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# Effect of Hydrothermal Temperature on the Synthesis of Palm Oil Shell-Based Zeolite

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**Abstract :**
Palm oil shells are one of the solid waste in palm oil processing plants, currently the use of palm oil shells is only used as activated charcoal. Though the mineral content potential contained in palm oil shell is very large, one of them is silica ($SiO_2$) of 71.1% with a large amount of this can be used as a source of silica.
The source of silica shell of palm oil in this research is used as the basic material of zeolite manufacture. Zeolite is a hydrated aluminasilicate compound which has many benefits such as catalyst, adsorbent, and ion exchanger. Zeolite fabrication method is a common and widely used hydrothermal method, because this process does not require a high temperature with a relatively short time. Palm oil shells are used to remove carbon in them and the ash is characterised using XRF. Palm oil ash was crushed together with NaOH they were melted at 500°C or 1 hour, and added with distilled water and soaked 24 hours, produced Sodium Silicate and characterised using FTIR. For Alumina, NaOH was reacted with Al(OH)3 to produce Sodium Aluminate and characterised using FTIR. Zeolite preparation was carried out by mixing the sodium silicate and sodium aluminate reactants and the zeolite crystallisation process was carried out using a hydrothermal reactor heated in an oven by varying the hydroternal temperature at 120˚C, 150˚C and 180˚C for 8 hours. Synthesized zeolite was characterised using XRF, XRD and SEM. FTIR analysis Sodium Silicate has been formed at wave number 981.19 cm-1 symmetric vibration Si-O (Na) strectching, and Sodium Aluminate has been formed at wave number 719.87 cm-1 with symmetric vibration Al-O (Na) stretching. The result of XRD characterisation at 120°C produces mixed zeolite of type 4A, Sodalit and Faujasit. At the temperatures of 150°C and 180°C formed Sodalite type zeolite. The best crystallinity was obtained at a hydrothermal temperature of 150°C and analysed using SEM, showing the small cubic crystal form bonding to each other to form an elongated geometry.

**Keywords**: Palm Oil, Zeolite, Sodium, Aluminate, Sodium Silicate

## 1. Introduction

Palm oil is one of the plantation commodities that Indonesia relies on to bringin foreign exchange every year. Indonesia is currently the second largest palm oil producer in the world after Malaysia with an average total production of 9.9 million tonnes per year since 2003. Projections for the next few years predict that Indonesia will occupy the first position. The market prospect for processed palm oil is quite promising, because the demand from year to year has increased considerably, not only domestically but also abroad.

In the palm oil or CPO processing industry, industrial waste will be obtained. Palm kernel shell is one of the wastes that amount to 60% of the production of kerneloil or PKO. Oil palm shell waste is grey-black in colour, irregular in shape and has ahigh hardness. Palm kernel shell has a main content of Silicon Oxide ($SiO_2$ ) which has reactive properties and good pozzolanic activity that can act into hard and stiff

materials. According to Hutahean (2007) palm kernel shell ash contains many minerals such as SiO2 58.02%; Al O23 8.7%; Fe O23 2.6%; CaO 12.65%; MgO 4.23%; Na2 O 0.41%; K2 O 0.72%; H2 O 1.97%; missing incandescence 8.59%.

Currently, the use of shells has not been maximised and only some of them areused to fill roads. One of the reasons is because this type of waste is very difficult to decompose naturally. One alternative technology that can be a solution to the problem of handling solid palm oil waste is the hydrothermal technique. With hydrothermal techniques, palm oil solid waste can be processed quickly to produce products, one of which is zeolite. The reason why oil palm shells are used as a source of silica insteadof natural silica sources such as pumice, fly ash, rice husk ash, kaolin, diatomite and smectite is because the use of these mineral materials is of low economic value andeasier to obtain.

Zeolite is a natural rock or mineral that chemically belongs to the silica mineral group and is expressed as hydrated alumina silicate, is fine, and is a secondaryproduct that is stable at surface conditions because it comes from sedimentation, weathering and hydrothermal activity in basic igneous rocks. This mineral is usually found filling the cracks or fractures of the rock. In addition, zeolites are also depositsof volcanic activity that contain a lot of silica.

