Effective utilizations of palm oil mill fly ash for synthetic amorphous silica and carbon zeolite composite synthesis

P S Utama1,2, E Saputra2, Khairat2
1Chemical Engineering Department Prince of Songkla University, Hatyai, Thailand
2Chemical Engineering Department University of Riau, Pekanbaru, Indonesia
E-mail: psutama@yahoo.com

Abstract. Palm Oil Mill Fly Ash (POMFA) the solid waste of palm oil industry was used as a raw material for synthetic amorphous silica and carbon zeolite composite synthesis in order to minimize the wastes of palm oil industry. The alkaline extraction combine with the sol-gel precipitation and mechanical fragmentation was applied to produce synthetic amorphous silica. The byproduct, extracted POMFA was rich in carbon and silica content in a significant amount. The microwave heated hydrothermal process used to synthesize carbon zeolite composite from the byproduct. The obtained silica had chemical composition, specific surface area and the micrograph similar to commercial precipitated silica for rubber filler. The microwave heated hydrothermal process has a great potential for synthesizing carbon zeolite composite. The process only needs one-step and shorter time compare to conventional hydrothermal process.

1. Introduction
Riau province is the largest Crude Palm Oil (CPO) producer and has the greatest palm oil plantation area in Indonesia. The crude palm oil production in 2015 was 7.8 million ton/year and the plantation area was 2.4 million ha [1]. According Kramanandita et al. (2014) production of one ton CPO will produce empty fruit bunch of 1.41 ton, fibers 0.9 ton and shells 0.3 ton [2]. Around 85% of fibers and 15% of empty fruit bunch and shells are used as fuel in palm oil industry to produce steam. It is estimated 5% of the fuel unburned and produce ash [3]. Therefore, it can be calculated in 2015 palm oil industry in Riau generated ash of 0.4 million ton. In order to minimize the waste of palm oil industry, the utilization of POMFA as a raw material for precipitated silica production has been done in the previous research. The alkaline extraction combine with the sol-gel precipitation and mechanical fragmentation was applied to produce precipitated silica, the result was 60% of silica from the ash can be extracted. The silica content in the POMFA was 39% so from 1 ton of POMFA only 234 kg silica can be extracted [4]. The process above still produces waste of 766 kg. However, if the waste can be processed further and produces valuable product the objective to minimize the waste can be fulfilled.

The main composition of POMFA is carbon of 30% and silica of 39% [4]. The extraction process will decreased the content of silica, make the POMFA richer in carbon and still has significant silica content. Moreover, the extraction process makes the carbon in the POMFA more porous because of part of silica leave the POMFA particle. Even though it can be predicted that the POMFA after extracted is a good material for adsorption but the content of carbon is too low and the content of ash is too high to be processed further as an activated carbon. One of the possible utilization of extracted POMFA is used as a raw material for synthesizing zeolite carbon composites. The zeolite carbon composite is a new material that has the properties of zeolite and carbon. The surface properties of carbon are usually hydrophobic and the nature of the zeolite surface is usually hydrophilic so that the zeolite carbon composite surface has both properties. This composite is particularly suitable for the adsorption of both organic and metal ions in the liquid and gas phases [5]. In the previous study, zeolite carbon composite was successfully synthesized from fly ash coal [6] and bottom ash coal [7]
by fusion process using NaOH at 750 °C followed by hydrothermal process at temperatures below 100 °C for more than 10 hours.

The hydrothermal process at temperatures of 80 to 110 °C and time of 2 to 8 hours was applied to synthesize the NaA zeolite carbon composite from rice husk ash [8]. This is possible because the silica derived from crop material is in amorphous form, which is more reactive than silica in the coal ash. According to Pathak et al. (2014) the use of conventional hydrothermal processes has the disadvantages of low yield, long process times and heterogeneous structures. This weakness can be fixed using the microwave as a heater. In microwave heating process, heat is radiated directly into the molecule present in the reactant without being affected by the conductivity of the wall of the reactor or the reactants themselves. The result is a rapid local heating of the molecules and makes the reactivity of the molecule increases [9].

In this research, firstly the POMFA was used as a raw material to produce synthetic amorphous silica that has similar properties to commercial precipitated silica for shoe sole and mechanical rubber good filler by alkaline extraction combine with sol-gel precipitation using H2SO4 and mechanical fragmentation. Secondly, the preliminary study of synthesizing carbon zeolite composite from the extracted POMFA as the raw material by microwave heating hydrothermal process.

