Study of Calcination Temperature and Concentration of NaOH Effect on Crystallinity of Silica from Sugarcane Bagasse Ash (SCBA)

NORHASYIMI RAHMAT[1]*, MOHD ALFIE SABALI[1], ANDREI VICTOR SANDU[2,3], NORSURAYA SAHIRON[1], IOAN GABRIEL SANDU[2]

[1] Faculty of Chemical Engineering, Universiti Teknologi MARA, 40450 Shah Alam

[2] Gheorghe Asachi Technical University of Iasi, Faculty of Materials Science and Engineering, 28 Mangeron Blvd., 700050, Iasi, Romania

[3] Center of Excellence Geopolymer and Green Technology (CEGeoGTech), School of Materials Engineering, Universiti Malaysia Perlis (UniMAP), Kangar, Perlis Malaysia

Sugarcane bagasse ash is a by-product produced from bagasse burning in sugarcane industry. SCBA contain high concentration of silica and some other elements such as aluminum, iron and alkaline earth oxide. In this study, an approach of ash preparation, acid washing and acid leaching have been proposed to extract silica from different concentration of sodium hydroxide, NaOH at 3M and 4M were prepared for silica extraction. The ash obtained after calcinations was characterized using X-ray Fluorescent (XRF) and the microstructure of silica particles were characterized by X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR). The x-ray fluorescent (XRF) result shown that the highest composition of silica obtained is 88.13% at temperature 1000°C for 4 h. At 1000°C, the peaks for silica quartz appeared at multiple angle compared to that of at 600°C. Moreover, significant intensity level difference was also observed. However, different concentration of sodium hydroxide (NaOH) used for silica extraction had shown insignificant effect on crystallinity level of silica quartz obtained.

Keywords: Sugarcane bagasse, silica, biomass waste, renewable resources

Sugarcane or *Saccharum officinarum L.* is a perennial grass that thrives in hot and humid locations. Sugarcane is commonly used in syrups, juices, and molasses. After juice was extract from stalks, the waste left is called sugarcane bagasse (SCB). Sugarcane bagasse ash (SCBA) is a residue resulting from the burning of bagasse in sugarcane or alcohol industry. Sugarcane stalks crushed to extract the juice and remaining fibrous residue is called bagasse. The disposal of this material is causing environmental problems and therefore wise management of handling this waste is gaining a priority.

Silica is a group of minerals composed of silicon and oxygen, which is commonly found in the crystalline state and rarely in amorphous state. Silica quartz is widely applied in medical, biotechnology [1] and advanced materials [2] research field. It has been thousands of years, which crystalline silica, primarily in the form of quartz has been mined. Single-crystal silica is high quality quartz with optical or electronic properties that make them useful for specialty purposes. Electronics grade crystals can be used in filters, frequency controls, timers, electronic circuits that become important components in cell phones, watches, clocks, games, television receivers, computers, navigational instruments and other products. This is due to unique property called piezoelectricity that converts mechanical pressure into electricity. Quartz also meets many needs in the field of optics due to its certain optical properties that is used in polarized laser beam. Prisms and lenses in optical instruments use smaller portions of high quality quartz crystals and scientist are experimenting with quartz bar to focus sunlight on solar-power applications. Today, quartz is used for a whole spectrum of products for high technology applications in the electronics and optical field to the everyday uses in the building and construction [3-5].

Based on previous studies by Teixeira et al., a composition analysis that was done on sugarcane bagasse ash mainly consisted of silica quartz. X-ray fluorescence was used in this characterization method [6]. As reported by Baharudin et al., sugarcane bagasse ash (SCBA) constituted about 70.97% of SiO_2 after it was burnt under controlled temperature of 600°C for 4 h [7]. Furthermore, Drummond et al. investigated the yield of silica from different preparation of sugarcane bagasse ash from natural burning (SCBA-NB) and from laboratory (SCBA-LP) which was burnt at 700°C in the muffle furnace for two hours followed by alkaline extraction. The study displayed slightly different yield, about 94.47% of silica from natural burning and 96.93% of silica from laboratory burning [8-10].

