PRODUCTION OF AMORPHOUS SILICA FROM RICE HUSK IN FLUIDISED BED SYSTEM

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ABSTRACT

Conventional methods for the preparation of amorphous silica (SiO_2) are very energy-intensive and expensive. Amorphous silica has wide industrial applications, with annual world consumption in the excess of 1 million tonnes valued at RM4,500 per tonne. Rice husk ash contains amorphous silica in the excess of 95 wt%. Thermal treatment of rice husk is deemed the most economical method to recover this amorphous silica from the readily available rice husk (approximately 0.5 million tonnes per annum in Malaysia). Hence, the purpose of this research was to recover amorphous silica from rice husk through thermal treatment in fluidised bed system. Experimental works were conducted in fluidised bed combustor systems to determine the optimum mixing parameters (sand size, fluidising velocity, static bed height) and combustion parameters (temperature, air supply, rice husk moisture content, feeding design) to produce amorphous, carbon-free silica from rice husk. The fly and bottom ashes were analysed for their residual carbon contents and silica structures through loss on ignition (LOI) tests and X-Ray Diffraction (XRD) analyses, respectively. Computational fluid dynamics (CFD) modelling using FLUENT was also conducted to optimise the fluidised bed design and to overcome problems encountered in experimental works. Experimental results showed that amorphous, siliceous ash with residual carbon content of down to 1.0 wt% could be obtained by burning water-washed rice husk that was free from alkali metal compounds (potassium oxide and sodium oxide). The short freeboard height of the experimental fluidised bed resulted in the incomplete oxidation of carbon and sand contamination in the ash. Modelling results showed that both problems could be overcome by increasing the height of the fluidised bed to 5000mm. In addition, the induction of swirling flows at the freeboard region was found to be beneficial in increasing the residence time of ash in the combustor, leading to higher carbon burnout.

ABSTRAK

Penyediaan silika amorfus (SiO_2) secara konvensional menggunakan banyak tenaga dan sangat mahal. Silika amorfus mempunyai penggunaan meluas di industri, dengan kadar penggunaannya di seluruh dunia melebihi 1 juta tan setahun dinilaikan pada RM4,500 per tan. Abu sekam padi mengandungi silika amorfus melebihi 95%. Rawatan haba ke atas sekam padi (dihasilkan pada kira-kira 0.5 juta tan setahun di Malaysia) adalah kaedah paling ekonomik untuk memperolehi silika amorfus. Oleh itu, matlamat penyelidikan ini adalah untuk mendapatkan silika amorfus daripada sekam padi melalui rawatan haba dalam lapisan terbendalir. Kerja eksperimen dilaksanakan dalam pembakar lapisan terbendalir untuk menentukan parameter percampuran (saiz pasir, halaju perbendaliran, ketinggian lapisan terbendalir) dan parameter pembakaran (suhu, bekalan udara, kelembapan sekam padi, rekabentuk sistem penyuapan) optimum bagi menghasilkan silika amorfus dan bebas karbon daripada sekam padi. Abu terbang dan abu bawahan dianalisis untuk menentukan baki karbon dan struktur silika masing-masing melalui analisis kehilangan jisim dan analisis belauan sinar-x. Permodelan pengiraan dinamik bendalir menggunakan kod program FLUENT juga dilaksanakan untuk pengoptimuman rekabentuk pembakar serta mengatasi masalah operasi semasa kerja eksperimen. Keputusan eksperimen menunjukkan abu sekam padi amorfus dengan kandungan karbon sisa serendah 1.0% dapat diperolehi dengan membakar sekam padi yang telah dibasuh dengan air (bebas dari sebatian logam alkali iaitu kalium oksida dan natrium oksida). Ketinggian pembakar yang tidak mencukupi menyebabkan pengoksidaan karbon tidak lengkap serta pencemaran pasir dalam abu terbang. Keputusan permodelan komputer menunjukkan masalah ini dapat diatasi dengan menambahkan ketinggian pembakar ke 5000mm. Penghasilan aliran pusaran di bahagian atas pembakar juga didapati berfaedah untuk meningkatkan masa mastautin abu di dalam pembakar, dan seterusnya menyebabkan kadar pengoksidaan karbon yang lebih tinggi.

