PRODUCTION OF AMORPHOUS SILICA FROM RICE HUSK IN FLUIDISED BED SYSTEM

NGO SAIK PENG

A thesis submitted in fulfilment of the requirements for the award of the degree of Doctor of Philosophy

Faculty of Chemical Engineering and Natural Resources Engineering
Universiti Teknologi Malaysia

FEBRUARY 2006
ACKNOWLEDGEMENT

I would like to express my most sincere gratitude and appreciation to my supervisor, Assoc. Prof. Dr Mohd Rozainee bin Taib for his guidance and supervision of this research works. Without his guidance, I believe this research would not have been completed.

I am also grateful to my fellow research partners, Mr Tan Kean Giap, Mr Anwar Johari, Mr Arshad Adam Salema, Mr Wan Ahmad Muhardi bin Wan Muhammad, Mr Lim Sin Yang, Mr Simon Looi Yat Seong, Mr Chong Yee Hwang and Ms Wong Cheng Teng for their valuable ideas, friendship and assistance. I am equally grateful to the Research Assistants involved in my research especially Mr Guee Boon Chye, whose assistance facilitated my experimental works.

My special thanks go to the School of Graduate Studies (SPS) who supported me financially through the UTM Fellowship Award. Lastly but certainly not the least, I am indebted to my parents for their endless support throughout the length of my study.
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 (SiO₂) 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 dinilai 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.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>CHAPTER</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>TITLE PAGE</td>
<td>i</td>
<td></td>
</tr>
<tr>
<td>DECLARATION</td>
<td>ii</td>
<td></td>
</tr>
<tr>
<td>ACKNOWLEDGEMENT</td>
<td>iii</td>
<td></td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>iv</td>
<td></td>
</tr>
<tr>
<td>ABSTRAK</td>
<td>v</td>
<td></td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>vi</td>
<td></td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xi</td>
<td></td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xxi</td>
<td></td>
</tr>
<tr>
<td>LIST OF PLATES</td>
<td>xxxii</td>
<td></td>
</tr>
<tr>
<td>LIST OF SYMBOLS</td>
<td>xxxiv</td>
<td></td>
</tr>
<tr>
<td>LIST OF APPENDICES</td>
<td>xl</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.1</td>
<td>Introduction</td>
<td>1</td>
</tr>
<tr>
<td>1.2</td>
<td>Benefits of Research</td>
<td>2</td>
</tr>
<tr>
<td>1.2.1</td>
<td>Amorphous Silica</td>
<td>2</td>
</tr>
<tr>
<td>1.2.2</td>
<td>Rice Husk as Silica Source</td>
<td>4</td>
</tr>
<tr>
<td>1.2.3</td>
<td>Market Review for Amorphous Silica from Rice Husk</td>
<td>8</td>
</tr>
<tr>
<td>1.2.4</td>
<td>Evaluation of Available Technologies for Production of Amorphous Silica from Rice Husk</td>
<td>11</td>
</tr>
<tr>
<td>1.2.5</td>
<td>Fluidised Bed as Selected Technology</td>
<td>16</td>
</tr>
</tbody>
</table>
1.2.6 Types of Fluidised Bed
1.3 Objectives of Research
1.4 Scopes of Research
1.5 Expected Results
1.6 Layout of the Thesis

2 LITERATURE REVIEW

2.1 Research History on Thermal Treatment of Rice Husk in Fluidised Bed
2.2 Effects of Fluidisation Parameters on the Mixing Characteristics of Rice Husk in Fluidised Bed
2.2.1 Fluidising Velocity
2.2.2 Sand Size
2.2.3 Static Bed Height
2.3 Effects of Operating Parameters on the Combustion Efficiency of Rice Husk in Fluidised Bed
2.3.1 Time
2.3.2 Temperature
2.3.3 Presence of Impurities in Rice Husk
2.3.4 Air Supply
2.3.5 Moisture Content of Rice Husk
2.4 Effects of Fluidised Bed Design on the Combustion Efficiency of Rice Husk in Fluidised Bed
2.4.1 Freeboard Height
2.4.2 Feeding Design and Position of Feed Entry

