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MODIFICATION OF CaO CATALYST WITH IMPREGNATION METHOD USING KOH IN BIODIESEL SYNTHESIS FROM WASTE COOKING OIL

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Abstract. Chicken eggshells can be used as raw material in the manufacture of CaO catalysts. Increased CaO catalyst activity can be done by the impregnation method. The purpose of this study was to determine the effect of %K on the wet impregnation of CaO catalyst using KOH and to find out the impregnation catalyst (CaO / K_2O) on the biodiesel yield. Prepared chicken egg shells were calcined at 900°C for 3 hours. Then the CaO obtained was impregnated using KOH with a variation of % K (5%, 7%, 9% and 12% (w / w)) while heated at 85°C. The impregnation product was calcined at 600°C for 5 hours. The impregnation catalyst (CaO K_2O) was applied to the biodiesel synthesis through a transesterification reaction with a mole ratio of 1:12 waste cooking oil: methanol, the amount of catalyst was 1.5% at a reaction temperature of 70°C for 2.5 hours. Based on the results of SEM-EDS analysis, the highest K_2O at 7% K was 21.99%), while the highest CaO content was at 9% K by 81.53%. For the highest surface area analysis at 7% K with a surface area of 71.22 m^2 / g, alkalinity was 2.59 mmol / g. The best biodiesel was obtained with a yield of 87.17%, kinematic viscosity of 2.89 cSt, water content of 0.032%, density of 0.819 g/ml, methyl ester level of 99.39%.

Keywords : Biodiesel, Impregnation CaO,, Transesterification, Waste Cooking Oil.

1. INTRODUCTION

Catalysts are compounds that accelerate reactions. The catalyst was divided into three, namely homogeneous catalyst, heterogeneous catalyst, and biocatalyst. In making a compound generally a homogeneous catalyst and heterogeneous catalyst are used. The disadvantage of a homogeneous catalyst is that it is difficult to separate from the solution of the process. Homogeneous catalysts also cannot be reused and will become hazardous waste if disposed directly. To avoid this weakness, therefore, heterogeneous catalysts are used.

CaO catalyst is a heterogeneous base catalyst which has been widely used because of its benefits, such as mild reaction conditions, relatively economical, a good alternative in the process of making biodiesel. Heterogeneous base catalysts can be easily separated from the reaction mixture so that they can be reused, and the impact is less on the environment and their solubility is lower in biodiesel [1-3]. CaO is made by calcining eggshells above a temperature of 600oC. Efforts made to improve the performance of the catalyst are by adding active sites in the form of bases with the impregnation method. Impregnation method aims to increase basicity by inserting metal into the catalyst.

Researches on the combination of CaO catalysts with other metal catalysts have been carried out, such as CaO / ZnO, CaO / Al_2O_3, CaO / Li and CaO / KF because it can increase catalytic activity, and can reduce the formation of soap in biodiesel production. In addition, the metal that can be used for impregnation is potassium (K) metal from KOH. KOH was chosen because the price is relatively cheap and easy to obtain. The CaO catalyst that has been impregnated can be used in the transesterification reaction in making biodiesel. Impregnation of CaO catalyst with KOH has been carried out with clam shell as a raw material, the best results were obtained on the addition of 5% KOH. However, based on analysis with XRD, there was still a component of $CaCO_3$ which

dominated after calcination. This was because the shells have a very hard layer. The biodiesel yield obtained was 81.5% with a catalyst weight of 3% of the weight, reaction temperature of 60ºC and reaction time of 3 hours [4]. Another study on the manufacture of CaO / C / KOH catalyst with wet impregnation method and applied to the manufacture of biodiesel from soybean oil, the best results of the catalyst at the addition of 25% KOH with biodiesel yield of 98%, reaction temperature of 65ºC, catalyst amount of 1.5% from total weight of oil [5].

For this reason, the impregnation of CaO catalyst from chicken egg shells using KOH will be varied in the concentration, accompanied by stirring and heating at 85ºC and its application to the manufacture of biodiesel with waste cooking oil.

2. METHODS

Material

The materials used, which are waste cooking oil and chicken egg shells, are obtained from street vendors around Samarinda, indicators of phenolptalein, NaOH 0.1 N, KOH, ethanol p.a, methanol p.a, aquadest and universal indicator paper.

