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PREPARATION OF CALCIUM OXIDE FROM CATTLE BONES AS CATALYST FOR CONVERSION OF WASTE COOKING OIL TO BIODIESEL

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ABSTRACT
Preparation of calcium oxide from cattle bones by thermal decomposition for 3 hours using various temperature at 400°, 500°, 800°, 900°, 1000°, and 1100°C. Calcium oxide was characterized using X-Ray Diffractometer. The results of XRD pattern showed of diffraction similar to CaO standard from JCPDS at 2θ: 32.2°; 37.3°; 53.8°; 64.1° and 67.3°. The CaO from heating cattle bones at 1000°C resulting of 2θ: 32.3°; 53.8° and 64.1°. Then, the metal oxide was characterized by FT-IR which showed the existence of CaO at wave number 362.2 cm^{-1} from CaO vibration. The CaO from cattle bones applied as catalyst on biodiesel synthesis from waste cooking oil and resulting viscosity value of biodiesel 5.93 cSt, density 0.876 g/cm^3, acid value 0.561 mg/KOH and iod number value 16.92 g/100 g, respectively all in the range of SNI standard.

Keyword: cattle bones, calcium oxide, catalyst, biodiesel, waste cooking oil

INTRODUCTION
The use of petroleum for various activities has led to the depletion of petroleum stocks. Therefore another alternative must be sought as a substitute for petroleum. One of the alternative fuels that have been developed over the years is biodiesel. Biodiesel is one of the attractive alternative fuels that can be produced from renewable sources. The standard process for biodiesel processing is by transesterification process. The synthesis of biodiesel by transesterification reaction will not take place without a catalyst. One type of catalyst used to synthesize biodiesel from triglycerides with alcohol, the base catalyst (Verma et.al, 2016).

Alkaline catalysts often used as NaOH, KOH, and calcium hydroxide ($Ca(OH)_2$) is a homogeneous alkaline catalyst system. However, the use of such catalysts has a disadvantage, i.e., the separation of the catalyst from the product is quite complicated. Other basic catalysts commonly used are metal oxide catalysts such as CaO, MgO (Lee et.al., 2014). The base catalyst of this metal oxide class has a heterogeneous system. The use of heterogeneous catalysts offers many advantages because this catalyst is separated from the product and can be reused. But the price of these metal oxide catalysts is expensive. Therefore, the research effort to find the source of the cheap heterogeneous catalyst obtained from nature and also friendly to the environment. There are several sources of calcium such as eggshells, mollusks, and bones. Bone consists of organic and inorganic materials. Approximately 20% of the bones are water, and the rest consists of inorganic materials such as calcium phosphate (65-70%), protein and collagen matrix (30-35%). Inorganic materials of natural sources contain the main components of calcium phosphate and calcium carbonate, with little magnesium, fluoride, and sodium, phosphorus, manganese, tin and copper (Prasuna et.al, 2004).

Sources of raw materials for synthesizing biodiesel include vegetable oils such as jatropha seeds, rubber, palm oil. Another source that can be used into biodiesel is waste cooking oil. The waste cooking oil is the rest of the household provided abundant forms the basis of an attractive and increase economic value into biodiesel.

Ho et.al. (2014) have synthesized biodiesel with raw materials from waste cooking oil using heterogeneous base catalyst which CaO derived from snail shells *(Achatina fulica)* calcinated at a temperature of 700 °C. The research shows the ratio of methanol and transesterification of waste cooking oil (40: 100) at a temperature of 65 ° C to form methyl ester is an average of 35 mL. In this study synthesized CaO catalyst from cattle bones was applied to transesterification reaction of biodiesel manufacture from wasteland oil to be utilized as a catalyst for an industrial process other than biodiesel (Minaria and Mohadi, 2017.

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EXPERIMENTAL SECTION
Chemicals and Instrumentation
The instrumentations are used in this research glasses flask, reflux apparatus, viscometer, water bath, pycnometer, Shimadzu Lab X-6000 X-ray diffractometer, Shimadzu FTIR Prestige-21, and SEM Jeol JED-2300. The materials used are cattle bone, phosphoric acid, methanol, phenolphthalein, potassium hydroxide, oxalic acid, Hanus solution (Iodine-Bromide Reagent), 15% potassium iodide, starch, chloroform, ethanol, sodium thiosulfate.