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A - Area, (m^2)

Ar - Archimedes number $\left(= \frac{\rho_f (\rho_p - \rho_f) g d_m^3}{\mu_f^2} \right)$, (dimensionless)

$C_{1\varepsilon}$, $C_{2\varepsilon}$ - Empirical constants, ($C_{1\varepsilon} = 1.42$, $C_{2\varepsilon} = 1.68$)

C_d, C_g - Constants in PDF equations, ($C_d = 2.0$, $C_g = 2.86$), (dimensionless)

C_D - Drag coefficient, (dimensionless)

C_p - Heat capacity, [J/(kg • K)]

d_b - Bubble size, (m)

d_{bm} - Limiting size of bubble expected in a very deep bed, (m)

d_{bo} - Initial bubble size, (m)

D_c - Column diameter or fluidised bed inner diameter, (m)

d_m - Mean particle diameter, (m)

d_p - Particle diameter, (m)

d_{pi} - Arithmetic mean diameter of screen apertures, (m)

d_{vs} - Volume-surface mean diameter $\left(= \frac{1}{\sum_{i=1}^{n} (x_i / d_{pi})} \right)$, (m)

f - Mixture fraction, (dimensionless)

$\overline{f}$ - Time-averaged value of f, (dimensionless)

f'^2 - Mixture fraction variance, (dimensionless)

f_c - Fractional conversion $\left(= \frac{m'}{m_{initial} - m_{final}} \right)$, (dimensionless)

F_D	-	Drag force, (N)
g	-	Gravitational acceleration, (= 9.81 m/s^2)
G_κ	-	Generation of turbulent kinetic energy, (m^2/s^2)
h_c	-	Natural or forced convection coefficient, [W/(m^2 • K)]
h_r	-	Radiation heat transfer coefficient, [W/(m^2 • K)]
H*	-	Instantaneous enthalpy, (kJ/kg)
$\Delta\hat{H}_c$	-	Heat of combustion of the fuel at reference temperature of 25^{o}C, (J)
$\hat{H}_i$	-	Specific enthalpy of the ith component at 25^{o}C, [J/(kg • K)]
H_v	-	Heat of vaporization of water, (J/mol)
k	-	Thermal conductivity, [W/(m • K)]
l	-	Latent heat of vaporisation, (J/kg)
L_e	-	Eddy length scale, (m)
l_{or}	-	Spacing between adjacent holes on a perforated plate, (m)
m	-	Mass, (kg)
m'	-	Instantaneous mass, (kg)
m_i	-	Local mass fraction, (dimensionless)
n	-	Number of mole, (kg-mol)
n_i	-	Mole of the ith component in the feed or product, (kg-mol)
N_{or}	-	Number of orifices on a perforated plate, (dimensionless)
p	-	Partial fraction, (dimensionless)
P	-	Pressure, (N/m^2)
$p(f)$	-	Probability Density Function i.e. fraction of time that the fluctuating variable f takes on a value between f and $f + \Delta f$, (s), (dimensionless)
p_1	-	PDF of f_{fuel}, (dimensionless)
p_2	-	PDF of p_{sec}, (dimensionless)
Q_c	-	Rate of heat absorbed by inlet air, (MJ/min)
Q_{loss}	-	Rate of heat loss through convection and radiation, (MJ/min)
Q_p	-	Rate of heat evolved from the combustion process, assuming complete reaction (MJ/min)
Q_s	-	Heat required for sustaining the combustion process, (MJ)

