

## Calcium Oxide Decomposed From Chicken's and Goat's Bones as Catalyst For Converting Discarded Cooking Oil to be Biodiesel

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**Abstract** - Thermal decomposition of calcium oxide from chicken's (*Gallus gallus domesticus*) and goat's (*Capra Hircus Aegragus*) bones was prepared at temperature variations of 400, 500, 800, 900, 1000, and 1100 °C respectively. X-ray diffractometer (XRD), FT-IR and SEM were used for calcium oxide characterization. XRD diffraction pattern of the bone's after thermal decomposition at 1100°C has similarity to the XRD standard diffraction pattern from Joint Committee on Powder Diffraction Standard (JCPDS). Diffractions of  $2\theta$  values being used are 34.2°, 37.3°, 58.3°, 64.1°, and 67.3°. Ca-O presence in the samples was detected by FT-IR characterization at wavenumber of 354,90 cm<sup>-1</sup>. SEM profile show reducing size of bones after decomposition in both chicken's and goat's bones. Furthermore, the prepared calcium oxide was applied for biodiesel synthesis from discarded cooking oil through transesterification reaction. By applying the catalysts decomposed from chicken's and goat's bones, the biodiesel product showed characteristics as follows: biodiesel applied the chicken's bone catalyst has fatty acid number of 0.56 mg/KOH, iod number of 22.41 g I<sub>2</sub>/100 g KOH, density of 0.88 g/cm<sup>3</sup> and viscosity of 5.91 mm<sup>2</sup>/s, while biodiesel applied the goat's bone catalyst has 0.56 mg/KOH, iod number of 21.57 g I<sub>2</sub>/100 g KOH, density of 0.88 g/cm<sup>3</sup> and viscosity of 6.34 mm<sup>2</sup>/s. Those biodiesel's characteristic values meet the National Standard of Indonesia (SNI) for biodiesel.

**Keywords:** Biodiesel; Biscarded cooking oil; Calcium oxide; Chicken's bone; Goat's bone

### Introduction

Nowadays, biodiesel has become an attractive biofuel; it offers several environmental benefits including environmental friendly fuel, renewable and essentially a sulfur- and aromatics-free energy (Hill *et al.*, 2009), these have increased the interest and demand for biodiesel (Kargbo, 2010). Biodiesel is known as a mono-alkyl ester of fatty acid with high energetic efficiency. Non-toxic fuel, no carbon dioxide, no sulfur emissions to the environment, and wider material resources available to be used are the considerable reasons for selecting biodiesel as transportation future fuel (Di Serio *et al.*, 2008). Various renewable sources such as vegetable oil, discarded cooking oil and animal fats can be synthesized into biodiesel (Ma and Hanna, 1999). The future of biodiesel as transportation fuel has received a considerable attention at this decade for fossil fuel substitution. Biodiesel can be synthesized through transesterification of alcohols with triglycerides from various renewable vegetable or fat oils catalyzed by base or acid (Di Serio *et al.* 2007).

Several catalysts have been prepared and reported as suitable for synthesis biodiesel, such as: conventional acid-base catalysts it has been applied for transesterification of vegetable or fat oils with methanol for biodiesel production. Examples of conventional acid-base catalysts currently used are hydrochloric acid, sulphuric acid, potassium hydroxide, and sodium hydroxide (Sharma *et al.*, 2008). These catalysts have been applied in homogeneous system; however they have many disadvantages such as they can reduce biodiesel as main product, it can cause corrosion in equipments and also it required expensive separation during its application, the cause of this was due to hydrolysis and saponification process. Acid catalyst is known for causing a serious environmental and corrosion problem (Noiroj *et al.*, 2009). Heydarzadeh *et al.* (2010) reported a heterogeneous  $\gamma$ -alumina-zirconia as an effective catalyst for biodiesel production for various fatty acids. Macroporous-mesoporous materials are also can be used for biodiesel synthesis (Dhainaut *et al.*, 2010). Other than those studies,

