

CHAPTER II

RICE HUSK SILICA EXTRACTION



2.1 Introduction

Thailand, one of the famous rice producing countries in the world, has shared a 3% annual increase in paddy production over the past decade. Reported by Department of Export Promotion, Ministry of Commerce in 2001, the local annual rice production is approximately 24 million metric tons. This amount results in the disposal of 5 million metric tons rice husk which is considered as an agricultural solid waste.

Although rice husk has been introduced as an effective biomass fuel, the utilization of rice husk for energy production has not been practical for small mills. In other words, there are not many uses for the husk after milling, so disposal of the husk has been a major problem contributing to serious environmental consequences. Many mills usually dump or burn the husk in the open area, even illegal dumping has been regulated. Open burning emits unfiltered smoke and ash leading to air pollution and health effects. Furthermore, natural decomposing husk releases methane, a major pollutant that contributes to global warming. However, a few of the large mills burn husk for advanced purposes such as to generate mechanical power, electricity and steam for drying paddies or parboiling rice. Besides those mentioned, many research efforts are working toward developing more practical and cost-effective techniques for the utilization of rice husk. [Hamdan, 1997; Kalapathy, 2000; Ajiwe, 2000; Della, 2002].

The recovery of valuable substances from agricultural wastes particularly agricultural residues is beneficial in raising the value of domestic agricultural output. Since, plenty of silica was found in rice husks and there is simple technique for its extraction, the recovery of pure silica from husk has been working increasingly attractive. This provides extremely positive benefits in terms of business and

environment that it not only reduces husk waste but also to make value-adding of extracted silica. This chapter emphasizes silica extraction beginning with literatures, methodology followed by product characterizations. The cost analysis of extracted silica would be mentioned in Chapter VII.

2.2 Objectives

This chapter mentions about the method of silica extraction from rice husk waste generated in Supanburi province, Thailand. The main objectives were proposed as follows:

1. To extract highly reactive silica from rice husk by using the acid leaching method.
2. To investigate economic benefits in terms of capital and operating costs throughout the extraction process.

2.3 Literature Reviews

2.3.1 General Information on Silica

Silica refers to the chemical compound, silicon dioxide (SiO_2). Most of silicas could be found in many natural compounds such as volcanic rock and ash, rich-silica plants and organisms. Synthesized silicas are chemically produced for specific purposes. Generally, silica can be classified into two types: crystalline silica and amorphous silica [Iler, 1979].

2.3.1.1 Crystalline silica

Crystalline silica is a mineral made of silicon and oxygen that is naturally abundant in the earth's crust. It may be found in more than one form. The polymorphisms of crystalline silica are alpha quartz, beta quartz, tridymite, cristobalite, keatite, coesite, stishovite, and moganite [Ampian and Virta, 1992; Heaney, 1994; Guthrie and Heaney, 1995]. Each polymorph is unique in its spacing, lattice structure, and angular relationship of the atoms dependent on the temperature and pressure of that synthesis. When temperature increases, various crystalline transitions are gradually developed in the order of quartz, tridymite and cristobalite and finally melting occurs. The atmospheric pressure transformations of crystalline silica at various temperatures were illustrated in Figure 2-1. In nature, the alpha form of quartz, the most common form, is so abundant that the term "*quartz*" is often used in place of the general term "*crystalline silica*" [Bom, 1992 and Virta, 1993].

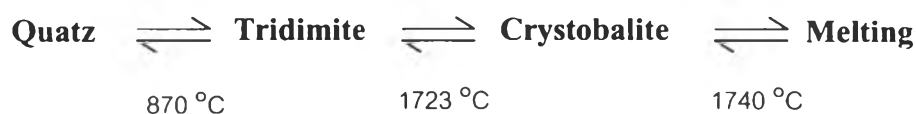


Figure 2-1 Transformations of crystalline silica at various temperatures [Iler, 1979].

2.3.1.2 Amorphous Silica

Amorphous silica is defined as a naturally occurring or synthetically produced oxide of silicon in two common forms: hydrated and dehydrated silica. Amorphous silica is highly reactive compared to that of crystalline silica and its applications are regularly found in the uses of chemical reactants and binders, such as an extender pigment, a flattening agent, and a desiccant. The amorphous phase is clearly distinguished by the absence of crystalline-based peaks and the broad absorbance of its X-Ray Diffraction patterns. Three types of amorphous silicas can be identified according to the production methods:

- Vitreous silica, made from fusing quartz.
- Silica M, formed by irradiation with high speed neutrons. This type is thermally unstable because it can be transformed to quartz at 930 °C within 16 h.
- Microamorphous silicas including sols, gels, powders, and porous glasses, generally consist of a fine particle less than a micron in size or have a specific surface area greater than 300 m² g⁻¹.

