

The Effect of Different Precursor Concentration on The Synthesis of CaO Nanoparticles with Coprecipitation Methods for Palm Oil Transesterification Catalysis

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Abstract

Calcium oxide nanoparticles was prepared by coprecipitation method using calcium acetate as precursor and calcined at 800 °C for 6 hours. This work studied the effect of different precursor concentrations on the size of calcium oxide obtained and its applicated for palm oil transesterification catalysis. Characteristics of samples were measured by XRD and SEM et al techniques. The results showed that the diffraction pattern of CaO has the same diffraction pattern as the XRD standard diffraction pattern from the Joint Committee on Powder Diffraction Standard (JCPDS). Calcium oxide analysis using SEM shows the morphology of particles that agglomerate almost all variations in precursor concentration. The particle size increases with increasing precursor concentration. The smallest particle size of 55.758 nm was produced on solid CaO from the lowest precursor concentration of 0.05 M. The catalytic activity of activated calcium oxide nanoparticle compound was tested in the production of methyl esters. The conversion of triglycerides in palm oil into methyl esters was 90.34%.

Keywords: nanoparticles, calcium oxide, coprecipitation, precursor, catalys, metyl ester

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INTRODUCTION

Nanoparticles are particles in the nanometer size, which is about 1-100 nm (Hosokawa *et al.*, 2007). Nanoparticles of a compound can have different properties and functions from the previous size. Calcium oxide nanoparticles are alkaline earth metal oxides with nanometer particle sizes that can be synthesized from a precursor and precipitating agent in a suitable solvent (Mirghiis *et al.*, 2014).

Calcium oxide nanoparticles can be synthesized by several methods including sol-gel, coprecipitation and thermal decomposition methods. Each method can produce different characteristics. The thermal decomposition method of direct high temperature calcination of CaCO₃ will produce micrometer-sized particles (Tang *et al.*, 2007). The sol-gel method can obtain CaO crystals up to 4 nm in size, but this is ineffective because it takes a long time and is high cost. Nanoparticle synthesis by coprecipitation is

included as a bottom-up method which involves chemical reactions of a number of precursors and other nanometer-sized materials are produced (Mikrajudin, 2008). The advantages of the coprecipitation method are the simpler operation, the less time consuming and the lower cost. Liu et al. (2010) synthesized CaO nanoparticles by the coprecipitation method, which is also used in biodiesel production. The method chosen in this study is the coprecipitation method, with a solution of calcium acetate as a precursor and oxalic acid as the precipitate.

The previous research was carried out by Rahmawati (2012), by synthesizing calcium oxide nanoparticles using the coprecipitation method and variations on the solvent, a good solvent in this study is a solvent that produces small particle sizes and large phase yields. Calcium acetate was chosen as a precursor and the precipitating agent used was acetic acid. The results of these studies indicate that the best solvent for the synthesis of calcium oxide is diethylene glycol, it is explained that diethylene glycol, which is not too polar or moderate in polarity, is able to produce colloids to form particles with small sizes and a large yield of calcium oxide phase. The calcination temperature used was 800 °C. The study did not carry out variations in the concentration of precursors, therefore in this study, variations in precursors were carried out to determine their effect on synthesis results, this is because according to Fernandez (2011) the concentration of precursors can affect the synthesis of nanoparticles.

CaO catalysts have high activity, are durable, low cost, and have high alkaline strength, while the transition metal oxides tend to be acidic, expensive, and obtain low yields (Liu et al., 2008). CaO is a heterogeneous catalyst, whose use in transesterification reactions can avoid unwanted soap formation due to reactions with free fatty acids (Nazar et al., 2013). However, the CaO compound used as a catalyst in the transesterification reaction is still micro-sized, as has been done by Xin (2009) and Mahreni and Sulistyawati (2011). Therefore, the researchers intend to apply calcium oxide nanoparticles as a catalyst in the transesterification reaction. Mahreni and Sulistyawati (2011), have produced biodiesel using a calcium oxide catalyst produced from calcined eggshells with a temperature variation of 200 - 900 °C. The catalyst is then applied to the transesterification reaction with variations in reaction time and variations in the weight ratio of methanol: oil and catalyst: oil used. The results obtained were the highest methyl ester product at the reaction time of 180 minutes at 99.41%. Therefore, in this study, the researcher intends to use calcium oxide nanoparticles as a catalyst for the transesterification reaction in 60 minutes, which is the lowest reaction time in previous studies.

