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Synthesis $Ca_3(PO_4)_2$ from tuna fish bone and potential as a catalyst in the transesterification reaction for biodiesel production

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ABSTRACT

Catalyst synthesis $Ca_3(PO_4)_2$ of waste tuna fish bones have been done. The catalyst was yielded by calcinations tuna fish bone powder on 600, 700, 800 and 1000 ^oC for two hours. Calcination of product was characterized with X-RD to Determine phase and crystalinity, SEM-EDS for analyze of metal and oxide composition. The result show that tuna fish bone have not been calcined showed a high peak at 2θ = 31.4° and 33.9°. The results of hydroxyapatite with high crystallinity nature formed on calcination temperature of 900 °C and 1000 ^oC. Analysis using SEM at a temperature of 1000 °C calcination, granule size particle is 1 μm to 2 μm with a composition there are 33.29% is P_2O_5, 0.53% is Na_2O, 0.68% is K_2O and 65.31 % is CaO.

Keywords: Catalyst, $Ca_3(PO_4)_2$, tuna fish bone, calcination, crystallinity, characterized.

INTRODUCTION

Increased demand for fuel is inversely proportional to supplies of petroleum reserves. Fuel oil is non-renewable and its availability is limited, its requires breakthroughs to find alternative energy sources that have ability to substitute fuels from petroleum, renewable and does not pollute the environment. One alternative fuels that can replace the role of oil is biodiesel. To be eligible the price, biodiesel produced should have a lower price in order to compete with diesel oil of fossil (oil) [1-7]. One method is to produce biodiesel via transesterification reaction involving methanol, catalyst and oil. Through this method, in order to get the product cheaper biodiesel can be done by modifying the type of catalyst.

Aplication of homogeneous catalysts such as KOH or NaOH in biodiesel production has the disadvantage of requiring the washing process is repeated for the purification of biodiesel, a catalyst was used can not be regenerated at the end of the reaction [8-9], finally catalyst will be removed along with the impurities and not reused (unreusable) [10-11]. Efforts are quite promising is utilization of solid catalyst such as CaO [12] and $Ca_3(PO_4)_2$ is sourced from fish bone [13-15]. The catalytic ability of the catalyst from both these sources in converting oil / lipid into biodiesel is high, the shells can convert palm oil and soybean oil 90% and 95% respectively and $Ca_3(PO_4)_2$ from waste fish bones Labeo rohita can convert soybean oil until 97.73% [16-17].

Tuna fishbone is a waste of tuna fisheries with the number reaching 15% of the body weight of fish. Bone naturally consist of 70% inorganic minerals, 20% organic matter and 10% water. The organic material is mostly made of collagen type I, whereas inorganic minerals comprised of carbonated hydroxyapatite [18]. Fish contains 60-70% of bone mineral, with the composition of 30% in the form of collagen protein and most bioapatite, including hydroxyapatite, carbonated apatite or dahlite. Constituent components of inorganic compounds predominantly fish bone calcium compounds (Ca) (135-233 g/kg) and phosphorus (P) (81-113g/kg) as well as smaller amounts of Mg, Fe, Zn, and Cu, with ratio Ca/P approached 1.67 [19,20]. Bioapatite crystal size and order fish and mammal bones are generally the same (Kim et al.1995) and contains hydroxyl (OH) is low, and also a low crystallinity. Based on this background on this research, synthesis of $Ca_3(PO_4)_2$ tuna fishbone that comes from the Maluku Islands potential

to be a catalyst for the production of biodiesel transesterification reaction. The analysis was performed with the synthesis, characterization and determination of the mineral composition of the oxide after synthesis.

EXPERIMENTAL SECTION

Tools and materials

The materials used in this study are tuna fish bones (Thunnus sp.) Obtained from the processing of tuna in Ambon, distilled water, N_2 gas, Whatman-42. The tools used are electric heaters Mammert, a magnetic stirrer (Science Ware), Balance analytical, mortar, Oven (Memert), means of calcination, thermometer 1000 ^oC, analytical balance, Quantachrome make-NOVA 4000E, canning electron microscope (SEM) (JEOL Lstd., Japan, JSM-5200), X-ray diffractometer SHIMADZU type XD610.