2. Methods
The raw material used in this experiment was POMFA from Sawee Industrial Palm Oil ltd. Chumporn, Thailand. The sodium hydroxide was NaOH laboratory grade with minimum content of 97% (dry basis). The sulfuric acid was commercial grade with minimum total acidity of 98% H2SO4 by mass. Aluminium oxide p.a. which has purity > 99.5% and average particle diameter < 10 µm (Sigma Aldrich, USA) was used as the aluminium source. The equipment and the optimum condition from the previous research was used to produce the synthetic amorphous silica. The extraction process was done in 2500 cm³ glass extractor. The extraction conditions were mass of POMFA 468.2 gram; the POMFA mass to NaOH volume ratio 0.2341 g/cm³; the concentration of NaOH 1.4 N and the stirring speed of 1065 RPM and time 60 min. The extract silica and the extracted POMFA were separated using vacuum filter. The sol-gel precipitation using H2SO4 10% (v/v) and mechanical fragmentation process were applied simultaneously in 1000 cm³ glass precipitator. The conditions of sol-gel precipitation and mechanical fragmentation was stirring speed of 1160 RPM, pH of 8.75 and precipitation time of 100 min [4n this experiment, sol-gel precipitation temperature of 90 °C was used instead of 30 °C as in the previous research in order to obtain specific surface area that suitable for rubber filler. The synthetic amorphous silica was characterized by a scanning electron microscope (SEM, JEOL JSM-5800LV, Japan), Energy-dispersive X-ray scanning electron microscope (SEM-EDX, JEOL JSM-5800LV, Japan) for element analysis and the specific surface area (SSA) were obtained by the Brunauer-Emmett-Teller (BET) method using a surface area analyzer (Quantachrome Nova 2000 e, USA). After extraction process, the extracted POMFA was washed and dried. The chemical composition of the extracted POMFA was analyzed using C, H, N and O analyzer and XRF (X-ray Fluorescence Spectrometer, PW 2400, Philips). In this preliminary study, synthesizing carbon zeolite composite the Si/Al ratio used were 5, 8 and 11 [10]; time 30 min and the input power of the microwave 800 W. The POMFA of 3 g were mixed with Al2O3 of 0.221, 0.128 and 0.085 g respectively to obtain the predetermined Si/Al ratio above. The mixture of fly ash and Al2O3 and 20 cm³ sodium hydroxide solution of 1 N were added into 100 cm³ polytetrafluoroethylene (PTFE) reactor. After zeolitization was performed the solid washed and dried. The dried solids obtained were characterized using XRD.

3. Results and discussions
3.1 Synthetic amorphous silica
The chemical composition of POMFA and extracted POMFA analyzed using C, H, N, O analyzer and XRF are listed in Table 1.
Table 1. Chemical composition of POMFA and extracted POMFA

| Oxide  | POMFA (%) dry weight | Extracted POMFA (%) dry weight |
|--------|----------------------|-------------------------------|
| SiO₂   | 39.02                | 24.50                         |
| Al₂O₃  | 1.19                 | 0.86                          |
| Fe₂O₃  | 1.71                 | 1.11                          |
| CaO    | 9.39                 | 7.64                          |
| MgO    | 4.11                 | 6.84                          |
| K₂O    | 6.20                 | 2.52                          |
| MnO    | 0.20                 | 0.18                          |
| P₂O₅   | 5.16                 | 4.27                          |
| SO₃    | 0.90                 | 0.22                          |
| CuO    | 0.06                 | 0.05                          |
| Rb₂O   | 0.03                 | -                             |
| SrO    | 0.04                 | 0.03                          |
| Na₂O   | -                    | 2.41                          |
| C      | 30.44                | 49.15                         |
| Total  | 99.63                | 99.79                         |

* (Utama et al., 2013 [4])

In the extraction process, part of silica in the POMFA was dissolved into sodium hydroxide solvent resulting the silica content in the extracted POMFA decreased. The decreasing silica content increasing the carbon content because of the carbon is insoluble in sodium hydroxide. If it is assumed that the carbon is fixed it can be calculated that of 60.11% silica can be extracted from the POMFA. This is in accordance with Utama et al., (2016) that reported at the similar conditions around 60% of silica can be extracted from POMFA [4].

The SEM micrograph of the synthetic amorphous silica obtained and the commercial precipitated silica depicted in Figure 1 and Figure 2 respectively. It can be seen that the microstructure of the synthetic amorphous silica and commercial precipitated silica is similar. The primary particle of both silica is quite uniform and posses spherical particle shape. The primary particle sizes are in the nano-scale, however the primary particle size of the commercial precipitate silica is smaller than the synthetic amorphous silica obtained. According Quarch et al. (2010) the primary particle size of the synthetic amorphous silica depend on the rate of gelation process [11]. There are many factors influenced the rate of gelation such as temperature, pH and ionic strength of the solution. The primary particle size can be tailored by varying the temperature and pH of the sol-gel precipitation process.
Figure 1. SEM micrograph of synthetic amorphous silica obtained.

Figure 2. SEM micrograph of the commercial precipitated silica.

The SEM EDX was used to determine the elements in the synthetic amorphous silica obtained. The energy dispersive X-ray spectrometry is depicted in Figure 3. It shown that the most element impurities were sodium and carbon. The carbon was found in the POMFA as a carbonate and as a char. In the extraction process, the char is insoluble but the carbonate soluble in the sodium hydroxide solvent form sodium carbonate. The sodium and the carbon as carbonate might be trap in the silica matrix and did not completely washed. The minor element K and Al were from the POMFA and S was from sulphuric acid was used to destabilize the extract silica in the sol-gel precipitation process were might be carried over into the synthetic amorphous silica obtained.

Figure 3. Energy dispersive X-ray spectrometry of synthetic amorphous silica obtained.