MATERIALS AND METHODS

Tools

Glassware, filter paper, furnace Muffle Furnace FH 14, stirrer magnetic, centrifugation, SEM

(Scanning Electron Microscopy) JEOL JSM-6360LA, XRD (X-Ray Diffraction) Rigaku Miniflex 600 and GCMS (Gas Chromatography-Mass Spectrometry) QP2010S SHIMADZU.

Materials

Ca(CH₃COO)₂·H₂O (Merck), demineralized aqua, oxalic acid (Merck), diethylene glycol (Merck), acetone (Merck), palm oil, methanol.

Preparation of Calcium Acetate Monohydrate and Oxalic Acid

The solution of Ca(CH₃COO)₂·H₂O can be done by dissolving Ca(CH₃COO)₂·H₂O 0.4 grams of in diethylene glycol in a 100 mL volumetric flask until it reaches the limit mark to produce a solution of Ca(CH₃COO)₂·H₂O 0.25 M, then steps are taken solution of Ca (CH₃COO)₂·H₂O 0.1 M and 0.05 M by dissolving 1.76 grams and 0.880 grams in diethylene glycol, respectively.

The preparation of an oxalic acid solution was done by dissolving 1.35 grams of oxalic acid in demineralized aqua in a 50 mL volumetric flask until the limit mark, resulting in a 0.15 M oxalic acid solution.

Synthesis and Characterization of Calcium Oxide Nanoparticles

The synthesis of CaO nanoparticles was carried out by slowly adding 50 mL of 0.15 M oxalic acid solution in a solution of Ca (CH₃COO)₂·H₂O at each concentration of 0.25 M; 0.1 M; 0.05 M accompanied by stirring using stirrer *magnetic* at 150 rpm for 12 hours at room temperature to produce calcium oxalate deposits. The precipitate can be obtained by centrifuge, followed by washing with demineralized aqua then washing with acetone, then separating by means of decantation. The next step is drying in an oven at 120 °C for 12 hours, the precipitate is then calcined in a furnace at 800 °C for 6 hours (Rahmawati, 2012). The sample was then characterized using X-Ray Diffraction and Scanning Electron Microscopy.

Preparation of Methyl Ester

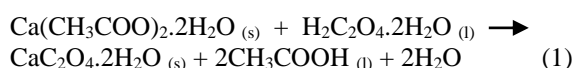
The resulting calcium oxide nanoparticles are used as a catalyst for the transesterification reaction with oil and methanol as raw materials. 2 grams of calcium oxide nanoparticles were mixed with 18 grams of methanol and stirred for 15 minutes at a stirring speed of 300 - 400 rpm. Furthermore, the mixture of methanol and catalyst is mixed with 20 grams of palm oil. The next step, the mixture is put into a three-neck flask equipped with a stirrer, thermometer and back cooler. The reaction is carried out for 60 minutes at a temperature of 60 - 65 °C. After the reaction is stopped, the reaction mixture is allowed to stand so that two layers are formed, namely the upper layer of the methyl ester and the lower layer of the glycerol layer consisting of (unreacted oil, glycerol and catalyst). The top layer is separated and weighed

as a methyl ester product. Furthermore, the sample was characterized by GC-MS (Gas Chromatography - Mass Spectrometry) to determine the formation of methyl esters (Mahreni and Sulistyawati, 2011).