Catalyst preparation

Tuna fish bones washed with distilled water until clean. Furthermore, both the catalyst base material is dried in an oven at 150^oC for 1 hour. Each 1 kg of the catalyst then crushed using a pestle until smooth and sieved to sizes of not passing ± 200 mesh.

Synthesis catalysts $Ca_3(PO_4)_2$ of tuna fishbone

Solids fish bones that have been sifted and weighed as much as five times each 150 g. The synthesis process $Ca_3(PO_4)_2$ bone fish is done by entering the solids that have weighed into the calcination apparatus. Calcination process is done by heating the solids with temperature variation of 600 ^oC, 800 ^oC, 900 ^oC and 1000 ^oC for 2 hours and flowed gas N_2 gas slowly. Furthermore, the sample was cooled l and the catalyst is inserted into the bottle and sealed.

Catalyst characterization

Characterization of the catalyst made by a spectrophotometer X-ray diffractometer (XRD) Shimadzu XD-3H, Perkin-Elmer TGA analyzer (Pyris Diamond TG / DTA), the make Quantachrome NOVA 4000E, scanning electron microscope (SEM) (JEOL Ltd., Japan, JSM -5200). Diffraktometer analysis by X-ray was done using Cu Kα radiation to 2 gram sample was placed in a cell split and spectra observed at 2θ = 2 - 80^o, the observed spectra are used to determine the type, structure and degree of crystallinity of the catalyst.

RESULTS AND DISCUSSION

Preparation synthesis $Ca_3(PO_4)_2$

In this research synthesis process was done using several stages in order to obtain a catalyst with high ability. The steps being taken are yan preparation stage consists of cleaning the bones of tuna and feathering bones into powder and sieved to 200 mesh, is the process of calcining to produce the catalyst and the latter is the characterization. Sources of raw materials to synthesize $Ca_3(PO_4)_2$ is hydroxyapatite (HAp) which apatite mineral compound that has a hexagonal structure. HAp is a crystalline phase of calcium phosphate compounds are most stable. The chemical formula of HAp is $CA_{10}(PO_4)_6(OH)_2$ has the lattice parameters: a = 9,433Å, c = 6,875Å, and the ratio of Ca / P = 1.67 [28]. Excess hydroxyapatite is porous, bioactive, non-corrosive and wear resistant. A synthetic hydroxyapatite material like bones that have a nature to bind to the bone as well. The nature of the calcium ion (Ca^{2+}) on hydroxyapatite can change ions of heavy metals that are toxic and absorb elements of organic chemistry in the body [21].

Properties of hydroxyapatite which is biocompatible and can be received by the body tissues makes this material is used as raw material for the manufacture of biomaterials (materials other than drugs derived from living things/synthetic) that can treat, augment, or replace tissue or organ function of the body, as well as a adsorbent, a photocatalyst , upholstery material, and plays a role in the field of biotechnology, for example used as support material for the immobilization of enzymes, as well as good for use as hard tissue implant, which is to improve bone and teeth. Hydroxyapatite as a major component of bone is a bioactive material which has a good osseointegration properties when used in the field of orthopedics. Osseointegration is a material's ability to fuse with the bone. Osseointegration is the main condition of the materials used for implants [22]. Hydroxyapatite has reached 69% by weight of the weight of natural bone and has a hexagonal structure which is the most stable compounds in body fluids and dried in air until 1200 ^oC.

Preparation of the catalyst $Ca_3(PO_4)_2$ begins with the process of cleaning the bones of tuna from the remnants of meat and washed with hot water several times until free of meat and fats are attached, then the drying process in oven at 100 ^oC for 24 hours to remove water as in Fig. 1. Bone tuna is completely dried, then crushed and then

ground with an iron mortar and sieved to 100 mesh size. Sieving process is carried out aiming to reduce the particle size so that its surface area becomes larger as shown in Fig. 1.

Figure 1 Tuna fishbone and powder

Catalyst synthesis $Ca_3(PO_4)_2$ of tuna fish bone waste

Tuna fish bone powder that has been sifted and weighed as much as five times each 50 g. The synthesis process $Ca_3(PO_4)_2$ of tuna fish bone waste is done by inserting a solid that has weighed into the furnace. Calcination process is done by heating the solids at 600 ^oC temperature variations, 700 °C, 800 ^oC, 900 ^oC and 1000 ^oC for 2 hours. Before calcination process, the compound of HAp in the bones of tuna is $CA_{10}(PO_4)_6(OH)_2$. After calcined the compound turned into $Ca_3(PO_4)_2$.

