

Silica Content and Structure from Corncob Ash with Various Acid Treatment (HCl, HBr, and Citric Acid)

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ABSTRACT

In this study, a simple method to obtain silica from corncob ash has been investigated using a nonthermal and thermal method. The Nonthermal method was done by various acid treatment with HCl, HBr and citric acid at room temperature. Thermal method was performed for HCl-leached, HBr-leached, and citric acid-leached corncob in the furnace at 750 °C for 5 hours. Corncob ash was characterized by Energy Dispersive X-ray fluorescence spectroscopy (EDXRF), Fourier transforms infrared spectroscopy (FTIR), X-Ray diffraction (XRD), and Scanning electron microscope-electron dispersive X-ray (SEM-EDX). In this study silica content increase after acid treatment (leaching) and combustion at high temperatures. The result established that silica is most obtained with HCl treatment that is equal to 79,95% with lower metallic oxide impurity content. The FTIR spectra with different intensity shows silanol group at 1636 – 1641 cm⁻¹, whereas siloxane group at 1037 – 1106 cm⁻¹, 616–797 cm⁻¹, and 459–469 cm⁻¹. X-Ray diffractogram shows silica transition of amorphous ($2\theta = 21 - 25^\circ$) to quartz crystalline ($2\theta = 26.66^\circ$) phase. The surface morphology of silica that characterized with SEM-EDX shows amorphous and crystalline silica corresponds to XRD result. The high intensity spectra of Si and O in EDX shows the presence of silica in corncob ash.

Keywords : corncob ash, silica, acid treatment

INTRODUCTION

Corn is the main of agricultural product in Indonesia. Corn production in 2015 reached 19.6 million tons (Badan Pusat Statistik, 2016). From that amount, we get corncobs waste of 5.88 million tons. Because it has no promising commercial value, corncob waste is usually only burned in the open air, causing air pollution and waste problems. A lot of effort has been made to make corncob waste be valuable. There have been several studies in the literature reporting corncob waste use. Corncob waste has been used as a mixture of animal feed (Umiyah and Wina, 2008), adsorbent (Hou et al., 2013; Sun et al., 2012), biofuel (Li et al., 2010), and cement (Adesanya and Raheem, 2010).

Corncob contains cellulose 40 - 45%, hemicellulose 30 - 35% and lignin 10 - 20% (Velmurugan et al., 2015). In 2009, Adesanya and Raheem reported while corncob ash contains more than 60% silica with a small percentage of metal elements. Based on these report, corncob ash has the potential source of silica. Silica is a chemical compound with the formula SiO₂ molecule (silicon dioxide) which can be obtained from mineral silica, vegetable (natural material) and synthesis (Bragmann and Goncalves, 2007).

Silica isolation from the natural material can be done by the nonthermal and thermal method. In the nonthermal method, organic and inorganic compounds can remove by acid treatment (leaching). The use of HCl as a hydrolyzing acid in silica isolation from the bottom ash of the sugar industry has been investigated by Amin et al. (2016). Silica can also be obtained from rice husk with carboxylic acid treatment (Umeda and Kondoh, 2008). The use of hydrolysis acid was expected to obtain a high content of silica from natural materials. The silica content can be increased by the thermal process through combustion at high temperatures (Fernandes et al., 2016).

The objective of the present work paper is to investigate silica in corncob ash by the nonthermal method with acid treatment and thermal method with combustion at high temperature. The acid used is hydrochloric acid (HCl), bromide acid (HBr), and citric acid. Citric acid is a more environmentally friendly organic acid is expected to produce high levels of silica. Bromide acid is chosen as hydrolyzing acid because it is theoretically stronger in acid than HCl. Therefore, an experimental investigation was conducted to explore the best acid to produce high silica content in corncob ash. To increase the silica

content in corncob powder, it was burned at high temperature 750°C for 5 hours. The corncob ash was measured by Energy Dispersive X-ray fluorescence spectroscopy (EDXRF) to analyze the content of silica and metallic oxide impurity in each ash. Identification the presence of silica functional group in each ash was analyzed by Fourier transform infrared spectroscopy (FTIR). The structure and morphology of corncob ash characterized by X-Ray diffraction (XRD) and Scanning electron microscope-electron dispersive X-ray (SEM-EDX) respectively.

