Zeolite Na-P1 Derived from Palm Oil Mill Fly Ash: Synthesis and Characterization

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Abstract. Palm oil mill fly ash is the solid waste of palm oil industry having silica content around 39 %. Synthetic Amorphous Silica (SAS) can be synthesized from the fly ash by alkaline extraction method combine with sol-gel precipitation. In this research, the SAS was used as the raw material for zeolite Na-P1 synthesis by hydrothermal process. The synthesis process was done in stainless steel autoclave and the operating conditions were: pressure of 200 kPa, temperature of 120 °C and time of 8 hours. The aluminium source was Al2O3, the Si/Al ratio used were 5, 8 and 11 while the sodium hydroxide concentration were 1, 2 and 3 N. The zeolite obtained was characterized using XRD and the diffraction pattern was compared to the zeolite Na-P1 from other references.

Keywords: palm oil mill fly ash, Si/Al ratio, synthetic amorphous silica, synthesis, zeolite Na-P1

1. Introduction
Alkali extraction combine with sol-gel precipitation can be used to synthesize Synthetic Amorphous Silica (SAS) from Palm Oil Mill Fly Ash (POMFA). The main composition of POMFA is 30% carbon and 39% silica. In the extraction process, about 60% silica can be extracted from POMFA [1,2,3]. The SAS obtained is in amorphous form, which is more reactive than silica in the form of quartz. In zeolite synthesis from coal fly ash, silica is in the form of quartz so it is need two stages process, the first step is smelting the fly ash using NaOH at temperature of 550 °C followed by a hydrothermal process for 12 hours [4]. Widiantuti et al. also applied the two stages processes to synthesize Na-X zeolite from coal fly ash [5]. While synthesis of zeolite from SAS only need one-step method without a smelting process, which requires high temperatures and energy, make the synthesizing process can be done in mild conditions. Sirisoonthorn et al. succeeded in synthesizing Na-A zeolite without the smelting process using amorphous silica extracted from rice husk ash [6].

The molecular formula of zeolite Na-P1 is Na₆Al₆Si₁₀O₃₂ˑ12H₂O, a synthetic zeolite that has a high ion exchange capacity because of the substitution of Si (IV) in the structure of zeolite by Al (III). This substitution causes the total charge to be negative as an adsorbent or a molecular sieve [7]. Further, according to Sharma et al. zeolite Na-P1 has characteristic micro-particles that have micro, meso and macro pores that are significant in increasing the diffusion rate of the processed molecules, reducing mass transfer resistance and maintaining the specific surface area of the micro-particles system [7].

In this research the synthesis of zeolite Na-P1 using SAS from POMFA by hydrothermal processes was studied. This is very important because the knowledge of effective and efficient zeolite synthesis can be applied and developed in the synthesis of other zeolite based catalysts. In addition, supported
by the results of previous research, the utilization of POMFA will increase the economic value of the palm oil industry and improving the image of the palm oil industry to be more environmentally friendly by implementing zero waste management.

2. Methods

POMFA was obtained from a palm oil mill in Petapahan, Kampar, Riau (PTPN V). The POMFA was dried at 110 °C and extracted using 1.4 N NaOH. The extracting condition were: the stirring speed of 1065 RPM, time of 60 minutes and the mass of POMFA to NaOH volume ratio of 0.23g/cm³ which were the optimum condition from previous studies [1,2]. The extract silica was separated from the solid using a vacuum filter and then acidified with 10% (v/v) H₂SO₄ so that pH 9 was reached and formed gel. The gel was left to stand for 18 hours and then broke and washed with distilled water and dried [9]. The Al₂O₃ with a purity of 99.5% and the average particle size is <10 µm (Sigma Aldrich, USA) was used as the aluminium source.

The method of Na-P1 zeolite synthesis applied in this research was adapted from Cardoso et al. and Sharma et al. [7,8]. The process of zeolite synthesis was carried out in a 5000 cm³ stainless steel autoclave reactor heated by electromagnetic induction. SAS as much as 2 g was placed in 50 ml crucible porcelain. The Al₂O₃ was added so that a mixture of silica and alumina with Si/Al ratios of 5, 8 and 11 were obtained and then NaOH 1N was added. The liquid to solid ratio in this study was 12.5 cm³/g. To study the effect of NaOH concentration, at the Si/Al ratio of 8, the NaOH concentration was varied of 1 N, 2 N and 3 N. The crucible porcelain containing a mixture of SAS, Al₂O₃ and NaOH solution above was put in the autoclave reactor and then the reactor was heated to a temperature of 120 °C and a pressure of 200 kPa for 8 hours.

The obtained zeolite was separated from the liquid with whatman filter paper and then dried. The obtained zeolite was analyzed using XRF (X-ray Diffractometer, Philips X'Pert MPD, Philips, Netherland) and the XRD diffraction results are shown in Figure 1. In the analitical procedure using XRF, the sample was heated at 1000 °C for 2 hours to convert the existing minerals into its oxide. So that the elements that detected by XRF can be used to calculate the chemical composition of samples by assuming the minerals were in the form of oxide. It can be seen that the largest impurity were sodium and sulphur. Both of these elements were from NaOH, solvents used in the extraction process, and sulphuric acid that was used for lowering pH in the sol-gel precipitation process. In the precipitation process the NaOH react with sulphuric acid forming Na₂SO₄.

