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Synthesis of Silica from Rice Husk by One-step Combustion, Fluidized Bed Combustion, and Alkaline Extraction

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Abstract

The objective of this research was to synthesize silica (SiO_2) from rice husk by three techniques: one-step combustion, fluidized bed combustion, and alkaline extraction. First, the rice husk was treated with 1 M of HCl for 3 hours. Then it was combusted in a box furnace under flowing of oxygen at varied temperature of 500, 600, 700, and 800 °C for 45 or 60 min. After determining the purity and specific surface area of obtained products, it was concluded that the optimum condition for the one-step combustion was firing at 700 °C for 60 min. The obtained product was amorphous having 99.9 % (wt.) SiO_2 and specific surface area of 315±5 m^2/g. The rice husk was also pyrolyzed in a fluidized bed burner at 550 °C for 15 min under flowing of nitrogen and then fired at 600 °C for 3 hours under flowing of air. The obtained silica was also amorphous having the purity of 99.8 % and the specific surface area of 331±6 m^2/g. For the last method, the rice husk ash was extracted by 1 M $NaOH$. This technique yielded 96.6 % SiO_2 having the highest specific surface area of 404±5 m^2/g

Key Words: Rice Husk, Rice Husk ash, Silica,

Introduction

Rice husk (RH) is an agricultural waste as a by-product from rice milling. Because Thailand exports large amounts of rice, millions tons of rice husk occur. Some rice husk is used as fuel, brick making, animal feed, and fertilizer. However, large amount of rice husk is left to decompose naturally. The major constituents of RH are organic compounds and hydrated silica. The organic materials consist mainly of celluloses and lignin.

Houston et al. (1972) found that when RH is burned in air the amorphous silica is obtained having the purity of 87-97% by weight. Therefore, RH is considered to be the most economical silica source. Phase, composition, and surface area of obtained silica depend critically on the combustion temperature of RH. Nakata et al. (1989) investigated properties of rice husk ash (RHA) obtained by combustion between 400 and 1500°C. The RH Combusted below 800°C was amorphous silica and above 900°C the silica in the RHA was cristobalite accompanied with small amount of tridymite. Kapur (1988, 1990) designed the tube in basket (TiB) for the RH combustion. He found that the silica in the RH was non-crystalline up to 600°C. The phase transformation of silica in the RH started at 600 to 800°C, first appearance of the cristobalite phase at 800°C. Next, the tridymite started to form at 1000°C approximately and became quite pronouncing above 1200°C. The cristobalite and tridymite phases coexisted at 1400°C.

To increase the purity of combusted RHA, the RH is pretreated by some acids, for example, HCl, H_2SO_4, HNO_3 and HF. Chakraverty et al. (1984, 1985) reported that the leaching of RH in 1 N HCl was effective to removing most of the metallic impurities. Additionally, the acid pretreatment did not affect the amorphicity of silica produced. The optimum condition for combustion RH was 500 °C for 6 hours. Real et al. (1996) found that the preliminary leaching of RH with HCl before combustion at 600 °C could obtain relatively pure amorphous silica (99.5%) and high specific surface area (260 m^2/g). Some alkaline such as $NaOH$ and NH_4OH have been also used to pretreated RH but the effect of alkaline pretreatment is not as good as that of acid pretreatment. Kalapathy et al. (2000) synthesized silica xerogel powder from alkaline extraction of RHA. The RHA was pretreated with HCl and extracted by 1 N $NaOH$. The obtained product was 93% silica containing traces of Ca, K, and Na oxides.

This work aims to increase the purity of the synthesized silica by means of 3 techniques: one step combustion in oxygen flowing atmosphere, fluidized bed combustion, and alkaline extraction. The obtained silica from each method was compared its purity and specific surface area. The obtained silica was then used to be a starting material for zeolite synthesis (did not presented in this paper).

Materials and Method

Preparation of Raw Material

RH was pretreated by boiling with 1 M HCl for 3 hours and then was rinsed with distilled water. It was dried at 120°C for 4 hours.