EXPERIMENTAL SECTION

Tools and materials

The tools used is glassware, Whatman filter paper, spray bottle, grinder, analytical balance, oven, magnetic stirrer, porcelain crucible, and furnace. The Instrument used is Energy-Dispersive X-ray Fluorescence spectrometer (EDXRF) MiniPal 4 at Energy and Environmental Laboratorium Institute Technology of Sepuluh Nopember, Fourier Transform-Infra Red (FTIR) Nicolet Avatar 360 at Analysis Laboratorium University of Islamic Indonesia, and X-Ray Diffraction (XRD) PANalytical at PSBTM-BATAN, Serpong. The required materials are corncob ash (*Zea mays*) Arjuna variety from the local agricultural field (Ciapus, Bogor, West Java), HCl 37% (Merck), Citric acid *Pro Analyst* (Merck), HBr *Pro Analyst* (Merck), and distilled water.

Experimental Procedure

Corncob washed with water until clean and drying in open air. Dry corncob cut into small pieces and grinded to powder. Corncob powder was leached using 250 mL acid (HCl, HBr, and citric acid) 3 M. Leaching is done by stirring the solution (100 rpm) at room temperature for 60 minutes. The leaching solution was filtered and the powder obtained was washed with distilled water. The powder is dried at 100 °C for 20 minutes. The obtained powder is labeled STJ1 (leached with HCl), STJ2 (leached with HBr) and STJ3 (leached with citric acid). The obtained powder then analyzed its chemical composition using EDXRF.

Corncobs without leaching (STJ0), STJ1, STJ2 and STJ3 were furnaced at 750 °C for 5 hours. Results obtained in the form of corncob ash labeled ATJ0 (corn ash without

leaching), ATJ1 (leached with HCl), ATJ2 (leached with HBr) and ATJ3 (leached with acid citric). The obtained ash is then analyzed its chemical composition using EDXRF.

The structure and the functional group of corncob ash (ATJ0, ATJ1, ATJ2 and ATJ3) observed using XRD and FTIR respectively. In XRD characterization, each ash sample measured its diffraction pattern at $2\theta = 20 - 80^\circ$ by the powder method. The diffractogram was observed and interpreted according to SiO₂ peak. In FTIR characterization, the ash samples were mixed with KBr and pellets were made. This pellet is measured its infrared absorption in the range of wave numbers 4000 - 300 cm⁻¹. The obtained FTIR spectra were observed and interpreted the characteristic spectra of SiO₂.

Surface observation of SiO₂ on corncob was done using SEM-EDX. The sample powder (ATJ0, ATJ1, ATJ2 and ATJ3) is first coated before in SEM-EDX. Samples of 100 mg placed spread on the carbon tape attached to the pin, the sample cleaned so that no dust is left behind. A pin inserted into sample holder for the coating process. The sample holder is then inserted into the SEM-EDX chamber. Based on the SEM-EDX micrograph obtained, the surface of SiO₂ is observed.

RESULT AND DISCUSSION

Chemical composition of corncob

Silica in corncob powder obtained via nonthermal and thermal methods. In the nonthermal method, corncob powder was leached using 3 acid variation are HCl, HBr, and citric acid. Acid treatment at room temperature is performed to remove other compounds in corncob powder. Faizul et al. (2013) have defined that leaching is performed to remove unwanted substances from a solid through a liquid medium in which case it is an acid. The study by Chakraverty and Kaleemullah (1991) about the rice husk, a nonthermal method with a strong acid is also effective for the removal of inorganic impurities which are usually present in small amounts. Strong acids not only can remove inorganic impurities, but also organic compounds such as cellulose, hemicellulose, and lignin. The chemical composition of corncob powder (STJ0 - STJ3) showed a chemical is dominated by silica (**Table 1**).