The significance of this study is to investigate the effect of calcination temperature and alkali concentration on cristallinity silica from sugarcane bagasse ash (SCBA). A new approach of acid washing using hydrochloric acid (HCl) is introduced and sodium hydroxide (NaOH) is used during the silica extraction acid leaching method. The structure of the silica particles obtained was characterized by X-ray diffraction (XRD) and Fourier Transform infrared spectroscopy (FTIR) for this initial study.

Experimental part

Materials and methodology

All chemicals are analytical grade and used without further purification. Hydrochloric acid (HCl) (37% ACS Specification), sodium hydroxide (NaOH) (98% ACS Specification) and sulphuric acid (H_2SO_4) (37% ACS Specification) are purchased from Sigma-Aldrich. The sugarcane bagasse is obtained from night market in Seksyen 18, Shah Alam. Distilled water is applied for all synthesis and treatment process.

a)Ash preparation

The sugarcane bagasse will be calcined for 2,3 and 4 h at different temperature of 600 and 1000°C in silica tray.

* *email: norhasyimi@salam.uitm.edu.my*

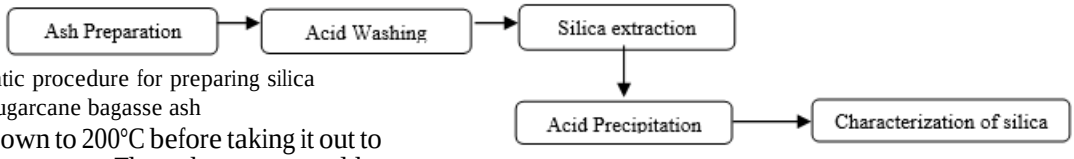

Fig. 1. The schematic procedure for preparing silica from sugarcane bagasse ash

Then, it will be cooled down to 200°C before taking it out to be cooled at room temperature. The ash was ground by the grinding machine. A significant increase of the ash specific surface area can be observed with the increase of grinding time.

b)Acid washing

5 g of sugarcane bagasse ash was dispersed in 30mL of distilled water, followed by washing it with 50mL of hydrochloric acid, HCl of 1 M. These dispersions were stirred for 2 h, filtered through Whatman No. 41 ashless filter paper which was then the SCBA residues washed with 50 mL of water. The residues were used for silica extraction. The filtrate and washings dried in an evaporating dish.

c)Silica extraction

The residue sugarcane bagasse ash dispersed in 50 mL of Sodium hydroxide solution at different concentration of 3M and 4M inside 250 mL conical flask. The mixture boiled for 4 h at constant stirring to dissolve the silica and produce sodium silicate solution. The solution was then filtered through an ashless filter Whatman No. 41 (Whatman Plc, Kent, England) to remove the carbon residue. The filtrate solution was sodium silicate, which subsequently was cooled to room temperature.

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_2 + H_2O$$

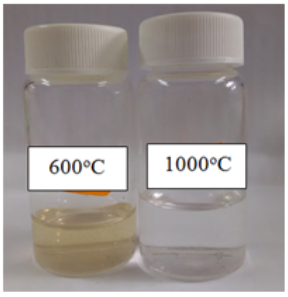

Fig. 2. Sodium silicate solution obtained at different temperature of 600°C and 1000°C

d)Acid leaching

The sodium silicate was titrated by using H_2SO_4 solution until the *p*H becomes acidic. The impure silica particles under constant stirring at 70 °C for 2 h before it was washed and dried at 100°C for 20 h to get the silica particles.

$$Na_2(SiO_2)_7 + H_2SO_4 \rightarrow 3.3SiO_2 + Na_2SO_4 + H_2O$$

e)Characterization of silica

The microstructures of the silica particles obtained were characterized by Fourier Transform Infrared spectroscopy (FTIR) and X-ray diffraction (XRD) analysis was used to obtain information on the crystallographic structure of silica.

