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Original Research Article

ZnO/CaO NANO Catalyst for Make Biodiesel from Avocado Seed Oil

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Abstract

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%. The test parameters are methyl 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%.
Keywords: Biodiesel, avocado, transesterification, nano catalyst, ZnO-CaO.

INTRODUCTION

Biodiesel is bioenergy made from vegetable oils, both new oil and used frying oil through the process of transesterification, esterification, or esterification-transesterification process as an alternative fuel instead of diesel (petrodiesel) that is environmentally friendly.

Avocado seeds are a waste that so many people throw away, after using the fruit meat. Even though avocado seeds contain vegetable fat which is composed of compounds that can produce oil. This compound is very unique because it has the same composition as diesel fuel. In addition, the levels of the nests in avocados are less than the levels of sulfur in diesel fuel. This makes combustion complete so that the exhaust gas will be more environmentally friendly. In addition, avocado seeds are biomass materials containing triglycerides and free fatty acid content (FFA) in low avocado seed oil which is 0.367% so that it can be used as biodiesel with the transesterification process.

The use of homogeneous catalysts such as alkali catalysts in the transesterification reaction causes easy saponification reactions to form soap. Istadi, I *et al.*, [1] explained that catalysts that are widely used in the biodiesel industry are homogeneous catalysts such as KOH or NaOH. Homogeneous base catalysts for transesterification reactions can react with free fatty acids to form soap, so that it will make it difficult to separate glycerol and reduce biodiesel yield.

Calcium Oxide (CaO) is an important inorganic material that can be used as a catalyst for transesterification reactions because it has many advantages including having high activity, durable, low cost and has a high base strength [2]. To increase the activity and productivity of the catalyst, the surface area per unit mass of the catalyst was increased by making nano-size CaO catalysts.

Ngamcharussrivichai, C *et al.*, [3] explained that the use of heterogeneous catalysts ZnO can be used repeatedly and the separation process is very easy. Heterogeneous catalysts such as ZnO can reduce the separation load and treatment of biodiesel industrial waste. Based on several research results it is stated that the use of catalysts on transesterification is cheaper, stable, can be used repeatedly and is available commercially and is environmentally friendly. For this reason, a heterogeneous catalyst that works is technically feasible and economically feasible because heterogeneous catalysts can provide results above the average.

Making biodiesel by transesterification previously uses an acid, base, one type of solid catalyst, or a size that is not nano. In general, this is done through a transesterification process and is followed by several stages with the addition of other ingredients. The transesterification of biodiesel is made by utilizing avocado seed waste and exploring the two catalysts, namely ZnO and CaO through stages that begin with catalyst preparation between ZnO and CaO and proceed with the esterification and transesterification process.

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%.

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

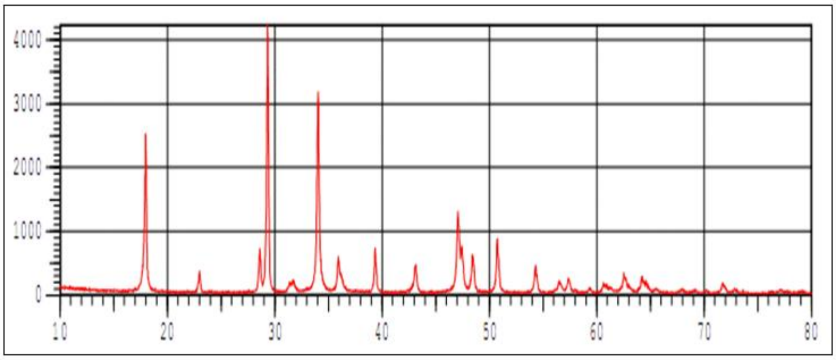
Making the biodiesel is started at esterifikasi step and continued transesterifikasi. At transesterifikasi, all of the mixture is heater for 1 hour and constant temperature and analyzed the percent of methyl ester produced.

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

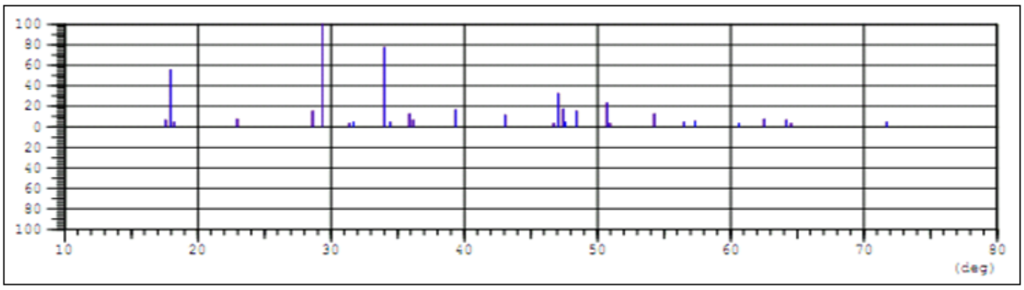


Fig-1: Identification of X-ray diffraction patterns (Sample ZnO/CaO)

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

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.

