

Synthesis and characterization of nanosilica from boiler ash with co-precipitation method

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Abstract—Boiler ash known as solid waste of sugar industry with high silicon dioxide. Nanosilica can be synthesized from boiler ash with co-precipitation method. Precipitation still produced amorphous and heterogenous nanoparticles because of reaction spontaneity. Modification using polysaccharides as dispersing agent improved its ability to synthesize homogenous silica nanoparticles. This study aimed to synthesize and characterize nanosilica from boiler ash with co-precipitation method. Polysaccharides that were used on this research include rice flour and agar powder with concentration 25% (w/w) silica. The characteristics of nanosilica were observed by particle size distribution, crystallinity, crystal size and morphology. Based on analysis, the use of polysaccharides as dispersing agent on precipitation method altered characteristics of nanosilica. Agar powder and rice flour reduced particle size and polydispersity index, turned crystallinity and crystal size, and formed unique particle morphology. The best characteristic of nanosilica was resulted by co-precipitation method using rice flour. It had average particle size 185.25 nm, polydispersity index 0.26, crystallinity 28.76%, average crystal size 22.44 nm.

scale sugar industry can produce 1.5-2.0% of the total sugarcane milled or about 1.7 to 2.3 million tons per year. Boiler ash has been utilized as the additional material for organic fertilizer, the fill of damaged roads and landslides [1]. Boiler ash is categorized as fly ash type F indicating that the boiler ash has a chemical composition of SiO₂, Al₂O₃ and Fe₂O₃ more than 70% and CaO less than 8%. It is this composition that makes boiler ash potential to be synthesized into silica. The synthesis of silica into nanosilica is carried out to expand the surface so that the reactivity increases.

The prevalent method of nanosilica synthesis is chemical precipitation, since it is excellent in the energy use efficiency and processing time. However, the use of precipitation method has not produced homogeneous nanosilica particles and a low degree of crystallinity [1]-[5]. An effort can be made to produce nanosilica particles with uniform size distribution is by the addition of a dispersing agent. In synthesis of nanosized oxide-based materials, polysaccharide played multiple roles, namely coating/capping, functionalizing, stabilizing, poring and or coordinating agent [6]. Polysaccharide is a type of dispersing agent which is abundantly available and the residue management is relatively simple. The polysaccharides could be used in this study are rice and agar. Rice was one of agricultural commodities which could be used as non-metallic bio-precursors to synthesize functional materials. Amylose and amylopectin of rice were representing the key structural elements for the synthesis of new functional nanomaterials [6]. Previously, rice used to synthesize zinc oxide nanoparticles [6]. Agar was a natural, biocompatible and biodegradable carbohydrate derived from marine algae. Agar was composed of agarose and agaropectin. Agarose was preferred due to that it was porous, cheap, and environmental friendly. It has been used to prepare alumina nanoparticle [7] and the result was relatively good. The polysaccharide concentration used in the synthesis process will greatly affect in its ability to control the particle sizes. Based on the research conducted by [8] for some types of polysaccharide-based dispersing agents, the polysaccharide concentration used was 25% (w/w).

I. INTRODUCTION

Boiler ash is a form of solid waste generated by the production activity of sugar industry. It is the result of chemical changes of pure bagasse burning at temperatures of 550-600°C for 4-8 hours. A large-

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II. MATERIALS AND METHODS

A. Materials

Boiler ash (BA) was obtained from PT Gunung Madu Plantation Lampung. BA from sugar factory cleaned by distilled water and burnt at 700°C for 7 hours. Sodium hydroxide (reagent grade), sulphuric acid and ammonium hydroxide (analytical grade) were purchased from Merck. Rice flour (RF) and agar powder (AP) was purchased from local market in Dramaga Bogor.

B. Synthesis of pure nanosilica from boiler ash

Ten grams BA on 80 ml 2.5 N sodium hydroxide solution was boiled in covered 250 ml erlenmeyer flask for 3 hours. The solution was filtered by whatman paper and the residues were washed with 20 ml boiling water. Then, the filtrate was allowed to cool down to room temperature and titrated 5 M H₂SO₄ until reached pH 2. Afterward, it was titrated again with NH₄OH until pH 7. Sol aged for 3.5 hours at room temperature then it was dried at 105°C for 12 hours [1][2][4].

C. Synthesis of nanosilica

Pure silica was refluxed on HCl 3 N for 6 hours. Thereafter, it was cleaned repeatedly with distilled water to free the acid. After that, it was dissolved on 2.5 N NOH by constant stirring on magnetic stirrer for 4 hours. Rice flour or agar powder 25% (w/w silica) was added into the solution after one hour. Then, 5M H₂SO₄ was titrated into solution to adjust pH 7.0-8.5. The precipitated silica was cleaned repeatedly with warm water to free the alkali. At the end, it was dried in the oven 60°C 3 hours and burned at 700°C for 4 hours to calcinate the polysaccharides.

