Chapter I

Introduction

1.1 Motivation, Objective, and Scope

Thailand exports large amounts of rice; in fact, the country ranks no. 5 in world production. As a by-product or waste from rice milling, millions of ton of husk occur. Until now, some husk is used as fuel, in brick making, etc. A substantial share is exported in the form of low-grade black husk ash, as shown in table 1.

Tab. 1. Husk ash export figures (1988-1990)

country	volume of export in ton	export value in Mio. Baht	average price in Baht per ton
1988:			
Belgium	37.5	0.160	4267
Germany	6463.6	19.069	2950
Hong Kong	112.0	0.303	2705
Japan	1134.1	3.754	3310
Netherlands	2719.2	6.793	2498
Saudi Arabia	110.9	0.723	6519
Spain	72.0	0.184	2556
Total	**10649.3**	**30.986**	**2910**

country	volume of export in ton	export value in Mio. Baht	average price in Baht per ton
1989:			
Belgium	1608.4	6.518	4052
France	53.0	0.273	5151
Germany	11168.8	34.790	3115
Hong Kong	23.3	0.076	3262
Japan	1932.5	6.839	3539
Netherlands	721.3	3.255	4513
Saudi Arabia	105.3	0.523	4967
South Korea	223.9	1.179	5266
Total	**14228.1**	**53.453**	**3757**
1990:			
France	100.1	0.515	5145
Germany	9919.7	33.424	3369
Japan	1550.2	6.417	4139
Netherlands	1392.0	4.342	3119
Saudi Arabia	432.0	1.576	3648
South Korea	1517.6	7.898	5204
U.A.E.	230.4	0.862	3741
Total	**15142.0**	**55.033**	**3634**

From: Trade Library, Department of Export Promotion

Until now there is abundance of waste husk not utilized in the country. The volume of low-grade husk ash export is increasing with time. This means we will get more money from exporting more cheap rice husk ash. But at the same time, considerable amounts of amorphous silica powder are imported from abroad. It is generally known that it is possible to extract amorphous silica from rice husk. But due to certain problems, extracting amorphous silica has failed to win the interest of industry so far. The objective of this thesis is to show that extracting high grade silica from rice husk is possible by a non-sophisticated technology. Silica from rice husk has excellent properties, i.e., high purity, high specific surface area, and fine colloidal structure.

1.2 Literature Survey

1.2.1 Utilization of rice husk

Much research work was cited on the utilization of rice husk as it is an abundant agricultural waste (Govindarao, 1980). Some study about rice husk was even started in the previous century. The scope of research about utilization of rice husk is very wide. Rice husk is used as fuel, animal feed, fertilizer, for the production of organic chemical products, of activated carbon production, etc. But only few applications were established on a large scale, such as utilization as fuel or fertilizer.

During the last decades, many researchers concentrated on materials science aspects. Several papers were published about rice husk as a source of silica compound, for preparation of new materials. They were based on the specific properties of rice husk ash, i.e., very fine structure and high reactivity. James and Rao (1986; 1,3) studied about silica in rice husk and concluded that the physical characteristics and the chemical reactivity of silica in rice husk ash depends on temperature and soaking time. In an X-ray diffraction pattern, husk ash showed a broad "amorphous" peak around 22.2^{o} and crystallization could not be detected below $700^{o}C$. Specific surface area of acid-leached silica was 195 m^2/g. For very long soaking time, the total pore volume with pore radius < 10 nm decreased, although no crystallization effects were detected yet. Other published research work by the same authors in the same year also described the reaction of silica in rice husk ash with lime to be used as lime rice husk ash cement.

For new materials preparation from rice husk, the preparation of silicon carbide was reported (Sharma, Williams, and Zangvil, 1984; Lee and Cutler, 1975) and silicon nitride (Rahman and Riley, 1989). The high price of these material motivated the use of rice husk as an inexpensive starting material.

As a high-technology material, silicon with solar cell grade purity was prepared (Amick, Milewski, and Wright, 1980; Amick, 1982; Banerjee, Sen, and Acharya, 1982; Bose, Govindacharyulu, and Banerjee, 1982; Hunt et al., 1984). The work is based on the fact that rice husk can be purified from cationic impurities at comparably low effort.