RESULTS AND DISCUSSION

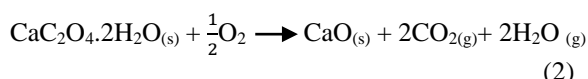
Synthesis of Calcium Oxide Nanoparticles

The reaction of calcium acetate in various concentrations with 0.15 M oxalic acid resulted in a white solution. This indicates that the solution is over saturated and calcium oxalate has formed. The following is the reaction that occurs (Kanade *et al.*, 2005).



The addition of the oxalic acid solution to the calcium oxide solution was carried out slowly and accompanied by stirring using a magnetic stirrer for 12 hours, this treatment was carried out so that the particles obtained from the reaction did not experience the formation of particles which could get bigger. The cloudy solution is centrifuged to obtain a precipitate in the form of calcium oxalate. The precipitate obtained was then washed with acetone and demineralized water, washing aims to remove the remaining oxalic acid and organic solvents in the precipitate. A white solid is produced after drying in an oven at 120 °C for 12 hours.

The calcination process was then carried out after the precipitate was dry, the solid was calcined at 800 °C for 6 hours. The decomposition temperature of oxalic acid is 189.5 °C so that this calcination process can remove residual oxalic acid. The following is a decomposition reaction of calcium oxalate to calcium oxide (Kanade *et al.*, 2005).

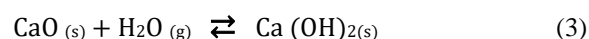


Characterization of Calcium Oxide Nanoparticles

Solid samples that have been synthesized can be analyzed using XRD to determine the phase formed, crystal structure, crystal size and degree of crystallinity. The light diffraction pattern is monitored at $2\theta = 5-90^\circ$. Comparison of the diffraction patterns of the prepared samples with variations in the concentration of precursors of 0.05 M, 0.10 M and 0.25 M is shown in Figure 1.

The content of the compounds in each sample can be seen through 2θ observations generated from XRD analysis. Based on the diffraction pattern obtained, it can be shown the presence of several typical peaks of CaO at each concentration. The resulting sample diffraction pattern was then matched with the diffraction pattern of pure CaO from the Joint Committee on Powder Diffraction Standards (JCPDS) data as a comparison. The peak CaO characteristics are confirmed and are close to the JCPDS data number

(37-1497). There is also a typical peak of $\text{Ca}(\text{OH})_2$ that appears. The appearance of $\text{Ca}(\text{OH})_2$ peaks is due to the reaction between CaO and water vapor, the more pores that are open in the CaO aggregate, the easier it is for water vapor to circulate in the pores, causing a lot of CaO to be converted to $\text{Ca}(\text{OH})_2$ (Lesbani, 2013). Research by Granados (2007) also shows that CaO left in the open air will hydrate to $\text{Ca}(\text{OH})_2$ very quickly. Granados (2007) also explained, when CaO is placed in an open space for ten days, CaO will be completely converted into $\text{Ca}(\text{OH})_2$. The following reaction occurs (Criado, 2014):



CaCO_3 peaks appear only at 0.25 M CaO concentration, the appearance of CaCO_3 peaks can be caused by the reaction of $\text{Ca}(\text{OH})_2$ which has been formed with CO_2 in the air. The following is the reaction that occurs (Guerrero *et al.*, 2017).



The diffract program in Figure 1. shows an increase in intensity with increasing concentration. The difference in high and low intensity occurs based on differences in each concentration. The difference in intensity values is quite close. The intensity value can show the percentage of crystallinity in each CaO sample.

The crystallinity relationship with variation in precursor concentration is shown in Table 1. % crystallinity is calculated based on the intensity of the diffraction peak of the CaO sample synthesized with a precursor concentration of 0.25 M at $2\theta = 34.015^\circ$, where the CaO sample has the highest intensity, so it is used as the intensity of comparison (*).