heteropolyacid nanoreactor with double acid sites was also reported to be important as facilitator catalyst for waste cooking oil transesterification (Zhang *et al.*, 2009). Metal oxide from Group II in periodic table of elements such as calcium, magnesium, or strontium is effectively used for biodiesel synthesis from vegetable oil (Refaat, 2011). On the other hand, these catalysts are relative expensive and searching renewable source as catalyst for biodiesel production is intriguing topic. One powerful catalyst for biodiesel synthesis is calcium oxide. In Industrial process calcium oxide is produced from lime in the nature. Therefore, development of solid renewable catalysts such as CaO has now gained much attention due to its ease of separation and lower environmental problems (Lopez *et al.*, 2007) Thus, the development of catalyst based on the metal oxide for biodiesel production is an interesting topic research. Our studies have reported the feasibility of calcium oxide from *Achatina fulica* as catalyst for the formation of biodiesel from waste cooking oil (Lesbani *et al.*, 2013). Previous studies reported formation mechanism of calcium oxide from decomposition of mollusk shell and their application for biodiesel synthesis from used frying oil (Agrawal *et al.*, 2012).

In this report, we aim to enlarge our study's scope by reporting the potential of using chicken's and goat's bones as the source of calcium oxide, other additional value can be added including its large source availability and its potency as a cheap catalysts. Calcium carbonate is main composition in both chicken's and goat's bones. Calcium carbonate can be transformed into calcium oxide by decomposition at an appropriate temperature. On the other hand, chicken's and goat's bones can be found easily and renewable sources for calcium oxide production due to composition of calcium carbonate in these bones. In this research, chicken's and goat's bones will be decomposed into calcium oxide at various temperatures before being used as catalyst for biodiesel production from discarded cooking oil. Discarded cooking oil is an attractive starting material that can increase the economical value of vegetable oil.

## Materials and Methods

### Preparation of calcium oxide from chicken's and goat's bones

Calcium oxides from chicken's and goat's bones were prepared according to the procedure from Nakatani *et al.* (2009). Dry bones (100 g) was placed into a silica cup, then they were decomposed by using an electric furnace for three hours at given temperature (400, 500, 800, 900, 1000, and 1100 °C). The combusted bones were cooled at room temperature and stored in desiccators over silica gels. The combusted bones were then characterized by using XRD powder followed by identification process using FT-IR spectroscopy and SEM-EDX. The XRD powder pattern for combusted bones at various temperatures were compared to the XRD powder pattern of calcium oxide produced by JCPDS. XRD samples values, which have the best fit to the XRD standard values was subjected to a further analysis by using FT-IR and SEM-EDX.

### Production of biodiesel from discarded cooking oil using decomposed fish' bones as catalyst

The biodiesel production's procedure was adopted from Viriya-Empikul *et al.* (2010) with a slight modification. 100 mL discarded cooking oil was poured into a 100 mL Schlenk flask, 40 mL methanol, and 4% (wt) combusted fish' bones were added, mixed and heated at 70 °C for three hours, the Schlenk flask was equipped with thermometer, magnetic stirrer, and condenser during the process. Reaction was stopped through quenching the mixture with 10 mL cold water. 1 mL phosphoric acid was added into the prepared mixture to neutralize the reaction mixture. The mixture was then stored overnight. The crude product of biodiesel was collected after separation from catalyst and glycerol. Pure biodiesel was obtained after distillation of crude biodiesel. Biodiesel was characterized through determination viscosity (ASTM D-445), density (ASTM D-1298), fatty acid value (ASTM D-974), and iod number (AOCS Cd 1-25).