Naturally, microamorphous silicas have been considered from either the vapor phase ejected from the volcanic eruption or deposited from supersaturated solution in natural water and in living organisms. Except for silica extracted from plants or diatoms, natural microamorphous silicas are highly contaminated by other minerals that brought about the limitations of their commercial uses. Therefore, plants are recognized as the high quality silica source for many specific purposes. The controlled conditions during the synthesis process provide many stabilized forms such as microscopic sheets, ribbons, fiber and spherical particles linked together in the three-dimensional network. Figure 2-2 presents the schematics of spherical silica in three volumetric patterns, discrete or separate particles in sols (a), aggregates with siloxane bonding at the contacted sites found in gels (b) and three-dimensional bulks of aggregated particles in aerogels, called pyrogenic silicas and dispersible silica powders (c).

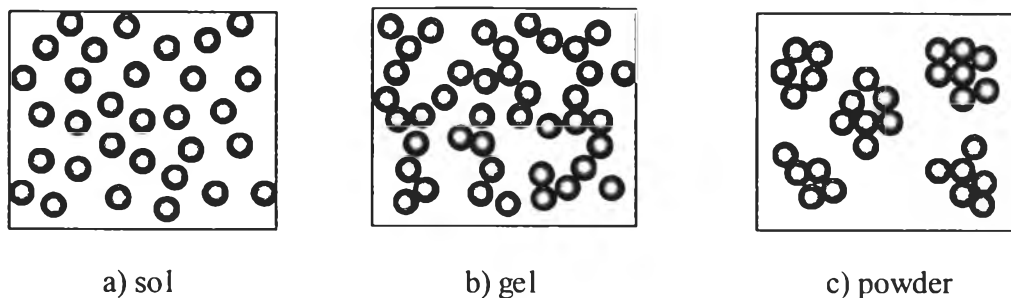


Figure 2-2 Ultimate particles in common forms of colloidal silica [Iler, 1979].

Anhydrous forms generally called “*pyrogenic*” or “*fumed*” silica are recovered from the gaseous phase at high temperatures. Vaporizing silicon dioxide in an arc or oxidizing the volatile silicon compounds such as SiH_4 or SiCl_4 with dry inert gas causes silica to condense as a white powder. Surface-hydroxylated amorphous silicas are nucleated slowly in the solution saturated with $\text{Si}(\text{OH})_4$ monomers, which then undergo to be dehydrated and precipitated out from the solution. The reaction takes place at an extremely slow rate and when the concentration of $\text{Si}(\text{OH})_4$ exceeds 2×10^{-3} M, the colloidal particles will be produced competitively. Particularly, the precipitation of silica from the supersaturated solution mostly provides spherical silica. However, other useful forms are particularly tailored by the control of pH, temperature, pressure and $\text{Si}(\text{OH})_4$ concentration. The effects of these parameters on the way of silica formations are reported. The synthesis of silica under hydrothermal conditions in the presence of solvent or water rapidly increases the rate of silica precipitation [Iler, 1979].

Silica in the form of soluble silicate is widely used in glass, ceramic, cement, pharmaceuticals, cosmetics and detergent industries. Additionally, it has been used as a major reactant for various synthetic chemistries such as catalyst, coating film and semiconductor [Kalapathy, 2000]. The development of simple and low energy techniques of silica extraction from natural resources has been attractive.

2.3.2 Rice Husk Silica

Rice husk, an abundant residue of rice milling and rich in silica, is commonly utilized as a fertilizer and feedstuff in agriculture, raw material in ceramic and metallurgical industries such as ceiling and partition products, brick making and as an energy resource in the combustion process. Rice husk can be used as fuel in heat generation for drying rice due to its high calorific power, approximately $16,720 \text{ kJ kg}^{-1}$ [Della, 2002]. Figure 2-3 shows the diagram of energy used for milling and electricity produced on the basis of a 1 ton paddy. Ramboll (1998) found out that the energy generated from rice husk (90-125 kWh) is much more than the energy used in rice production (30-60 kWh) and if all the rice husk in our country was used to generate energy, that would amount to approximately 2,400 GWh electricity per year. By direct combustion, the conversion is as low as 40% with particulate emissions in the flue gases in excess of $3000 \text{ mg (Nm}^3)^{-1}$. In this combustion, rice husk ash (RHA) is produced. The burning of rice husk in air always leads to the formation of silica ash, which varies from gray to black depending on inorganic impurities and unburned carbon amounts.