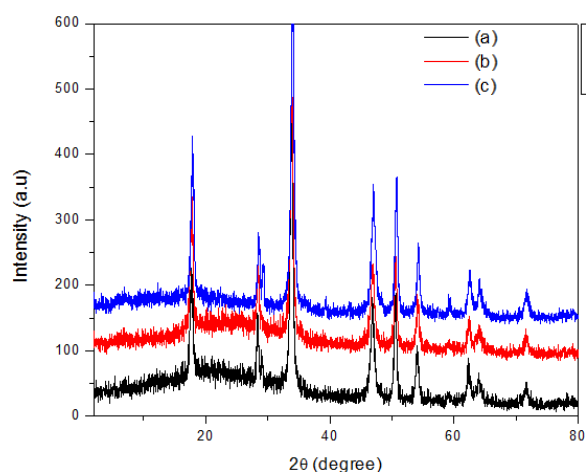


Figure 1. X-Ray Diffraction Patterns of Calcium Oxide Nanoparticles (a) X-ray diffraction patterns of CaO concentrations 0.05 M (b) The X-ray diffraction pattern of CaO with a concentration of 0.10 M (c) The X-ray diffraction pattern of CaO with a concentration of 0.25 M.

Table 1. Sample CaO crystallinity Relations
Synthesis on Concentration Variations Precursor

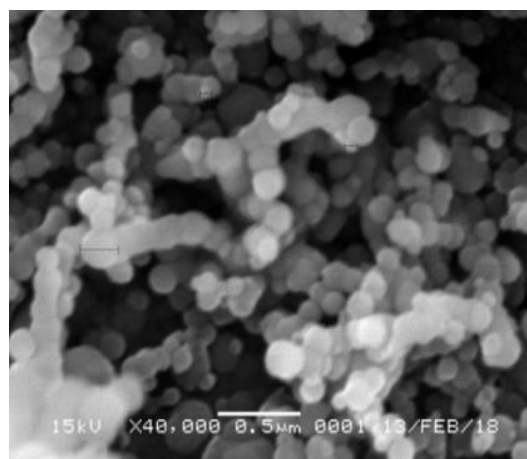
Concentration	2 θ (°)	High Peak	% crystallinity
0.05 M	33.814	1604	76.45
0.10 M	33.860	1733	82.60
0.25M	34.015	2098*	100

Table 1 shows that % crystallinity is at a concentration of 0.05 M < 0.10 M < 0.25 M. These results are in accordance with the research conducted by Widiarti and Rahayu (2016) in making CaO/SrO catalysts, which explains that more the higher the percentage of the catalyst that is carried, the higher the crystallinity produced. This is because CaO samples at a concentration of 0.25 M form crystals that contain more CaO than samples with a concentration of 0.10 M, and CaO with a concentration of 0.10 M contains more CaO than CaO with a concentration of 0.05 M. resulting in a high intensity scattering beam captured by the XRD machine and translated into a sharp high peak with a narrow 2 angle (Jacub, 2011).

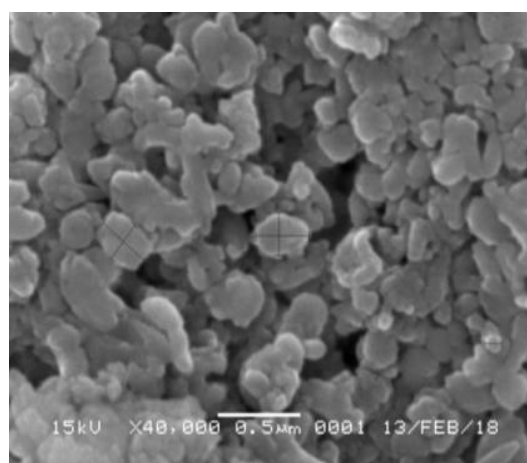
Samples that have gone through the calcination process are then analyzed using SEM to determine the surface morphology of the sample, so that the size and uniformity of the particles can be determined. The sample consisted of three different concentrations, namely 0.05 M; 0.10 M; 0.25 M was analyzed with a magnification of 40000. The results of the analysis of samples of various concentrations using SEM are shown in Figure 2.