Q_v	-	Rate of heat consumed to vaporise the moisture content in the feed material, (MJ/min)
r	-	Radius, (m)
R	-	Effects of rapid strain and streamline curvature, (kg/s^4)
Re	-	Reynolds number $\left(= \frac{\rho_f U d_p}{\mu_f} \right)$, (dimensionless)
S_m	-	Transfer of mass from reacting particles into gas phase, [$kg/(m^3 \bullet s)$]
T	-	Temperature, (K)
T_{ad}	-	Adiabatic flame temperature, (K)
t_{cross}	-	Particle eddy crossing time, (s)
T_L	-	Fluid Lagrangian integral time $\left(T_L \approx 0.15 \frac{\kappa}{\varepsilon} \right)$, (s)
u	-	Velocity component or velocity component in *x*-direction, (m/s)
u'	-	Fluctuating component of u, (m/s)
$\bar{u}$	-	Instantaneous velocity component, (m/s)
u_i, u_j	-	Time-averaged velocity component
U, U_o	-	Fluidising gas velocity, (m/s)
U_b	-	Bubble rise velocity, (m/s)
U_{mf}	-	Minimum fluidising velocity, (m/s)
$U_{mf,m}$	-	Minimum fluidising velocity of a mixture of bed particles, (m/s)
U_{ms}	-	Minimum spouting velocity, (m/s)
v	-	Velocity component in *y*-direction, (m/s)
V_m	-	Bubble ejection velocity, (m/s)
w	-	Velocity component in *z*-direction, (m/s)
x_i	-	Mass fraction of the *i-th* size range in the particles screen analysis, (dimensionless)
z	-	Height of bed of particles, (m)

Greek Letters

α_ε	-	Inverse effective Prandtl number for turbulent dissipation rate, (dimensionless)
α_κ	-	Inverse effective Prandtl number for turbulent kinetic energy, (dimensionless)
α_s	-	Swirl constant, (dimensionless)
δ	-	Empirical constant, (dimensionless)
ε	-	Turbulent dissipation rate, (m^2/s^3)
ξ	-	Emissivity of the combustor surface, (dimensionless)
ϕ_i	-	Instantaneous species concentration, density or temperature, ($kmol/m^3$, kg/m^3 or K)
ϕ_s	-	Particle sphericity, (dimensionless)
$\varnothing$	-	Inner diameter of fluidised bed column, (m)
ς	-	Normally distributed random number, (dimensionless)
Ω	-	Swirl angular velocity, (rad/s)
ρ	-	Density, (kg/m^3)
σ_t	-	Constant in PDF equations (= 0.7), (dimensionless)
τ	-	Particle relaxation time (s)
τ_e	-	Characteristic lifetime of the eddy, (s)
τ_i	-	Fraction of time that f spends in the Δf band, (s)
θ	-	Bragg angle in x-ray diffraction analysis, (^{o})
κ	-	Turbulent kinetic energy, (m^2/s^2)
μ	-	Dynamic fluid viscosity, (kg/m·s)

Subscripts

a	-	Air
feed	-	Feed
final	-	Final
fuel	-	Fuel
i	-	i-direction or chemical species i

initial	-	Initial
j	-	j-direction or chemical species j
m	-	Mixture
s	-	Sand
sec	-	Secondary fuel
t	-	Turbulent conditions
w	-	Water

Abbreviation

ASEAN		Association of South-East Asian Nations
ASTM	-	American Society for Testing Materials
BET	-	Brunauer, Emmett and Teller
CFD	-	Computational Fluid Dynamics
DRW	-	Discrete Random Walk
EC	-	European Commission
FKKKSA		Fakulti Kejuruteraan Kimia dan Kejuruteraan Sumber Asli
FSDP	-	Full-Scale Demonstration Project
HHV	-	Higher HeatingValue
IARC	-	International Agency for Research on Cancer
ID	-	Internal Diameter
LCD	-	Liquid Crystal Display
LHV	-	Lower Heating Value, (MJ/kg)
LOI	-	Loss on Ignition
LPG	-	Liquefied Petroleum Gas
LPM	-	Litre per Minute
MSW	-	Municipal Solid Waste
NIOSH		National Institute for Occupational Safety and Health
NO_x	-	Nitrogen Oxides
PDF	-	Probability Density Function
PMET	-	Pittsburg Mineral & Environmental Tech. Inc.
RHA	-	Rice Husk Ash
RM	-	Ringgit Malaysia
RMS	-	Root Mean Square

SEM	-	Scanning Electron Microscopy
TDH	-	Transport Disengaging Height, (m)
USD	-	United States Dollar (USD 1 = RM 3.80)
UTM	-	Universiti Teknologi Malaysia
XRD	-	X-Ray Diffraction