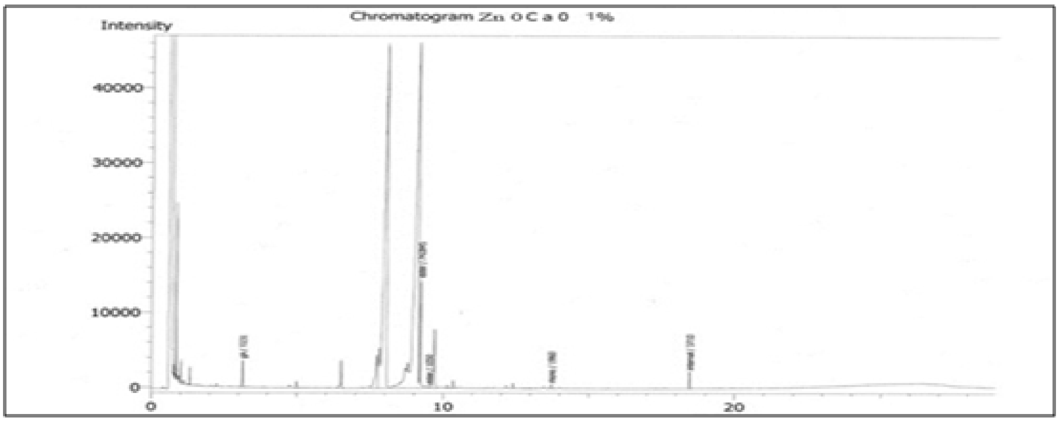


Fig-2: Chromatogram GC Analysis of Transesterification Result of Avocado Seed Oil with ZnO / CaO catalyst with ZnO loading 1%

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				

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.

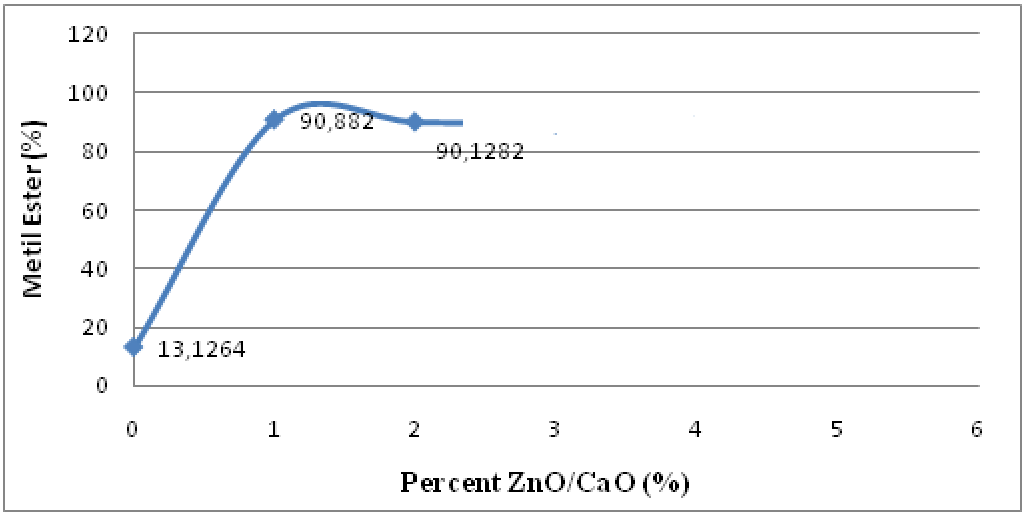


Fig-3: Percent ZnO/CaO (%) vs Metil Ester (%)

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 90.1282%. 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 [4]. 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 [1].

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% of methyl ester yield was decreased from 90.1282% 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% compared to that of 1% approximated by measurement of other competing reactions. When compared with [7], transesterification results with a 1% to 2% 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 [8].

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 65^0C, 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 [9]. The results of the amount of glycerides obtained can be seen in Table-4. 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 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 [10] 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.

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

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