Methods
Base catalyst preparation from cattle bone

Cattle bone is taken from several locations in a traditional market in Palembang City. The cattle bones that have been obtained are washed and dried in an oven at a temperature of 100 °C to remove water. Cattle bones are crushed and sifted to a 100 mesh size.

Preparation of waste cooking oil sample

Waste cooking oil was taken from food stalls in the Indralaya District. Waste cooking oil was filtered using Whatman No.40 filter paper to clean it. The filtered oil is store in a plastic container.

Fatty acids determination in waste cooking oil by titration

Cooking oil of 5 grams is weighed, then added with 96% ethanol of 10 mL, refrigerated to boiling, then shaken until completely dissolved. The resulting sample is titrated with PP indicator using a KOH titrant to produce a pink color.

Fatty acid formula:

$$= \frac{\text{ml KOH x N KOH x 56.1}}{\text{Weight of sample}}$$

Standardization of KOH

A total of 102 mg of oxalic acid were included in a 250 mL Erlenmeyer, then 25 mL aquadest were added. The mixture is added with PP indicator and titrated with 0.1 N KOH which will be standardized until the solution is pink in color. Iteration was performed three times.

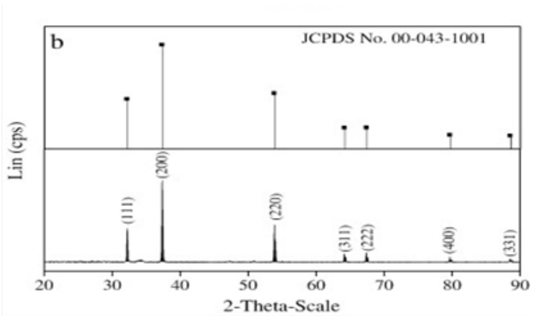

Figure 1. Difactogram of CaO

Table 1. Data 2θ (JCPDS) for the compounds of CaO, $Ca(OH)_2$, $CaCO_3$

Compounds	2θ				
CaO	34.2°	37.3°	53.8°	64.1°	67.3°
$CaCO_3$	29.4°	39.4°	43.2°	47.4°	48.5°
$Ca(OH)_2$	28.6°	34.1°	47.1°	50.8°	-

Determination of iodine number in waste cooking oil by Hanus method

The waste cooking oil is weighed as much as 0.5 g and then loaded into Erlenmeyer. 10 ml of chloroform solution and 25 ml of Hanus solution (Iodine-Bromide Reagent) are added, shaken until all oil is well blended and let stand in a dark room for 30 minutes. 10 ml of 15% KI solution added. Titration is done with a solution of $Na_2S_2O_3$ 0.1 N and the indicators used are starch 1%, titration until a clear solution. $Na_2S_2O_3$ 0,1N use was recorded.

$$\text{Iod Numbers} = \frac{(b-a) \times NNa_2S_2O_3 \times 12.69)}{(g\ sample)}$$

Where :
A = Number of mL thio solution for the titration of the sample
B = Number of mL thio solution for blank titration

Preparation and characterization of base catalyst cattle bones

Cattle bones that pass a 100 mesh sieve as much as 100 grams of calcined with a furnace in oxygen atmosphere conditions at various temperature variations. The temperature variations used were 400, 500, 800, 900, 1000, and 1100 ° C for 3 hours. After the cold solids are then it stored in the desiccator for 24 hours. Characterization is performed by using X-ray diffraction. The result of the obtained characterization compared with JCPDS data which is standard for XRD diffraction pattern data.

Study of transesterification of cooking oil with preparation catalyst Into biodiesel

The transesterification reaction was performed using a 500 mL three-neck flask equipped with a pumpkin flap. A total of 100 mL of waste cooking oil was added 40 mL of anhydrous methanol followed by the addition of a basic catalyst of cattle bone as much as 0.2 g. The reaction was heated at 65 ° C. for 3 hours. The reaction is stopped by using ice water. The reaction product was left overnight to obtain multiple phases, followed by separation by addition of 1 mL H_3PO_4 for the neutralization process.

Determination of viscosity value of biodiesel product

The sample is inserted into the viscometer, then covered with a rubber ball, then the lid is opened, and the sample is allowed to flow. The sample flow time is recorded from the first line to the second line in seconds. If the flow time is less than 200 seconds, then the determination is repeated using a viscometer that has a smaller factor. The same treatment is done for biodiesel after distillation.