## Results and Discussion

Decomposition of chicken's and goat's bones at various temperatures was characterized by using XRD. The patterns are shown in Figure 1 (chicken's bone) and Figure 2 (goat's bone). XRD patterns in Figure 1 are compared to the calcium oxide standard from JCPDS. Diffraction  $2\theta$  from

JCPDS for calcium oxide being used is at 32.2, 37.3, 53.8, 64.1, and 67.3 deg. Therefore; we emphasized the patterns in Figure 1 with these values. The XRD pattern of the chicken's and goat's bones show broad peaks at 30-35 deg, the patterns indicate the presence of calcium on those bones. Decompositions of chicken's and goat's bones were conducted at various temperatures in the range of 400-500 and 800-1100 °C. XRD patterns of decomposed chicken's and goat's bones at temperature of 400 and 500 °C show similarity patterns with original chicken's and goat's bones, thus we start the decomposition from 800 °C. The Decomposition of chicken's bone starts to show an increasing signal at 700 °C, and the high and the sharp peak of the decomposition was clearly shown at 800 °C (Figure 1). While the decomposition of goat's bone at 800 °C show XRD pattern with a high and a sharp peak (See Figure 2), these high and sharp peaks indicated appearance of high crystallinity. There are similarity pattern between XRD pattern found in the decomposed chicken's and goat's bones at 800 °C and those at 900-1100 °C, thus we concentrate to select the same calcium oxide' pattern with JCPDS data at temperature 900-1100 °C (Blanton and Barnes, 2005).

Characteristic pattern of decomposition at 900 °C shows a present of calcium oxide at 32.3, and 64.1 deg, while, that process at 1000 °C was found at 32.3, 53.8, and 64.1 deg. Further detailed study shows decomposition evidence at 1100 °C and the result has a similarity pattern with the decomposition at 900 °C. Thus, it can be concluded that the decomposition at 1100 °C has nearest pattern with JCPDS of calcium oxide. Further characterization was carried out using FT-IR spectrophotometer and SEM analysis. FT-IR spectrum of calcium oxide and chicken's and goat's bones are presented in Figure 3 while SEM photo analysis is shown in Figure 4.

FT-IR spectrum of both chicken's and goat's bones show appearance of samples' peaks with similar vibrations. The broad peaks were shown at similar wavenumbers which is at  $1041.0\text{ cm}^{-1}$ . This peak is related to calcium carbonate peak at the same wavenumber to the wavenumber of JCPDS standards. The FT-IR result shows absorbance band for Ca-O that belongs to both chicken's and goat's bonds at wavenumber of  $354.90\text{ cm}^{-1}$ . This band is strengthened by the appearance of the other bands at wavenumber of  $870.0\text{ cm}^{-1}$ . The O-C-O stretching bond of carbonate for all of the measured bones samples appeared at wavenumber of  $1627.92\text{ cm}^{-1}$ . This is similar to the appearance of peak at wavenumber of  $1041.56\text{ cm}^{-1}$  for Ca-O standard, this is a unique vibration for calcium oxide, which is indicated vibration of Ca-O (Tang *et al.* 2013). Detailed of characterization was carried out using SEM photo analysis.

