J. Mater. Environ. Sci. 7 (7) (2016) 2369-2374 T. Chanadee et al.
ISSN : 2028-2508
CODEN: JMESC

Preparation and Characterization of Low Cost Silica Powder from Sweet Corn Cobs (*Zea mays saccharata L.*)

T. Chanadee[*], S. Chaiyarat

Materials Science Program, Department of Materials Science and Technology, Faculty of Science,
Prince of Songkla University (PSU), Hat Yai, Songkhla 90112, Thailand

Received 25 Mar 2016, Revised 11 May 2016, Accepted 16 May 2016

**Corresponding author. E-mail: tawat.ch@psu.ac.th (T. Chanadee); Phone: +6674288382; Fax: +6674446925*

Abstract

Preparation and characterization of silica powder from sweet corn cob were carried out in this work. Corn cobs were burned in air at 600 and 800 °C for 2 hours to obtain corn cob ash (CCA). Silica powder was produced by dissolving CCA with sodium hydroxide (NaOH) solution to form sodium silicate (Na_2SiO_3) solution. The pH of the solution was adjusted to7.0 by adding hydrochloric acid (HCl) to form silica gel followed by drying to form silica powder. As-prepared silica powder was characterized using XRF, XRD, FT-IR, and SEM techniques. As-prepared silica powder with 90.6% silica content was obtained from CCA after burning at 600 °C. In addition, XRD patterns revealed amorphous structure and FT-IR spectra indicated the presence of siloxane and silanol groups in as-prepared silica powder from CCA burned at 600 °C.

Keywords: Agricultural waste, Corn cob ash, Silica, Sol-gel, Sweet corn

1. Introduction

Sweet corn (*Zea mays saccharata L.*) is one of the significant agricultural crops. In Thailand, production capacity of sweet corn is about 1.48 million tons per year [1]. This includes fresh stalk, frozen or canned.

The factories sort out corn seeds for further processing and leaving in corn cobs as industrial waste. Biodegradation of corn cobs by microorganisms is a long process. Incineration is simple and fast, however, it releases green house gas (CO_2) to atmosphere and causing global warming. Moreover, smoke from the process to cause directly affect to public health [2]. According to the above mention, corn cob industry is concerned environmental pollutions, therefore, suitable process to dispose or convert corn cob waste to valuable product is crucial.

From the literature [3-5] it was reported that corn cob composes of cellulose and lignin and consists of significant elements such as silicon (Si, 0.133 wt%), calcium (Ca, 0.022 wt%) and aluminium (Al, 0.052 wt%).

Relatively high content of silicon was found in corn cobs which could be converted into silica (SiO_2) in form CCA. Purified CCA silica can be obtained from burning corn cobs in air followed by extraction with alkaline or acid solutions [6]. This process provides a promising source of silica, which is essential reactant for further advanced material synthesis.

The objective of this work is to prepare silica powder from sweet corn cobs by dissolving CCA in NaOH solution followed by HCl solution. Furthermore, the effect of burning temperatures of corn cobs to CCA was investigated. From this method, silica powder can be produced at low cost and agricultural wastes can be reduced to prevent pollution. As-prepared silica powder was characterized by using XRF (X-ray fluorescence), FT-IR (Fourier transform infrared spectroscopy), XRD (X-ray diffraction), and SEM (Scanning electron microscopy) techniques.

2. **Experimental**

2.1. *Preparation of CCA powder*

Sweet corn cob was collected from local Songkhla province, Thailand. Firstly, bulk corn cobs were washed and then dried at 110 °C for 24 h. 500 g of dried-corn cobs were ground into small crumbs. Powder of CCA was obtained by burning corn cobs in air at 600 and 800 °C for 2 hours.