Viscosity formula: KV = F x t
Where:
KV = Kinematic Viscosity
F = The viscometer factor used
T = Flow time of example

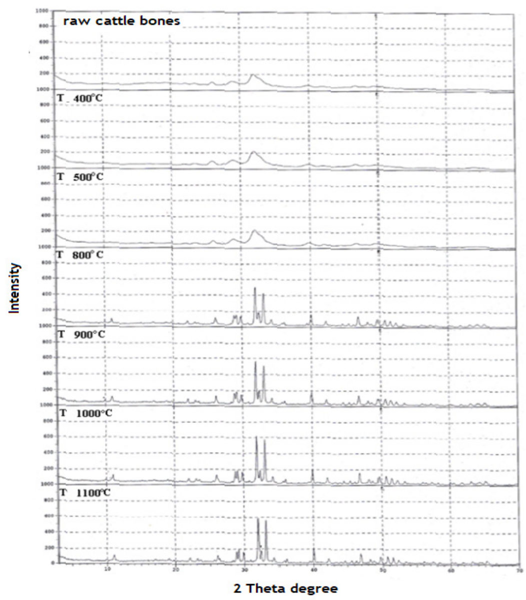

Figure 2. Diffractogram of Cattle bones Heating Results at Various Temperatures

Determination of density value of biodiesel product

Density measurements carried out in the water bath at a temperature of 40 °C empty pycnometer first weighed, then pycnometer filled with a biodiesel product that is obtained, then weigh it. Repetition is done three times. The same test performed for aquadest as a comparison.

RESULTS AND DISCUSSION

Identification of CaO metallic oxide of preparation from cattle bone using XRD

Calcium oxide analysis resulting from the calcination process using XRD. Data XRD diffractogram generates patterns derived calcium compounds include CaO, $Ca(OH)_2$ and $CaCO_3$ as the main compound. Pattern diffractogram produced consistent with the patterns of calcium oxide released by the *Joint Committe on Powder Diffraction Standard* (JCPDS) as presented in Table 1. Characteristics of calcium compounds at any temperature variation is analyzed through the observation of 2θ according to the standards.

In accordance to the JCPDS diffractogram in the Figure. 2, the selection of CaO to be used as a base catalyst in the synthesis of biodiesel from cooking oil through a transesterification reaction process is the cattle bone heated at a temperature of 1000ºC. This can be seen from the resulting CaO peaks approaching the standard JCPDS diffractogram for CaO. The 2θ value of cattle bones 1000ºC heating is 32.3°; 53.8° and 64.1° with the intensity values sequentially by 117.13 and 15. A value of 2θ from cattle bones 1100ºC heating is 32.2°; 53.2° and 64.1° with successive intensity values of 165.33 and 17.

Identification of calcium oxide that results from the preparation of cattle bones decomposition with analysis using FT-IR spectroscopy

In this study, cattle bone heating at 1000 ° C was analyzed by FT-IR. The measured FT-IR spectra are presented in Figures 3. In Figure 3 shows that the presence of functional groups in the region 400-4000 cm^{-1} wave number. The wave number range can be divided into two main areas namely in the range of 400-1000 cm^{-1} wave numbers as an area for identification of inorganic compounds and local wave number range 1000-4000 cm^{-1} as a base uptake organic compounds to facilitate the observation. In the wave number around 3400 cm^{-1} contained in the cattle bone as shown in Figure 3 which shows the -OH group. This indicates the presence of crystal water formed at CaO where the wavelength indicates the shifting vibration of the -OH group. A number range calcium carbonate and hydroxide legible at 400-1000 cm^{-1} (Tang et.al, 2013).

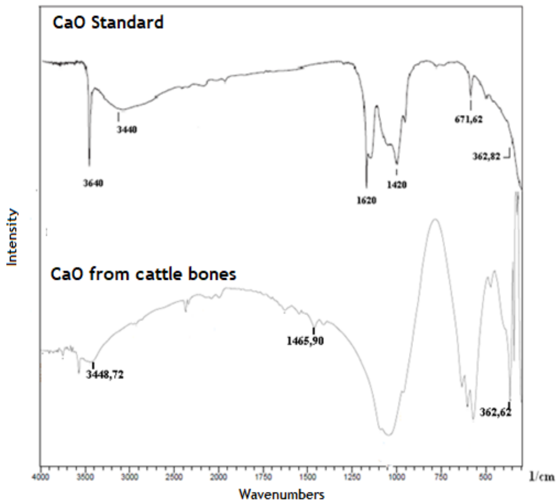

Figure 3. FT-IR spectra of CaO from Cattle bones heating at 1000 ˚C and CaO Standards.