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CHAPTER 1

INTRODUCTION

1.1 Introduction

The purpose of this research was to produce amorphous silica fom rice husk through thermal treatment using the fluidised bed technology. Rice husk ash contains among the highest amount of biogenic silica still in its amorphous form (in the excess of 95 wt% silica, SiO_2) (Kaupp, 1984; Kapur, 1985; James and Rao, 1986) compared to other biomass materials, such as ash from sugarcane bagasse (57 – 73% SiO_2) (Jenkins et al., 1996; Natarajan et al., 1998b; Stephens et al., 2003). In addition, the percentage of ash in rice husk is many times higher (at 13 – 25 wt%, dry basis) (Jenkins et al., 1998; Natarajan et al., 1998b; Armesto et al., 2002) compared to that of sugarcane bagasse (at only 1.9 – 6.8 wt%, dry basis) (Jenkins et al., 1998; Natarajan et al., 1998b; Das et al., 2004). Further, it was reported that such a high percentage of silica is very unusual within nature and that no other plant waste even approaches the amount of silica found in rice husk (Beagle, 1974). The recovery of amorphous silica from rice husk is deemed the most economical source of silica due to the presence of abundant source of rice husk around the country, with annual generation rate of approximately 0.5 million tonnes (in the year 2003, Department of Statistics Malaysia). Rice husk has a high calorific value, which at approximately 13 MJ/kg is sufficient to promote sustainable combustion process, thus reducing the cost of fuel required for the conversion process. This is in contrast with the conventional preparation methods which are either energy-intensive (vapour-phase reaction and thermal decomposition technique) or involves high raw

material costs (alkaline extraction method), all of which result in high production costs.

1.2 Benefits of Research

1.2.1 Amorphous Silica

Silica or silicon dioxide (SiO_2) exists in two forms, amorphous and crystalline. Processing of silica of specific quality results in several types of specialty silicas, such as colloidal silica, fumed silica, fused silica, high-purity ground silica, silica gel and precipitated silica (McDonald, 1991). The global demand for specialty silicas is growing at an annual rate of 3% with revenue generation of more than RM 9.5 billion (USD 2.5 billion) (MineSet Partners LLC, 2004). Currently, the Asia Pacific region is the leading consumer in specialty silica with demand exceeding RM 3 billion (USD 800 million) in 2003 (MineSet Partners LLC, 2004).

Among these specialty silicas, silica in its amorphous form has wider industrial applications (as high-purity ground silica and fumed silica) since crystalline silica is carcinogenic to humans and is categorised as an IARC (International Agency for Research on Cancer) Group 1 agent, whereby its exposure could lead to the risk of silicosis. Amorphous silica is used mainly in specialty coatings, plastics, rubber, electronics, abrasives, refractories and optics (McDonald, 1991). It is also a much sought after raw material for the synthesis of various fine chemicals (sodium silicate, zeolite catalysts, aerogel, very pure silicon, silicon nitride, silicon carbide and magnesium silicide). Since 1997, the world consumption of amorphous silica is estimated to be in the excess of 1 million tonnes per annum valued at approximately RM 4,500 per tonne (Chemlink Pty Ltd., 1997). The price of amorphous silica is highly dependent on its grade (particle size and level of impurities) and could range from RM 440 (USD 120; coarse, impure form) to RM 21,000 (USD 5,500; ultra-fine, highly pure form) (McDonald, 1991). By processing into higher end products such as sodium silicate, its economic value is

further elevated. For example, the production of one tonne of sodium silicate requires approximately 135 kg of amorphous silica as raw material. Thus, one tonne of amorphous silica will produce an equivalent of 7.4 tonnes of sodium silicate, which in turn commands a price of RM 2,100 per tonne (USD 550 per tonne; Chemical Market Reporter, 1999). Sodium silicate is then used for the synthesis of nano-chemicals such as aerogel, with selling price of up to RM 19 million per tonne (USD 500 per 100 g; The Star, 2003).