The center of interest for the present thesis is the preparation of high purity amorphous silica (Chakraverty, Mishra, and Banerjee, 1988).

1.2.2 Composition of rice husk

The composition of rice husk depends on agricultural methods, on geographical and meteorological factors. Reported data may also be influenced by sample preparation, and method of analysis. The major components are presented in the table below after (Sharma et al., 1984).

Tab. 2. Main organic and inorganic components in rice husk

component	typical range
ash content	13-29 %
cellulose	34-44 %
lignin	19-47 %
sugar*)	17-26 %

*) D-xylose, L-arabinose, methlyglucoronic acid and D-galactose

Rice husk also contains a little protein, moisture, and very small amounts of vitamins.

The most outstanding property of rice husk ash is its very high amount of silica (> 90 % SiO_2). The following table shows the chemical composition of different types of plant ash.

Tab. 3. Ash composition of different wood ashes in comparison to rice husk ash (Matthes, 1990)

plant	SiO_2	P_2O_5	MgO	CaO	Na_2O	K_2O	Cl_2
beech wood	5	6	10	50	6	20	-
birch wood	12	8	14	30	9	23	-
oak bark	3	3	8	57	2	26	-
pine wood	10	9	6	25	9	27	-
spruce wood	2	4	6	30	6	7	43
rice husk	96	-	└ 1.5 ┘		└ 1.5 ┘		-

The extent of contamination of husk with bran, which evidently depends upon the technique used for milling of paddy, may also contribute to the differences in composition. Some specific impurities may depend on the origin of the rice as well as on the applied fertilizer. The following values are found according to different sources (Amick, 1982; Hunt et al., 1984).

Some impurities, for example, the Al and Fe contents significantly vary when soil dust is washed away before the analysis.

Tab. 4. Impurities levels (ppm) in rice husks of different origin

cation	USA1	USA2	USA3	Japan	Malaysia
Al	200	-	200	-	-
Mn	1500	500	500	200	200
Fe	900	-	-	-	-
Na	400	-	-	-	-
K	-	4000	2000	8000	1200
Mg	3000	900	600	200	300
Ca	4000	1000	1000	1000	1000

1.2.3 Chemical treatment of rice husk

Although rice husk ash contains silica in amorphous form, crystallization can occur quite easily during heat treatment due to cationic impurities acting as mineralizers. Some reports (Xu et al., n.d.; Nakata et al., 1989) indicated that eutectic compounds of impurities and silica eventually formed and glazed the inner surface, thus hampering the further access of oxygen or release of volatiles. It was also reported that adhering soil dust can act as mineralizer. So, washing and impurity extraction by chemical means are absolutely needed when an amorphous silica is the target. Many researchers preferred impurity extraction by acid leaching. For instance, 1:1 and 1:3 of HCl/H_2O (Hunt et al., 1984; Amick, 1982). At too low concentration and temperature of reaction (1:10 HCl, 50°C, 5 h after Hunt et al., 1984) the effect for purification is reduced. Silica content of untreated and acid treated husk ash are distinctly different. Acid leached husk ash can be upgraded to silica contents ≃ 99 %. Unfortunately, one of the most important parameters for leaching, i.e., the ratio husk/acid was never reported in the previous papers. To summarize: extraction of impurities does not only improve the purity (silica content in ash) but also reduces the danger of crystallization and preserves the nanostructure of silica in rice husk.

1.2.4 Combustion of rice husk

The combustion of rice husk has been investigated by differential thermal analysis (DTA) and thermogravimetry / differential thermo-gravimetry (TG-DTG). Figure 1 illustrates the reaction peak at around 330°C and 425°C; the reaction is completed at ≃ 650°C. Compared with TG-DTG figure 2, weight of rice husk remains constant after 600°C. Cellulose material can be broken down thermally by two mechanisms a) dehydration followed by charring and b) depolymerization and volatilization of hydrocarbons. From ash color (Chakraverty et al., 1988) it was found that the lowest incineration temperature to get white ash is 500°C (5 h); at 700°C, only 1.5 h are required.