The compositions of compounds contained in rice husk are 16% ash, 35% cellulose, 22% hemicellulose, 13% lignin, 3% soluble and 9% moisture. It is evident that hemicellulose and lignin can be hydrolyzed in HCl, H_2SO_4 , HNO_3 and HBr and digested into simple species, while cellulose is only partially digested and finally leaves a non-hydrolyzed product as silica. The difficulty of digesting cellulose may be related to its partially crystalline nature. After burning out impurities, more than 95 % of amorphous silica remains in rice husk ash [Hunt, 1984]. The chemical compositions of rice husk ash before and after burning were examined as presented in Table 2-1.

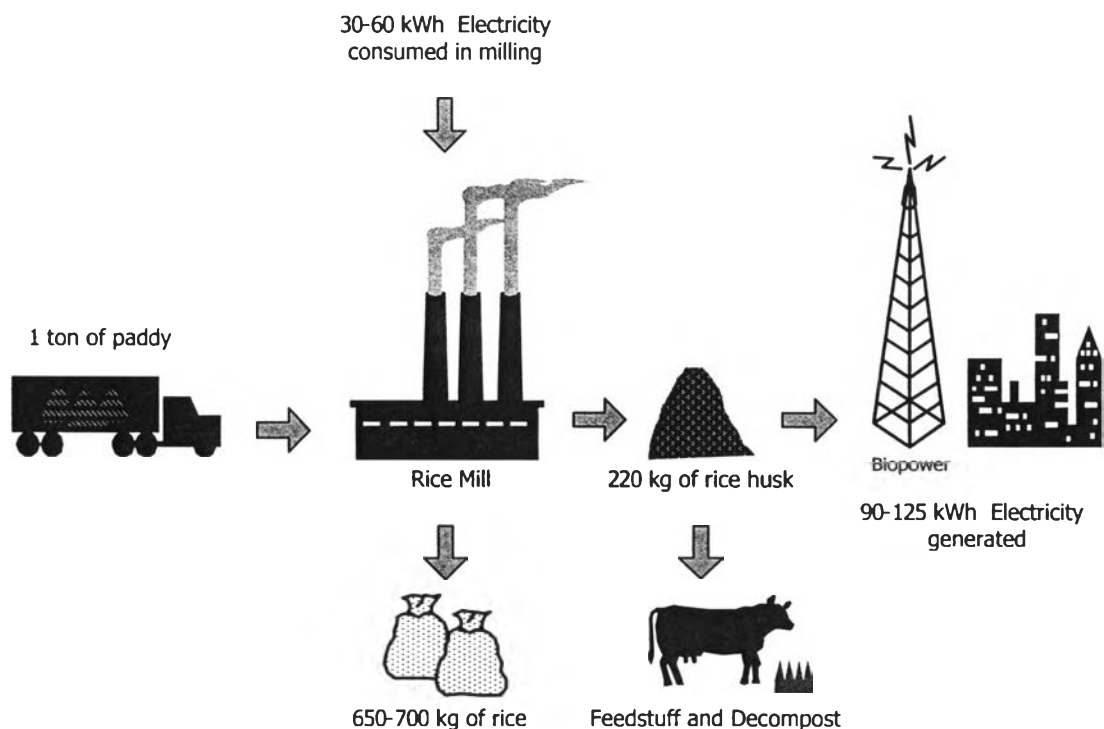


Figure 2-3 Equilibrium of energy used for milling and electricity produced on the basis of a 1 ton paddy adapted from Ramboll (1998).

The utilization of rice husk ash (RHA) in terms of waste management has gradually developed over the decades. Since 1938, the discovery of high silicon content deposited in rice husk has resulted in several studies for the preparation of elementary silicon and a number of silicon compounds; especially silica, silicon carbide, and silicon nitride [Della, 2002]. Recently, rice husk ash in blackish form is used as water soaking material and some of them are exported to the European countries for the utilization as a silica source for the electronic industries [Krishnarao, 2001]. The benefit of rice husk ash has been recognized as an additive for cement and concrete fabrication [Ajiwe, 2000].

Rice husk ash mainly consists of hydrated amorphous silica and trace amounts of metals depending on the variety, climate and geographic location. As shown in Table 2-2, rice husk produced from Asia contains a higher silica content than that found in Tanzania [Stroeven, 1999]. The composition of rice husk ash generated in Thailand was reported by Lohsoontorn (2002). It was also reported that the obtained

ash possessed an amorphous phase with the density of 1.83 g cm^{-3} , specific surface area of $332 \text{ m}^2 \text{ g}^{-1}$, and average pore size of 59 \AA .