Calcium oxide is the expected target solids in this study was observed in the range of 250-400 cm^{-1} wave number. FT-IR spectra of cattle bones heating at a temperature of 1000 ˚ C and FT-IR spectra of standard CaO is presented in Figure 3 shows the peaks that appear to vibration almost identical between the standard cattle bones and CaO. CaO absorption bands in cattle bone decomposition at temperatures of 1000 ˚C seen in the area around 362.2 cm^{-1} that indicates vibration of the metal oxides CaO preparation results. OCO bond stretching of carbonate appears at wave number 1465.9 $cm^{-1.}$

Early identification of cattle bone using SEM-EDX analysis

The result of SEM-EDX analysis for the bone of cattle bone can be seen in Figure. 4 and Figure. 5. the surface morphology of cattle bone before heating with 1000x magnification is seen not homogeneous due to different composition between cattle bone.

The composition of cattle bone can be seen from EDX data in Figure 8 which is carbon 64.14%, oxygen equal to 24.82%, sodium equal to 0.25%, magnesium equal to 0.24%, posfor equal 3.64% and calcium 6.92%.

The EDX data of cattle bone before heating process at various temperature variation obtained low calcium element content. Although calcium is not the main component in cattle bones a but can be used as a candidate to obtain CaO.

SEM-EDX analysis on cattle bones heated at 1000 ˚C

Cattle bones that have been through the process of heating at various temperatures and have done XRD analysis that produces the best CaO from cattle bones at a temperature of 1000 ˚C subsequently analyzed by SEM-EDX. The results of SEM-EDX analysis for cattle bones at 1000 ˚C can be seen in Figure 6 and 7.

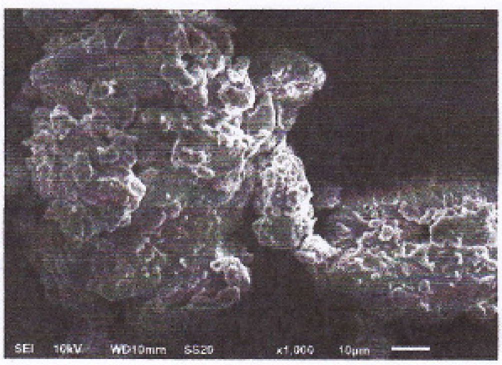

Figure 4. Results of SEM photograph of Cattle bones

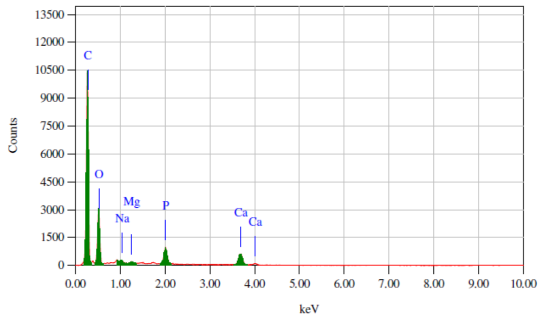

Figure 5. EDX Analysis Results from Cattle bones

In Figures 6, there is a significant difference with cattle bones before heating process. Cattle bones composition, from heating at 1000 ˚C can be seen from the data in Figure 7 namely EDX carbon by 11.21%, 44.21% oxygen, sodium at 2.01%, amounting to 1.14% magnesium, phosphorus amounted to 14.37 % And calcium by 24.83%. The high carbon content initially decreased, but the calcium content grew by 6.91% to 24.83%. From the SEM-EDX data in Figures 6 and 7 it is clear that the structure of the heating cattle bone has a higher homogeneity than before heating.

The application of CaO from cattle bone as a catalyst in the synthesis of biodiesel from cooking oil

The transesterification process is carried out for 3 hours through a reflux process to achieve the value or the maximum amount of methyl esters formed. The use of pure H_3PO_4 was added as a solvent reactant strongly acidic alkaline neutralizing acidic conditions in the transesterification process. Methyl ester which is biodiesel obtained through transesterification reaction with heated CaO catalyst is 20 mL, with calculation yield obtained is 14.28%.