Conventional methods for preparation of amorphous silica requires the use of high temperature (in the excess of 1500^{o}C) and pressure for extracting silicon in pure form from natural deposits of quartzite rock or quartz sand, such as through the thermal decomposition technique and vapour-phase reaction (Tanner et al., 2000; Wu et al., 2000; Sadasivan et al., 1998, Bogush et al., 1988 and Dielt et al., 1981). Quartz sand is used as the raw material as it is the second most common mineral on earth, therefore making it the most common form of crystalline silica. Another preparation method is the sol-gel process but it involves high raw materials cost (Tomozawa et al., 2001). Such preparation methods results in extremely high production costs, which is subsequently reflected in its high market price.

Rice husk is found to contain amorphous silica in the range of 20 – 25 wt% (Hamad, 1981 – 1982; Hanna et al., 1984; Patel et al., 1987; Nakata et al., 1989; Real et al., 1996; Liou, 2004), which upon thermal degradation yields an ash product with an excess of 95 wt% silica. In addition, rice husk is a form of waste from the rice milling industries and is produced in abundance around the country. The amorphous nature of silica in rice husk makes it extractable at a lower temperature range (Kalapathy et al., 2002) and hence, thermal treatment of rice husk to produce amorphous silica is viewed as a more economical process having the potential to replace the conventional high temperature processes. This is because thermal treatment of rice husk actually produces energy instead of consuming energy. The energy produced could be recovered in the form of heat or electricity.

1.2.2 Rice Husk as Silica Source

The presence of silica in rice husk has been discovered as far back as 1938 (Martin, 1938; Chandrasekhar et al., 2003) while its recovery potential had been realised since 1984 (Kaupp, 1984). It is considered a good source of silica having the potential for large-scale production due to the following reasons:-

a) High Silica Content with Amorphous Characteristic

Rice husk contains silica in the range of 20 – 25 wt% (Real et al., 1996; Patel et al., 1987, Conradt et al., 1992 and Chouhan et al., 2000). The silica (SiO_2) in rice husk exists in the hydrated amorphous form like silica gel. Thermal degradation and pyrolysis of rice husk, followed by combustion of the char, result in a highly porous and amorphous silica particulate mass with a varying percentage of unburnt carbon (Kapur, 1985). Combusted at moderate temperature, the white ash obtained from rice husk contains approximately 92 – 97 wt% amorphous silica (Mishra et al., 1985 and Chakraverty et al., 1988) and some amount of metallic impurities that can be further removed by a simple acid-leaching treatment. Other studies consistently reported that rice husk ash contains very high silica content such as Armesto et al. (2002) (87.7 wt% as SiO_2), Liou (2004) (>90 wt% silica), Kapur (1985) (>95 wt% silica) and Houston (1972) (87 – 97 wt% silica).

b) Abundant and Cheap Source of Silica

Rice is cultivated in more than 75 countries (Natarajan et al., 1998a) and over 97% of rice husk are generated in developing countries (Armesto et al., 2002). Rice husk accounted for 14 – 35 wt% of the paddy harvested, depending on the variety, with an average of 20 wt% (Jenkins, 1989 and Mahin, 1986). Thus, worldwide annual husk output is estimated at 80 million tonnes (Kapur, 1985).

Closer to home, the annual paddy output in Malaysia, up to 2003, was 2.26 million tonnes (Department of Statistics Malaysia) and considering rice husk accounted for 22% of this value, the amount of rice husk generated was approximately 0.5 million tonnes per annum. Rice husk is considered as a form of waste from rice milling processes and are often left to rot slowly in the field or burnt in the open. Although a

small portion of the rice husk is used as a component in animal beddings, the fact that it is a cheap and abundant source of silica remains largely unrealised. To some extent, rice husk has been utilised as fuel for cooking and parboiling of paddy rice in some developing country, but it is neither fully nor efficiently utilised. Such under-utilisation clearly shows the wastage and loss of resources which in reality could generate revenue through the recovery of silica via methods such as combustion.