2.2 *Preparation of silica powder*

Silica powder was achieved by adapting the purifying method of selected-CCA powder burned at 600 °C from Shim, J. *et al* [6]. A 10 g of CCA powder was stirred in 60 mL of a 1 N NaOH aqueous solution. The solution was stirred in a covered beaker for 3 h with a constant heating at 80 °C to dissolve silica and produce a sodium silicate (Na_2SiO_3) solution (reaction (1)). After that, residues of K_2O, P_2O_5, CaO, etc. were separated from Na_2SiO_3 solution by filtering through filter paper, Whatman No. 41, assisted with a pump inlet.

$$SiO_{2(s)} + \text{residues}_{(s)} + NaOH_{(aq)} \rightarrow Na_2SiO_{3(aq)} + H_2O_{(l)} + \text{residues}_{(s)} \quad (1)$$

$$Na_2SiO_{3(aq)} + HCl_{(aq)} \rightarrow 2NaCl_{(aq)} + H_2O_{(l)} + SiO_{2(s)} \quad (2)$$

In general, insoluble ionic compounds have higher lattice energy than hydration energy. The energy provided by hydration of dissolved ions is inadequate to break down the ionic lattice, thus the ionic compounds remain mostly undissolved [7].

In order to remove residues, sodium silicate solution was washed with hot water several times until the solution was clear. The clear solution was allowed to cool to room temperature. pH of the solution was adjusted to 7.0 by using 1 N HCl at a constant stirring and then incubated to encourage gel formation for 12 h (as expressed in reaction (2)). This step was followed by several washings and centrifugation at 4000 rpm for 5 min. After that, the supernatant was removed. Next, the acquired gel was dried at 80 °C for 24 h to obtain as-prepared xerogel. Finally, xerogel was washed with deionized water at least 3 times and dried at 80 °C to produce 8 g of as-prepared silica powder.

2.3 *Characterization of silica powder*

The silica content in CCA powder and as-prepared silica powder were investigated by using XRF (PHILIPS PW2004, the Netherlands). X-ray diffraction pattern of as-prepared silica powder was obtained from XRD (PHILIPS X' Pert MPD, the Netherlands) using CuK_α radiation of 1.54 Å and a scan range of 20-80° with a step size of 0.05°. A Fourier transform infrared spectrum of as-prepared silica powder was obtained from FT-IR (Bruker TENSOR 27, USA) recorded in a wave number range of 4000 - 400 cm^{-1}. 1 mg of as-prepared silica powder was mixed with 100 mg of KBr in ZrO_2 mortar and then pressed into a thin pellet. KBr is essential in order to improve the transparent and prevent the scattering of the incident light at the samples surface. The morphology of CCA powder and as-prepared silica powders were investigated by SEM (Quanta 400, FEI, USA). Prior to SEM analysis, the samples were coated with a very thin film of gold (Au) using a sputter coater (SPI, 12150 AX, USA).

3. **Results and discussion**

Elemental analysis of sweet corn cobs used in this work was presented in Table 1.

Table 1: Composition of corn cobs from XRF analysis.

Element	Concentration (wt%)
Si	0.31
K	0.61
Cl	0.27
Ca	0.15
Trace elements	Balance

Physical characteristics of corn cob and CCA powder were shown in Fig. 1. The composition of CCA powder was presented in Table 2.

