The Utilization Of CaO Catalyst Impregnated With KOH In Biodiesel Production From Waste Cooking Oil

Syarifuddin Oko, Irmawati Syahrir, Muh. Irwan

Abstract: Transesterification of used cooking oils with methanol was produce methyl esters (biodiesel) by using CaO as catalyst dissolved by KOH. The CaO obtained from the shelled chicken shells mixed with KOH with variations of % K (0 %, 5 %, 7%, 9 % and 12 %) is accompanied by heating at 85 ^{0}C, while the catalytic properties are performed by XRD, Base and SEM.-EDX. The catalysts obtained are then used for the biodiesel production, the best biodiesel yields by producing 87.17% in catalysts of 7% K and oils : methanol (1:12) moles ratio, 1.5 % total oil catalysts, reaction time of 2, 5 hours, the reaction is 65 ^{0}C, biodiesel characteristics, kinematic viscosity of 2.89 cSt, 0.032 % water content, density 0.819 g / ml, methyl ester content 99.39 %.

Keywords: Biodiesel, Chicken egg shell, Transesterification, Used cooking oil, CaO Catalysts Impregnation.

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1 INTRODUCTION

For decades, many different ways have been developed to get as much energy as possible without using limited resources. Each year, billions of rupiah are spent on green energy research to find new sources of energy. Biodiesel is a renewable fuel whose combustion properties are similar to fossil fuels. Biodiesel is produced through a transesterification of vegetable oils or animal fats with short chain alcohol using acids, bases and enzymes as catalysts [1]. Biodiesel is a clean, non-toxic and renewable fuel. Unlike diesel from fossils, biodiesel has a role in reducing the release of harmful gases such as CO, SOx, and hydrocarbons. Some homogeneous catalysts, such as H_2SO_4 and NaOH have been used in biodiesel production. Compared to heterogeneous catalysts, homogeneous catalysts are usually associated with higher reaction rates and lower reaction temperatures. However, homogeneous catalysts are associated with some disadvantages. They are corrosive. In addition, it is difficult to separate these catalysts from their reaction products and their reagents. Therefore, sustainable production is negatively affected by the presence of homogeneous catalysts. Homogeneous catalysts also cause secondary pollution or pollution to the environment [3]. Some studies on the use of CaO oxidizing catalysts include Yang, et al (2012), with KOH / CaO 15% (w / w) catalysts, soybean oil cation ratio: methanol (1 : 16), 4% catalyst temperature 65 ^{0}C and 1 hour reaction time obtained by methyl ester 97.1%. Using CaO/C/KOH as catalysts with wet filling processes, such as variants of reaction temperature, amount of catalyst, reaction time and molar ratio of soybean oil and methanol [7].

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The best result with 98% of yield, 65 ^{0}C reaction temperature, 1.5 % of catalyst volume and 1 : 10 molar ratio. Rachim, et al (2017) uses catalyst CaO/ZnCl$_2$ from crab skin through transesterification reaction between cooking oils used and methanol with the addition of CaO-ZnCl$_2$ catalysts of 3% by weight of oil. The molar ratio between used cooking oil and methanol used is 1 : 12 and the result is 77.94 %. In this study impregnation of CaO catalyst from chicken egg shells will be carried out using KOH which has been varied and applied to making biodiesel from used cooking oil.

2 MATERIALS AND METHODS

2.1 Materials
The materials used in this study include: used cooking oil, chicken egg shell, indicator PP, 0.1 N NaOH, KOH, 95% ethanol, methanol, catalyst CaO/K, aquadest and universal indicator paper.

2.2 Preparation of Catalysts Raw Materials
Weighing 1000 grams of egg shell, wash with water until clean and dry in an oven at 110 ℃ for 24 hours. Next, crush the eggshell into powder and sieve with a sieve -200 + 325 mesh. Then the eggshell powder is calcined at 900 ℃ for 3 hours. The calcination results are then stored in a desiccator to keep the catalyst conditions dry.