Preparation of catalyst raw materials

Weighing 1000 grams of egg shells, washing with water until clean and drying them in the oven at 110 ℃ for 24 hours. Then breaking the egg shell to powder and screening with a sieve of -200 + 325 mesh. Then the eggshell powder was calcined at 900 ℃ for 3 hours. The calcination results were then stored in the desiccator to keep the catalyst condition dry.

Manufacture of catalyst CaO/K_2O

As much as 50 grams of CaO from the first calcination was dissolved in 200 mL of KOH solution with variations of 0%, 5%, 7%, 9% and 12%, then impregnated by heating the mixture with a temperature of 85oC while being stirred until dry. The impregnated catalyst was then dried in an oven at 105oC for 24 hours, then calcined at 600ºC for 5 hours. The impregnated catalyst was analyzed for its basicity, BET, SEM EDX and XRD.

Estertification Reaction on Waste Cooking Oil

Heating the waste cooking oil that has been weighed before to a temperature of 60°C. Mixing waste cooking oil with 40 grams of methanol and 1 gram of H_2SO_4. Reacting them for 1 hour, keeping the mixture temperature at 60°C. Inserting it into a separating funnel and letting it sit for 1 hour, then taking the triglycerides at the bottom layer.

Transesterification Reaction (Biodiesel)

Weighing 1.5% of the weight of CaO / K_2O catalyst oil which was previously impregnated with a variety of % K into a round bottom flask. Adding methanol then stirring for 60 minutes. Inserting waste cooking oil into a round bottom flask (ratio 1:12 with methanol). Increasing the temperature to 65°C then refluxing it for about 3 hours. Cooling the reflux results then separating the reflux results with CaO catalyst. Inserting the mixture into a separating funnel and storing it at room temperature for 1 hour then separating between the top layer and the bottom layer. Washing the top layer with ± 80°C temperature water. Next evaporating the water content contained in biodiesel at a temperature of 105°C. Analyzing the biodiesel products produced includes GC-MS, density, kinematic viscosity, water content, yield, and flash point analyses.

3. RESULTS AND DISCUSSION

The manufacture of CaO catalyst is done by calcining the eggshells that have been washed and dried. The purpose of eggshells calcination is to remove carbonate dioxide compounds through the decomposition reaction of calcium carbonate contained in eggshells to obtain calcium oxide compounds. In this study, calcination of eggshells is carried out for 3 hours at a temperature of 900℃. The reactions that occur in the calcination process are:

$$CaCO_3 \xrightarrow{950℃} CaO + CO_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

From the calcium oxide compounds obtained then impregnation process is carried out using KOH. Impregnation aims to increase the catalytic activity of the catalyst. The principle of impregnation is to enter the precursor into the support pore (catalyst) while stirring and heating. This will affect the characteristics of the catalyst, namely basicity, surface area, morphological shape, and composition of the catalyst.

Basicity

One way to increase catalytic activity is to increase alkalinity. Basicity can be improved by the impregnation method. KOH is used as a precursor for the impregnation process on CaO catalysts. The impregnation process causes the basicity of the catalyst to increase. The greater the basicity of the catalyst, the more the catalytic activity of the catalyst will increase [4]. Basicity before and after impregnation can be seen in Figure 1.