III. CHARACTERIZATION

Particle size distribution of nanosilica was observed by *Vasco Particle Size Analyzer*. Exactly 0.1 grams nanosilica powder was dispersed into distilled water. Then, it was stirred on magnetic stirrer for 10 minutes and sonicated for 1 minute. Nanosilica particles were scanned by PSA for 2-5 minutes.

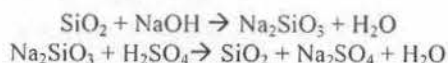
The diffraction pattern, crystallinity, size and phase of crystal was observed by *Shimadzu XRD-7000 Maxima X* with Cu-Kα radiation, voltage 40 kV, impedance 30 mA, and λ=1.54Å. Diffractograms was scanned at 10-60° with scanning rate 2°/minute on room temperature. Crystallinity of nanosilica was calculated by XRD-7000 software while crystal size of nanosilica was calculated by Scherrer Formula.

IV. RESULT AND DISCUSSION

A. Transformation of boiler ash became nanosilica

Boiler ash (BA) in this study was burned at 700°C for 7 hours in order to eliminate trash materials and change the crystallinity. Fresh BA was composed of 82.76% silicon dioxide and other compounds. Silicon dioxide compound increased after burning process became 99.00%. The crystallinity also increased from 50.26% became 97.56%.

The silica was extracted by sodium hydroxide with hydrolysis process at 90-100°C for 3 hours to form natrium silicate. Natrium silicate and silicon dioxide was obtained via the following reactions:



Natrium silicate was precipitated by sulphuric acid to reach stability of silica sol. The sol of silica reach stability at pH 8.5 and aging time 3.5 hours at 60 °C.

Synthesis of nanosilica was done by extraction process with high concentration of hydrochloric acid. The particle size of silica would be reduced in this process. The smaller particle was precipitated again with same reaction. The second precipitation process resulted the sol with smaller droplet size.

B. Particle size distribution of nanosilica

The use of synthesis method affected homogeneity of nanosilica particle sizes. *Fig. 1(a-c)* shows a shift in the value of particle size distribution. The average size and polydispersity of nanosilica particles decreased, regardless of the methods start from precipitation, co-precipitation AP, until co-precipitation RF. The curve width lessened with the use of polysaccharide in the precipitation process which showed the decline in the size range and dispersity of particles in the dispersion media.

Nanosilica as the result of precipitation had a maximum size of 9774.96 nm and the minimum 28.19 nm. The range of nanosilica particle sizes shifted and became narrower when agar was used as a dispersing agent with the largest particle size of 4676.59 nm and the smallest 23.45 nm. The size distribution curve shifted, becoming narrower when rice was used as a dispersing agent with the largest particle size of 1288.58 nm and the smallest 29.52 nm.

The precipitation could synthesize nanosilica with an average particle size of 269.42 nm, with a polydispersity index of 0.9190. The high index value of polydispersity indicated that the nanosilica particles produced by precipitation technique had a deficient particle size distribution. Extraction with hydrochloric acid was able to reduce the size of nanosilica but had not been able to prevent the agglomeration of particles spontaneously[1].

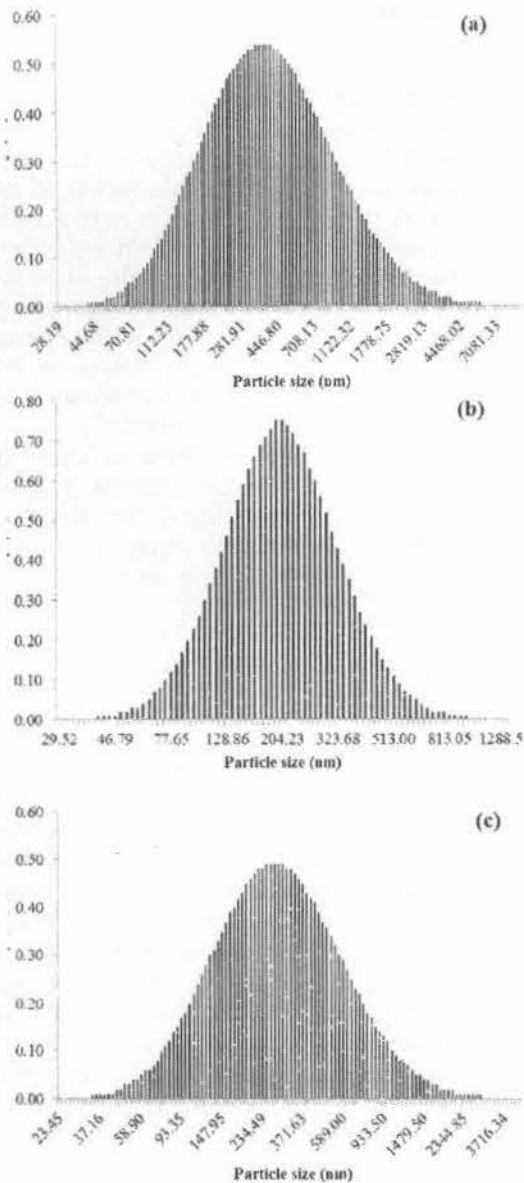


Fig. 1. Particles size distribution of nanosilica with different synthesis method (a) precipitation (b)co-precipitation RF (c)co-precipitation AP.