Results and discussions

FTIR spectra in figure 4 prove to show that silica structure present in synthesized bagasse ash. The broad wave band

Fig. 3. Silica, SiO_2 in crystalline structure for characterization

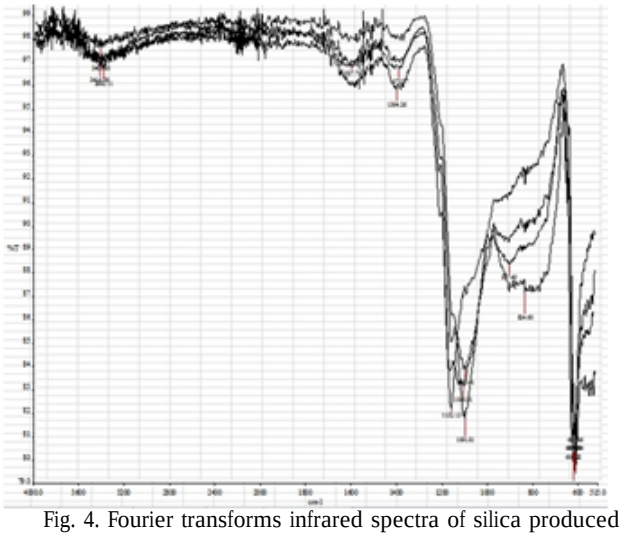

Fig. 4. Fourier transforms infrared spectra of silica produced from SCBA

observed at 3410 to 3470 cm^{-1} is due to the stretching vibration of the O-H bond from the silanol groups (Si-OH) which adsorbed water molecules on the silica surface. The band at 1070 to 1090 cm^{-1} is due to Si-O-Si asymmetric stretching vibration, while the band at 791 to 806 cm^{-1} has been identified as the network of Si-O-Si symmetric bond stretching vibration [8].

Determination of silica composition in the Sugarcane Bagasses Ash (SBA) at difference temperature and time

The effect of times and temperature to the composition of silica present is shown in table 1. Based on the analysis result, 4 h burning time were gave higher silica composition than 2 and 3 h burning time. The acid washing method was used in this study to improve the silica composition of raw ash. All samples that have been treat with hydrochloric acid, HCl was give higher silica amount than raw ash samples. Therefore, table 1 clearly shown at 1000°C with 4 hours burning time and involve of acid washing method give the highest silica composition which is 88.13%. Therefore, suitable combination of time and temperature would help to improve the silica composition present.

Temperature (°C)	Composition (% wt)					
	Raw Ash			After Acid Washing		
	2 h	3 h	4 h	2 h	3 h	4 h
600	37.76	40.25	47.41	74.14	76.83	80.76
1000	52.39	56.26	67.17	86.72	87.63	88.13

Table 1
COMPOSITIONS OF SILICA IN SCBA AT DIFFERENT TEMPERATURE AND TIME

The effects of different calcined temperature at NaOH concentration of 3M

The effect of SCBA on the calcination temperature at 600 and 1000^{O}C was investigated in this study. At 600^{O}C the intensity percentage (I%) are less compared to 1000^{O}C. At 600^{O}C, quartz silica intensity peaks presence in X-ray diffraction (XRD) spectral only at high angle of 50 to 55 (2θ) and 59 to 67 (2θ) with the highest intensity percentage of 10.5% as shown in figure 6 and table 2. While at 1000^{O}C, the intensity peaks can be seen both at high angle from 40 to 60 (2θ) and 68 (2θ) and low angle at 21.01 (2θ) with the highest intensity of 18.8% as in figure 6 and table 2. The presence of quartz silica at low angle spectral of 1000^{O}C is due to recrystalization of crystobalite silica to quartz silica with the change in intensity and miller indices (hkl).

In addition, some reasonably sharp and intense peak starts to show up as temperature increasing (Teixeira et al., 2008). Recrystallisations of amorphous silica happen when crystalline increases as temperature increases. At 1000^{o}C, the SCBA becomes highly crystalline as evident from sharp reflection peaks.