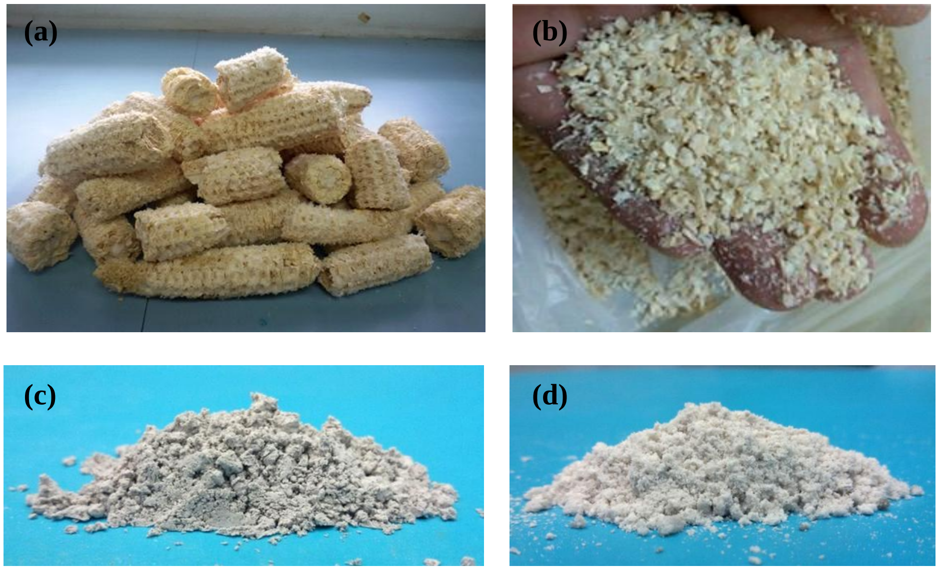

Figure 1: Macrostructural images of corn cob in different forms (a) dried-bulk corn cobs, (b) ground-corn cobs, (c) CCA powder burned at 600 °C, and (d) CCA powder burned at 800 °C.

Table 2: Composition of CCA powder from XRF analysis.

Compound	**Concentration (wt%)**	
	600 °C	**800 °C**
SiO_2	28.02	25.37
K_2O	31.93	31.93
P_2O_5	13.86	19.39
CaO	3.09	8.12
Trace compounds	Balance	Balance

As-prepared gel, as-prepared xerogels and as-prepared silica powder were shown in Fig. 2(a)-(c), respectively.

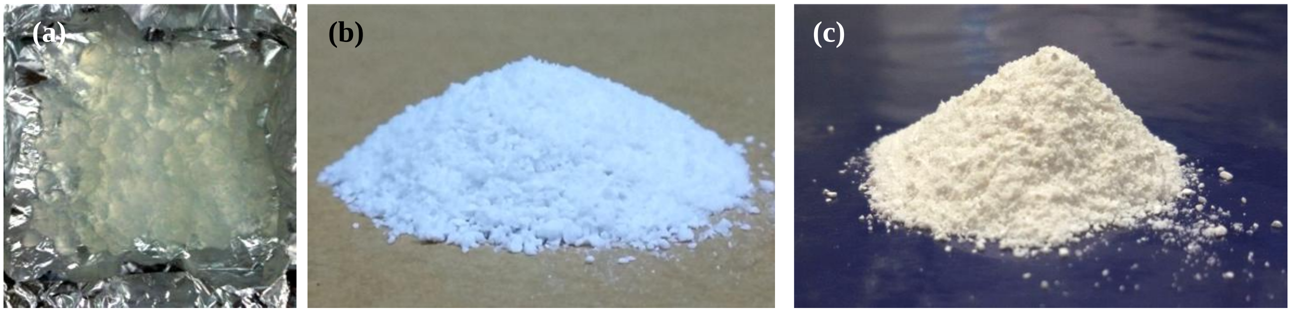

Figure 2: Macrostructural images of (a) as-prepared gel, (b) as-prepared xerogels, and (c) as-prepared silica powder derived from CCA burned at 600 °C.

Table 3 shows yield of CCA calculated according to ASTM E1756-01 reported by Sluiter, A. *et al* [8-9] as shown in equation (3)-(5).

$$\mathrm{ODW}=\frac{\mathrm{Weight}_{\text{air dry sample}}}{100}\ \mathrm{x}\ \%\text{Total solids} \qquad (3)$$

$$\%\text{Total Solids}=\frac{(\mathrm{Weight}_{\text{dry crucible plus dry sample}}-\mathrm{Weight}_{\text{dry crucible}})}{\mathrm{Weight}_{\text{sample as received}}}\ \mathrm{x}\ 100 \qquad (4)$$

$$\%\mathrm{Ash}=\frac{(\mathrm{Weight}_{\text{crucible plus ash}}-\mathrm{Weight}_{\text{crucible}})}{\mathrm{ODW}}\ \mathrm{x}\ 100 \qquad (5)$$

where ODW is oven-dry weight of corn cob.
$\mathrm{Weight}_{\text{air dry sample}}$ is air-dry weight of corn cob.
$\mathrm{Weight}_{\text{dry crucible plus dry sample}}$ is crucible plus corn cob weight dried at 105 ± 3 °C.
$\mathrm{Weight}_{\text{dry crucible}}$ is crucible weight dried at 105 ± 3 °C.
$\mathrm{Weight}_{\text{sample as received}}$ is moist weight of corn cob.
$\mathrm{Weight}_{\text{crucible plus ash}}$ is crucible plus CCA weight burned at 600 and 800 °C.
$\mathrm{Weight}_{\text{crucible}}$ is crucible weight burned at 600 and 800 °C.