2.3 Creates CaO Impregnation Catalyst
A total of 50 grams of the first calcined calcined solution was dissolved in 200 ml of KOH solution with variations of 0%, 5%, 7%, 9% and 12% KOH, then diregregated by mixed heating to 85 ^{0}C while stirring until dry. The impregnation catalyst was then dried at ovne at 105 ^{0}C for 24 hours, then classified at 600 ^{0}C for 5 hours. The catalyst results from alkaline impregnation analysis, BET, SEM EDX and XRD.

2.4 Determination of Free Fatty Acid
Weighing a 5 gram sample into a 250 ml erlenmeyer then adding 50 ml of 95% ethanol which was neutralized with 0.1 N NaOH with the help of phenolpthalein (PP) indicator. Add 5 drops of PP indicator to the sample. Minimized with 0.1 N NaOH which has been standardized previously, pp indicator is added to pink.

Calculate of free fatty acid with the formula:

% FFA = (VNaOH × NNaOH × Molecul Weight of Free Fatty Acid) / (Sample Mass x 1000) x 100%

2.5 Transesterification Reaction

Weighing 1.5% of the weight of CaO / K catalyst oil which was previously impregnated with various % K into a round bottom flask. Adding methanol then stirring for 60 minutes. Put used cooking oil into a round bottom flask (ratio 1 : 12 with methanol). Increasing the temperature to 65 °C then reflux for approximately 3 hours. Cooling the reflux results then separating the reflux results with CaO catalyst. Insert the mixture into a separating funnel and store at room temperature for 1 hour then separate it between the upper layer and the lower layer. Wash the top layer with ± 80 ° C temperature water. Then evaporate the water content contained in the biodiesel at 105 °C. Analyzing the biodiesel products produced include GC-MS analysis, density, kinematic viscosity, water content, yield and flash point.

Yield (%) = (Product Weight) / (Raw Material Weight) x 100 %

3 RESULTS AND DISCUSSION

The preparation of CaO catalyst is done by slicing the chicken eggshells which have been washed and dried. The purpose of egg spinning is to remove the carbonate dioxide compound by calcium carbonate decomposition reaction contained in egg shells to obtain calcium oxide compounds. In this study, egg intake was performed for 3 hours at 900 ℃. The reaction that occurs in the tuning process is: $CaC_{O3} \rightarrow_{950} CaO + CO_2$ From the calcium oxide compound obtained then impregnation using KOH is carried out. Impregnation aims to increase catalytic activity. The principle of impregnation is to insert the precursor into the support pores (catalyst) with stirring and heating. This will affect the characteristics of the catalyst, namely alkalinity, surface area, shape, and composition of the catalyst.

3.1 XRD Analysis

XRD analysis is useful to see the catalyst components produced, but cannot determine the number of these components. This component can be seen in Figure 1.
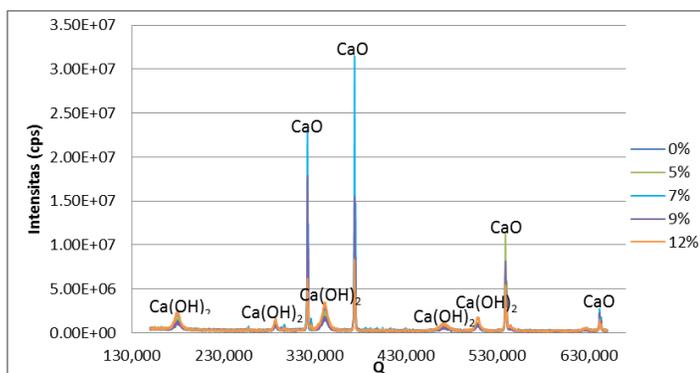

Figure 1. The catalyst diffractogram using XRD

The results of XRD analysis showed that the dominating components were CaO and Ca (OH)$_2$. Calcination in this study aims to form CaO which is used as a heterogeneous base catalyst. However, if the CaO is in contact with air it will form Ca (OH)$_2$, Ca (OH) 2 compounds reduce the alkalinity and

catalytic surface area so that catalytic catalytic activity decreases.