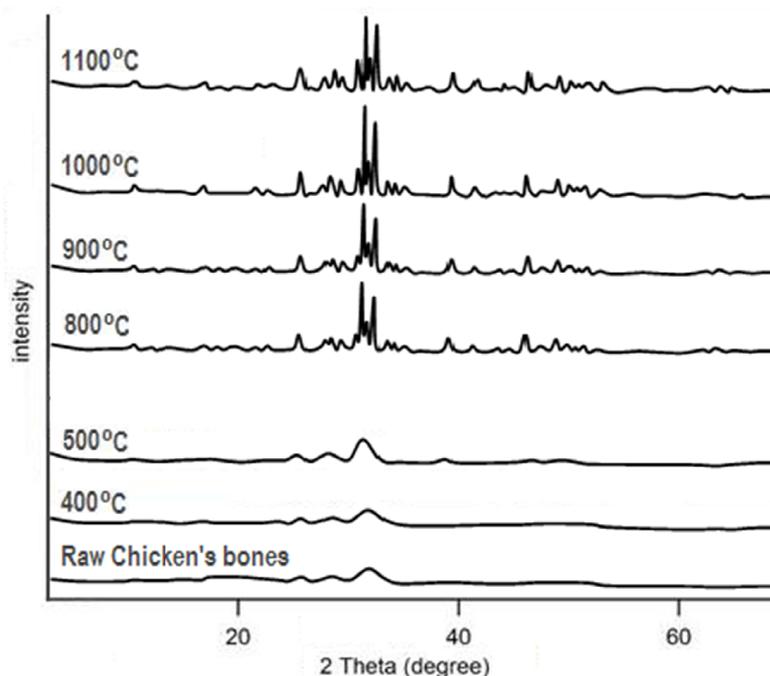


Figure 1. XRD patterns of chicken's bones with various decomposition temperatures.

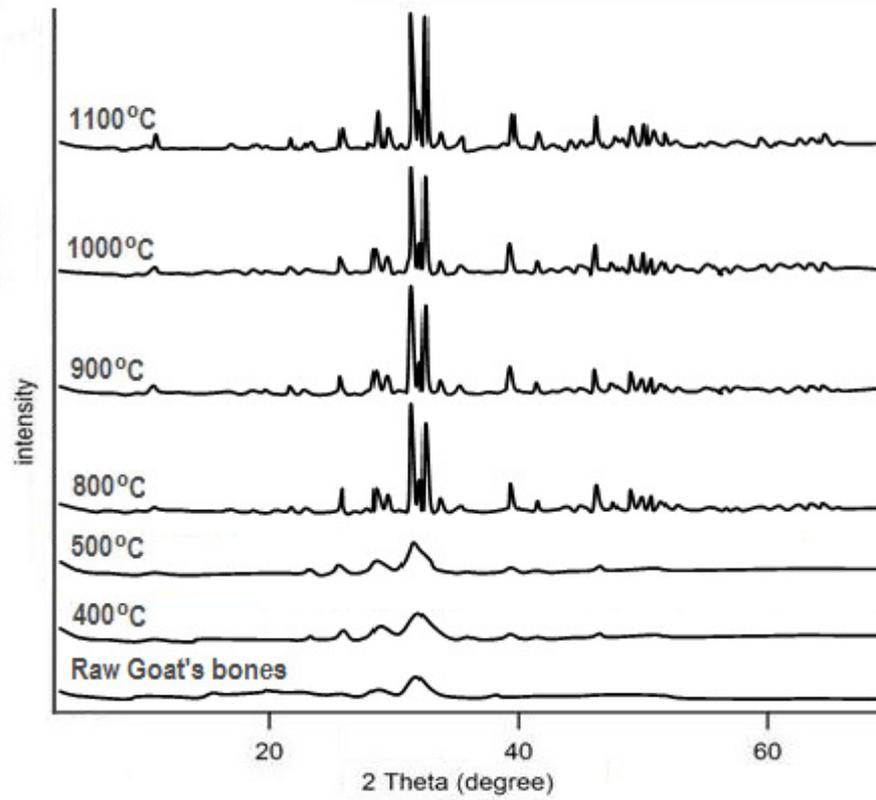


Figure 2. XRD patterns of goat's bones with various decomposition temperatures.