Table 2-1 Compositions of rice husk ash (blackish form) before and after burning out at $700 \text{ }^\circ\text{C}$ for 4 h, based on % by weight [Della, 2002].

Minerals	RHA as received	RHA after burning
SiO ₂	72.1	94.95
K ₂ O	0.72	0.94
Na ₂ O	0.50	0.25
CaO	0.43	0.54
MgO	0.70	0.90
Fe ₂ O ₃	0.15	0.26
P ₂ O ₅	0.06	0.74
MnO	0.15	0.16
TiO ₂	0.05	0.02
Al ₂ O ₃	0.30	0.39
Loss on fire	24.3	0.85

Table 2-2 Compositions of rice husk ash analyzed by using the X-ray Fluorescence characterization (% by weight) obtained from different countries.

Minerals	Thai RHA [Lohsoontorn, 2002]	Vietnamese RHA [Stroeven, 1999]	Tanzanian RHA [Stroeven, 1999]
SiO ₂	99.66	96.7	88.9
Al ₂ O ₃	0.10	0.08	0.3
Fe ₂ O ₃	0.02	0.03	0.19
CaO	0.19	0.30	0.43
K ₂ O	0.03	0.73	3.67
MgO	-	0.16	2.07

After the combustion, more than 96% by weight of silica remains in the white ash. Rice husk silica in an amorphous form is approximately 30-47 μm in particle size. A combination of Back Scattered Electron (BEI) and X-ray images of rice husk, presented in Figure 2-4, shows the porous structure in which silica is concentrated mostly under the outer surface of husk. [Stroven, 1999].

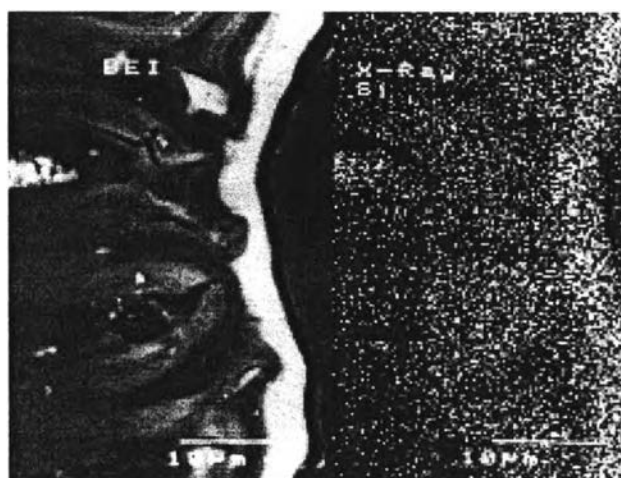


Figure 2-4 Combined Back Scattered Electron and X-ray images revealing porous husk structure and silica concentration at the outer surface [Stroven, 1999].

Finger print X-ray diffraction of amorphous silica shown in Figure 2-5 appears at 2θ close to 23° . Fourier transform infrared data illustrated in Figure 2-6 indicates the functional groups found in rice husk silica. Amorphous silica consists of siloxane (Si-O-Si) and silanol groups (Si-OH). The increasing in the number of absorption peaks is related to the more completeness of silica crystallization. If silica tetrahedral can be connected to form chain, ring or more complicate network, the absorbance in the range of 1200 and 700 cm^{-1} will be occurred [Ibrahim, 1980; Kamath, 1998].

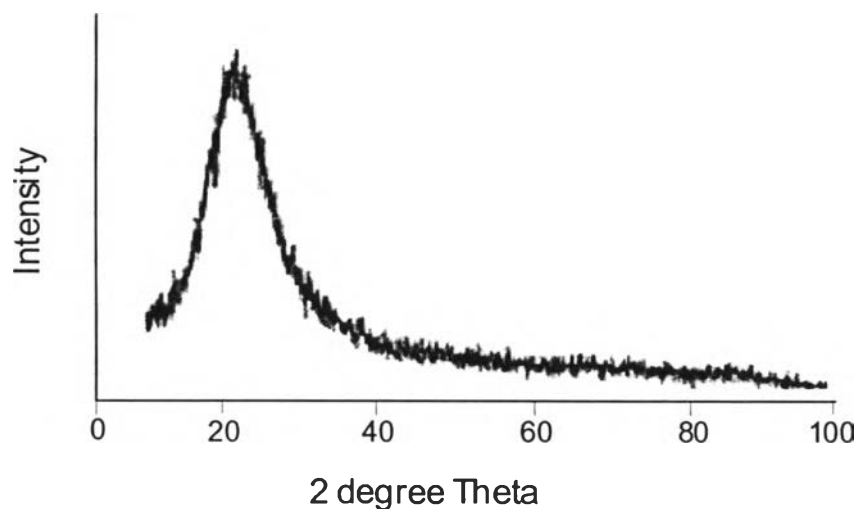


Figure 2-5 X-Ray Diffraction pattern of amorphous silica produced from rice husk ash [Kalapathy, 2000].

