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BIODIESEL FROM AVOCADO SEED OIL WITH ZnO/CaO NANO CATALYST

PRATIWI PUTRI LESTARI and SUKMAWATI

Department of Chemical Engineering Institut Teknologi Medan
Jl. Gedung Arca No. 52, North Sumatera, 20217,
Indonesia.
E-mail address : pratiwiputri@itm.ac.id

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ABSTRACT

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. ZnO doping into metal oxides can increase activity of heterogeneous catalyst in 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 65 ^{0}C, 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 metyl ester content obtained from the results of transesterification reaction with gas chromatographi analysis. In this study, ZnO/CaO nanocatalysts were synthesized and doped with sol gel method and calcined at 450 ^{0}C in air for 60 min. The synthesized ZnO/CaO nanoparticles were characterized by XRD. From the experiment, the highest yield of methyl ester was obtained on ZnO/CaO 1% catalyst with yield of 90,8820%.

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.

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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 a lower activation energy.

The ideal heterogeneous catalyst (not activated by water, stable, active at low temperatures and having 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 increase the methyl ester formation reaction of PFAD (Palm Fatty Acid Distillate) 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 that 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 is very easy to do separation process. The use of ZnO/CaO nano particle catalysts can increase the methyl ester formation reaction of PFAD (Palm Fatty Acid Distillate).

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So in this study can be expressed the formulation of the problem, among others: How the transesterification process of making biodiesel from avocado seed oil using nano catalyst ZnO/CaO, How the effect of ZnO/CaO nano catalyst in transesterification process of making biodiesel from avocado seed oil.

This study aims to: Know the process of transesterification of biodiesel production from avocado seed oil by using ZnO/CaO nano catalyst, Knowing the effect of nano catalyst concentration of ZnO/CaO on transesterification process of making biodiesel from avocado seed oil.

RESEARCH METHODOLOGY

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

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

Analyzed for the catalyst done catalyst preparation (ZnO/CaO) by wet impregnation method. Impregnation method for this analyzed is mixture of CaO

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and ZnO heated and mixed by magnetic stirrer with 300 rpm for 2 hours. After that dried and calcinations at 450^{0}C temperature for 1.5 hours.

Making the biodiesel is started at esterifikasi step and continued transesterifikasi. At transesterifikasi, all of the mixture is heater for 1 hour and constant temperature and analyzed the percent of methyl ester produced.

Results Analysis, ZnO/CaO catalyst is characterized using XRD analysis and Methyl Ester Analysis are analyzed by gas chromatography.

RESULTS AND DISCUSSION

Table.1 Analyzed for the raw material

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

Analyzed ZnO/CaO

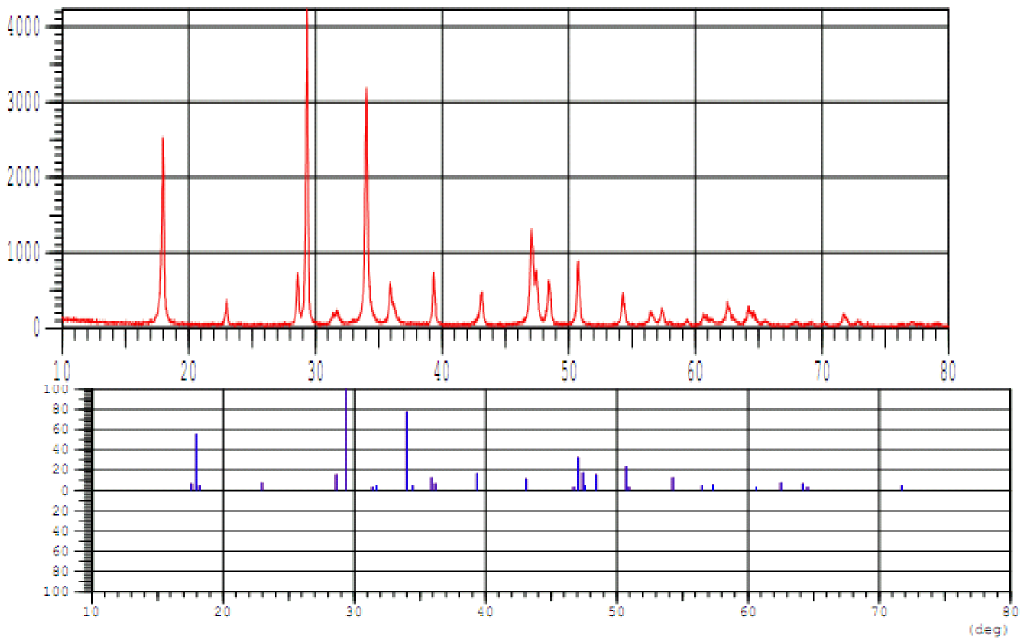

Fig.1 Identification of X-ray diffraction patterns (Sample ZnO/CaO)

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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.