3 METHODOLOGY

3.1 Introduction
3.2 Research Materials
### Experimental Techniques

#### 3.3.1 Thermal Treatment in Muffle Furnace

#### 3.3.2 Fluidisation Study in 80-mm Inner Diameter Fluidised Bed Column

#### 3.3.3 Combustion Study in 80-mm Inner Diameter Fluidised Bed Combustor

#### 3.3.4 Combustion Study in 210-mm Inner Diameter Fluidised Bed Combustor

### Analytical Techniques

#### 3.4.1 Determination Silica Structure and Presence of Contaminants in Rice Husk Ash through X-Ray Diffraction (XRD) Analysis

#### 3.4.2 Determination of Residual Carbon Content in Rice Husk Ash through Loss on Ignition (LOI) Test

#### 3.4.3 Determination of Particle Size Distribution of Rice Husk Ash through Sieve Analysis

#### 3.4.4 Determination of Oxygen Level in Combustion Gas

### Modelling Technique through Computational Fluid Dynamics (CFD) Code of FLUENT

#### 3.5.1 Governing Equations

#### 3.5.2 Numerical Solutions

---

### RESULTS AND DISCUSSIONS ON COMBUSTION OF RICE HUSK IN FLUIDISED BED TO PRODUCE AMORPHOUS SILICA

#### 4.1 Basic Combustion Characteristics of Rice Husk

#### 4.2 Effect of Temperature and Residence Time on the Formation of Silica Crystals in Rice Husk Ash
4.3  Effects of Fluidisation Parameters on the Mixing of Rice Husk in Fluidised Bed

4.3.1  Sand Size

4.3.2  Fluidising Velocity ($U_{mf}$ Number)

4.3.3  Static Bed Height

4.4  Effect of Fluidisation Parameters on the Mixing of Rice Husk in Fluidised Bed during Combustion Process

4.4.1  Sand Size

4.4.2  Fluidising Velocity

4.5  Effect of Mixing Parameters on the Combustion Efficiency of Rice Husk in Fluidised Bed

4.5.1  Fluidising Velocity

4.5.2  Static Bed Height

4.6  Effect of Temperature on the Combustion Efficiency of Rice Husk in Fluidised Bed

4.6.1  Bed Temperature

4.6.2  Freeboard Temperature

4.6.3  Heat Loss

4.7  Effect of Washing of Rice Husk on Its Combustion Efficiency in Fluidised Bed

4.7.1  Determination of Pretreatment Method for Rice Husk

4.7.2  Effect of Alkali Metals Removal in Rice Husk on Its Combustion Efficiency in Fluidised Bed

4.7.2.1  Primary Stage Combustion

4.7.2.2  Secondary Stage Combustion

4.8  Effect of Air Supply on the Combustion Efficiency of Rice Husk in Fluidised Bed

4.8.1  Primary Air Factor

4.8.2  Primary-to-Secondary Air Ratio

4.8.3  Pneumatic Air Feeding Velocity
4.9 Effect of Moisture Content in Rice Husk on Its Combustion Efficiency in Fluidised Bed 241