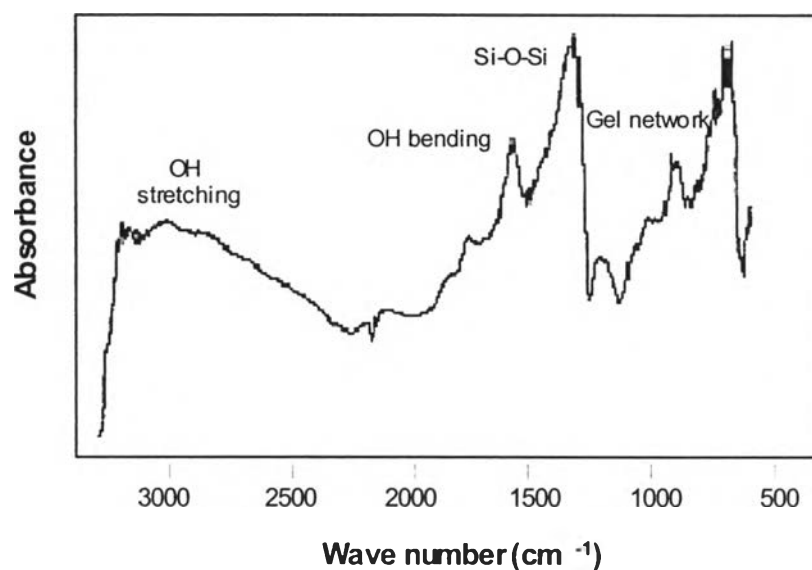


Figure 2-6 Fourier Transform Infrared spectra of amorphous silica produced from rice husk ash [Kalapathy, 2000].

The conventional production of pure silica is by smelting quartz at a high temperature. During the last decade, it was successfully to extract silica from silica-rich vegetables such rice husk. Acid leaching has been found to be a cost effective method requiring a low amount of energy to retrieve amorphous silica from rice hull. The extracted silica was reviewed as an economically viable raw material for the production of silica gels and powders [Rahman, 1997; Kamath, 1998; Chakraverty, 1991]. The solubility of amorphous silica was very low at the pH less than 10 but it

increased sharply at the pH more than 10. This behavior led to the precipitation of silica from silicate solution [Chakraverty, 1991]. The quality of silica utilized from rice husk was determined on the basis of the impurities removal with low effort and high specific surface. Banerjee (1982), cited in Riveros (1986), presented the method of silica extraction which began with washing the rice husk with water, followed by sun drying and burning at 400 °C to get white ash (SiO₂) but the ash contained many mineral contaminants such as sodium, potassium and calcium. Many authors have concluded that the preliminary leaching of rice husks with a solution of HCl, HBr, HNO₃, H₂SO₄, NaOH and NH₄OH, boiled before thermal treatment in the temperature ranges from 500-1400 °C, proved to be effective in the removal of metallic impurities, which provided white ash silica and the high specific surface area.

Riveros (1986) proposed the acid leaching of rice husk in the boiling solution of 1:3 HCl:H₂O for 1 h and dried the husk in hot air before calcination. After this process, there was a significant decrease in the amount of impurities, approximately 300 ppm. The better method was improved by Kalapathy (2000) technique. Acid leaching followed by alkali washing and final water rinse effectively reduced some mineral impurities to less than 100 ppm and 99% purity of silica was obtained from this technique.

In 1998, Farone et al. patented a method of removing silica from hydrolyzed cellulose in sugar cane using the alkali treatment (5-10% NaOH) at 80-90 °C to produce silicic acid. Silicic acid was preferably transformed to silica gel and sodium silicate, then used as a silica source for zeolite synthesis. The metal hydroxide was neutralized with sulfuric acid and removed by distilled water rinses. This patent contributed to high efficiency and economic feasibility according to low temperature required and atmospheric synthesis condition, which was recommended for rice husk as well.