3.2 Analysis of Alkalinity

One way to increase the catalytic activity of catalysts is to increase the ability. The spirit can be enhanced by the impregnation method. KOH is used as the precursor for the impregnation process of the CaO catalyst. The impregnation process causes the catalysts to increase. The greater the catalyst will increase the catalytic activity of the catalyst. The level of pre and postural immunity can be seen in Figure 2.
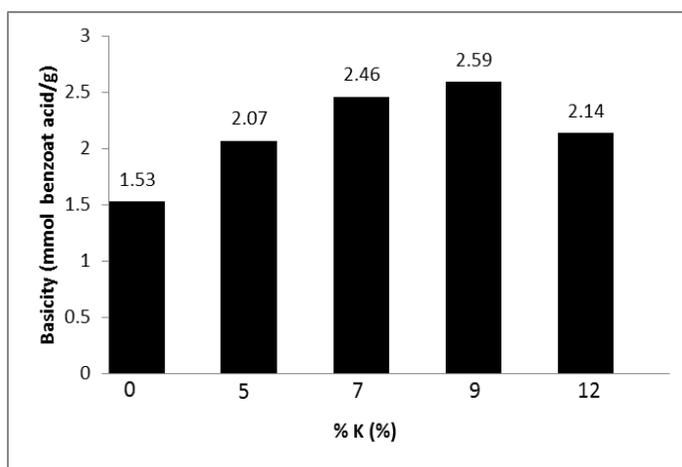

Figure 2. Effect of % K on alkalinity

Determination of impregnation catalysts by using acid - base titration method, prior to impregnation, the catalyst was 1.53 mmol of benzoic acid/g. After impregnation, the catalyst is increased to 2.07-2.59 mmol of benzoic acid/g. Decrease of noise at 12% K, this is due to the distribution of K metal in CaO pores less evenly and also due to the mixer being too small so that it can not reach the entire surface of the glass of the impregnated chemicals and solutions that are so strong that stirring is done manuals and samples that stick to the glass that are difficult to separate.

3.3 SEM-EDX Analysis

To see the impression of % K variation in the impregnation process, can be seen by analysis using SEM-EDX. SEM aims to look at the surface shape of the sample and EDX aims to see the chemical component of the catalyst. The shape of the catalyst surface can be seen in Figure 3 and the catalyst composition can be seen in Table 1.
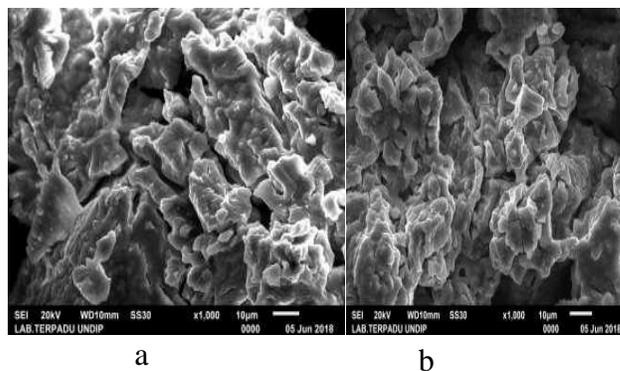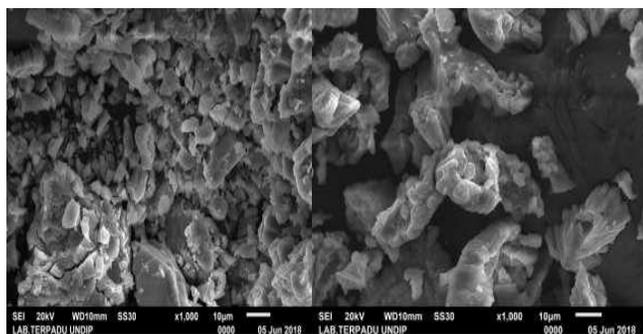

a   b

Figure. 3 *Form of catalyst surface through SEM. a) 5%, b) 7%, c) 9%, d) 12%*

The shape of the surface of the catalyst in each% K looks different in Figure 3. The difference in surface shape is influenced by differences in the composition of the catalyst. The imperfections of the impregnation process and the effect of the second calcination temperature cause a difference in the composition of each variation% K. This is because KOH compounds are not only converted into K_2O compounds but also form K_2CO_3 compounds. According to Blasi et al. (2008), at a temperature of 300 ^{0}C, KOH will be converted to K_2O, H_2O, and K_2CO_3 by reaction:

$$2\ KOH \longrightarrow K_2O + H_2O$$
$$K_2O + CO_2 \longrightarrow K_2CO_3$$
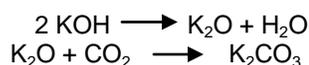
At temperatures above 427 ^{0}C, melting KOH will react with carbon compounds to form K_2O and K_2CO_3 by reaction :

$$4\ KOH + C \longrightarrow K_2O + K_2CO_3 + 2\ H_2$$

Table 1.
CaO impregnation catalyst composition (SEM-EDX)