Kaupp (1984) noted that the ash content of approximately 20 wt% in rice husk (which comprise of over 95 wt% silica) would make rice husk utilisation systems become very economically attractive. According to Kapur (1985), when rice husk is burnt under controlled conditions, the resulting ash is easily the cheapest bulk source of highly reactive silica with a BET (Brunauer, Emmett and Teller method) surface area which can be as high as 80 m^2/g or more. Further, since the ash is obtained as a fine powder, it does not require further grinding (James and Rao, 1986) and thus, making it the most economical source of nanoscale silica (Liou, 2004).

c) Quality of Silica Comparable with Other Expensive Sources of Silica

As reviewed by Real et al. (1996), a number of published literatures (such as Mishra et al., 1985; Chakraverty et al., 1988; and James and Rao, 1986) had concluded that rice husk are an excellent source of high-grade amorphous silica. The silica obtained from rice husk ash is a good material for synthesis of very pure silicon (Amick et al., 1980; Amick, 1982 and Hunt et al., 1984), silicon nitride (Real et al., 1996; Yalçin and Sevinç, 2001), silicon carbide (Krishnarao and Subrahmahyam, 1995; Gorthy and Pudukottah, 1999) and magnesium silicide (Ghosh et al., 1991). In addition, this silica has been claimed (Amick, 1982; Chakraverty et al., 1985; and Hunt et al., 1984) to be an excellent source of very pure silicon, useful for manufacturing solar cells for photovoltaic power generation and semiconductors. In the manufacture of silicon carbide from rice husk silica, the processing temperature could be lowered to 1500^oC due to the high surface area and intimate contact available from carbon and silica in rice husk. This is considered to be less energy-intensive compared to conventional methods using coal and quartz sand in electric furnaces (Hanna et al., 1984), whereby the processing temperatures are in the order of 2500^oC. With silica content in the excess of 95 wt%, rice husk ash can also be used as a substitute for silica in cement manufacture. Preliminary study conducted by Ajiwe et al. (2000)

showed that the produced cement had similar standard compared to commercial cement.

d) Disposal Problem

The current practices to dispose of the large quantities of rice husk through open burning or rotting in field are not environmental-friendly. Open burning results in air pollution with the formation of smoke and particulate matters in the form of char and ash. Rotting in field, on the other hand, results in formation of methane (CH_4), which is a potent greenhouse gas. Combustion of biomass such as rice husk can actually reduce the greenhouse effect by converting emissions that would have been methane into the less potent greenhouse gas carbon dioxide. Since CH_4 is some 25 times more potent as a greenhouse gas than carbon dioxide (CO_2), and since the two gases have similar atmospheric residence times, trading off CH_4 emissions for CO_2 emissions from combustion leads to a large net reduction of the greenhouse effect associated with the disposal of rice husk. Rotting in the field leads to a slow decay of the material, with eventual emissions of approximately equal amount of CH_4 and CO_2 from the carbon that is released during the decay (Morris et al., 1991).