The effect of acid, incineration temperature and time resulted in silica structure, porosity and purity. The amorphous phase was typically performed under thermal combustion of which temperature was employed in the range of 400-700 °C. Pre- and post-treatment using 3 % (v/v) of HCl or 10% (v/v) of H₂SO₄ for 2 h aging at a ratio of 50 g husk L⁻¹ and calcinations at 600 °C for 4 h gave high quality 99.66 %

amorphous silica [Yalcin, 2001]. The color change from gray to black after air burned product was attributed to the completeness of the combustion process, the presence of inorganic impurities and the transformation of silica structure. By treating with 3 N HCl and calcination temperature up to 700 °C, the formation of black particles, carbon fixed, can be diminished and bright white silica with homogeneous particle size distribution was produced [Della, 2002; Krishnarao, 2001].

Due to the fact that rice husk ash is cheap and highly reactive, the recovery of silica from the ash is the attractive process which not only minimizes waste but also an increase in waste value is concerned. Recently, rice husk silica was successfully applied as a silica source for zeolites synthesis. The highly reactive silica for zeolite A and Y was obtained by the digestion of rice husk in NaOH at a hydrothermal condition then precipitating and burning 100 g sample in muffle furnace purged with air at 700 °C and 1000 °C respectively. This method provided the most reactive silica in the amorphous form: $\text{Si}(\text{OSi})_4$ tetrahedral units without SiOH groups [Hamdan, 1997]. Similarly, Wang et al. (1998) reported that silica from gasification ash reacted proportionally with alumina and alkali metal oxide was utilized to produce zeolite ZSM-48, which exhibited high selectivity for the conversion of olefin to methane. Even carbonaceous ash, it was able to produce high quality NaA zeolite by using carbon based silica dissolved in an aqueous solution as a reactant [Nur, 2001]. Up to the present, no literature on the use of rice husk silica for mesoporous molecular sieve synthesis has been published. Therefore, we are interested in another alternative use of rice husk silica for the preparation of silicate mesoporous material, as its applications are widely recognized in many environmental and chemical fields.

2.4 Experimental

The most common technique employed in this work was acid hydrolysis. The extracted silica product was characterized by standard methods for chemical compositions and functional group analysis. The details of the extraction procedures are presented below.

2.4.1 Materials and Chemicals

- Rice husk (from the rice mill located in Supanburi, Thailand)
- Hydrochloric acid (37% m/m, Lab-Scan)
- Deionized water

2.4.2 Apparatus and Instruments

- Glass wares
- Desiccator
- Digital balance
- Universal indicator
- Muffle furnace (Carbolite 201, maximum temperature up to 1000 °C)
- X-ray diffractometer (Bruker: model axs D5005 X- diffraction)
- BET surface analyzer (Micromeritic: model ASAP 2010)
- Infrared spectrometer (Nicolet: model Impact 400D)

2.4.3 Methodology

The silica extraction employed in this work was acid hydrolysis modified from Yalcin and Sevinc (2001). The procedure was orderly presented in the following.

1. Rice husk was ground to 16 mesh-size particles, sieved, and washed with water to remove sand and small scarp.
2. After drying, 30 g of dried husk was gently refluxed in 300 mL of 5 M Hydrochloric acid at 80 °C for 1 h.

3. The hydrolyzed husk was rinsed repeatedly with deionized water until the pH of the aging acidic solution was neutral tested by universal indicator.
4. The husk was dried in the oven at 110 °C for 3 h then calcined in muffle furnace purged with air at 650 °C for 4 h.
5. The silica obtained from rice husk ash was characterized by XRD, XRF, FTIR and the silica content was examined by the quantitative technique referred to ISO 3262-1975 (E).

2.4.4 Sample Characterizations

2.4.4.1 X-Ray Diffraction (XRD) Analysis

In order to examine whether the extracted silica was amorphous silica, the powder XRD patterns were carried out using the Bruker model axs D5005. The sample was homogeneously ground and firmly packed in a sample holder. The X-ray was operated using Cu K α which generated a current of 40 mA and a potential of 40 kV. The scanning was performed at 2 θ rotated from 0-60 degree with the rate of 1.25 degrees per minute.

2.4.4.2 Quantitative X-Ray Fluorescence Spectroscopic (XRF) Analysis

The element compositions of prepared catalysts were analyzed by Wavelength Dispersive X-Ray Fluorescence (WDXRF) spectrometer, model: PW 2400. The 6 g of dried sample were mixed with a binder (H₃BO₃) and pressed manually at 30 N m⁻² to make the pellet sample. Afterwards, it was transferred to a sample holder before the measurement. The quantitative elemental analysis was performed on various referent elements with the current of 100 mA and the potential of 24 kV at the scan speed set of 0.6 degrees per minute.