Figure 4 shows nitrogen adsorption–desorption isotherms of amorphous silica obtained. The type of physisorption isotherm is similar to the type II reversible isotherm in IUPAC classification that
indicates unrestricted monolayer-multilayer absorption of non-porous or macro-porous adsorbent. The hysteresis loop of the isotherm is similar to H3 hysteresis loop. The H3 loop represents an assemblage of particles that are loosely coherent and have slit shapes pores. This fact is in accordance with the SEM micrograph that shows the primary particles of synthetic amorphous silica are form aggregates that are loosely coherent [12].

The BET-SSA analysis of the synthetic amorphous silica obtained gives SSA of 53.590 m²/g. The SSA of the silica is similar to SSA of Ultrasil* 360 of 55 m²/g which suitable as a rubber filler for shoe sole and mechanical rubber goods [13].

3.2 Carbon zeolite composite.
The slurry of extracted POMFA, alumina and sodium hydroxide solution in PTFE reactor was heated by microwave for zeolitation process. The solid obtained after zeolitation process was analyzed using XRD, the result is depicted in Figure 5. It can be seen that for the Si/Al ratio of 5 (F1) the peaks of the XRD diffraction indicate there were silica as quartz and alumina as corundum. The peaks of XRD diffraction for the Si/Al ratio of 11 (F3) indicate there were silica as quartz, alumina as corundum and carbon as graphite. The peaks of XRD diffraction for the Si/Al ratio of 8 (F2) indicate there were alumina as corundum and aluminium silicate as kyanite. Even though the zeolitation process by microwave heated hydrothermal has not formed zeolite yet, however for the Si/Al ratio of 8 in a relative short time and only using one-step can made the silica and alumina react to form aluminium silicate. In this experiment, the sodium hydroxide concentration used was 1 N and the liquid volume to solid ratio used was 6.66 (cm³/g). The sodium hydroxide concentration and the liquid volume to solid ratio might be too low and made the zeolite cannot be formed. The carbon zeolite synthesis can be explored further by using higher sodium hydroxide concentration and volume liquid to solid ratio.
Figure 5. The XRD diffraction of solid obtained with variation of Si/Al ratio (A= alumina as corundum; C = carbon as graphite; S = silica as quartz and AS = aluminium silicate as kyanite).

4. Conclusions
The sodium hydroxide extraction combine with sol-gel precipitation using sulphuric acid and mechanical fragmentation have been successfully applied for producing synthetic amorphous silica from the POMFA. The synthetic amorphous silica obtained has chemical composition, microstructure and specific surface area similar to commercial precipitated silica that is suitable for mechanical rubber goods and shoe sole filler. The microwave heated hydrothermal process shows great potential to be applied for synthesizing carbon zeolite composite from extracted POMFA. Even though the zeolitization process by microwave heated hydrothermal has not formed zeolite yet, however the ratio of Si/Al ratio of 8 in a relative short time and only using one-step can made the silica and alumina react to form aluminium silicate.

Acknowledgments
This work was supported by DPRM, Ministry of Higher Education and Research Technology Indonesia through Penelitian Produk Terapan grant.
References
[1] Badan Pusat Statistik Propinsi Riau 2017 *Riau dalam angka 2015* (Pekanbaru: Badan Pusat Statistik Propinsi Riau)
[2] Kramanandita R, Bantacut T, Romli M and Makmoen M 2014 *Chem. Mater. Res.* **6 (8)** 46-53
[3] Tay H and Show K 1995 *Cement Concrete Comp.* **13** 27-36
[4] Utama P S, Yamsaengsung R and Sangwichien C 2016 *Key Eng. Mater.* **673** 183-192
[5] Babic B, Kokunesoski M, Gulicovski J, Prekajski M, Pantic J, Radosavljevic-Mihajlovic A and Matovic B 2011 *Process Appl. Ceram.* **5** (2) 91-96
[6] Miyake M, Kumar Jha V, Kimura Y and Matsuda M 2008 *Trans. Ecol. Environ.* **109** 203-212
[7] Widiastuti N, Zhely M, Hidayah N, Praseytoko D and Fansuri H 2014 *Adv. Mater. Lett.* **5** (8) 453-458
[8] Sirisoonthon S, Jiemsirilers S, Nilpairach S, Wasanapianpong T, Sujaridworakun P and Chuankrekkul N 2014 *Key Eng. Mater.* **608** 241-246
[9] Pathak C Y, Debananda R and Sumanta D 2014 *World J. Civil Eng. Constr. Technol.* **1** (1) 2-11
[10] Cardoso A M, Paprocki A, Ferret L S, Azevedo C M N and Pires M 2015 *Fuel* **139** 59-67
[11] Quarch K, Durand E, Schildc, Kwade A and Klind M 2010 *Chem. Eng. Res. Des.* **88** 1639-1647
[12] Sing K S W, Everett D H, Haul R A W, Moscou L, Pierotti R A, Rouquerol J and Siemieniewska T 1985 *Pure Appl. Chem.* **57** (4) 603-619
[13] Evonik Resource Efficiency GmbH 2017 *Product information ULTRASIL*® **360** (Wesseling: Evonik)