Table 1. Chemical content of Corncob Powder (% weight)

	SiO ₂	CaO	MgO	K ₂ O	Na ₂ O	Fe ₂ O ₃	Al ₂ O ₃
STJ0	27.8	14.03	9.5	18.49	ND	4.69	5.7
STJ1	43	8.4	ND	ND	ND	8.02	4
STJ2	22.5	3.3	ND	ND	ND	6.77	ND
STJ3	35	10	0.95	0.7	ND	11.15	ND

Based on the results of the analysis with EDXRF, the highest silica content, 43%, was found in corncob powder leached using HCl (STJ1). The enhancement of silica content is accompanied by the decline of other impurities. The alkali metal oxides of CaO, MgO, and K₂O are the main impurities in corncob powder. This alkali metal oxide content is less after the leaching of acid in corncob powder.

The metal impurities bound with Cl⁻ and Br⁻ in corncob powder which leached with HCl and HBr. Umeda and Kondoh (2008) found that using carboxylic acids for leaching, cause metal impurities can be reduced through chelate reactions between carboxyl groups (-COOH) and metallic element. The leaching result using carboxylic acid is in good agreement with the present study that uses citric acid for leaching. The three acids are capable reducing the metal oxide compounds with different abilities based on their reaction to the metal oxide.



Figure 1. Corncob ash (a) ATJ0, (b) ATJ1, (c) ATJ2 and (d) ATJ3

The thermal method is carried out to obtain corncob ash which contains more silica. **Figure 1** shows a different color appearance of the corncobs ash. Corncob ash without acid leaching (ATJ0) are gray while the ashes of leaching (ATJ1, ATJ2, and ATJ3) are both light brown but with different brightness. ATJ1 is the brightest than ATJ2 and ATJ3. Different colors of ash may be affected by impurities that remain behind. The impurities are carbon

or other metal oxides. Based on the appearance of the ash, it can be said that the silica obtained is not a pure silica. According to Della et al. (2012), longer combustion times with higher temperatures can remove carbon impurities, but the formed silica will transition from amorphous to crystalline.

The appearance of the ash color in **Figure 1**, is seen that ATJ1 is the brightest, so it can be said that HCl is the best acid to leach impurities. Hydrolysis using hydrochloric acid has been done by Chandra et al. (2012) that isolate the silica from rice husks. The burning of rice husks after hydrolysis using HCl results in a whiter rice husk ash because at the time of burning the metal content and organic compounds in rice husks have been lost before. The use of HCl as a hydrolyzing acid in silica insulation has also been carried out by Amin, et al. (2016). Ash that has leach with acid and burns at high temperature is highly desirable because it contains a higher content of silica (**Table 2**).

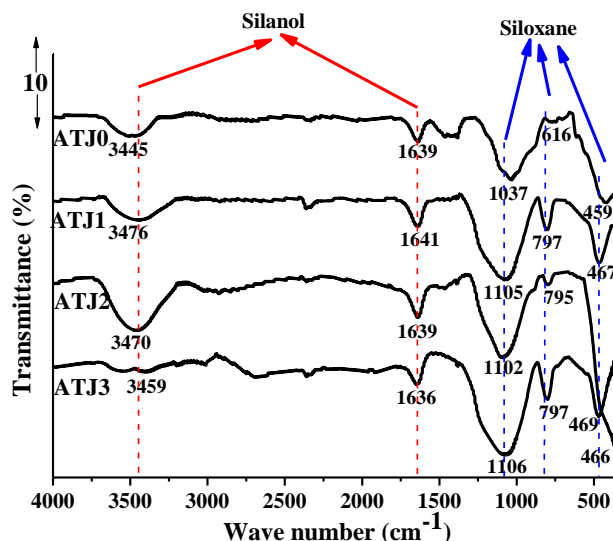
The silica content in corncob ash without acid treatment did not increase significantly. The level of silica in corncob ash with acid treatment use HCl and citric acid has increased almost twice as much. The enhancement in silica content reached almost threefold occurred in corncob ash HBr acid treatment. Although the use of each of these acids can increase the silica content, HCl is the most effective acid used because it can produce corncob ash with the highest silica content.

FTIR characterization

Characterization with FTIR was performed to identify major chemical groups present in the corncob ash is shown in **Figure 2**. In addition to chemical groups, information about bonds through shifts in absorption wave numbers due to the formation of silica structures in corncob ash can also be observed by FTIR spectra.