2.4.4.3 Fourier Transform Infrared Spectroscopic (FTIR) Analysis

Two grams of rice husk silica were ground consistently with 200 g of spectroscopically pure KBr powder. The mixture was then pressed with the hydraulic

press about 150 kg cm^{-2} for 1 minute and inserted into the V-mount cell. The maximum of the absorbance occurred in the region $400\text{-}4000 \text{ cm}^{-1}$.

2.4.5 Results and Discussion

2.4.5.1 X-Ray Diffraction Spectroscopy

The X-ray diffraction pattern of rice husk after calcination at $650 \text{ }^\circ\text{C}$ is presented in Figure 2-7. The broad peak of diffractogram appeared at approximately 2θ equal to 23 performs a characteristic of amorphous silica as similar to that found in references [Hamdan, 1997; Kalapathy, 2000; Yalcin, 2001]. The fluctuation of lines shown in the figure resulted from the coarse scanning of characterization. Even if no other metal signals were observed from the XRD diffractogram, it has not been concluded that the rice husk ash contains only the silica element unless the purity of obtained ash is determined.

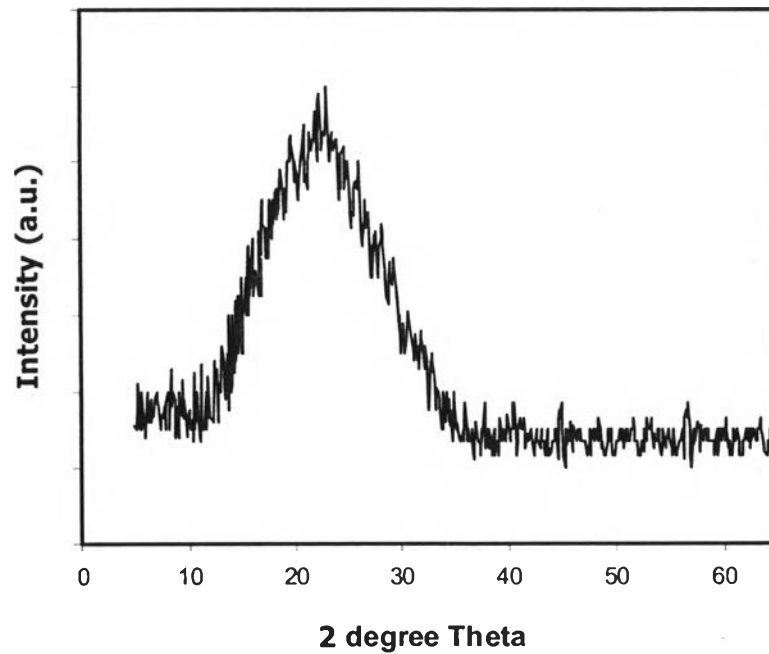


Figure 2-7 XRD spectrum of the extracted silica.

2.4.5.2 X-Ray Fluorescence Spectroscopy

After hydrochloric treatment, the hydrolyzed rice husk was calcined and left white residue ash. There was no black particle deposited in the extracted silica. The XRF results in Table 2-3 indicates few metallic impurities found in the sample but in trace amounts and the main element contained in rice husk ash is silica. This can be confirmed with the high intensity peak shown in Figure 2-8. The peak at 2θ equal to $108-110^\circ$ is silica which corresponding to $\text{SiK}\alpha$ crystal scanned at 24 kV. The results from XRF analysis are found in good agreement with the determination of silica content in the ash according to the standard method ISO 3262-1975 (E). The analysis result reported by Department of Science Service confirmed that up to 99.7% by weight of purified silica was obtained from rice husk ash.

Table 2-3 Compositions of rice husk ash obtained from this work analyzed by quantitative XRF (% by weight).