Synthesis of Silica

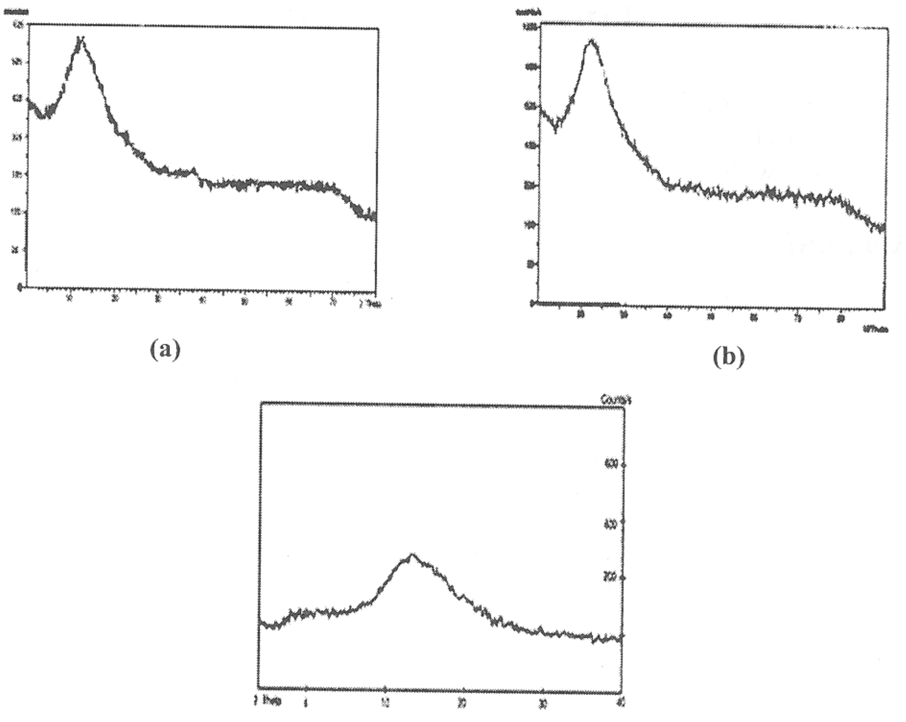
There were three techniques used to synthesize silica from pretreated RH in this experiment. First, the pre-treated RH was combusted in a box furnace under flowing of oxygen atmosphere at 500°C, 600°C, 700°C, and 800°C for 45 or 60 min. Second, the pretreated RH was pyrolyzed in a fluidized bed burner at 550°C for 15 min under flowing of nitrogen and then burned under flowing of oxygen at 600°C for 3 hours under flowing of air following Pongsak's (1992) method.

For the last method, the RHA obtained from the first technique was extracted following the methods of Kamath et al. (1998) and Kalapathy et al. (2000). Ten grams of RHA was dispersed in 60 ml. of distilled water and adjusted pH to 1 using 6 M HCl. Then it was stirred for 2 hours, filtered through ashless filter paper (Whatman no. 41). The residue was rinsed with water before extracted with 60 ml. of 1 M $NaOH$. The mixture was stirred and boiled for 1 hour. The residue was removed by the filtration. The filtrate was allowed to cool to room temperature and then titrated with 1 M HCl to pH 7. The solution was aged to form gel for 18 hours at room temperature. Next, 100 ml of deionized water was added while stirring rigorously. The slurry was centrifuged for 15 min at 2500 rpm. The clear supernatant was discarded. The obtained paste was rinsed and dried at 80°C for 12 hours.

The obtained silica from each method was analyzed its crystallinity by an X-ray diffractometer (XRD, Philips X'pert) using a $Cu-K$ line as a source and a nickel as a filter at 30 kV and 30 mA, specific surface area by a multipoint BET (adsorption) method (High Speed Gas Sorption Analyzer, Quantachrome NOVA 1200), and chemical composition by an X-ray Analytical Microprobe (XAM, Horiba XGT 2000W) at 50 kV and 1.0 mA. Finally, the morphology of silica was viewed by mean of Scanning Electron Microscope (SEM, Jeol JSM-5600 LV).