The use of polysaccharides in the precipitation process was able to synthesize nanosilica particle size distribution better than the synthesis result with ordinary precipitation. Rice flour as a dispersing agent in the precipitation process produced nanosilica particles with an average size of 185.45 nm, with a polydispersity index of 0.2540. Rice has starch granules consist of amylose molecules and amilopectin. In nanosilica synthesis, the carbon matrix have a helix shape in amylose and have a role in providing the morphological form and the uniformity of nanoparticle sizes. The hydroxyl groups of amylopectin could be involved both in intra- and/or intermolecular supramolecular association. It had ability to coordinate transition metal ions, maintaining the nanoparticles highly aggregated [6].

RF on this research was obtained from high amylose rice, so that in nanosilica synthesis, amylose had more ability to control shape and size of particle.

As a result, the average size of synthesized nanosilica with co-precipitation AP was 252.22 nm, with a polydispersity index of 0.6520. The outcome of nanosilica formed still did not have a good size distribution. Resemble with rice, agar has granules which is consist of agarose and agarpectin. The high aggregation of nanosilica particle suspected due to the presence of high agarose relatively in the agar which was used as a dispersing agent. Agarpectin has the ability to associate into intra- or inter-molecules as a balancing agent Si^{2+} ion transition and maintaining a high aggregation between silica particles.

C. XRD analysis of nanosilica

The diffractograms in Fig. 2 illustrates the nanosilica diffraction pattern as a result of precipitation which had a value of 2θ with high intensity at 32.03° , 33.90° , 19.06° , and 28.07° . The highest intensity was at 32.03° which indicated the phase of cristobalite crystal [1]. Points 2θ 19.06° and 28.07° showed the presence of tridymite phase while the peak point (33.90°) indicated the presence of mullite phase. Domination of cristobalite phase showed that precipitated silica nanoparticles had good thermal stability. Cristobalite known as crystal phase of silica which was formed at $700-800^\circ C$.

The precipitated silica nanoparticles with agar powder as the dispersing agent, had a diffraction pattern similar to precipitated nanosilica with higher intensity. The peak point with the highest intensity was found at 31.99° , 33.86° , 19.01° , and 28.04° . Based on Fig. 2c, there was not the peak point of agar. It indicates that agar was eliminated by calcination process at $700^\circ C$.

Meanwhile, nanosilica as a result of a synthesis with rice as the dispersing agent had the strongest peak at an angle of 2θ $22-23^\circ$ which indicated an amorphous silica phase. Amorphous silica phase could be opal-A, opal CT or opal C. Crystalline phase was showed by the strong peak at 31.58° (cristobalite), 19.16° (trydimite) and 33.97° (mullite).

The degree of crystallinity indicated the proportion of the crystal phase which existed in the material. The nanosilica synthesis using the precipitation method produced particles with a crystallinity of 33.22% with a dominant silica cristobalite phase. The rice flour used as the dispersing agent was able to reduce the crystallinity of the particles up to 28.76%. Meanwhile, the agar flour was able to increase the crystallinity of the particles up to 59.53%. This crystallinity change was related to the composition of amylose in rice and agarose agar since both of the major compounds forming crystallinity.