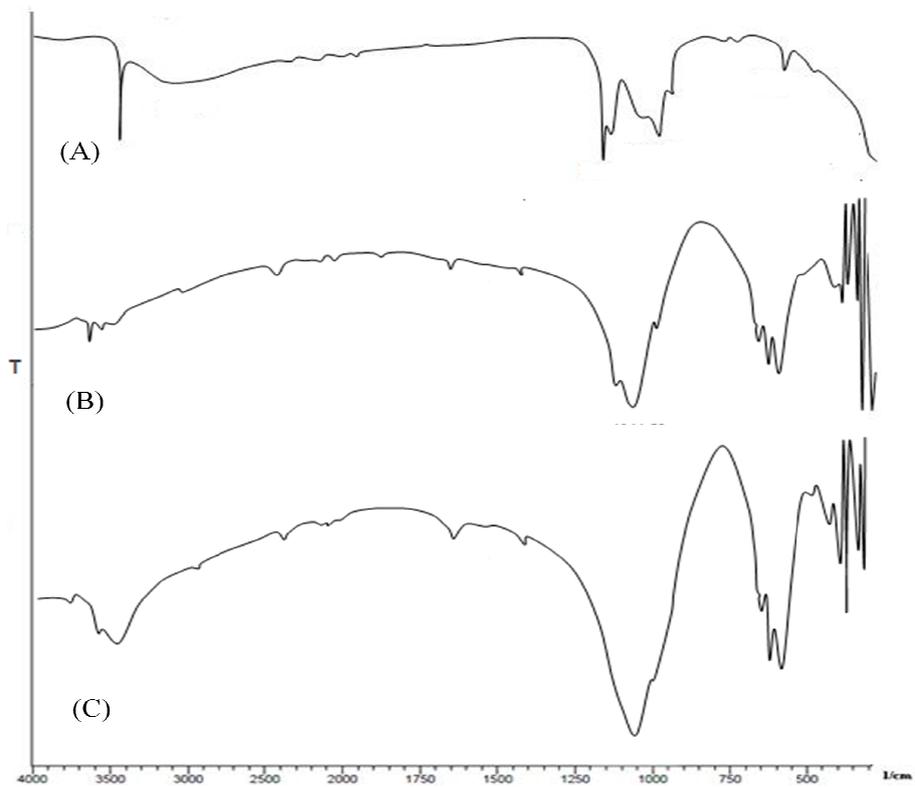


Figure 3. FTIR spectrum of calcium oxide (A), chicken's (B) and goat's (C) bones.