The value of fatty acid number of biodiesel product

The result of the determination of fatty acid number on biodiesel production from waste cooking oil by titration method got the average value of repetition 3 times equal to 0.561 mg/KOH using CaO catalyst from cattle bone. According to the data of SNI 04-7182-2006, the maximum value of fatty acid number found in biodiesel is 0.8 mg/KOH. The data shows that the biodiesel product has a value that is in accordance with the standard. High acid numbers can cause sediment in the fuel system and corrosion of the media. The higher the acid number the lower the quality of biodiesel (Pinyaphong, 2011).

Iod value of biodiesel product

The result of the determination of Iodine number of biodiesel product obtained average value from repetition 3 times is 16.92 g/100 g for cattle bone catalyst. The result of the analysis shows that iodine number in biodiesel from synthesis according to standard biodiesel value determined by SNI (Lesbani et.al, 2015). Biodiesel with a high content of iodine number exceeds constant biodiesel quality standard maximum of 115 g/100 g will lead to a tendency to polymerization and formation of deposits on injectors noozle and piston rings at the start of combustion.

Density value of biodiesel product

Density provides information on how the fuel will work in diesel engines. According to the standard ASTM D-1298 (1999), a specific gravity of diesel fuel specifications in the range of 0.85 to 0.89 g / $cm^{3.}$ The test was performed on methyl ester with measurement according to ASTM standard with laboratory scale. The use of high temperature to the transesterification reaction will increase the saponification reaction. The presence of impurities such as glycerol from the saponification reaction so that the impurities formed form the mass of the biodiesel species to become larger. High mass types indicate some impurities contained in biodiesel (Pinyaphong, 2011). The results of the analysis of methyl ester density were measured with three repetitions of the average values obtained are 0.8844g/cm^3 for cattle bones catalyst. These results indicate that the resulting product meets the ASTM standard of density used.

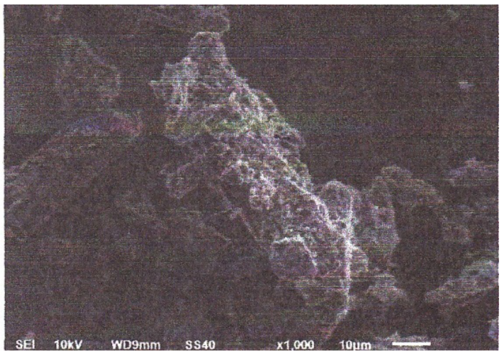

Figure 6. SEM photograph of Cattle Bones Heated at 1000 ˚C

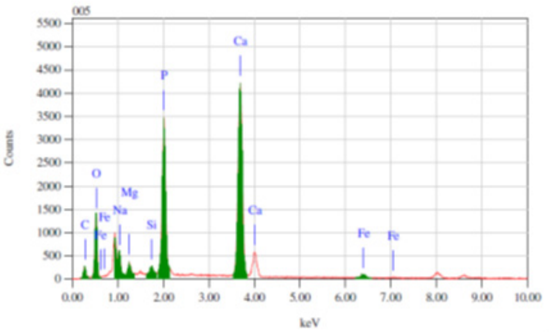

Figure 7. EDX Analysis of Cattle Bone Heating Results 1000 ˚C

Viscosity value of biodiesel product

Viscosity is defined as fluid resistance to the flow rate of a mm-sized capillary. The test results obtained after three times the viscosity repetition obtained an average of 5.93 cSt and 6.03 cSt. The recommended restriction is ASTM D-445 with a viscosity of diesel fuel specification that is in range 2.3 – 6.0 cSt. If the price of viscosity is too high it will be big friction losses in the pipeline, the pump work will be heavy, the filtration is difficult and the possibility of the dirt come too big, and difficult to disregard the fuel. Conversely, if the viscosity of biodiesel it will result a thin lubrication.

CONCLUSION

Cattle bone heating at a temperature of 1000 ˚C was produced CaO as a catalyst. The XRD data of cattle bones 1000 ˚C has a value of 2θ: 32.3°; 53.8°, and 64.1°. The FT-IR data showed that CaO appears at the wave number 362 cm^{-1}. As well as from SEM-EDX data the surface morphology of cattle bones after heating at 1000 ˚C was seen to be more homogeneous compared to not heated. Biodiesel product from waste cooking oils catalyzed by CaO from cattle bones have a viscosity of 5.93 cSt, the density of 0.876 g/cm^3, the acid number of 0.561 mg/KOH and an iodine number of 16.92 $GI_2/100$ g in accordance to the biodiesel standards.

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