K (%)	Compound	Mass (% weight)	K (%)	Compond	Mass (% weight)
5	C MgO K_2O CaO	21,11 1,59 12,73 64,46	9	K_2O CaO	4,38 81,53
7	C MgO K_2O CaO	25,72 2,71 21,99 46,72	12	C MgO K_2O CaO	39,53 1,01 9,58 45,98

3.4 Application of Impregnation CaO Catalyst in Biodiesel Production

Early stage of biodiesel manufacturing analyzes the level of free fatty acids and the kinematic viscosity of cooking oil used as raw materials for making biodiesel. Free fatty acids are very influential in the production of biodiesel because high fatty acids contained in oil samples will react with alkaline catalysts to form soap, as the base will react to neutralize oil-free fatty acids [2], while the viscosity analysis is done to see the viscosity of the oil itself to be compared to the biodiesel obtained. From the analysis of free fatty acids found free fatty acids in 0.74% oil samples and kinematic viscosity 33.09 cSt. Aesthetic reactions do not need to be done, because the level of free fatty acids is less than 5%. In the transcription response, the first catalyst reacts with methanol to form a

methoxy species that is the originator of the reaction of the transaction. The reaction mechanism is listed in Figure 4 below:
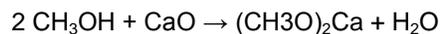
$$2\ CH_3OH + CaO \rightarrow (CH3O)_2Ca + H_2O$$

Figure 4. *Mechanism of formation of methoxy group*

Transcription reaction was carried out at a temperature of 62 - 65 °C for 3 hours, obtained 3 layers consisting of catalyst, glycerol and biodiesel. The catalyst layer and glycerol were separated then the top layer which was biodiesel washed using warm aquadest (temperature ± 80 °C). The washing process is carried out repeatedly until the washing layer is clear and the pH of the washing layer is the same as the pH of the aquadest used as washing water. This repeated washing aims to remove glycerol, methanol, and catalysts that are still contained in biodiesel. The biodiesel that has been washed is then heated at 105 $^\circ$C for 30 minutes to remove the remaining washing water.

3.5 Characteristics of Methyl Esters from Used Cooking Oil

The characteristics of methyl esters consisting of density, kinematic viscosity, and water content can be seen in Table 2 below:

Table 2. *The results of the analysis of density, viscosity, moisture content and yield of biodiesel*

Catalyst (%)	Ratio	Density(gram/mL)	Viscosity (cst)	Water Content (%)	Flash Point (^{0}C)	Yield(%)
0%	1:9	0.8701	4.28	0.0459	174	59.41
	1:12	0.8715	5.38	0.034		49.69
	1:15	0.8558	4.13	0.0479		78.26
5%	1:9	0.8625	4.01	0.042	180	52.12
	1:12	0.8644	3.53	0.0459		47.75
	1:15	0.8716	5.18	0.036		24.14
7%	1:9	0.8635	3.27	0.032	176	62.75
	1:12	0.8599	2.89	0.032		87.17
	1:15	0.8656	4.26	0.0379		73.49
9%	1:9	0.8667	3.61	0.042	174	44.55
	1:12	0.8672	4.13	0.046		60.165
	1:15	0.8663	4.15	0.034		80.765
12%	1:9	0.9027	21.66	0.0459	>280	75.245
	1:12	0.8936	16.64	0.0419		72.75
	1:15	0.8976	17.8	0.0459		61.82