Table 2. Chemical content of Corncob Ash (% weight)

	SiO ₂	CaO	MgO	K ₂ O	Na ₂ O	Fe ₂ O ₃	Al ₂ O ₃
ATJ0	26.9	16.45	1.35	26.55	ND	8.66	1.85
ATJ1	79.95	1.24	ND	1.52	ND	3.9	5.15
ATJ2	63.65	1.93	ND	4.04	ND	4.83	20.05
ATJ3	70.6	3.37	ND	2.59	ND	8.26	3.6

**Figure 2.** FTIR Spectra of Corncob Ash

The main chemical groups in silica are silanol and siloxane (Rafiee et al., 2012; Amin et al., 2016). The corncob ash (ATJ0 - ATJ3) has silanol and siloxane groups with varying intensity. The absorption band of the silanol group comprises a vibrational absorption band OH bonding of Si-OH at wave numbers 1636, 1639, 1641 cm^{-1} and a broadband at wave numbers 3445, 3459, 3470, and 3476 cm^{-1} is due to water-bending molecular vibration bound to the silica matrix. The absorption bands of the siloxane groups are shown in the three regions of wave numbers. The vibration asymmetry of siloxane bonds (Si-O-Si) is 1037, 1102, 1105, and 1106 cm^{-1} . The vibration symmetry of Si-O-Si framework is 616, 795, and 797 cm^{-1} . The bending vibration of the O-Si-O framework is 459, 466, 467 and 469 cm^{-1} .

The FTIR corncob ash spectra exhibited nearly identical absorption band patterns but had different intensities seen in their relative transmittance percentage values. The absorbing vibration band of symmetry of Si-O-Si framework on corncob ash without acid treatment has a relatively low % of transmittance with sloping peak. It is shown that the siloxane group has not been formed clearly. The FTIR's result is consistent with

the EDXRF's results which shows that the content of silica in corncob ash without acid treatment is much lower than corncob ash with acid treatment. The absorption bands of the silanol and siloxane groups are increasingly apparent in corncob ash through the highest intensity treatment of ATJ1. The results of this study indicate that silica structure begins to form well when corncob powder leach uses HCl rather than the other two acids. The difference of intensity and the shape of the top of the silanol and siloxane bands on corncob ash with three different acids leaching indicates structural and silica bonds differences.

XRD characterization

Characterization using XRD was performed to look at the presence of silica and identify its phase through the diffraction peaks that appeared at $2\theta^\circ$ in the $20 - 80^\circ$ range. Diffractograms of corncob ash indicate different patterns and intensities (**Figure 3**). In ATJ0 the diffractogram pattern looks more sloping, widened, and has a low intensity in the region $2\theta^\circ = 20 - 35^\circ$. Diffractogram shows that amorphous silica is formed on corncob ash without leaching using acid (nonthermal treatment).