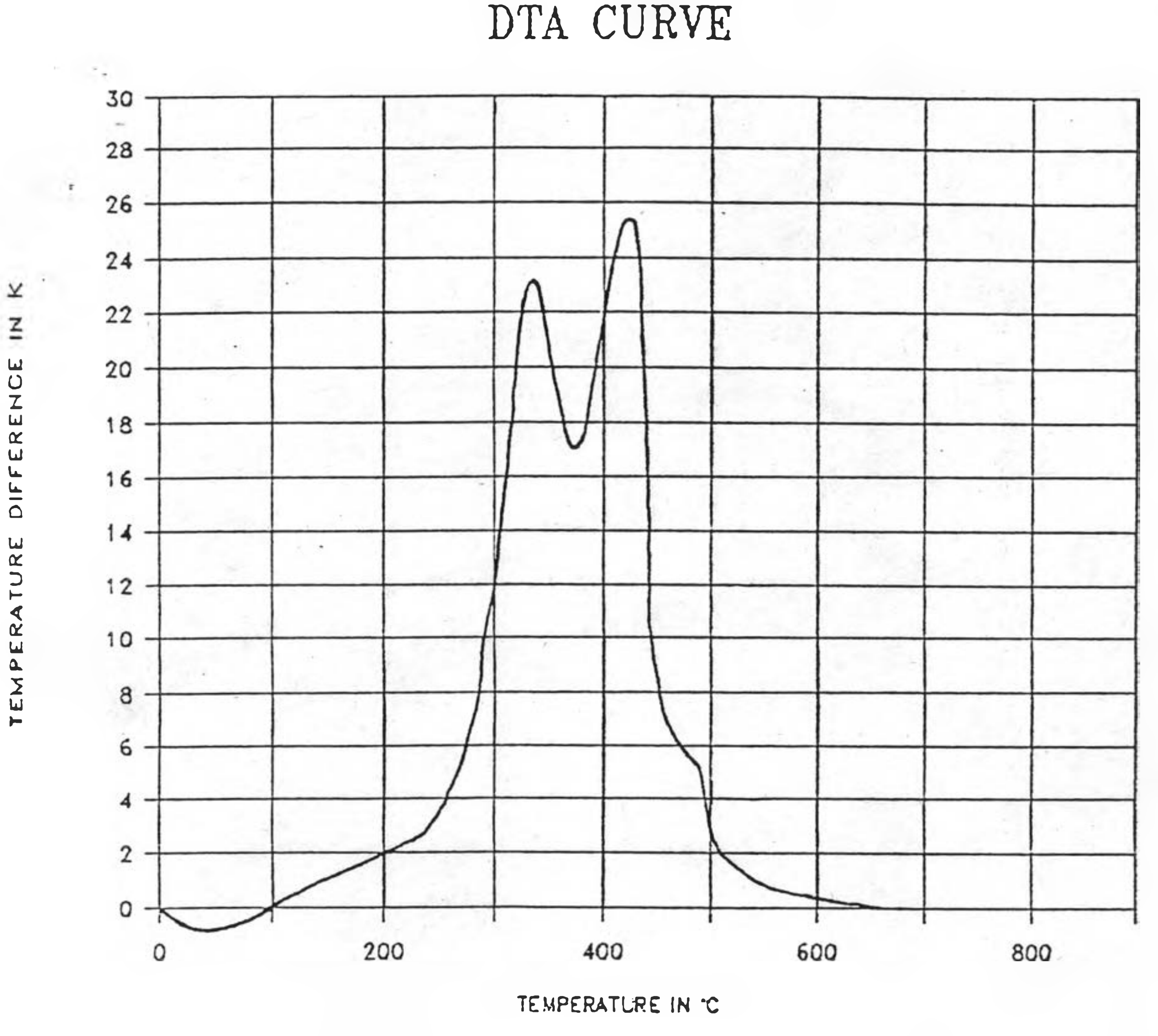

Fig. 1. DTA graph for the combustion of rice husk in air, after Ibrahim, Kabish, and Kamal, 1987