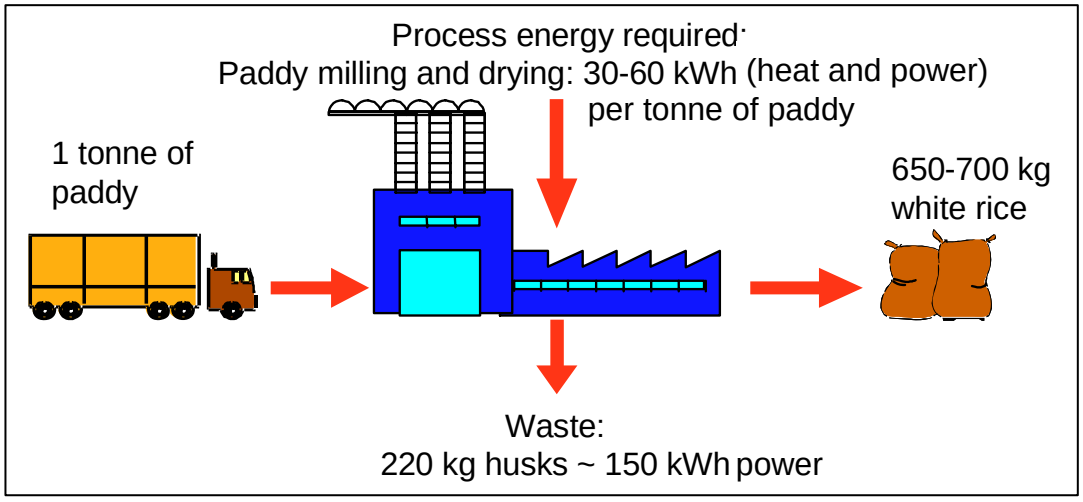
e) High Energy Content

Rice husk has an average lower heating value (LHV) of 13 – 16 MJ/kg (Jenkins, 1989; Mahin, 1986 and Kapur, 1985). Comparisons by Natarajan et al. (1998a) indicated that the LHV of rice husk is about one-third that of furnace oil, one-half that of good quality coal and comparable with sawdust, lignite and peat. It was also reported that the world annual energy potential of rice husk is 1.2×10^9 GJ, with a corresponding heating value of 15 MJ/kg. Thus, rice husk is a good renewable energy source. Apart from solving its disposal problems, combustion offers the potential for energy recovery from this waste.

In Malaysia, with a reported annual generation rate of rice husk at 0.424 million tonnes in the year 2000, the potential energy generation from rice mills is 263 GWh per annum. This translates to a potential capacity of 30 MW (National Energy Balance Malaysia Year 2000 Report). The pressure to search for renewable energy sources is mounting due to the depletion of fossil fuels and the rapid increase in

energy demand, from 25,558 toe (tonne of oil equivalent or equivalent to 42 GJ of lower heating value) in 1998 to 31,515 toe in 2001 (National Energy Balance Malaysia Reports for Year 1998 and 2001). In the Eighth Malaysia Plan (2001 – 2005), the Government replaces the Four-Fuel Diversification Policy with the new Five-Fuel Diversification Policy, which adds renewable energy as a potential source alongside existing four fuels utilised for power generation (oil, gas, coal and hydro). The renewable energy focus is on biomass and the target contribution towards the total electricity generation mix is 5% by 2005 and 10% by 2010. Utilising only 5% of renewable energy could save the country RM5 billion over five years (NSTP, 29th June 2002).

The use of rice husk as renewable energy has already been practised in Malaysia, whereby Bernas and a private rice miller operate a few small (< 1 MW) rice husk cogeneration plants to produce electricity and steam for paddy drying. As shown in Figure 1-1, milling of 1 tonne of paddy produces about 220 kg of rice husk or equivalent to approximately 150 kWh of potential power. In the year 1997, a Full-Scale Demonstration Project (FSDP) under COGEN 3 using rice husk as fuel had been implemented in Ban Heng Bee Rice Mill (1952) Sdn. Bhd. with the commissioning of its 450 kW rice husk-fired cogeneration plant. COGEN 3 is the third phase of the EC-ASEAN cooperation programme initiated by the European Commission (EC) and the Association of South-East Asian Nations (ASEAN). It is financed by the European Commission. COGEN 3 accelerates the implementation of proven, clean and efficient cogeneration projects using biomass, coal or gas as fuel. The projects are implemented through partnerships between ASEAN industrial companies and European equipment suppliers.



Source: EC-ASEAN COGEN Programme

Figure 1-1: Power generation potential from rice husk mills

1.2.3 Market Review for Amorphous Silica from Rice Husk Ash

Currently, the two major commercial applications for amorphous silica from rice husk ash (RHA) are as pozzolan in the cement industry and for manufacture of sodium silicate in the fine chemicals industry. It can also be used in the steel industry as insulator during the steel casting process. However, since it will transform into crystalline form at the end of the steel making process due to prolonged heating at high temperatures (i.e. 1500^{o}C for 4 hours), it is more economically-feasible to use crystalline rice husk ash for such purpose since the price of amorphous ash is higher compared to crystalline ash. The market for crystalline ash (up to 1.0 wt% crystals, carbon content 2.5 – 5.0 wt%) in the steel industry is well-established, with an average price of RM 570 per tonne (USD 150 per tonne) (Bronzeoak, 2003).

a) Cement Industry

Amorphous RHA has been widely researched as mineral cement replacement material (MCRM). The two main research areas for the utilisation of RHA in the cement industry are in the manufacture of low cost building blocks and in the production of high quality cement. Traditionally, silica fume, which is a byproduct

of metallurgical industry, is used for exactly the same purpose but its supply is becoming limited and expensive for developing economies. The current price of silica fume is reported to be RM 4,560 per tonne (USD 1,200 per tonne) in India (Torftech News, 24th November 2003).