Table 2

QUARTZ SILICA XRD PEAK ID REPORT FOR 3M NAOH AT 600^{O}C

List	2-Tetha	Intensity (%)
a	50.843	0.4
b	54.777	4.2
c	55.398	1.8
d	59.699	10.5
e	67.7	6.6

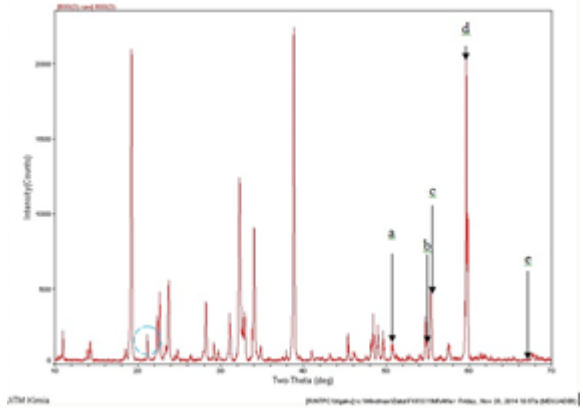

Fig. 5. Quartz silica at 3M NaOH at 600^{O}C

Table 3

QUARTZ SILICA XRD PEAK ID REPORT FOR 3M NAOH AT 1000^{O}C

List	2-Tetha	Intensity (%)
a	21.021	18.8
b	45.917	3.4
c	50.423	0.4
d	57.359	0.2
e	68.613	4.9

Identification of sodium silicate functional group using Fourier Transform Infrared Spectroscopy (FTIR)

The functioning group for the commercial sodium silicate and extracted sodium silicate from SCBA was illustrated in figure 7. The comparison spectrum structure of commercial sodium silicate and extracted sodium silicate is shown. Theoretically, Fourier Transform-Infrared Spectroscopy (FTIR) measures the absorption of infrared spectrum radiation by the sample material versus wavenumber. The infrared absorption bands will identify molecular structures and components exist in the sample.

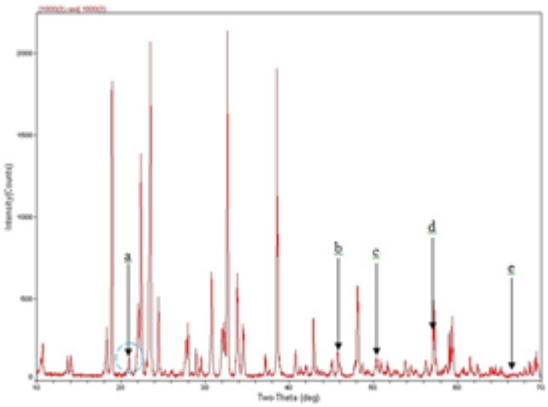

Fig. 6. Quartz silica at 3M NaOH at 1000^{O}C

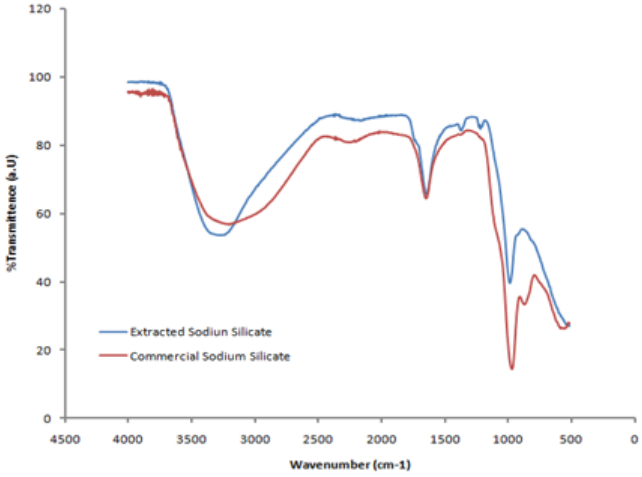

Fig. 7. The FTIR spectrums of commercial sodium silicate and extracted sodium silicate from SCBA

When a sample is irradiated with infrared radiation, absorbed IR radiation usually excites molecules into a higher vibration state. The wavelength of light absorbed by a particular molecule is a function of the energy difference between the at-rest and excited vibration states. The wavelengths that are absorbed by the sample are characteristic of its molecular structure.