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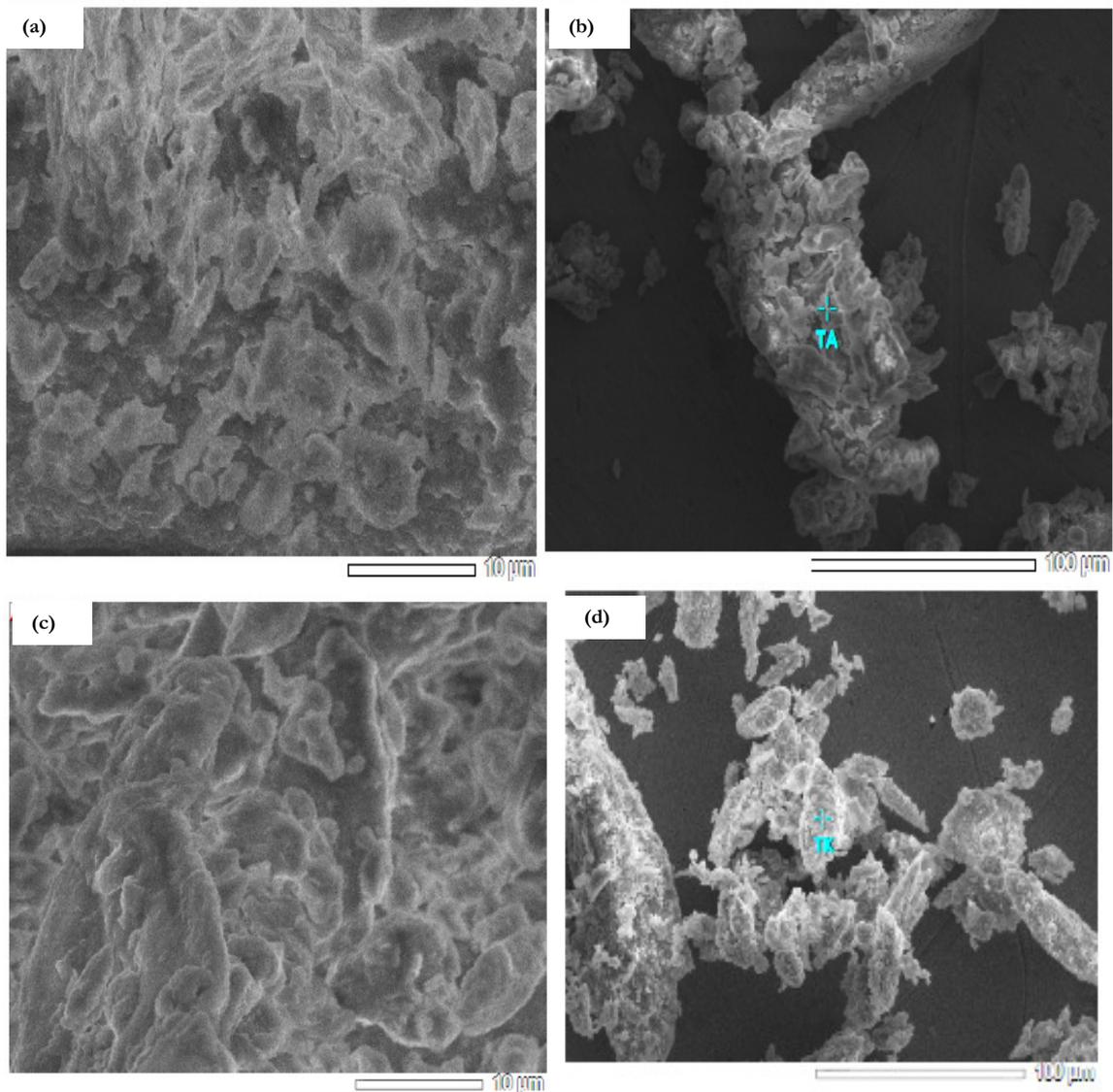


Figure 4. Scanning electron microscope (SEM) analysis for chicken's bone (a) and calcium oxide from chicken's bone (b), goat's bone (c) and calcium oxide from goat's bone (d)

SEM analysis for Comparison of SEM-EDX photo between both chicken's and goat's bones before and after decomposition at 1100 °C are showed in Figure 4. There are differences between both in their sizes and structures. Identification by SEM-EDX for the bones before and after thermal decomposition shows different particle's distribution and shape (i.e. tree like shape), it can be seen in Figure 4. These different is due to decomposition at high temperature. Calcium carbonate from chicken's and goat's bones form calcium oxide at appropriate temperatures and this is relevant with literature (Chakraborty & Banerjee, 2011). EDX data of thermal decomposition for both bones at 1100 °C show in Figure 5a and 5b. Mass percentage for the chicken's bone as measured by EDX data are as follows: oksigen (40.70%), fosfor (19.08%), calcium (34.09%), while for goat's bone contained carbon (10.78%), oksigen (36.65%), magnesium (1.32%), phosphor (17.17%) and calcium (34.09%). Compared goat's bone, the carbon content in chicken's bone decreased, while carbon and oxygen content in goat's bone increased.

Biodiesel was characterized through determination of its density, viscosity, iod number, and fatty acid value; these parameters were measured by standard method. The results of analysis of biodiesel are shown in Table 1. The four chosen parameters for biodiesel analysis were selected from the other fourteen parameters based on their simplicity without minimizing their confidence for testing

biodiesel product to meet the SNI standard. Based on the results analysis on Table 1, all of those characterization data except the goat's bone viscosity, all of them meet the SNI standard. In summary calcium oxide from chicken's bone decomposition at 1100 °C is more appropriate as base catalyst for biodiesel production (SNI 04-7182-2006) compared to that from goat's bone due to all biodiesel parameter in the range of SNI standard.