In research conducted by Mimin (2016), zeolite 4A has been successfully synthesised from palm waste ash which is used as a source of silica. And in previous studies the raw materials used were palm coir ash and palm kernel shell fly ash, thenthe variations used in the synthesis of zeolite 4A ranged from stirring time, gel heating time and stirring speed (Murni (2006), Yelmida (2012) Zahrina (2012)). In the research conducted by Jahro *et al.* (2015) who successfully synthesised zeolites 4A and 13X from oil palm shells by looking at the quality of the synthesised zeolites which were influenced by the Si / Al ratio in the synthesis base material and gel formation. In research conducted by Alim (2015), successfully synthesised zeolite from *Fly Pofiia* with the results of characterisation using XRD, FTIR and SEM showingthat at T = 150 ° C has the best crystallinity with the type of Sodalite zeolite with the chemical formula Na6 [AlO4 SiO ]46 .8H2 O with a cubic crystal structure.

Zeolites can be synthesised by several methods, one of which is the melting method followed by a hydrothermal process. The use of this method produces zeolites with higher purity than direct hydrothermal. Hydrothermal is formed from the word hydro which means water and thermal which means heat, so it can be estimated that the hydrothermal method uses heat and water whose properties change the solutioninto solids. In practice, this method involves heating reactants in a closed container (autoclave) using water. In a closed container, the pressure increases and the water remains as a liquid. The hydrothermal method (using water as a solvent above its boiling point) must be carried out in a closed system to prevent loss of solvent when heated above its boiling point.

## 2. Research Methods

### Tools and Materials

The materials used in this research are oil palm shells from PT PN VI Bunut, Sodium Hydroside (NaOH), Aluminium Hydroxide $Al(OH)_3$ and distilled water.

Tools that will be used to support this research include analytical scales, glass cups, erlenmeyers, measuring cups, funnels, measuring *fiilasks*, spatulas, stirring rods, mortar, pestle, *shaker*, *Fourier Transfiiorm Infiira Red* (FT-IR), *X-ray Flourescence (*XRF), *Scanning electron microscope (*SEM), *X-Ray Difiifiiraction* (XRD), motor stirrer, magnetic stirrer, oven, muffle furnace, pH meter, dropper pipette and sieveshaker.

### Preparation and Characterisation of Palm Kernel Shell Ash

Oil palm shell samples were obtained from PT Perkebunan Nusantara VI which is a by- product of oil palm processing. The sieved shell ash was initially characterised using an XRF instrument to determine the content of compounds contained in the oil palm shell ash. The results of the XRF analysis can be seen in Table 1.

Table 1. XRF analysis of palm kernel shell ash

| Elements | Content (%) |
|---|---|
| Si | 71,10 |
| Ca | 12,90 |
| K | 5,96 |
| Mg | 4,83 |
| Al | 1,44 |
| Fe | 1,10 |
| S | 1,01 |
| Zn | 0,69 |
| P | 0,64 |
| Mn | 0,09 |

From the results of XRF analysis, it is known that Silica in the palm kernel shell ash sample is the most content of 71.1%. With the amount of silica contained in this sample,it can be utilised in the process of making zeolite.

**Zeolite Preparation**

Zeolite is a porous alumina silica crystal material with a three-dimensional structure formed from alumina tetrahedra and silica tetrahedra with cavities containing metal ions, usually alkali or alkaline earth metals (mainly Ca and Na) and water molecules that can move freely in the zeolite cavity (Payra et al, 2003). The preparation of zeolites was carried out using palm shell samples as a source of silica with the addition of aluminate, with the method used being the hydrothermal method.Water Content Testing (ASTM D 3173-03)