According on Table 2 it is known that biodiesel water content has confounded SNI specification on biodiesel quality requirements of less than 0.05 %, whereas for the density parameters and kinematic viscosity of biodiesel obtained using catalysts with K concentration at CaO by 12% still exceed SNI standard. This is because there is still a residual catalyst that floats on the biodiesel washing process so that the catalyst can react with the fatty acids forming the soaps or the biodiesel formed to react again with the catalyst so that the react switch towards the reactant. Flash point of uncontaminated material is the lowest temperature when it can evaporate to form a mixture that can ignite the fire in the air. Measuring the flash point requires ignition sources. At the flash point, the steam can stop to burn when the ignition source is out. Based on the standard SNI 7182 : 2015 flash

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point for biodiesel is at least 100 ^{0}C, from the results of the study shows that the biodiesel produced meets the standard, except for % K of 12 % do not face this due to the high viscosity obtained ie above 280 ^{0}C. Molar ratio used cooking oil to methanol is one of the most influential factors in the transientification process. In general, the transertification of the reaction requires 3 mol alcohol and 1 mol triglyceride to produce 3 mol esters (biodiese) and 1 mol of glycerol as by product. In this study using ratio 1 : 9, 1 : 12 and 1 : 15 (Oil : Methanol). The use of excess methanol aims to make the reaction of the equilibrium more shifted towards the product as the transertification reaction is an alternating reaction. The best result was obtained yield of 87.17 % with K 7% catalyst and methyl ester (biodiesel) 99.39 % based on GC-MS analysis.

3.6 Optimization of Transesterification Process Variable

To prediction optimum yield of biodiesel was the verified by carrying out three repeated experimental runs using the suggested optimum condition. The repeated experiments gave an average optimum yield of 87.17 %. The results obtained in this optimization study was compared with the results reported by other researchers for the production of biodiesel from various oil feedstocks. It was found that the yield obtained in this study is the highest as compared to those reported by other researchers.
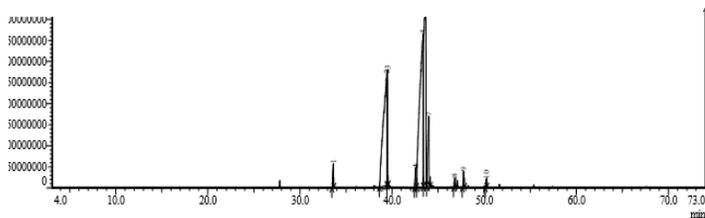
Peak#	R.Time	Area	Area%	Height	Name
1	33.620	293324096	1.08	56602654	Tetradecanoic acid, methyl ester (CAS)
2	39.410	6969108136	25.55	264598705	Hexadecanoic acid, methyl ester (CAS)
3	39.505	1309525132	4.80	274663551	Hexadecanoic acid, methyl ester (CAS)
4	42.555	509800207	1.87	45416713	9,12-Octadecadienoic acid (Z,Z)-, methyl ester (CAS)
5	43.357	9601925705	35.20	362677332	Spiro[4,5]dec-8-en-7-one, 1,8-dimethyl-4-(1-methylethyl)- (CAS)
6	43.655	6927846213	25.40	440394409	9-Octadecenoic acid (Z)-, methyl ester (CAS)
7	43.968	1345649444	4.93	164701286	Octadecanoic acid, methyl ester (CAS)
8	46.774	101212105	0.37	22279249	Hexadecanoic acid, 2-hydroxy-1,3-propanediyl ester (CAS)
9	47.760	151617208	0.56	37452989	Eicosanoic acid, methyl ester (CAS)
10	50.215	70041426	0.26	19322414	DI-(9-OCTADECENOYL)-GLYCEROL
		27280049672	100.00	1688109302	

Figure 5. *GC-MS biodiesel chromatogram (methyl ester)*

4 CONCLUSION

From the results of the research that has been done, can be concluded as follows:
1. From the result of catalytic analysis of CaO / K; SEM-EDS contains CaO and K2O from CaO impregnation, the highest K2O is 7% K variation 21.99 %), while the highest CaO content is 9 % K at 81.53%. For the highest surface area analysis at 7 % K with surface area of 71.22 m2 / g, the base is 2.59 mmol /g.
2. The best biodiesel results with 87.17 % yield, kinematic viscosity of 2.89 cSt, 0.032% water content, 0.819 g / ml density, 99.39 % methyl ester content.

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