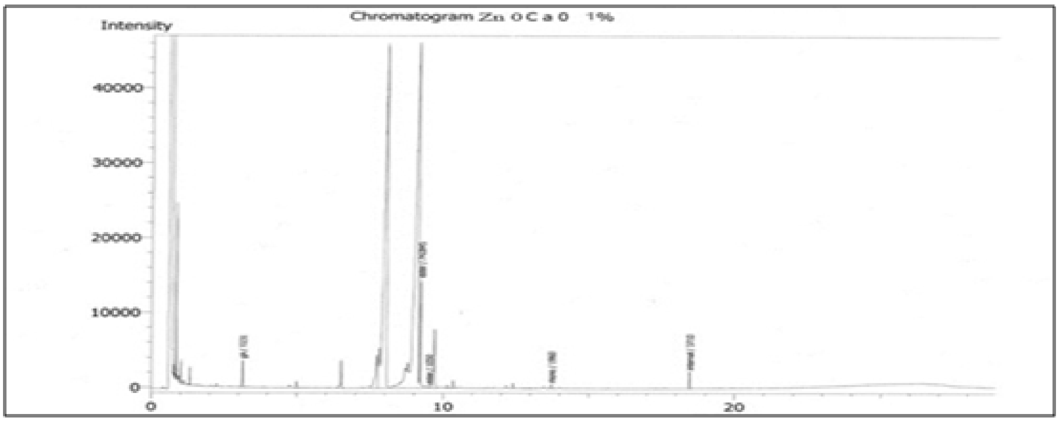

Figure. 2 Chromatogram GC Analysis of Transesterification Result of Avocado Seed Oil with ZnO / CaO catalyst with ZnO loading 1%.

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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				

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 free fatty acid level of 0.73%. In this research, transesterification reaction has been done using calcined CaO catalyst at 450^0 C.

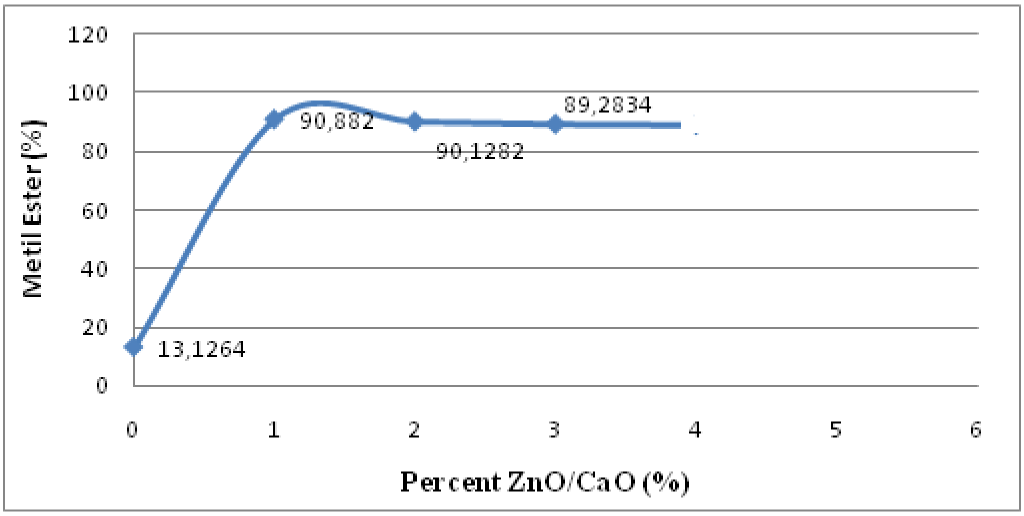

Fig.3 Percent ZnO/CaO (%) vs Metil Ester (%)

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The content of methyl esters formed by gas chromatography analysis. The increase of ester formation rose drastically from 0% loading to the use of CaO catalyst with ZnO doping of 1%, ie 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 to 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 the methanol and avocado seed oil. The catalyst can provide an alternative reaction path with a smaller activation energy (minimum energy required 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

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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].

Determination of the Best Use of Catalyst Doping

In this study also obtained data composition of glyceride transesterification process. Operating conditions used are Avocado Seed Oil: Methanol = 1:10, reaction temperature 65^{0}C, 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, ie methyl esters and glycerol with monoglycerides and diglycerides as intermediate products. The transesterification reaction ideally runs consis- tively of triglycerides being diglycerides, then diglycerides to monoglycerides and finally mono glycerides to esters [10]. The results of the amount of glycerides obtained can be seen in Table 4.3. The above table can be obtained that the use of doped CaO catalyst ZnO 0% shows a much higher glyceride composition than with 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

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0% is thought to be due to high free fatty acids that can cause saponant reactions. Thus the catalyst is unable to direct the reaction toward the methyl ester product.

Based on the results of research conducted by [(11)] stated that the use of raw materials with free fatty acid content above 1% leads to increased yield of side reactions, ie 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 reactorbatches. 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.

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CONCLUSION

1. The use of ZnO / CaO nanoparticle catalysts can improve the methyl ester formation of avocado seed oil with ALB levels of 0.73%
2. The highest methyl esters were obtained on the use of CaO catalyst with ZnO doping of 1% is 90.882%
3. 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.

ACKNOWLEDGEMENT

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