3. Results and discussions

3.1 Synthetic amorphous silica

The intermediate material obtained, SAS, was analysed for its chemical composition by XRF and characterized by XRD to determine whether the silica was amorphous. The results of the XRF can be seen in Table 1 while the XRD diffraction results are shown in Figure 1.

| No. | Oxide | (% dry weight) |
|-----|-------|---------------|
| 1   | Na₂O  | 3,62          |
| 2   | Al₂O₃ | 0,20          |
| 3   | SiO₂  | 82,00         |
| 4   | SO₃   | 4,56          |
| 5   | K₂O   | 1,13          |
| 6   | LOI   | 8,49          |

Table 1. Chemical composition of SAS obtained
Other impurities such as $\text{Al}_2\text{O}_3$ and $\text{K}_2\text{O}$ were from POMFA which dissolved in the extraction process. These salts and oxides might be trapped in the silica gel matrix so that it was difficult to remove in the washing process. The composition of silica and alumina were used to determine the amount of alumina that have to be added so that a suitable Si/Al ratio can be obtained.

![Figure 1. XRD diffraction pattern of SAS from POMFA](image)

From figure 1, it can be seen that there is no sharp peak pattern, indicating the absence of crystalline minerals. According to Kamath and Proctor the diffraction of amorphous silica XRD was characterized by the existence of a sloping hill shaped pattern at position $2\theta$ between 15$^\circ$ and 35$^\circ$[10]. The peak is at position $2\theta$ of 23$^\circ$, this is in accordance with the results reported by Music et al. and Martinez et al. that the amorphous silica peak position $2\theta$ were of 21.9$^\circ$ and 23$^\circ$[11,12].

### 3.2 Zeolite synthesis

The condition of zeolite synthesis and the XRD characterization of zeolite obtained can be seen in Table 2.

| No | Synthesis condition | XRD characterization                  |
|----|---------------------|---------------------------------------|
|    | Si/Al ratio | [NaOH] (N) | Na-P1, SiO$_2$, Al$_2$O$_3$ |
| 1  | 5          | 1        | Na-P1, SiO$_2$, Al$_2$O$_3$ |
| 2  | 8          | 1        | Na-P1, SiO$_2$, Al$_2$O$_3$ |
| 3  | 11         | 1        | Na-P1, SiO$_2$, Al$_2$O$_3$ |
| 4  | 8          | 2        | Analcim, SiO$_2$, Al$_2$O$_3$ |
| 5  | 8          | 3        | Sodium tecto-hexaaluminohexasilicate carbonate, SiO$_2$, Al$_2$O$_3$ |

The effect of Si/Al ratio was studied by varying the Si/Al ratio of the samples. After hydrothermal process the liquid and the solid was separated using whatman filter paper and then washed with distilled water until the pH of washing water $<$10. Solid obtained was then dried and characterized using XRD, the diffraction results can be seen in Figure 2.
Zeolite species P from the phillipsite group can be identified from peaks pattern of the diffractogram. The zeolite P have 11 peaks pattern, as shows in the Figure 2 there are 6 peaks in the samples at Si/Al ratio of 5, 8 and 11 which have the same position of 2θ with the zeolite P. While the other peak patterns show that there is residual alumina and silica that not react to form zeolite. This is in accordance with the work of Sharma et al. that the zeolite Na-P1 can be synthesized at Si/Al ratio from 5 to 11. The Si/Al ratio affect the zeolite synthesis, the increasing Si/Al ratio increase the height of the peaks pattern. It is indicating that higher Si/Al ratio made the process synthesis better.

Further experiments were carried out by varying NaOH concentrations from 1N; 2N and 3N at Si/Al ratio of 8. XRD diffraction results can be seen in Figure 3.

As shown in Figure 3 the concentration of NaOH greatly affects the type of zeolite obtained. At NaOH concentration of 1N, the Na-P1 zeolite was obtained, at NaOH concentration of 2N the identified zeolite was analcim. Whereas in the NaOH concentration of 3N the zeolite identified is Sodium tecto-hexaaluminohexasilicate carbonate. Cardoso et al. reported that the zeolite Na-P1 can be synthesized from coal fly ash using NaOH concentration of 2N and 3N [7]. In this research the lower NaOH concentration was used because the raw material for silica source were SAS which is more reactive compare to coal fly ash.

Figure 2. Diffractogram of zeolite obtained at different Si/Al ratio
Figure 3. Diffractogram of zeolite obtained at different NaOH concentration

4. Conclusion
Na-P1 zeolite can be synthesized from POMFA through 2 stages process. The first process is extraction with NaOH combined with precipitation sol-gel to obtain SAS from POMFA. The SAS obtained was used to synthesize Na-P Zeolite with a hydrothermal process at a pressure of 200 kPa at 120 °C for 8 hours. The operating conditions that produce Na-P1 zeolite were Si/Al ratio = 8 and 11; NaOH concentration of 1N with a ratio of liquid volume to solid of 12.5 cm³/g.

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