Table 1. The results of calcination process powder tuna fisbone at various temperatures

Temperature	Times	Initial weight	Final weight	Percentage
600 ^oC	2 h	4.0426 g	1.9238	47.59 %
700 ^oC	2 h	4.0874 g	1.8702	45.76 %
800 ^oC	2 h	4.0832 g	1.8459	45.21 %
900 ^oC	2 h	4.0605 g	1.8191	44.79 %
1000 ^oC	2 h	4.0414 g	1.6910	41.84 %
Average				47.37 %

Table 1 shows that the mass mass before calcination and after calcination is reduction in the average percentage of the mass efficiency calcination results in the amount of 45.04%. The observations show that the higher the calcination temperature (sintering temperature), the yield of the resulting smaller. Calcination process at a temperature of 1000 ^oC produce yield 41.84%, calcination at 900 °C resulted in yield 44.79%, calcination 800 °C resulting yield of 45.21% and 700 ^oC resulting yield 45.76%. Calcination at 600 °C produces the most yield is 47.59% with the color gray powder. This condition indicates that the powder is still contained organic components and have not shown a high degree of purity [23]. The use of sintering temperature of 600 °C on a tuna fish bone powders are still gray [24] the same conditions was obtained as in Figure 2.

Other researchers [23] states that the value of the yield in the range of 60% or less with a color change to white indicating a more pure hydroxyapatite. The decline in the yield on the calcination process allegedly because of the loss of water and organic material contained in the material powder fish bones. Two inflection points on the bone powder tuna is at a temperature of 100.5 °C and 365.6 °C, which indicates the loss of water and organic materials.

Figure 2 Tuna fish bones colour after calcination

The inflection point at a temperature of 365.6 °C indicates a loss of collagen and other organic materials. Calcination at a temperature between (200-300) °C there was a slight loss of weight of components a combination of water and organic material [25]. Losing weight will happen drastically at the sintering temperature (300-500) °C, due to the decomposition of organic materials, namely collagen, fat and protein are associated with other components in the bone. Compounds that are left on the calcination temperature of 600 °C is Hap [26].

Characterization of catalysts

Tuna fish bones catalyst characterization by XRD

Catalyst characterization was performed using X-ray diffraction, SEM and EDX in this study aims to assess the data crystal $Ca_3(PO_4)_2$ bone tuna used. There are four phases contained in fish bones early namely apatite carbonate type A (AKA) with the molecular formula ($CA_{10}(PO_4)_6(CO_3)_2$), apatite carbonate type B (IMR) with the molecular formula ($CA_{10}(PO_4)_3(CO_3)_3(OH)_2$), tricalcium phosphate (TKF) with the molecular formula ($Ca_3(PO_4)_2$) and octa calcium phosphate (OKF) with the molecular formula ($Ca_8H_2(PO4)_6.5H_2O$). The mineral apatite phase is already contained in the fish with a low crystallinity [27-28].