**Sodium Silicate Recombinant Preparation**

The palm kernel shells were sieved to a size of 100 mesh to homogenise the particle size. The sieved palm kernel shells were refined at 600°C for 8 hours. From 10 grams of palm kernel shells, only about 0.8-0.9 grams of amorphousash was produced. The ash obtained was added to NaOH while being crushed.Ash and NaOH were melted at 500°C for 1 hour. This melting aims to separate the silicate in the amorphous solids of palm kernel shell ash so that it reacts with NaOH and forms sodium silicate which is the main component of zeolite (Sutarno, 2000 ). The reaction that occurs:

$$2NaOH(s) + SiO_2(s) \rightarrow Na_2SiO_3(aq) + H_2O(aq)$$

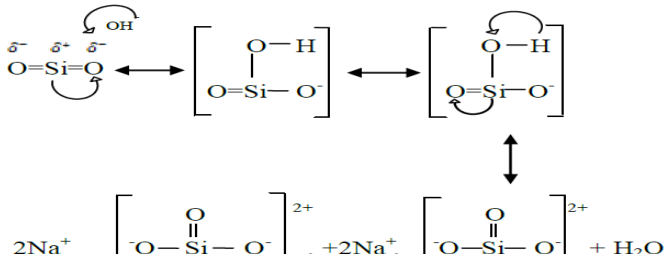

Figure 1. Reaction mechanism of sodium silicate formation (Alex, 2005)

**Sodium Aluminate Reactant Preparation**

Aluminate is made by reacting NaOH solution with $Al(OH)_3$. The addition of $Al(OH)_3$ into NaOH solution forms a white colloid. The process of making Sodium Aluminate must be in an alkaline atmosphere with the aim of balancing because the O atom in NaOH has a higher electronegativity price than Si/Al so that $H^+$ will be bound to the O atom (Trisunaryanti, 2006).

Sodium Aluminate formation reaction:

$$NaOH(aq) + Al(OH)_3(s) \rightarrow NaAlO_2(aq) + 2H_2O(aq) \rightarrow NaAlO_2(aq) + 2H_2O(l) \rightarrow NaAl(OH)_4(aq)$$

Reaction mechanism :

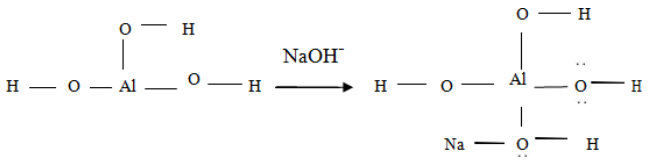


Figure 2. Formation of sodium aluminate (Putriani, 2018)

**Zeolite Synthesis Process**

The process of making zeolite is done by reacting sodium silicate solution with sodium alimunate. The result of mixing this solution forms a white gel which isthen stirred for 3 hours. The formation of the gel shows the interaction between Silicate and Alimunat in the formation of the core and the growth of zeolite crystals. Crystallisation in zeolite formation is achieved from the solution phaseto the gel phase and then to the solid phase. The process occurs continuously starting with the condensation reaction and followed by the polymerisation of saturated solutions forming Si-O-Al bonds (Hamdan, 1992). Furthermore, the crystallisation process is carried out by hydrothermal treatment using a reactor by varying the hydrothermal temperatures of 120°C, 150°C and 180°C for 8 hours.

Temperature can affect the type of product that crystallises, increasing temperature will increase denser products because the resulting porous product decreases as the water fraction in the liquid phase decreases. In the crystal formation stage, the amorphous gel will undergo rearrangement in its structure by heating so that a crystal core embryo is formed.

The results of the hydrothermal process with temperature variations of 120°C, 150°C, and 180°C are in the form of solids. The colour of the solids formed varies based on temperature variations. For a temperature of 120 ° C, a white solid is obtained and a temperature of 150 ° C, a brownish white solid is obtained.

Then the solids were washed with distilled water until the filtrate was clear. The purpose of this washing is to remove the remaining NaOH in the zeolite. After washing, the solids were dried at 80°C for 4 hours to reduce the water content in the synthesised zeolite so as to obtain dry solids with constant weight.