The functioning group of the single molecules was represented according to the result, absorption bands in the range of 400 cm^{-1} to 4400 cm^{-1} wavenumbers are typically due to functional groups Si, O and H. The patterns of the result obtain almost the same, at peak 969 cm^{-1}, the wavenumber represent the Si-O-Si stretching. Both spectrums appear at peak 3239 cm^{-1} confirms the presence of hydroxyl group in the sample. Peak observed at 1646 cm^{-1} confirm the presence of H-O-H (water adsorption) and at peak 871 cm^{-1} confirm the presence of SiO_4 tetrahedron. Absorption bands in this region are generally due to intramolecular phenomena and are highly specific to each material. Therefore, all peak that present in commercial sodium silicate also present in extracted sodium silicate from sugarcane bagasse ash.

The effects of different sodium hydroxide (NaOH) concentration

Different concentrations of 3M and 4M of sodium hydroxide (NaOH) are used for the silica extraction method. Insignificant effect can be observed in the quartz crystalline structure for different concentration of NaOH at 3M and 4M. However, at 600^{O}C, a decreasing pattern in the presence of quartz silica peaks was displayed between these two different concentrations. At 1000^{O}C, the presence of quartz silica peaks at concentration of 4M was higher than concentration at 3M. This could be due to an intense beam of X-ray strikes the quartz silica crystalline

structure. In general, crystal diffracts the X-ray beam differently, depending on its structure and orientation and then collected by an area detector.

The effect of alkaline solution concentration mostly effect for the formation of crystobalite silica. This supported by Haruto et al. studies on crystallization of silica gel in alkaline solution by using different concentration of NaCl in 1% of KOH solution said that by increasing the NaCl concentration influence the formation of SiO_2-Y and crystobalite. Furthermore, addition of NaCl seems to avoid the formation of SiO_2-X_2, which formation of crystobalite directly from SiO_2-Y. The conversion crystalline phase reaction path shown as in figure 8:

$$\text{Amorphous} \rightarrow SiO_2 - Y \rightarrow SiO_2 - X \rightarrow \text{Crystobalite}$$

Fig. 8. Crystalline Phase Reaction Path

Table 4

QUARTZ SILICA XRD PEAK ID REPORT FOR 3M NaOH AT 600°C

List	2-Tetha	Intensity (%)
A	50.843	0.4
B	54.777	4.2
C	55.398	1.8
d	59.699	10.5
e	67.7	6.6

Table 5

QUARTZ SILICA XRD PEAK ID REPORT FOR 4M NaOH AT 600°C

List	2-Tetha	Intensity (%)
a	55.4	1.8
b	57.442	0.2
c	59.681	10.5

Table 6

QUARTZ SILICA XRD PEAK ID REPORT FOR 3M NaOH AT 1000°C

List	2-Tetha	Intensity (%)
a	21.021	18.8
b	45.917	3.4
c	50.423	0.4
d	57.359	0.2
e	68.613	4.9

Table 7

QUARTZ SILICA XRD PEAK ID REPORT FOR 4M NaOH AT 1000°C

List	2-Tetha	Intensity (%)
a	21.122	18.8
b	45.997	3.4
c	50.725	0.4
d	54.636	4.2
e	55.257	1.8
f	57.401	0.2
g	64.097	2
h	67.562	6.6

Table 4 above shows the presence of silica quartz peaks for 3M NaOH at 600°C only at high angle of 50.843, 54.777, 55.398, 59.699 and 67.7 (2θ). The highest percentage intensity (I%) was at angle 59.699 (2θ) with 10.5%.

Table 5 above shows the presence of silica quartz peaks for 4M NaOH at 600°C only at high angle of 55.4, 57.442, and 59.681 (2θ). The highest percentage intensity (I%) was at angle 59.681 (2θ) with 10.5%.

Table 6 above shows the presence of silica quartz peaks for 3M NaOH at 1000°C at both low angle of 21.021 (2θ) and high angle of 45.917, 50.423, 57.359, and 68.613 (2θ). The highest percentage intensity (I%) was at angle 21.021 (2θ) with 18.8%.