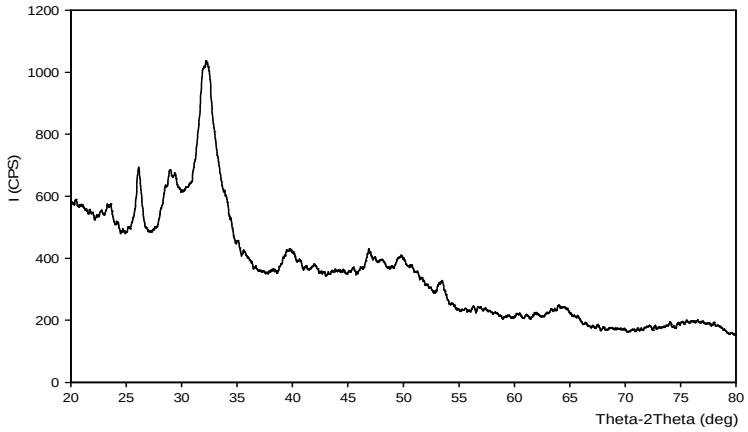


Figure 3 Diffractogram of tuna fish bone iniatially

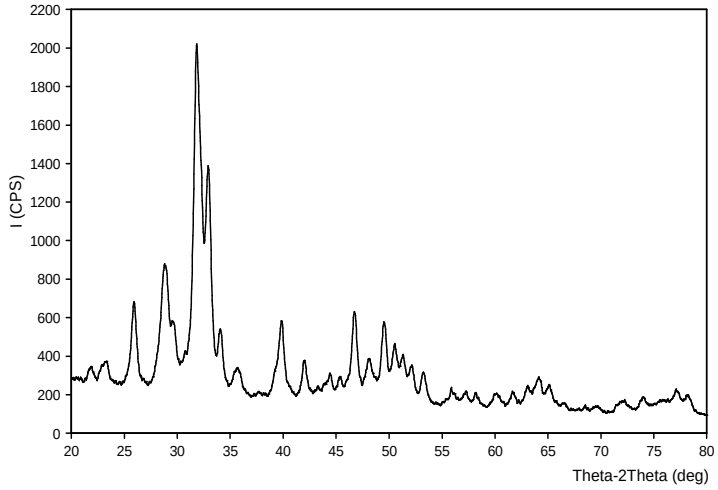


Figure 4. Diffractogram of tuna fish bone after calcination at 600 °C

In identifying compounds calcination phase dicalcium triphosphate results can be analyzed using XRD. X-ray diffraction patterns of tuna fish bone powder before calcination at the calcination temperature of 600 °C, 800 °C, 900 °C and 1000 °C is presented in Figure 3 to Figure 7. XRD diffraction patterns produced showed that the peaks of the XRD patterns are shifting as with calcination temperature increases. Before calcination obtained the highest peak at 2θ = 31.4° and 33.9° which is characteristic of hydroxyapatite phase.

At the time of the calcination at a temperature of 600 °C not show significant peak shifts in samples of tuna fish bones. Another emerging phase in addition to hydroxyapatite after calcination at a temperature of 800 °C (Figure 8) is a carbonate apatite type A, tricalcium phosphate and phosphate oktakalsium. Carbonate apatite type A was

detected at 2θ = 21.8°, oktakalsium phosphate detected at 2θ = 29.9° and 41° while the tricalcium phosphate is detected at an angle 2θ = 35.6°, 44.5°, 51.2° and 57.0°.

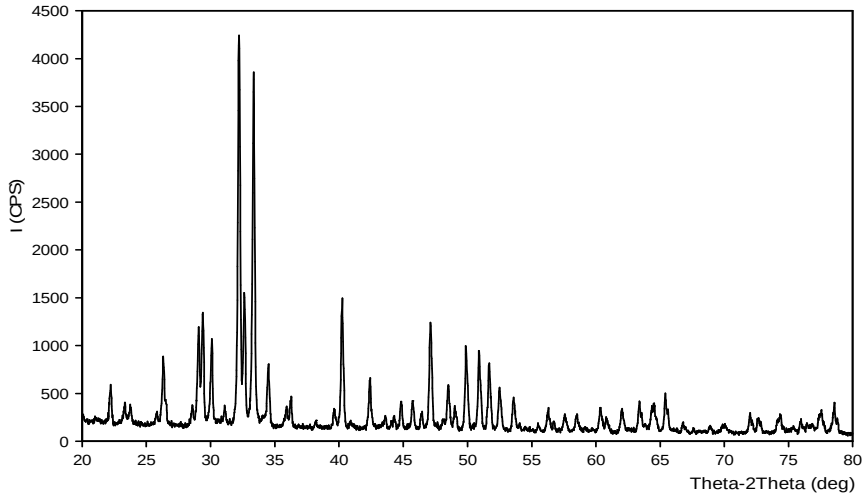


Figure 5 Diffractogram of tuna fish bone after calcination at 800 °C

Phase compound tricalcium phosphate (TCP) which appear indicating the process of decomposition of HAp compound in the sintering process 1.200 °C (Prabarakan and Rajeswari 2006). X-ray diffraction pattern at a temperature of 800 °C showed the highest peak of Hap with 2θ = 33.7°. The result diffraction pattern is dominated by the phase of hydroxyapatite, but there are others, namely phase carbonate apatite type B (51.0°), and oktakalsium phosphate (22.9°, 32.6°, 42°, and 43.9°).