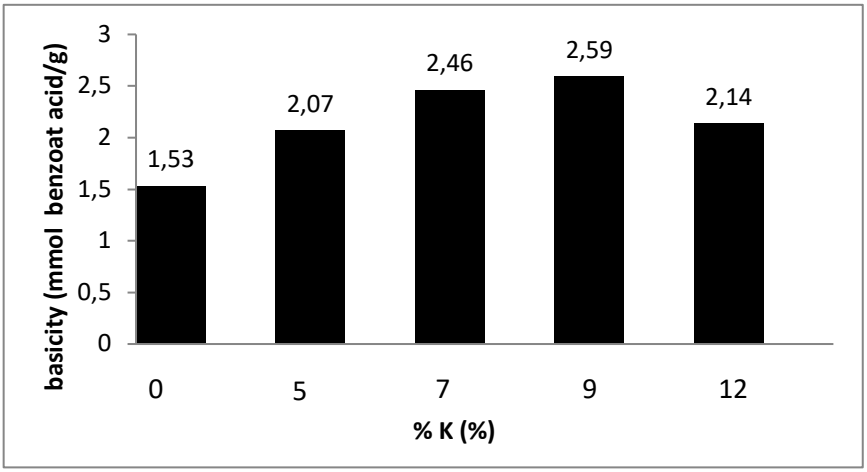

Figure 1. Effect of % K on basicity

Determination of the basicity of the impregnation catalyst using the acid-base titration method, before impregnation, basicity of the catalyst was 1.53 mmol benzoic acid / g. After impregnation, the catalyst alkalinity increased to 2.07-2.59 mmol benzoic acid / g. The decrease of alkalinity is at 12% K, this is due to the distribution of K metal in CaO pores which is not evenly distributed and is also caused by stirrers that are too small so they cannot reach the entire surface of the beaker in the impregnation process and the solution becomes very thick so that the stirring is done manually and samples attach to beakers that are difficult to separate.

Surface area

The surface area of the CaO impregnation catalyst is determined by the compounds contained therein and the compounds that cover the pores of the catalyst. The surface area of the catalyst can be seen in Figure 2.

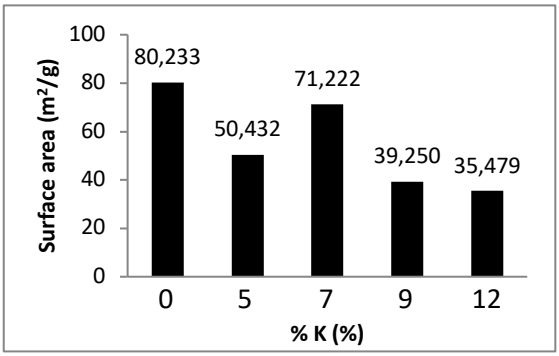

Figure 2. Effect of % K on Catalyst Surface Area

The catalyst before impregnation had the largest surface area of 80.233 m^2 / g, compared to the catalyst after impregnation. According to [4], the pores of CaO are filled with K_2O and K_2CO_3, causing a decrease in surface area. The decrease in surface area is also caused by the formation of Ca $(OH)_2$. The size of the surface area is directly proportional to K content except in the variation of 12%.

SEM-EDX

The effect of variations in% K on the impregnation process can be seen by using SEM-EDX analysis. SEM aims to see the shape of the sample surface and EDX aims to see the chemical components of the catalyst. The shape of the surface of the catalyst can be seen in Figure 3 and the composition of the catalyst can be seen in Table 1.

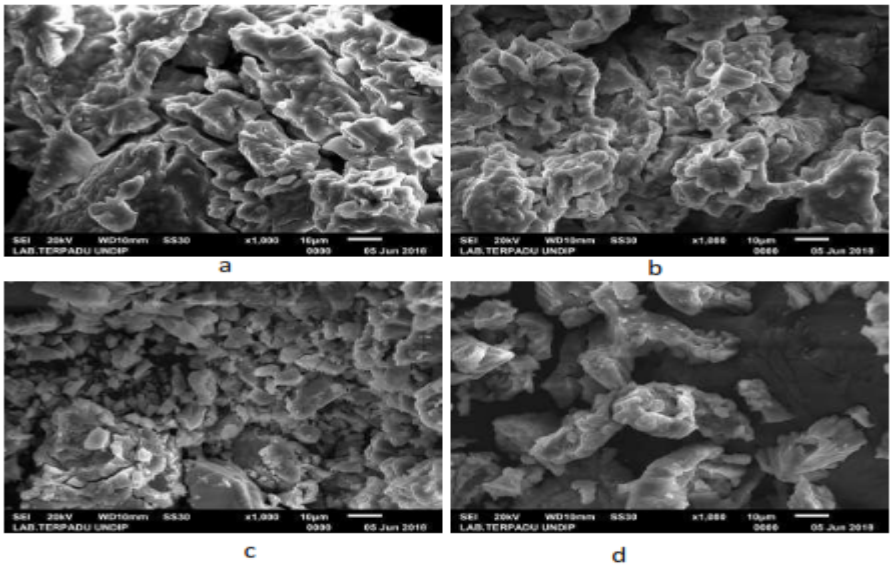

Figure 3. The surface of the catalyst through SEM. A) 5%, b) 7%, c) 9%, d) 12%

The shape of the catalyst surface 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 differences in the composition of each variation of % K. This is because the KOH compound is not only converted into K_2O compounds but also forms K_2CO_3 compounds. At temperatures of 300°C, KOH will be converted to K_2O, H_2O, and K_2CO_3 [6], by reaction:

$$2KOH \rightarrow K_2O + H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

$$K_2O + CO_2 \rightarrow K_2CO_3 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