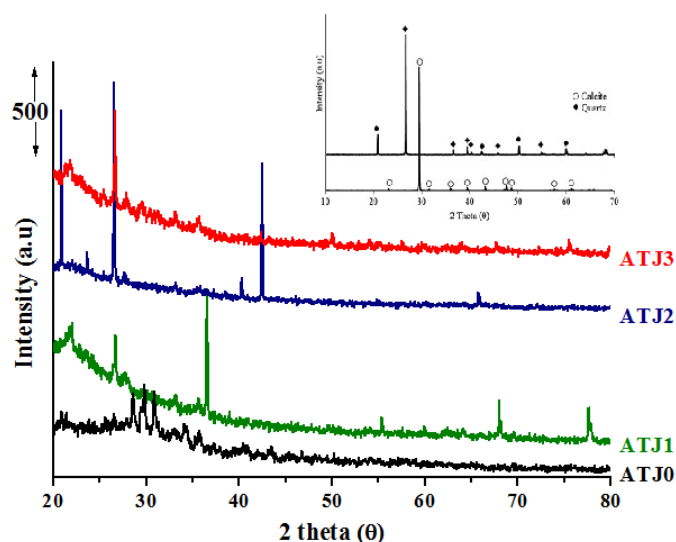


Figure 3. Corncob Ash Diffractogram

The diffractogram corresponding with a study conducted by Zhao, et al., 2016 which shows that amorphous mesoporous silica is at $2\theta = 15 - 30^\circ$. The amorphous phase silica begins to transition into a crystalline phase in ATJ1, ATJ2, and ATJ3. The ATJ1 diffractogram still clearly shows the amorphous phase silica at $2\theta = 21 - 25^\circ$ and began to appear sharp peaks with low intensity at $2\theta = 26^\circ$. According to the NIOSH manual of Analytical Methods (2003) which deals with amorphous silica, the peak that appears at $2\theta = 26.66^\circ$ indicates that the type of silica structure is quartz. ATJ2 diffraction shows a more crystalline silica phase when compared to ATJ0, ATJ1, and ATJ3. At ATJ2 the peak intensity indicating the emergence of amorphous silica begins to disappear, and the peak intensity indicating the presence of silica in the form of quartz looks higher and more sharply. The amorphous silica peak is still visible on ATJ3 although not the peak marks produced by ATJ1 at $2\theta = 21 - 25^\circ$. In ATJ3, silica peaks in quartz form look increasingly sharp with high intensity.

The silica structure of a corncob ash that leached with three types of acid and combusted at 750°C for 5 hours showed different phases. Although the amorphous phase of SiO_2 can be obtained by burning ash at temperatures up to 750°C (Mohanraj et al., 2012) in this study, the type of acid used for the leaching process before the thermal process also affected the silica structure. The amorphous phase of silica is still apparent when used HCl and $\text{C}_6\text{H}_8\text{O}_7$ as

leaching agent and begin to form peaks indicating phase transitions from amorphous to crystalline. While at HBr as leaching agent, the peak intensity of corncob ash diffractogram indicates that the presence of the amorphous phase is less dominant than the peak indicating the presence of the crystalline phase. It shows that HCl is a leaching agent which can maintain the silica phase in the amorphous phase during the thermal process 750°C for 5 hours. Increased temperature and burning time is likely to increase the crystallinity of the silica structure.

SEM-EDX characterization

The morphology of silica in corncob ash is characterized by SEM-EDX to observe the shape and structure of the particles. The SEM-EDX results also provide data on the percentage of composition of corncob ash. The morphological observation of corncob ash without leaching with acid and leaching with acid (ATJ0 - ATJ3) is shown in magnification 2500 times (**Figure 4**).

The results obtained in **Figure 4(a) - 4(d)** shows the surface shape of corncob ash which is seen more clearly. The intensity of the ash surface color that tends to be less bright when compared with the other three micrographs shows that in ATJ0 there is still more impurities in the form of organic and inorganic substances as seen in the data of other components of the larger element compared with the other three ashes.

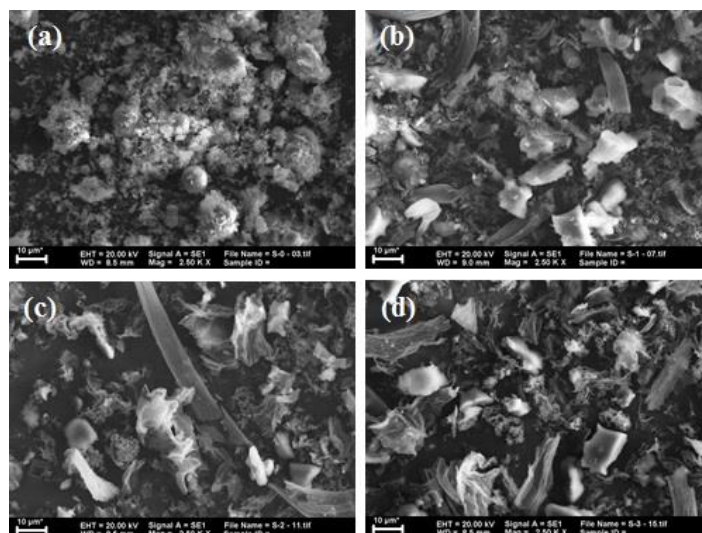


Figure 4. Corncob Ash Micrograph with 2500 Times Magnification (a) ATJ0, (b) ATJ1, (c) ATJ2, and (d) ATJ3