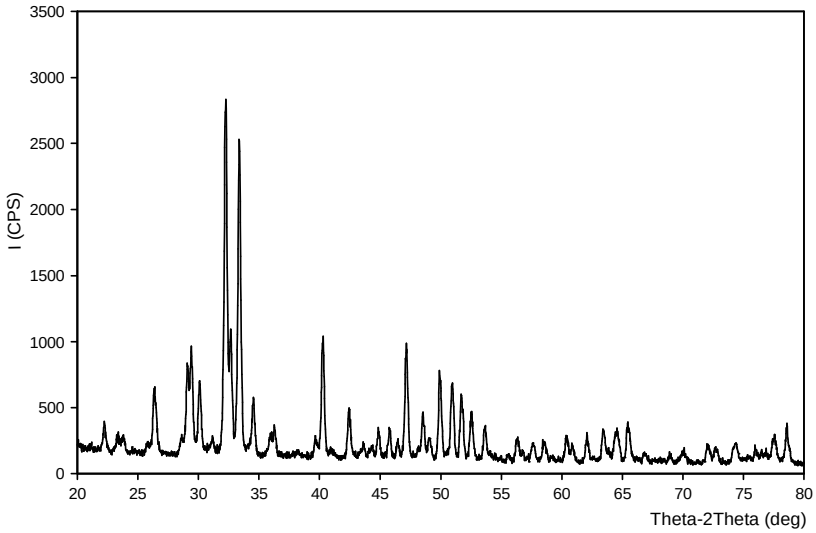


Figure 6 XRD result of tuna fish bone after calcination at 900 °C

The results of hydroxyapatite with high crystallinity nature formed on calcination temperature of 900 °C and 1000 °C views from the highest peak compared to the peak at calcination temperature of 600 °C and 800 °C. The highest peak in the diffraction pattern of the sample with calcination temperature of 900 °C and 1000 °C is found at an angle 2θ = 33.9°. Hydroxyapatite is formed there are other phases, namely AKA, AKB, OKF, and TKF. AKA phase shape can be formed at high temperatures and replace Hap-OH in the structure, while the AKB phase can be formed at lower temperatures by replacing ion $(PO^4)^{3+}$ [26].

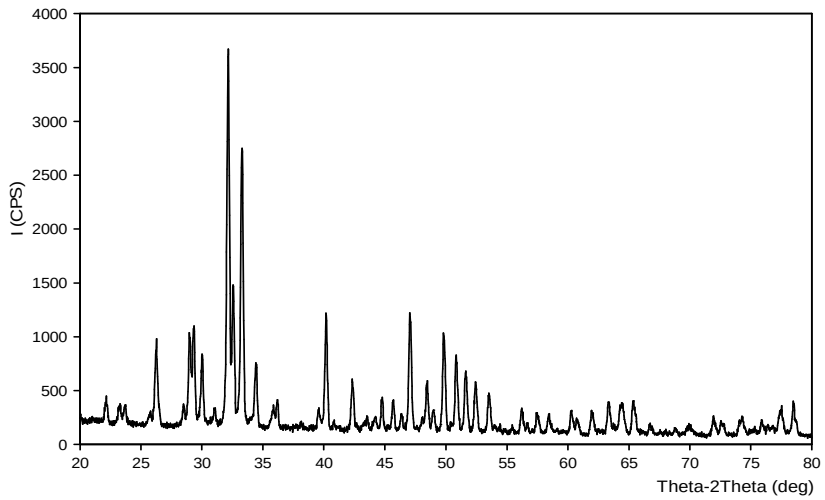
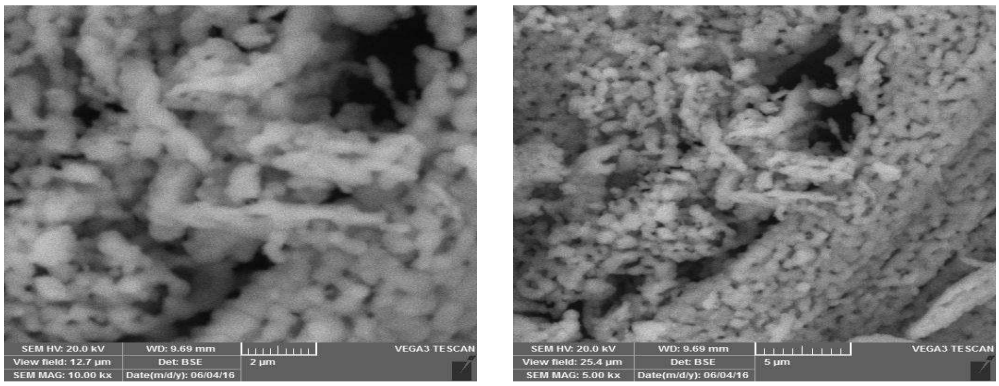