Minerals	RHA	RHA	RHA
	[this work]	[Lohsoontorn, 2002]	[Cook, 1985]
SiO_2	99.766	99.66	86.90 – 97.30
K_2O	0.007	0.03	0.58 – 2.50
CaO	0.009	0.19	0.20 – 1.50
Al_2O_3	0.099	0.10	-
Fe_2O_3	0.032	0.02	~ 0.54
P_2O_5	0.071	-	0.2 – 2.85
SO_3	0.016	-	0.1 – 1.13

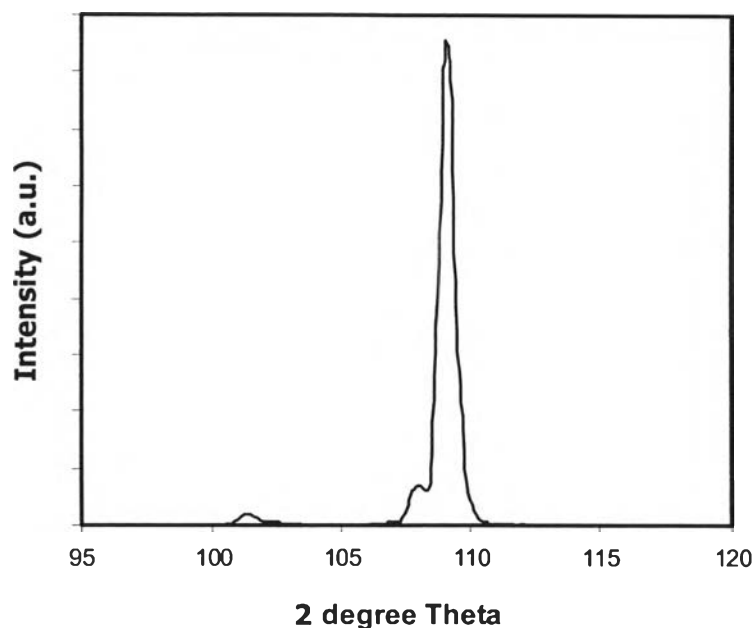


Figure 2-8 XRF pattern corresponding to silica element found in rice husk ash.

2.4.5.3 Fourier Transform Infrared Spectroscopy

The major chemical groups contained in rice husk silica were identified by FTIR spectra shown in Figure 2-9. The broad band between 2,800 and 3,700 cm^{-1} corresponds to the silanol (Si-OH) groups. The predominant sharp peak at 1,100 cm^{-1} is due to siloxane bonds (Si-O-Si). The spectrum which appeared at 800 cm^{-1} is characteristic of Si-O-Si stretching modes while the peak at 480 cm^{-1} is due to Si-O bending mode. The presence of Si-O-Si bonds associated with the Si-O bonds are found to be distinctive patterns attributed to the gel network forming more complicated structures [Handam, 1997]. The contaminant peak found at 1636 cm^{-1} responded to carbon dioxide detection.

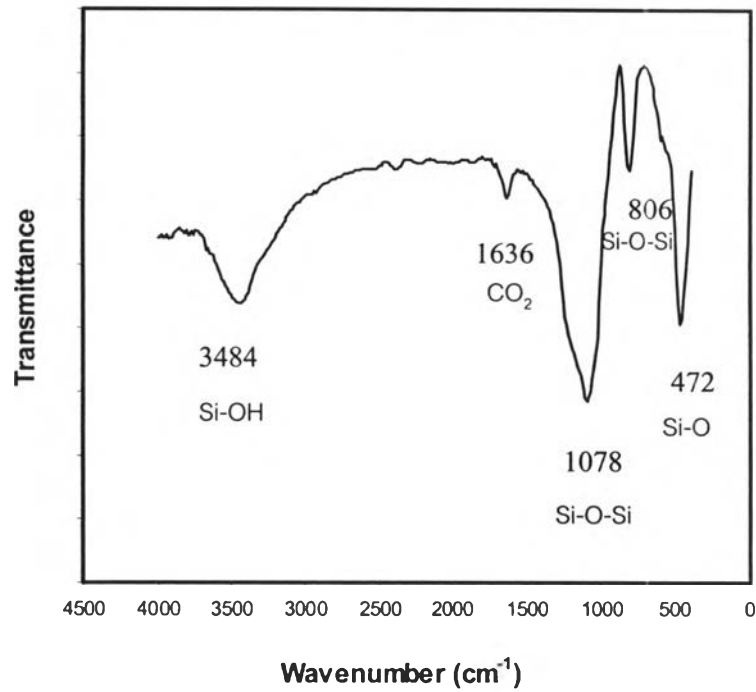


Figure 2-9 FTIR spectrum of the extracted silica.

2.5 Summary

The extraction of rice husk silica was carried out by acid leaching. Rice husk was refluxed in 5 M HCl at 80 °C for 1 h. This promising method provided the simple, efficient and cost-effective method for upscale implementation. The characterization results from XRD spectrum and silica content examination pointed to the high quality of amorphous silica (more than 99% purity) retrieved from rice husk ash. This led to success in the utilization of husk waste as a natural silica source for MCM-41 synthesis that will be discussed further in Chapter III.