Results and Discussion

The XRD patterns of obtained silica are shown in Figure 1. From the broad peaks, it clearly indicates that all samples are amorphous phase.



(a)

(b)

(c)

Figure 1: XRD patterns of silica from (a) one-step combustion at 600°C, 60 min, (b) fluidized bed combustion, and (c) alkaline extraction.

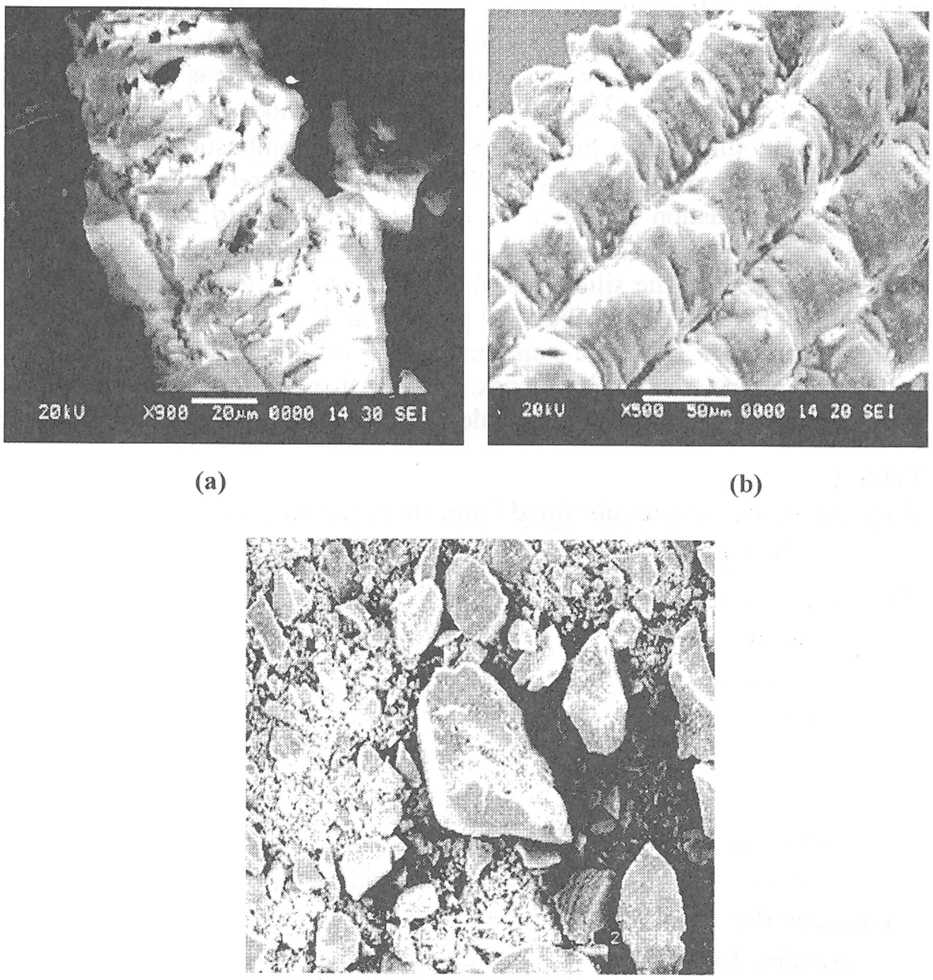
The purity of synthesized silica is presented in Table 1. For the one-step combustion, increasing temperature and time increase the obtained silica purity, except at 800°C, 60 min at which the purity is decreased. This may be due to the formation of other metal oxides (e.g. CaO, K_2O, Fe_2O_3) were enhanced at higher temperature. The one-step combustion at 700°C, 60 min and the fluidized bed combustion gave the silica purity above 99% (wt.) while the alkaline extraction method yielded lower purity (96.6%). The average specific surface areas and average pore radii of selected samples are shown in Table 2. The sample from the alkaline extraction method has the highest area followed by that of fluidized bed method and one-step combustion method, respectively. All samples have the areas larger than the previous works (Houston et al., 1972; Nakata et al., 1989; Kapur, 1988 and 1990; Chakraverty et al., 1984 and 1985; Real et al., 1996; and Kalapathy et al., 2000) in which the obtained areas were found in the range of 60 to 260 m^2/g. The fluidized bed method at 600°C, 180 min yielded higher silica purity than that of the one-step combustion at 600°C, 60 min. This can be explained that the fluidized bed method was conducted at the longer combustion time and the RH was pyrolyzed to remove organic compounds prior to oxidation. However, the one-step combustion at 700°C, 60 min can produce the silica with the same purity as that of the fluidized bed method. Figure 2 shows the SEM pictures of selected samples from each method. The silica from one-step combustion and fluidized bed method is still in the original shape of rice husk. On the other hand, the silica from the extraction method is aggregated powder.