To identify the resulting zeolite, characterisation was carried out using *X-Ray Fluoresence* (XRF) to determine the composition of the resulting zeolite, X-Ray Diffraction (XRD) to determine the crystal structure, type of zeolite and crystallinity and *Scanning Electro Microscope* (SEM) was used to see the morphological shape of the synthesised zeolite.

**Data Analysis**

Data - the results of research that has been collected in the form of quantitative data. The data obtained were statistically analysed using Variance (ANOVA) used to determine the real effect or not the variation of raw material temperature on the qualityand quality of zeolite produced. Calculation of analysis of variance is done using the hydrothermal stage test

## 3. Results and Discussion

**Zeolite Synthesis Process**

The process of making zeolite is done by reacting a solution of Sodium Silicate with Sodium Alimunat. The result of mixing this solution forms a white gel which is then stirred for 3 hours. The purpose of this stirring is to homogenise the mixture and accelerate the reaction between Sodium Silicate and Sodium Aluminate due to stirring so that the frequency of collision of molecules will occur greater and the reaction will take place quickly. Based on research conducted (Yelmida et al, 2011) which synthesised zeolite from palm *fiily ash*, the best variation of stirring effect was obtained at 3 hours at room temperature. Mixing between sodium silicate and sodium aluminate accompanied by stirring will form a white gel.

**Analysis of Zeolite in the Hydrothermal Process**

Characterisation of Zeolite at 120 and 150 with X-Ray Diffraction (XRD)

After knowing the Si/Al ratio in the zeolite synthesised at 1200 C, 1500 C, so to prove the type of zeolite formed, analysis using X-Ray Diffraction (XRD) which is a qualitative analysis method that provides information aboutthe crystal structure of a particular mineral. The crystallinity of the sample isseen from the diffractogram pattern. Difactograms that have clear separation of peaks and high peak sharpness intensity have good crystallinity. XRDresults for zeolite at 120°C, 150°C,

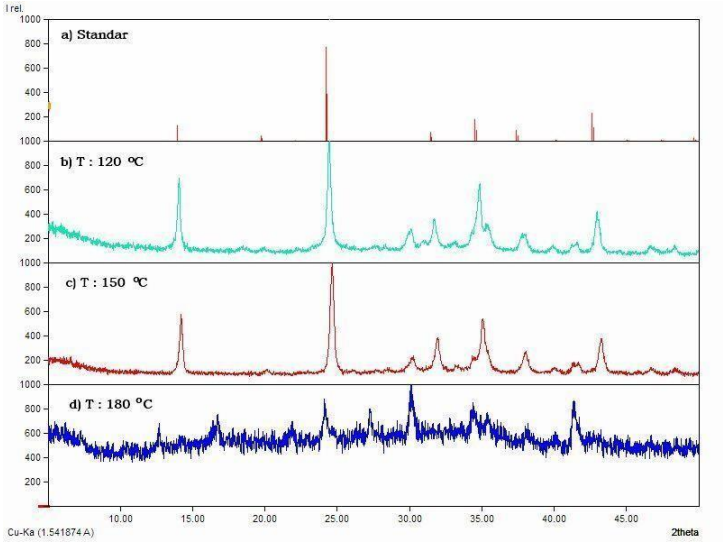


Figure 3.XRD pattern for zeolites at temperatures of (a)120°C, (b)150°C, and (c)1800 C and JCPDS Standard

From Figure 3, it is known that different temperatures give different diffractogram results with different peak intensities. At 120°C there are 12 *peaks* and 150°C there are 8 peaks at 2θ (Table 1)

Table 1. 2θ angle position of zeolite 120° and 150°C

| No . | Zeolite T: 120°C (Pos. [°2Th.]) | Zeolite T: 150°C (Pos.[°2Th.]) |
|---|---|---|
| 1 | 14.09 | 14.22 |
| 2 | 24.41 | 24 .66 |
| 3 | 30 .18 | 30.30 |
| 4 | 31.73 | 31.97 |
| 5 | 34.84 | 35.08 |
| 6 | 35.43 | 38.08 |
| 7 | 37.74 | 41.70 |
| 8 | 39.91 | 43.30 |
| 9 | 41.64 | |
| 10 | 42.95 | |
| 11 | 46.71 | |
| 12 | 48.37 | |