Research such as that conducted at FEUP (Faculdade de Engenharia, Universidade do Porto or Faculty of Engineering of University of Porto) in Portugal had shown that RHA concrete performed better than silica fume concrete. Further, studies by Nehdi et al. (2003) showed that depending on the addition rate, RHA increased the compressive strength of concrete by up to 40% at 56 days and was thus deemed superior compared to silica fume. They also concluded that the performance of RHA in reducing the rapid chloride penetrability of concrete was comparable to silica fume and was slightly more efficient than silica fume in resisting surface scaling due to deicing salts. Preliminary studies conducted by Ajiwe et al. (2000) also showed that RHA-formulated cement (RHA substitution of 24.5 wt%, based on the analysis by Bogue (1989) that the theoretical percentage fraction of silica in tricalcium silicate or Portland cement was 26.3 wt%) had similar standard in terms of its compressive strength and setting time compared to commercial cement.

The market of RHA for cement industry is not as well-developed as steel, but there is a great potential due to the pozzolanic properties of RHA that are comparable to cement. The potential is also driven by the absence of any health issues associated with the use of crystalline ash (as in the steel industry) due to the use of amorphous ash. In the United States of America, RHA has already been used commercially by Pittsburg Mineral & Environmental Tech. Inc. (PMET) which is part of Alchemix Corporation, Arizona, as a substitute for silica fume in the production of specialist concrete. PMET specifies that the RHA for use as substitute for silica fume should contain less than 1% of crystalline silica (>99% amorphous), carbon content less than 6% and mean particle size of 7 – 9 μm (passing 45 μm sieve). The current market prices for RHA sold to the cement industry were shown in Table 1-1. The price could reach as high as RM 2,280 per tonne (USD 600 per tonne) for high quality amorphous RHA with more than 85% silica content.

Table 1-1: Market prices for amorphous rice husk ash for use in cement industry

No.	Source/Reference	Price (per tonne)		Remarks
		RM	USD	
1	Torftech Application Description (August 2002)	1,140	300	-
2	The Hindu Newspaper (19th January 2003)	1,900 – 2,280	500 – 600	Price for super pozzolana (RHA containing high silica content in the excess of 85%)

b) Fine Chemicals Industry

The emerging use of amorphous RHA is for the manufacture of water glass (sodium silicate or Na_2SiO_3), which in turn is an intermediate raw material for synthesis of a wide array of fine chemicals. The current market price for water glass is RM 2,100 per tonne (USD 550 per tonne, Chemical Market Reporter, 18th January 1999).

The conventional process of manufacturing sodium silicate is through the fusion of silica sand with high-purity soda ash in furnaces at high temperatures (1300 – 1500^{o}C), forming water glass (a solid) which is then crushed and dissolved in water and digested under pressure with steam. According to Stephens et al. (2003), the production of water glass through this route formed the foundation of all commercial processes for making sodium or other soluble silicate solutions today. Both the high-temperature fusion and high-temperature and pressure digestion processes are very energy-intensive, thus very expensive. In addition, the silicates produced generally contain metal contaminants found in the earth in amounts ranging from 400 to 10,000 ppm.

The potential for obtaining this expensive sodium silicate solution through the relatively less costly process of caustic digestion of RHA had been reported by Stephens et al. (2003). In their patent (U.S. Patent No. 6,638,354) describing the synthesis of precipitated silicas and silica gels (with and without deposited carbon), the sodium silicate solution required for the synthesis was obtained from digestion of amorphous RHA in a caustic solution of sodium hydroxide. Maintaining the amorphous structure in the RHA is important for its use in the synthesis of chemicals as the silica maintains a porous skeletal structure which provides better chemical reactivity and solubility, especially during operations such as caustic