Figure 7 XRD result of tuna fish bone after calcination at 1000 ºC

Tuna fish bones catalyst characterization by SEM

Fishbone generally contain hydroxyapatite with a very low degree of crystallinity. Fish bones will turn into hydroxyapatite with high crystallinity on the heating temperature (800-1200) °C [27]. Catalysts Ca_3 $(PO_4)_2$ is generally made from fish bones through a calcination process at temperatures > 600^oC. At a temperature of 600 ^oC visually would seem that the hydroxyapatite powder is composed of stacks that are still solid. Visual analysis of the catalyst made by using a SEM to fish bone powder at a temperature at 600 ^oC with a magnification range can be seen in Figure 8.



(a) **(b)**

Figure 8 Analysis of the morphology of the tuna fish bones on the calcination temperature 1000 ° C magnifications (a) 5000 times (b) 10000 times

SEM characterization by calcination at temperature of 600 ^oC showed that the constituent particles of samples that form hydroxyapatite is not all either change the structure or a constituent. There are some parts that have undergone changes give clues already a fraction the constituent change their structure and form other compounds. This visualization indicates that the calcination process at a temperature of 600 ^oC has not been able to change hydroxy apatite into pure $Ca_3(PO_4)_2$.

After calcination at 1000 °C was obtained visualization of changes in the structure of the fish bone powder form uniform particles. According to [27] that the hydroxyapatite is not spherical, the particle form varied and resembles a crystal form. The composition and distance constituent particles of hydroxyapatite samples are also irregular. Microcrystals contained in fish bones are very small, the size of the crystal particles of 5-10 µm. The microstructure of hydroxyapatite vary in size and are influenced by temperature treatment is used [27].

The morphology of hydroxyapatite which has undergone a process of heating crystalline and the crystal crumbled / irregular, alleged that the crystal size increases with increasing temperature used [23]. Samples with calcination temperature of 1000 °C has a granule size larger particle is 1 µm to 2 µm. Granule size difference thought to be caused due to the calcination process is carried out.

Tuna fish bones catalyst characterization by EDS

Elemental composition of the oxide catalyst calcination results conducted to identify the content of the catalyst that has been synthesized. Samples analyzed were the result of calcination at a temperature of 600 ^{o}C and 1000 ^{o}C. Based on the results of EDS analysis of elemental composition of the oxide can be seen in Figure 9.

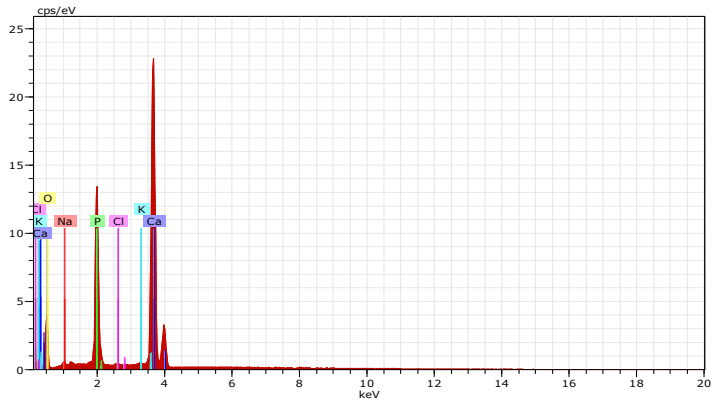


Figure 9 The catalyst composition of fish bones at the calcination temperature of 600 ^{o}C

Based on the results of EDS analysis using the obtained information that the calcination temperature of 600 ^{o}C the main content of the sample is shown by the high calcium intensity obtained. The complete kompiosisi calcined catalyst at a temperature of 600 ^{o}C summarized in Table 2.