Table 3: Ash yield of CCA powder after burning at different temperature.

Temperature (°C)	Ash yield (%)
600	7.6
800	1.3

It was observed that CCA powder obtained from burning corn cob at 600 °C (Fig. 1(c)) appeared as dark-gray powder due to existing of carbon residue (remaining from the decomposing of cellulose and lignin), whereas CCA powder from burning corn cob at 800 °C appeared as milky white powder. At high burning temperature, carbon was oxidized and burned off, thus the presence of unburned black carbon decreased. The color of metal oxide constituents that are in the CCA influenced the color of CCA, resulting in milky white obtained [10]. Table 2 shows XRF results producing composition of CCA after burning at different temperatures. The compositions of CCA were SiO_2, K_2O, P_2O_5 and CaO as major components. In addition, the minor composition was composed of unburned carbon and other residues of CCA. It can be seen that CCA obtained from burning at 600 °C is the optimum condition because it contained higher amount of silica than CCA obtained from burning at 800 °C. It also shows that CCA powder obtained from burning at 800 °C contained higher amounts of metal oxides (e.g. P_2O_5, CaO) due to greater formation of these compounds at higher temperature [11]. Moreover, burning at 600 °C led to higher ash yield compared to CCA obtained from burning at 800 °C (see Table 3).

The chemical composition of as-prepared silica powder obtained in this work was presented in Table 4.

Table 4: Composition of as-prepared silica powder from XRF analysis.

Compound	Concentration (wt%)	
	600 °C	800 °C
SiO_2	90.60	88.43
P_2O_5	1.74	4.77
Trace compounds	Balance	Balance

It can be observed from Table 4, that chemical treatments (alkaline and acid treatment) led to higher silica concentration and also decreased the concentration of heavy metals. Fig. 3 showed an XRD pattern of as-prepared silica powder in range of 2θ = 0 - 80°. A broad peak was observed at 2θ = ~17 - 29° corresponding to the formation of amorphous silica according to ICDD data base No. 01-080-3750. However, trace compound peaks were obtained in as-prepared silica powder in agreement with the XRF result.

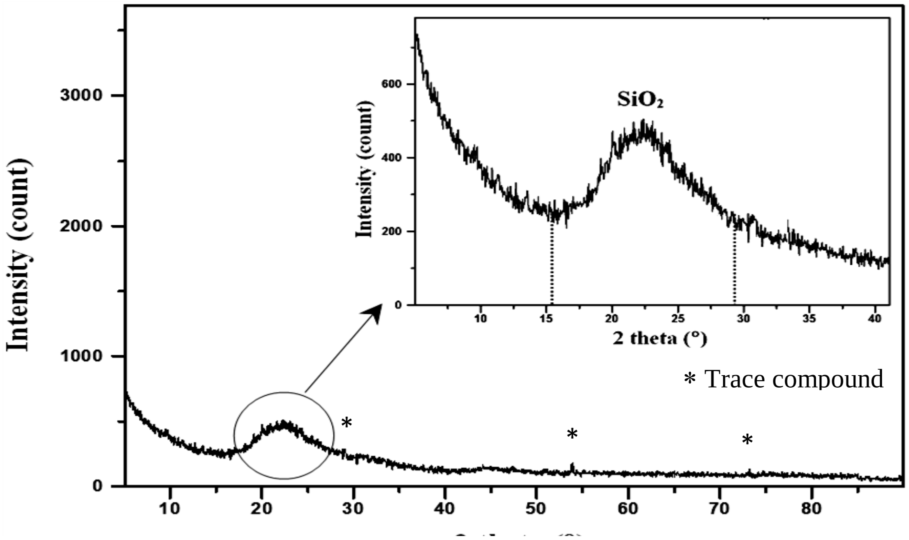

Figure 3: XRD pattern of as-prepared silica powder derived from CCA burned at 600 °C.

