics of soybean oil transesterification at reactor batches. The results of this study indicate that the conversion of triglyceride to diglyceride is the slowest step and the rate determinant of the reaction while the conversion step of monoglyceride to methyl esters is the fastest stage. Monoglycerides are the most unstable compounds among other intermediate compounds and will soon be converted to glycerol and methyl esters because the reaction rate constant is the fastest. The same study was also obtained by (11) who conducted the kinetics study of transesterification of palm oil and conducting the study of kinetics of transesterification of sunflower oil and Brassica carinata oil. Both studies showed that the conversion stage of triglyceride to diglyceride is a penigration stage because it is the slowest stage. Data on the amount of glycerides obtained can be made comparisons between triglycerides, diglycerides, and monoglycerides.

CONCLUSION

i. The use of ZnO/CaO nanoparticle catalysts can improve the methyl ester formation of avocado seed oil with ALB levels of 0.73%
ii. The highest methyl esters were obtained on the use of CaO catalyst with ZnO doping of 1% is 90.882%
iii. The reaction of the catalyst with high free fatty acid may affect the transesterification reaction so that the methyl ester content obtained is not maximal.

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