The sample with a concentration of 0.05 M has a morphology as in Figure 2. (a), in the figure it can be seen that the particles are spherical and connected to one another. This collection of particles has a more homogeneous size and tidier edges when compared to particles at other concentrations. The average of particle size was 55,758 nm. The morphology of the sample with a concentration of 0.10 M is shown in Figure 2. (b), showing particles that have a flat but irregular round shape and untidy edges, the particles also look not homogeneous with a size of 250.903 nm. Furthermore, for the sample with a concentration of 0.25 M in Figure 2. (c) has a different morphology from the two previous concentrations, it can be seen that the particles have clear edges, are round in shape with some elongated particles. The average of particle size was 479.405 nm.

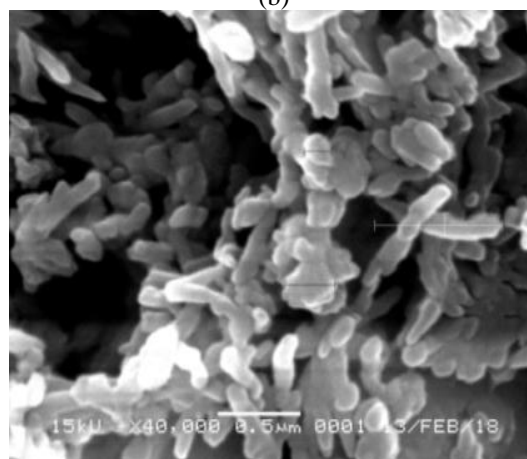
The morphology of samples of all concentrations is agglomerated and almost entirely inhomogeneous, especially at high concentrations, this can be caused by several things, the high concentration in the solution contains more particles than low concentrations, when stirring occurs centrifugal force can make atoms are homogeneously distributed, but the number of particles in a solution with high concentrations will be difficult to distribute properly because the slower movement of particles can cause



(a)



(b)



(c)

Figure 2. SEM Morphology of Calcium Oxide Nanoparticles (a) SEM morphology of CaO with a concentration of 0.05 M; (b) SEM morphology of CaO with a concentration of 0.10 M; (c) SEM morphology of CaO with a concentration of 0.25 M

the particle growth rate to increase, this allows particle buildup, and particle uniformity can also be reduced (Prasetya, 2006). High concentrations contain many particles, where the more particles the smaller the distance between the particles, making it easier and

faster for the formation of large particles (Oskam, 2006).

Application of Calcium Oxide Catalyst in the Transesterification

The transesterification reaction of oil with alcohol using a calcium oxide nanoparticle catalyst results with a precursor concentration of 0.05 M was carried out at 60 °C for 60 minutes. The product as shown in Figure 3 is obtained in the form of two layers, the upper yellow layer is methyl ester, and the lower yellow layer is darker as glycerol.

Two products resulting from the transesterification reaction are methyl ester and glycerol which are separated into two layers because of the difference in density, methyl ester has a density smaller than glycerol so that the methyl ester is at the top (Romano and Sorichetti, 2011).



Figure 3. Products of the Transesterification Reaction

The resulting mass of methyl ester is 17.85 g, from this mass it can be seen that the percentage conversion of triglycerides in oil to methyl ester is 90.34%. When compared with the conversion results from the transesterification of CaO synthesized by Santos et al (2019) with a larger size of CaO, the activity is greater, but the activity will be smaller when compared to the CaO nanoparticles synthesized by Bharti et al (2019) with a size of 8 nm. This is presumably because the smaller the size, the larger the surface area so that the area of contact with the reactants will be larger.