FT-IR spectrum of as-prepared silica powder derived from CCA burned at 600 °C was shown in Fig. 4. A broad band around 3500 cm^{-1} corresponded to stretching vibration of the O-H bond from the silanol groups (Si-OH) that adsorbed water molecules on the silica surface [6, 12]. The band of Si-O asymmetric stretching vibration appeared at 1100 cm^{-1} [13] and the band of Si-O symmetric stretching vibration appeared at 800 cm^{-1} [6]. The band at 460 cm^{-1} attributed to the bending vibration of Si-O-Si called siloxane bonds [13, 14]. In addition, the band at 1600 cm^{-1} corresponded to the bending vibration of water molecules that bounded or trapped to the matrix of silica [6, 15].

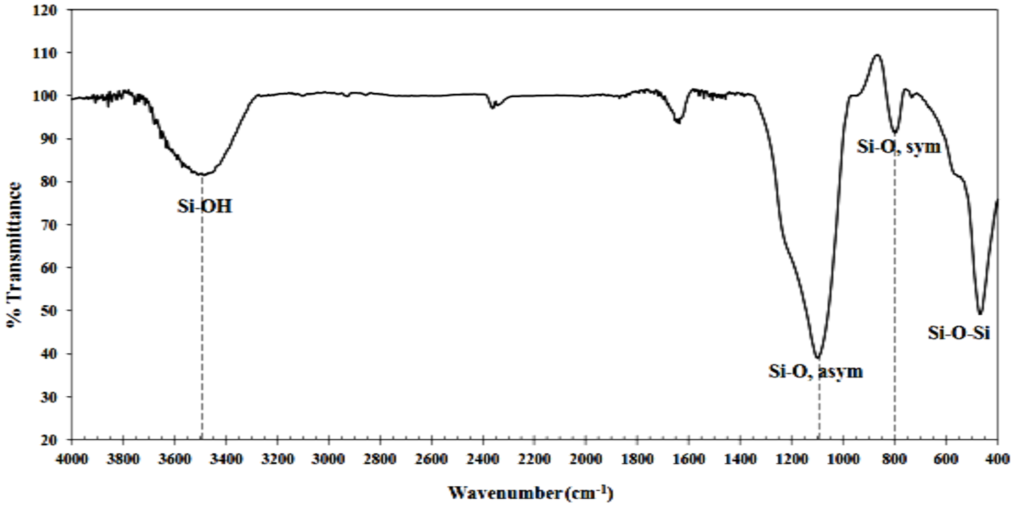

Figure 4: FT-IR spectrum of as-prepared silica powder derived from CCA burned at 600 °C.

The morphology of obtained powders received from different experimental steps were depicted in Fig. 5. Fig. 5(a) showed agglomerated particles of the received CCA burned at 600 °C. Fig. 5(b) showed large particles of as-prepared xerogels. It can be seen that as-prepared silica derived from CCA burned at 600 °C were small an average particle size and irregular in shape (Fig. 5(c)).