Table 2 Contents of the element and oxide catalysts tuna fish bones at the calcination temperature 600 oC

Elements	Weigth (%)	Compounds	Weight (%)
Sodium	0.4	Na_2O	0.53
Phosporus	14.53	P_2O_5	33.29
Calsium	46.67	CaO	65.31
Potasium	0.57	K_2O	0.68
Clorine	0.19		
Oxigen	28.88		

Table 2 provides information about the quantity of catalyst oxides contained the bones of tuna which are synthesized by calcination at a temperature of 600 ^{o}C. At this temperature calcination the catalyst contains oxides are as much as 33.29% P_2O_5, Na_2O as much as 0.53%, 0.68% K_2O and CaO as much as 65.31%.

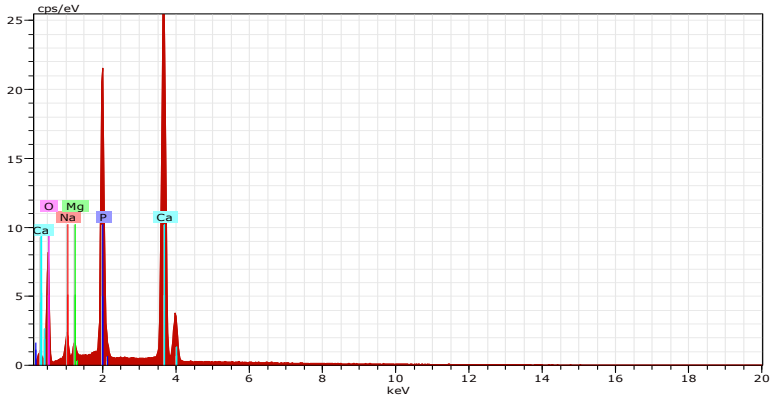


Figure 10 The catalyst composition of tuna fish bones at the calcination temperature 1000 °C

The catalyst composition is calcined at a temperature of 1000 ^{o}C visible in Figure 10 shows that the elemental composition of Ca contained in the sample decreased from 47.67% at 600 ^{o}C calcination temperature becomes 39.91% on calcination using temperatures 1000 ^{o}C. This fact strongly supports the hypothesis that the calcination process can be used to improve the content of tricalcium diphosphate is contained in the bones of tuna.

Table 3 Content of element and oxide catalysts tuna fish bones at the calcination temperature 1000 ^{o}C

Elements	Weigth (%)	Compounds	Weight (%)
Sodium	2.93	Na_2O	3.94
Magnesium	1.04	MgO	1.73
Phosphorus	16.80	P_2O_5	38.49
Potasium	39.91	CaO	55.84
Oxigen	39.33		

In addition Table 3 also shows in addition to the content of tuna fish bones are calcined at a temperature of 1000 ^{o}C formed. CaO content is 55.84% indicates that this material can serve as a catalyst for the transesterification reaction transeterifikasi mainly used oil into biodiesel. Improving the ability of these catalysts in the transesterification reaction is supported also by the presence of MgO in this material. These oxides have a catalytic ability large enough. By maximizing the function of these two oxides as catalysts is expected to speed up the reaction tranesterifikasi to produce biodiesel using heterogeneous catalyst [12].

CONCLUSION

Based on the research that has been done, it can be concluded as follows:
1.The tuna fish bones that have not been calcined showed a high peak at 2θ = 31.4° and 33.9° which is characteristic of hydroxyapatite phase. Calcination at a temperature of 800 ^{o}C obtained carbonate apatite type A, tricalcium phosphate and phosphate oktacalsium.
2. The results of hydroxyapatite with high crystallinity nature formed on calcination temperature of 900 °C and 1000 ^{o}C
3.Visual analysis at 600 ^{o}C showed that the constituent particles of samples that form hydroxyapatite is not all either change the structure or a constituent.
4.Samples with calcination temperature of 1000 °C has a granule size larger particle is 1 μm to 2 μm with a composition that is as much as 33.29% P_2O_5, Na_2O as much as 0.53%, 0.68% K_2O and CaO as much as 65.31 %.
5.The catalyst composition calcined at a temperature of 1000 ^{o}C shows the elemental composition of Ca decreased from 47.67% at 600 ^{o}C calcination temperature becomes 39.91%
6.The composition of CaO and MgO tuna fish bones transesterification potential as a reaction catalyst for biodiesel production

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