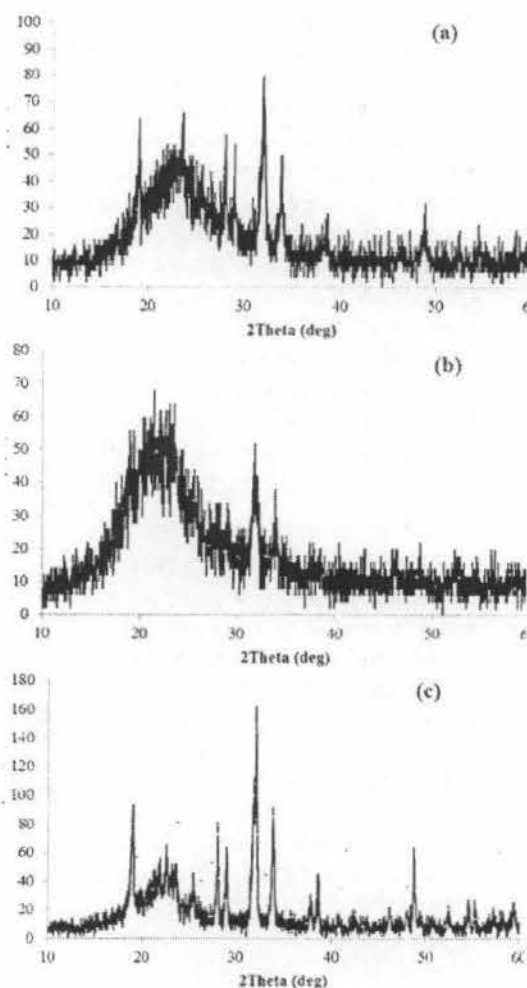


Fig. 2. Diffraction pattern of nanosilica with different synthesis method (a) precipitation (b)co-precipitation RF (c)co-precipitation AP.

In aqueous solution, rice granules swelled and their semi-crystalline structure was lost as smaller amylose molecule. The small amylose molecules could form a complex with Si^{2+} because of their high number of functional groups. Silicon ions and starch molecule would be associated then nucleation and initial crystal growth occurred within regions of their high concentration. Van der Waals interaction between the surface molecules formed the driving force for self-assembly. Then, SiO_2 nanocrystals can be assembled to reach larger size [6]. Similar to rice, agar granules also swelled in aqueous solution and formed large agarose molecules. Agarose had same role with amylose, could be associated with silicon ions to form the nanocrystalline silicon dioxide.

Despite its fairly low degree of crystallinity, the crystal formed from the synthesis process had a relatively small size (Table 1). The crystal size was obtained by calculating the average size of the crystal with high intensity. It was given by Scherrer formula [7].

$$D = \frac{k\lambda}{\beta \cos\theta}$$

where D crystallite size (nm), k Scherrer constant (0.9), λ wavelength of Cu (0.154 nm), β full width at half maximum (FWHM), θ diffraction angle (deg).

The highest crystal size was obtained from nanosilica precipitation with an average crystal size of 27.17 nm, followed by agar nanosilica co-precipitation 26.80 nm and rice co-precipitation 22.44 nm. The third sample of nanosilica crystal size was smaller than the size of silica 91.53 nm. In general, the three methods of nanosilica synthesis were able to reduce the silica crystal size up to 70-75%. Acid hydrolysis of this process broke structure of silica crystal.

TABLE I
THE CRYSTAL SIZE OF NANOSILICA WITH DIFFERENT SYNTHESIS METHOD

Nanosilica									Crystal phase
Precipitation			Co-precipitation RF			Co-precipitation AP			
2 θ (deg)	D(nm)	β (rad)	2 θ (deg)	D(nm)	β (rad)	2 θ (deg)	D(nm)	β (rad)	
19.06	26.28	0.0053	19.16	10.81	0.0126	19.01	27.05	0.0050	trydimite
22.65	25.05	0.0056	20.06	7.49	0.0181	22.60	18.63	0.0073	quartz
28.07	30.00	0.0047	28.01	30.42	0.0045	28.04	36.45	0.0038	seifertite
29.02	28.99	0.0049	29.16	66.07	0.0021	28.98	38.85	0.0036	crystalite
32.03	18.87	0.0079	31.85	12.28	0.0113	31.99	17.46	0.0080	crystalite
33.90	28.33	0.0051	33.97	21.11	0.0066	33.86	29.06	0.0048	crystalite

Despite of crystal properties, XRD analysis could be used to analyze chemical composition of silica nanoparticles. It would be very important to assure purity of silica. Qualitative analysis of XRD on silica nanoparticles showed that SiO_2 had high percentage 90-99% while another metal oxide had 1-10% in percentage. Functional group of silica by infra red spectra not to be expressed because the main characteristics of silica nanoparticle more enough.

Silica nanoparticle which produced by co-precipitation RF had better properties if it to be applied for electrolyte membrane additive. Based on FTIR analysis [9], the band at 1072 cm^{-1} illustrated the presence of Si-O-Si, the band at 902 cm^{-1} for Si-O-H. Amorphous silica is known to have the ability as a semiconductor material due to its mechanical resistance, electricity, and good selectivity of chemical modification.

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VI. CONCLUSION

Nanosilica can be synthesized from the boiler ash of sugar industry using both precipitation method and co-precipitation method. Modification of the precipitation process with agar powder and rice flour as a dispersing agent proved able to reduce the particle sizes, increase the particle size distribution, lower the crystal size, and change the crystallinity of nanosilica. The rice flour used in the precipitation produced nanosilica with the best characteristic, that is, with a particle size of 185.45 nm, polydispersity index of 0.2540, crystal size of 22.44 nm.

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