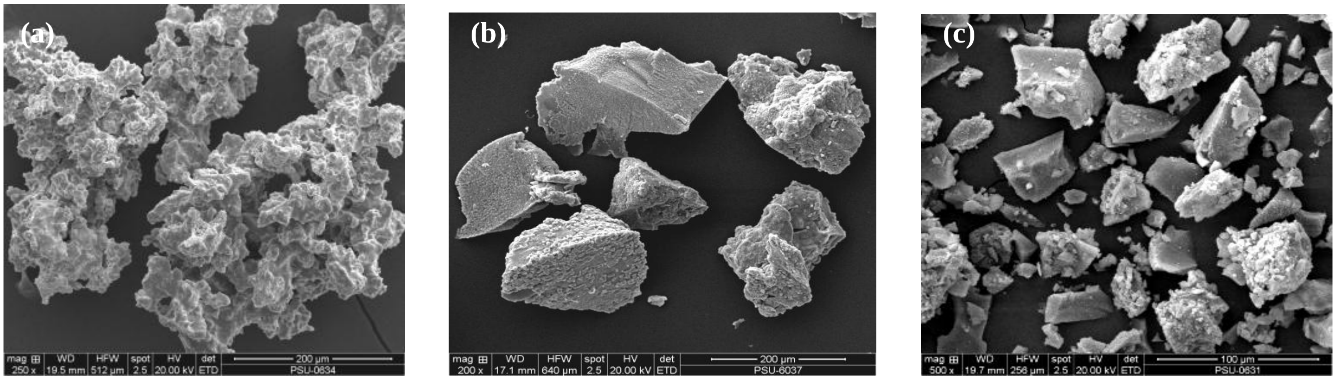

Figure 5: Microstructural images of (a) CCA powder burned at 600 °C, (b) as-prepared xerogels, and © as-prepared silica powder derived from CCA burned at 600 °C.

Conclusion

The efficacy of sweet corn cob (*Zea mays saccharata L.*) ash (CCA) as a potential source of silica powder was investigated. This work revealed that the burning temperature played an important role in the chemical and physical properties of powder products. The results indicated that the optimum burning temperature of corn cobs to produce CCA for preparing of silica powder was 600 °C. This temperature highly achieved ash yield of CCA and as-prepared silica powder. XRD analysis showed the amorphous nature of as-prepared silica powder. In addition, FT-IR data indicated the presence of silanol and siloxane groups in as-prepared silica powder.

Acknowledgments-The authors gratefully acknowledged the assistance provided by Assoc. Prof. Dr. Sumetha Suwanboon and Dr. Sirinya Chantarak in proof-reading the manuscript.

References

1. Centre for agricultural information., Office of agricultural economics., Thailand foreign agricultural trade statistics, *Agricultural Statistics Report,* 403 (2013) 1.
2. Department of Agricultural Extension. Maize: Annual Report, The Agricultural Co-operative Federation of Thailand, Limited, (2015).
3. Pinto J., Paiva A., Varum H., Costa A., Cruz D., Pereira S., Fernandes L., Tavares P., Agarwal J., *Energ. Buildings*. 43 (2011) 1985.
4. Pinto J., Cruz D., Paiva A., Pereira S., Tavares P., Fernandes L., Varum H., *Constr. Build. Mater*. 34 (2012) 28.
5. Owoeye S., Oji B., Aderiye J., *Int. Journal. Eng. Technol. Innov*. 2(3) (2015) 1.
6. Shim J., Velmurugan P., Oh B., *J. Ind. Eng. Chem.* 30 (2015) 249.
7. John Kotz., Paul T., Gabriela W. Chemistry and Chemical Reactivity, Thomson Learning, Inc, (2006).
8. Sluiter A., Hames B., Ruiz R., Scarlata C., Sluiter J., Templeton D., *Technical Report, Technical Report: Laboratory Analytical Procedure (LAP),* NREL/TP-510-42622 (2008) 1.
9. Sluiter A., Hames B., Hyman D., Payne C., Ruiz R., Scarlata C., Sluiter J., Templeton D., Wolfe J., *Technical Report, Laboratory Analytical Procedure (LAP),* NREL/TP-510-42621 (2008) 1.
10. Terzioglu P.,Yucel S., Rababah T., Özçimen D., *Bio. Res.* 8(3) (2013) 4406.
11. Sumran M., Kongkachuichay P., *KKU. Eng. J.* 30(2) (2003) 165.
12. Okoronkwo E., Imoisili P., Olusunle S., *Chem. Mater. Res.* 3(4) (2013) 68.
13. Djangang C., Mlowe S., Njopwouo D., Revaprasadu N., *J. Applicable Chem.* 4(4) (2015) 1218.
14. Indhumathi P., Syed P., Saraswathy P., *Int. J. Adv. Eng. Technol.* 2(4) (2011) 421.
15. Saleem M., Rustam M., Naqvi H., Jabeen S., Akhtar A., *Sci. Int. (Lahore)*. 27(1) (2014) 265.