Table 2. Phases formed from the synthesized solids

| Sample | Zeolite A (Pos. [°2Th.]) | Sodalit (Pos. [°2Th.]) | Faujasit (Pos.[°2Th.]) | Products |
|---|---|---|---|---|
| **120°C** | 31.73, 39 .91 41.64, 46.71, 48.37 | 14.09, 24.41, 34.84, 35.43, 37.74, 42.95 | 30 .18 | Zeolite A, Sodalite, Faujasite |
| **150°C** | - | 14.22, 24 .66 35.08, 38.08, 43.30 | - | Sodalit |
| **Standard** | 10.15, 12.45, 16.09, 21.64, 23.96, 27.08, 29.91, 34.15 (ASTM no. 39-222) | 14.06, 19.94, 22.30, 24.48, 28.33, 31.77, 34.89, 37.78, 41.53, 42.66, 44.16, 47.34. | 10.11, 11.86, 15.60, 20.27, 27.70, 30.62, 32.32, 34 .50 (Breck, 1974) | |

The zeolite phases formed in Table 2 show that at 120°C the mixed zeolite phases are Zeolite A, Sodalite and Faujasit. Zeolite type A is classified in 3 different types namely 4A, 5A and 6A the process and main components are the same only different types of cations.

Table 2 shows the values of 2θ = 31.73, 39.91 41.64, 46.71, 48.37 at 120°C which makes the zeolite 4A formed not much different from the standard zeolite 4A and previous research literature.

Another type of zeolite that appears at 120°C is Sodalite, there are 6 peaks at2θ that show Sodalite peaks. Figure 5(c) shows the results obtained at 150°C there are 6 main peaks with good intensity and in accordance with the standard. The 6 peaks appearing at 2θ = 31.73, 39.91, 41.64, 46.71, 48.37 are identified as peaks belonging to Sodalite with increasing intensity. Meanwhile, zeolite 4A and Faujasit were no longer identified at 150°C from the XRD analysis results due tothe absence of peaks from zeolite 4A and Faujasit. According to Treacy (2001), Sodalite appears at 2θ = 13.93°; 24.26°; 31.55°; 32.53°; 34.61°; 37.44°; 41.53°;42.66°; 44.16°; 47.34°, for Faujasite appears at 2θ = 30.18° which is the skeleton of zeolite X.

Zeolite 4A and Faujasit are zeolites composed of *cage* Sodalite which bindsto the double ring D4R and D6R. Not forming zeolite 4A and Faujasit at 150 ° C can be indicated that zeolite 4A and Faujasit formed at 120°C is still in a less stable state so that the phase of zeolite 4A and Faujasit dissolves at 150°C. From Figure 3 it can be seen that the increase in temperature from 120°C to 150°C produces a better level of crystallinity and also the purity of zeolite obtained is getting better because no more mixed zeolite is formed.

Zeolites produced in this research at 150°C hydrothermal temperature conditions have a better level of crystallinity compared to crystallinity at 120°C hydrothermal temperature. Previous research conducted by Mimura et al (2001) higher hydrothermal temperatures will obtain hydrothermal products have better crystallinisation. Pure zeolite with high crystallinity will produce a very clear narrow peak with a low and flat baseline (Attkins, 1999).

**Zeolite Characterisation with Scanning Microscope (SEM)**

Analysis using SEM aims to look at the morphology of the particle shape on the surface. In principle, surface analysis involves surface radiation with a source of energy sufficient to penetrate and cause emission from the surface of the energy beam that can be analysed. The following are the results of SEM analysis for Sodalite at 150°C.