Table 1
Silica purity of samples obtained from three techniques.

Technique	SiO_2 (% wt.)
One-Step Combustion	
- 500°C, 60 min	91.20
- 600°C, 45 min	89.50
- 600°C, 60 min	94.63
- 700°C, 45 min	94.55
- 700°C, 60 min	99.90
- 800°C, 45 min	99.12
- 800°C, 60 min	97.55
Fluidized Bed Combustion	99.80
Alkaline Extraction	96.60

Table 2
Surface characterization of silica obtained from three techniques.

Technique	Spec. Surf. Area (m^2/g)	Avg. Pore Radius (Å)
One-Step Combustion		
- 600°C, 60 min	314±5	29
- 700°C, 60 min	315±5	28
Fluidized Bed Combustion	331±6	28
Alkaline Extraction	404±5	27



(a) **(b)**

(c)

Figure 2 : SEM pictures of products from (a) one-step combustion at 600°C, 60 min, (b) fluidized bed combustion, and (c) alkaline extraction.

Conclusion

Three different techniques, one-step combustion, fluidized bed combustion, and alkaline extraction, were used to synthesize silica from rice husk. The obtained products have high content of amorphous silica (96.6 to 99.9 % wt.) and high average specific surface areas (314 to 404 m^2/g). The optimum condition for the one-step combustion is firing at 700°C for 60 min. The alkaline extraction yielded the silica that has the lowest purity among the three methods but having the highest specific surface area.

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References

[1] Houston, D. F. (1972) Rice: Chemistry and Technology. American Association of Cereal Chemists, Inc., St Paul, MN.

[2] Nakata Y., Suzuki M., Okutani T., Kikuchi M., and Akiyama T. (1989) Preparation and properties of SiO_2 from rice hulls. J. Ceram. Soc. Jpn. 97: 842-852.

[3] Kapur, P.C. (1985) Production of reactive bio-silica from the combustion of rice husk in a tube-in-basket (TiB) burner. Powder Technol. 44: 63-75.

[4] Chakraverty, A.; Mishra, P.; Banerjee, H. D. (1988) Investigation of combustion of raw and acid-leached rice husk for production of pure amorphous white silica. J. Mater. Sci. 23: 21-26.

[5] Chakraverty A., Banerjee H.D., Mishra P. (1990) Production of amorphous silica from rice husk in a vertical furnace. AMA Agric. Mech. Asia Afr. Lat. Am. 214:69-76.

[6] Real C., Alcala M.D., Criado J.M. (1996) Preparation of silica from rice husks. J. Am. Ceram. Soc. 79: 2012-2020.

[7] Kalapathy, U., Proctor, A., Shultz, J. (2000) A simple method for production of pure silica from rice hull ash. Bioresour. Technol. 73: 257-264.

[8] Pongsak Phongpech. (1992) Preparation of Silica from rice husk by Fluidized bed Method. Master Thesis, Department of Chemical Technology, Chulalongkorn University.

[9] Kamath, S. R., and Proctor A. (1998) Silica gel from rice hull ash: Preparation and characterization. Cereal Chem. 75: 484-493.