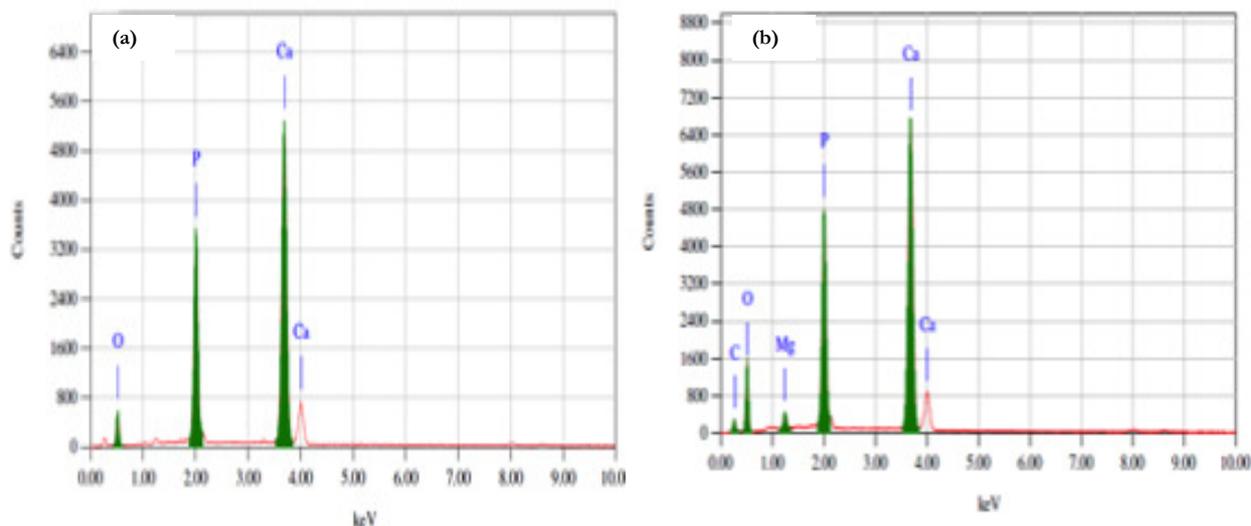


Figure 5. (a) EDX of calcium oxide from chicken's bone, (b) EDX of calcium oxide from goat's bone

Table 1. Analysis of biodiesel

No.	Parameters	SNI standards	Chicken's bone sample	Goat's bone sample
1	Iod Number	Max. 115 g I <sub>2</sub> /100 g KOH	22,42 g I <sub>2</sub> /100 g KOH	21,57 g I <sub>2</sub> /100 g KOH
2	Density	0.85-0.89 g/cm <sup>3</sup>	0.88 g/cm <sup>3</sup>	0.88 g/cm <sup>3</sup>
3	Viscosity	2.3-6.0 mm <sup>2</sup> /s (cSt)	5.91 mm <sup>2</sup> /s (cSt)	6.34 mm <sup>2</sup> /s (cSt)
4	Fatty acid value	Max. 0.8 mg/KOH	0.56 mg/KOH	0.56 mg/KOH

## Conclusion

Decomposition of chicken's and goat's bones to calcium oxide was achieved at 1100 °C. XRD patterns of decomposed chicken's and goat's bones at 1100 °C similar with calcium oxide from JCPDS standard. The data also was confirmed by FT-IR data, which fitted to the standard vibration, the specific vibration at wavenumber of 354.90 cm<sup>-1</sup> close to the specific vibration of calcium oxide. SEM photo profile show homogeneous size and distribution particle after decomposition of chicken's and goat's bones. Calcium oxide was applied for synthesis of biodiesel from discarded cooking oil resulted biodiesel characteristic values meet the National Standard of Indonesia (SNI) for biodiesel.

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