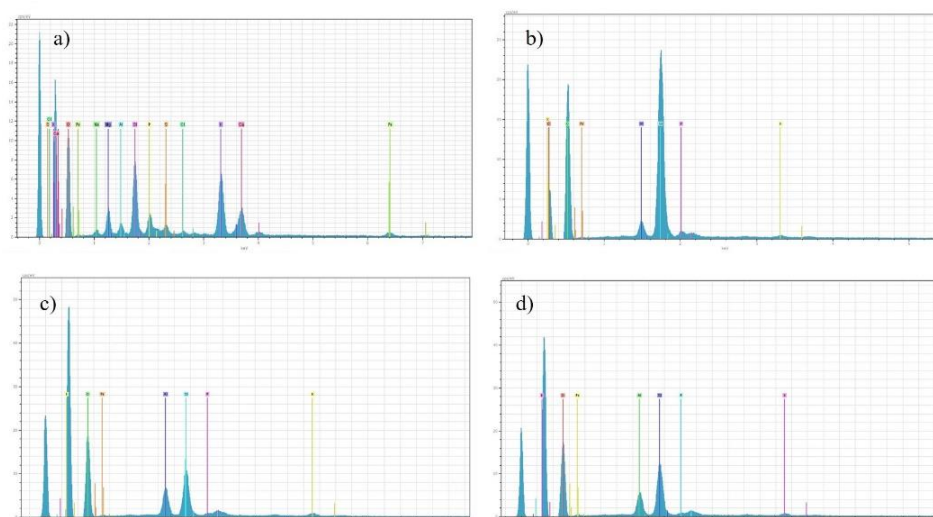


Figure 5. EDX Spectra of Corncob Ash (a) ATJ0, (b) ATJ1, (c) ATJ2, and (d) ATJ3.

Table 3. Element composition of corn cob ash

No.	Corncob Ash Code	Element Percentage (%)							
		Si	P	Ca	Mg	K	Na	Fe	Al
1	ATJ0	4.14	1.58	3.40	2.01	6.21	0.48	1.31	0.55
2	ATJ1	15.34	1.06	ND	ND	0.32	ND	0.8	1.34
3	ATJ2	5.92	1.49	ND	ND	0.66	ND	0.87	4.31
4	ATJ3	7.75	1.53	ND	ND	0.61	ND	0.72	4.15

The ash surface of corn cob with acid treatment (ATJ1 - ATJ3) shows a different shape with ATJ1. With the acid treatment and combustion at 750 °C for 5 hours, the surface of corn cob ash began to change its shape into small pieces of silica-shaped structure that began to transition from the amorphous phase to the crystalline phase. It is shown on a more regular surface form almost resembling a long

cylinder and an irregular cube. The form of powder and fibers as seen on the surface of ATJ0 begins to decrease (ATJ1 and ATJ3) and is almost invisible (ATJ2). The silica profile in SEM micrograph corresponds to the results of FTIR and XRD characterizations on ATJ1 - ATJ3 which indicates that the structure of silica begins to form clearly. The shape of the

silica structure begins to change its phase from amorphous to crystalline.

In ATJ1 - ATJ3 the intensity of the ash color is lighter and cleaner when compared to ATJ0, it indicates that impurities in the form of organic and inorganic substances begin to be reduced. The percentage of organic and inorganic substances in the corncob ash showed in EDX spectra (**Figure 5**). A strong intensity of Si and O peaks appear in **Figure 5 (b), (c), and (d)**, confirming the presence of silica. Silica is predominant in these ash corresponds to SEM images. The composition percentage of corncob shown in **Table 3**.

CONCLUSION

In this study, the silica of corncobs can be obtained by nonthermal treatment with HCl as hydrolyzing acid and thermal treatment at 750 °C for 5 hours. The silica content obtained on corncob ash from EDXRF analysis was 79.95%. Structure characterization with FTIR shows that silica structure presents a bond of silanol and siloxane groups already formed. The silica structure identified by XRD indicates that transitions an amorphous phase into a crystalline phase. The morphology of the silica surface observed with SEM-EDX shows amorphous and crystalline silica according to XRD results.

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