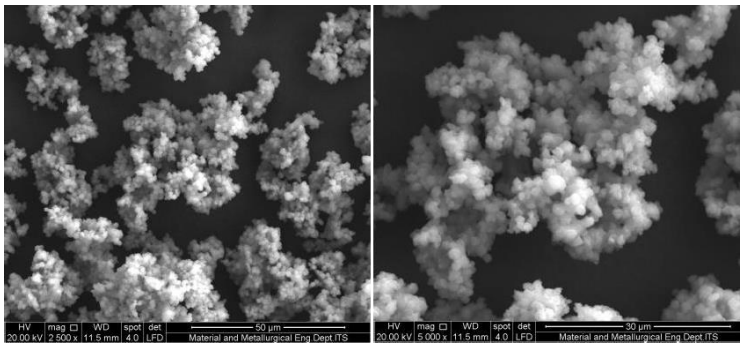

Figure 4. SEM images of Sodalite magnification 30.0µm (2500x), 20.0µm (5000x)

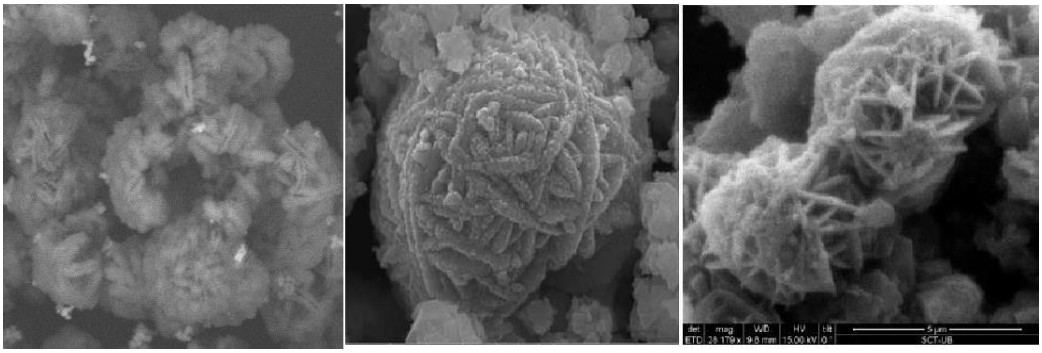

Figure 5. (A) Sodalite T:150°C, (B) Sodalite (Fajar, 2012) and (C) Sodalite (Daniela et al, 2010).

From the results of SEM analysis Figure 5(A) Sodalite has the same shape similarity with the results of research (Fajar et al, 2012) Figure 5(B) and research (Daniela et al, 2010) Figure 5(C). Cube-shaped crystals with small and smooth and elongated sizes that are bonded together are the crystal form of Sodalite. Cubes of small size that bind together to form elongated geometry are more dominant when compared to cubes of larger size. The morphology of SEM results shows the presence of pores formed in each Sodalite crystal (Wajima, 2005). One of the properties or characteristics of zeolite is porous because zeolite crystals are a framework formed from a tetrahedral mesh of SiO4 and $AlO_4$ (Lobo et al, 2001). The SEM results also show uniform crystal shape and no other crystal shapes. This shows that in the hydrothermal results with a temperature of 150°C the best temperature zeolite formed the most and there is no mixture of other zeolites is Sodalite.

**Conclusion**

From the results of the research conducted, it can be concluded that:

1. The preparation of zeolites from palm kernel shells was carried out by melting palm kernel shell ash with NaOH base to obtain Sodium Silicate and reacted with Sodium Aluminate using a hydrothermal reactor.
2. Hydrothermal temperature variations produce different types of zeolites with different levels of crystallinity. At T = 120 ° C produces mixed zeolites namely 4A, Sodalite and Faujasit, at T = 150 ° C produces Sodalite and at T = 180 ° C is more likely to be amorphous.

3. The results of characterisation using XRF, XRD and SEM show that at T=150°C has the best crystallinity with the type of zeolite Sodalite with the chemical formula $Na_6[AlO_4SiO]_{46}.8H_2O$ with a cubic crystal structure.

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