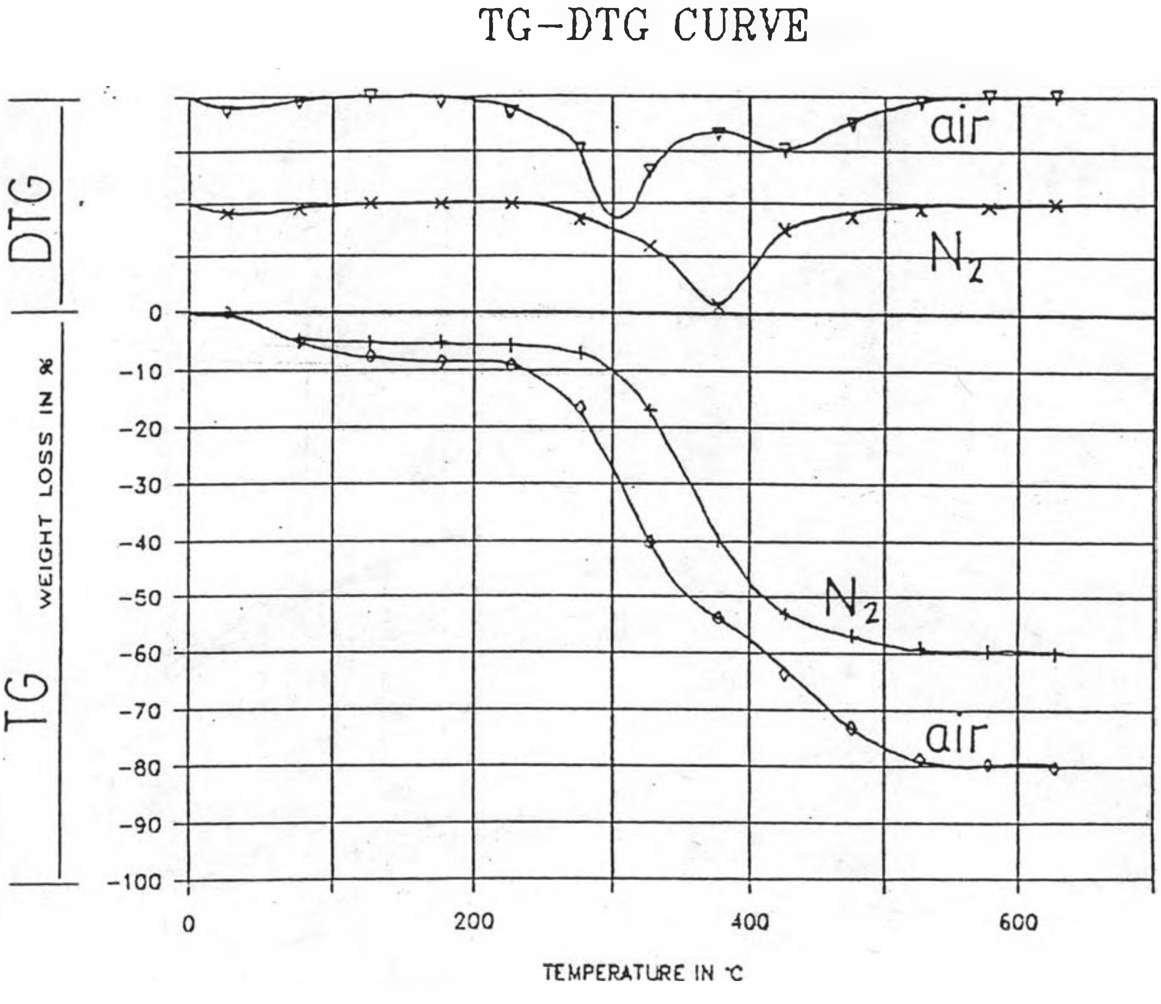

Fig. 2. TG-DTG graph for the combustion of rice husk in air and in N_2 atmosphere, after James and Rao, 1986, 3

With too high temperature and too low soaking time, crystallization occurs after a collapse of pore size smaller than 10 nm. To preserved amorphous nanostructure, 600°C - 650°C at less than 10 h were recommended. This temperature range is very low for combustion of organic matter, but this is the highest temperature to preserve the natural properties of rice husk ash. This requires further investigation.

A study presently performed elaborates the matter: For a successful treatment of rice husk, only a narrow T "window" is available. Complete incineration under favourable condition requires a minimum T of combustion. Charred material, and carbon black require distinctly higher T for incineration. This may even require temperatures where

- the pore nanostructure starts to collapse,
- grain agglomeration becomes tighter,
- nucleation starts (which does not lead to detectable amounts of crystalline matter, but makes the material prone to crystallization),
- crystallization starts.

Therefore, the possible lowest temperature was envisaged.