At temperatures above 427°C, the melted KOH will react with carbon compounds to form K_2O and K_2CO_3 by reaction:

$$4KOH + C \rightarrow K_2O + K_2CO_3 + 2H_2 \quad \ldots\ldots\ldots\ldots 4$$

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

K (%)	component	composition(% wt)	K (%)	Component	composition (% wt)
5	C	21,11	**9**	K_2O	4,38
	MgO	1,59		CaO	81,53
	K_2O	12,73			
	CaO	64,46			
7	C	25,72	**12**	C	39,53
	MgO	2,71		MgO	1,01
	K_2O	21,99		K_2O	9,58
	CaO	46,72		CaO	45,98

Application of CaO / K_2O Catalyst in Biodiesel Synthesis

The initial stage in making biodiesel is analyzing the levels of free fatty acids and kinematic viscosity from waste cooking oil which is used as a raw material for making biodiesel. Free fatty acids are very influential in the process of making biodiesel because the high free fatty acids contained in oil samples will react with alkaline catalysts to form soap, because bases will react to neutralize free fatty acids from oil [6], while viscosity analysis which is done to see the viscosity of the oil itself can be compared with the biodiesel obtained. From the analysis of free fatty acid content, the free fatty acid content in the oil sample was 0.74% and kinematic viscosity was 33.09 cst. The aesthetic reaction does not need to be done, because the reaction serves to reduce the levels of free fatty acids contained in oil while the oil requirements used as a raw material for making biodiesel are free fatty acid levels of less than 5% [7].

In the transcription reaction, the catalyst is first reacted with methanol to form a methoxy species which are the initiator of the transesterification reaction. The reaction mechanism is listed in the reaction below:

$$2CH_3OH + CaO \dashrightarrow (CH_3O)_2Ca + H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 5$$

$$2CH_3OH + K_2O \dashrightarrow 2CH_3OK + H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 6$$

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

Characteristics of methyl esters from waste cooking oil

The characteristics of methyl esters which consist of density, kinematic viscosity, and moisture content can be seen in table 2 below

Table 2. Analysis results of density, viscosity, water content and yield of biodiesel

catalyst (%)	Density(g/mL)	Kinematic Viscosity (cst)	Water Content (%)	Yield (%)
0	0.8715	5.38	0.034	49.69
5	0.8644	3.53	0.0459	47.75
7	0.8599	2.89	0.032	87.17
9	0.8672	4.13	0.046	60.165
12	0.8936	16.64	0.0419	72.75

Based on Table 2, it is known that the biodiesel water content has met the SNI specification regarding biodiesel quality requirements which is less than 0.05%, while the parameters for kinematic density and viscosity for biodiesel obtained using catalysts with 12% K concentration at CaO still exceed SNI standards. This is because there are still remaining catalysts floating in the biodiesel washing process so that the remaining catalyst can react with fatty acids to form soap or biodiesel which is formed to undergo reaction again with the catalyst so that the reaction shifts towards the reactants.

The mole ratio of oil to methanol is one of the most influential factors in the transesterification process. In general, the transesterification reaction requires 3 moles of alcohol and 1 mole of triglycerides to produce 3 moles of fatty esters and 1 mole of glycerol. In this study, a ratio of 1:12 (Oil: Methanol) is used. The use of excess methanol is intended so that the equilibrium reaction shifts more towards the product because the transesterification reaction is an alternating reaction. The best results were obtained with the yield of 87.17% with a K catalyst of 7% and the methyl ester of 99.39% based on GC-MS analysis.

4. CONCLUSION

Based on the results of the research that has been done, conclusions can be drawn as follows:

1. From the analysis of the CaO / K2O catalyst; SEM-EDS analysis showed that the content of CaO and K2O as follows: K2O was the highest in the variation of 7% K at 21.99%), while the highest CaO content at 9% K was 81.53%. In surface area analysis, it was found that the highest surface area was at 7% K with surface area of 71.22 m2 / g and alkalinity of 2.59 mmol / g.
2. The best biodiesel product was with yield of 87.17%, kinematic viscosity of 2.89 cSt, moisture content of 0.032%, density 0.819 g / ml, and methyl ester content of 99.39%.

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