Table 7 above shows the presence of silica quartz peaks for 4M NaOH at 1000°C at both low angle at 21.122 (2θ) and high angle of 45.997, 50.725, 54.636, 55.257, 57.401, 64.097, and 67.562 (2θ). The highest percentage intensity (I%) was at angle 21.122 (2θ) with 18.8%.

Conclusions

Crystal solid of silica particles was successfully prepared from sugarcane bagasse ash due to the presence of network Si-O-Si from Fourier Transform Infrared spectra (FTIR). The x-ray fluorescent (XRF) result shown that 88.13% is highest composition of silica obtained at temperature 1000°C for 4 h with acid washing method. The study on crystallinity of silica based on calcination temperature at 600 and 1000°C shows the recrystalization of crystobalite silica to quartz silica when the temperature increases and more quartz silica peaks obtain from X-ray Diffraction (XRD) spectral. There is no significant effect can be observed in the quartz crystalline structure for the effect can be observed in the quartz crystalline structure for the effect on different concentration of NaOH at 3M and 4M. The patterns of the result obtain from Fourier Transform-Infrared Spectroscopy (FTIR) analysis was almost the same, the peak present at 969 cm^{-1}, 3239 cm^{-1}, 1646 cm^{-1} and 871 cm^{-1} wavenumbers are typically due to present of functional groups Si, O and H, hydroxyl group, Si-O-Si stretching, H-O-H (water adsorption) and SiO_4 tetrahedron respectively. Therefore, the property and functional group exist in extracted sodium silicate from sugarcane bagasse ash (SCBA) was same as commercial sodium silicate in the market.

AcknowledgementsThis project is funded by Fundamental Research Grant (FRGS/2/2013/TK05/UITM/03/2) from Ministry of High Education Malaysia. Special thanks to Research Management Institute (RMI) Universiti Teknologi MARA for the special assistance in alleviating the execution of this project.

References

1.PASQUA, L., CUNDARI, S., CERESA, C., CAVALETTI, G., Current Medicinal Chemistry, **16**, 2009, p. 3054.

2.CESARINI, E., LORENZINI, M., CAGNOLI, G., MARTELLI, F., PIERGIOVANNI, F. & VETRANO, F., Journal of Non-Crystalline Solids, **357**, 2011, p. 2005.

3.TEIXEIRA, S.R., DE SOUZA, A.E., DE ALMEIDA SANTOS, G.T., VILCHE PEÑA, A.F., MIGUEL, Á.G., Journal of the American Ceramic Society, **91**, 2008, p. 1883.

4.UCHIMA, J.S., RESTREPO-BAENA, O.J., TOBON, J.I., Construction and Building Materials, **118**, 2016, p. 286.

5.NORDIN, N., ABDULLAH, M.M.A.B., TAHIR, M.F.M., SANDU, A.V., HUSSIN, K., International Journal of Conservation Science, **7**, no.1, 2016, p. 161.

6.TEIXEIRA, S.R., SOUZA, A.E., CARVALHO, C.L., REYNOSO, V.C.S., ROMERO, M., RINCON, J.M., Materials Characterization, **98**, 2014, p. 209.

7.BAHURUDEEN, A., SANTHANAM, M., Cement and Concrete Composites, **56**, 2015, p. 32

8.REIG, F. B., ADELANTADO, J.V.G., MOYA MORENO, M. C. M., Talanta, **58**, 2002, p. 811.

9.KADIR, A.A., RAHIM, A.S.A., SANDU, I.G., ABDULLAH, M.M.A., SANDU, A.V., Rev. Chim. (Bucharest), **67**, no. 5, 2016, p. 978.

10.SHAHEDAN, N.F., ABDULLAH, M.M.A.B., HUSSIN, K., SANDU, I., GHAZALI, C.M.R., BINHUSSAIN, M., YAHYA, Z., SANDU, A.V., Mat. Plast., **51**, no. 3, 2014, p. 258

Manuscript received: 12.02.2016