GC-MS analysis was used to identify the compounds contained in the methyl esters of palm oil. The chromatogram results of GC-MS analysis are shown in Figure 4. Analysis with a mass spectrometer can show the estimation of compounds from the 4 highest peaks of the chromatogram, which is comparing them with the MS instrument library which has a value. *similarityindex* (SI) is high. The suspected compounds can be seen in Table 2.

Each methyl ester compound (Table 2) has a different retention time, it can be seen that the longer the carbon chain, the longer the retention time. This is because in the column there is a process of separating compounds based on the principle *like dissolve like*, methyl ester compounds that have a longer carbon chain tend to be nonpolar, so they will be held longer in the nonpolar column. This causes the methyl ester to have a longer retention time than the methyl ester with a shorter carbon chain (Hutami *et al.*, 2012).

Table 2. Mass Spectrometer Analysis Results of Palm Oil Methyl Ester Samples

Peak	Retention Time, tR (Minutes)	Peak Area (%)	Suspected Compound	Molecular Formula
2	34,735	0.78	Methyl Tetradekanoate (Methyl Miristate)	C ₁₅ H ₃₀ O ₂
6	39,372	36.06	Methyl Hexadecanoate (Methyl Palmitate)	C ₁₇ H ₃₄ O ₂
8	42.969	57.89	Methyl cis-9-Oktadecenoate (Methyl Oleate)	C ₁₉ H ₃₆ O ₂
9	43,263	4.17	Methyl Octadecane noate (Methyl Stearate)	C ₁₉ H ₃₈ O ₂

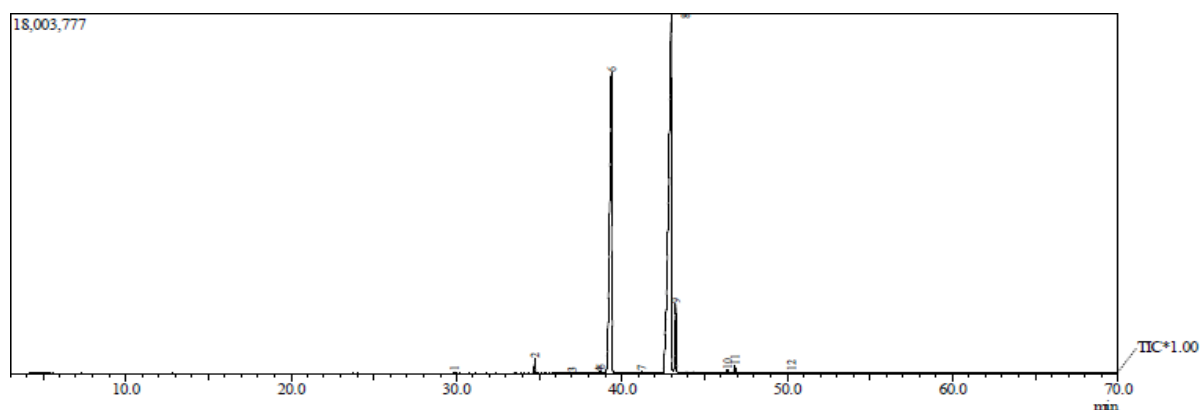


Figure 4. GCMS Chromatograms of Palm Oil Methyl Ester Samples

CONCLUSION

The higher the concentration of the precursor, the larger the size of the particles, while the lower the concentration of the precursor, the smaller the particle size. The same thing happened to the effect of variations in precursor concentrations on crystallinity. The higher precursor concentration also increases the crystallinity of the synthesized CaO. Of the 3 variations in precursor concentrations used in the synthesis of CaO nanoparticles, only a precursor concentration of 0.05 M resulted in a nanoparticle CaO with a more homogeneous particle size and fairly good crystallinity. Meanwhile, the conversion of triglycerides in palm oil to methyl esters in the transesterification reaction using CaO catalyst was 90.34%.

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