4.10 Effect of Feeding Design on the Combustion Efficiency of Rice Husk in Fluidised Bed 246

4.10.1 Vortex Feeding 246

4.10.2 Vortex Feeding with Higher Fluidising Velocity 263

4.11 Summary of Findings 273

5 RESULTS AND DISCUSSIONS ON IMPROVEMENT IN DESIGN AND OPERATION OF THE FLUIDISED BED THROUGH CFD MODELLING 277

5.1 Increase in Fluidised Bed Freeboard Height 277

5.2 Improvement of Feeding Conditions 284

5.2.1 Feeding Velocity 284

5.2.2 Vortex Feeding 292

5.3 Summary of Findings 310

6 CONCLUSIONS AND RECOMMENDATIONS 313

6.1 Conclusions 313

6.2 Recommendations for Future Study 323

REFERENCES 325
# LIST OF TABLES

<table>
<thead>
<tr>
<th>TABLE</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 1-1:</td>
<td>Market prices for amorphous rice husk ash for use in cement industry</td>
<td>10</td>
</tr>
<tr>
<td>Table 1-2:</td>
<td>Existing methods and technologies for preparation of amorphous silica from rice husk</td>
<td>12</td>
</tr>
<tr>
<td>Table 1-3:</td>
<td>Performance of existing thermal treatment technologies in producing low carbon content rice husk ash</td>
<td>18</td>
</tr>
<tr>
<td>Table 2-1:</td>
<td>Properties of sewage sludge and rice husk (wt% dry basis)</td>
<td>30</td>
</tr>
<tr>
<td>Table 2-2:</td>
<td>Sand size and corresponding fluidisation velocity reported in literature for combustion of rice husk in fluidised bed</td>
<td>31</td>
</tr>
<tr>
<td>Table 2-3:</td>
<td>Minimum fluidising velocity of sand of various size ranges</td>
<td>33</td>
</tr>
<tr>
<td>Table 2-4:</td>
<td>Static bed height used for the combustion of rice husk as reported in existing literatures</td>
<td>34</td>
</tr>
<tr>
<td>Table 2-5:</td>
<td>Temperature limits reported in various literatures for the onset of crystallisation of silica in rice husk ash</td>
<td>43</td>
</tr>
<tr>
<td>Table 2-6:</td>
<td>Chemical properties of wheat straw and rice husk</td>
<td>54</td>
</tr>
<tr>
<td>Table 2-7:</td>
<td>Optimum air factor reported in literature (as reviewed by Natarajan et al., 1998a) for combustion of rice husk in fluidised bed</td>
<td>57</td>
</tr>
<tr>
<td>Table 2-8:</td>
<td>Different rice husk feeding arrangements reported in literature</td>
<td>64</td>
</tr>
<tr>
<td>Table 3-1:</td>
<td>Chemical properties of rice husk</td>
<td>68</td>
</tr>
<tr>
<td>Table 3-2:</td>
<td>List and identifications of combustion parameters investigated in the 210-mm inner diameter fluidised bed combustor</td>
<td>89</td>
</tr>
<tr>
<td>Table 3-3:</td>
<td>Diffraction peaks of crystalline silica</td>
<td>90</td>
</tr>
<tr>
<td>Table 3-4:</td>
<td>Properties of particles used in modelling the effect of feeding method on rice husk combustion in the 210-mm inner diameter fluidised bed combustor</td>
<td>113</td>
</tr>
<tr>
<td>Table 4-1:</td>
<td>Real-time tracking of combustion of a batch (4 g) of water-washed rice husk particles in the muffle furnace (650 – 750°C)</td>
<td>118</td>
</tr>
<tr>
<td>Table 4-2:</td>
<td>Effect of temperature and residence time on the formation of black char particles during thermal treatment of raw rice husk in the muffle furnace</td>
<td>122</td>
</tr>
<tr>
<td>Table 4-3:</td>
<td>Effect of temperature and residence time on the formation of black char particles during thermal treatment of water-washed rice husk* in the muffle furnace</td>
<td>123</td>
</tr>
<tr>
<td>Table 4-4:</td>
<td>Effect of temperature and residence time on the formation of black char particles during thermal treatment of water-washed rice husk* (submerged particles) in the muffle furnace</td>
<td>124</td>
</tr>
<tr>
<td>Table 4-5:</td>
<td>Effect of temperature and residence time on the formation of black char particles during thermal treatment of water-washed rice husk* (floating particles) in the muffle furnace</td>
<td>125</td>
</tr>
<tr>
<td>Table 4-6:</td>
<td>Diffractograms of rice husk ash samples from thermal treatment of raw rice husk in the muffle furnace at different temperatures and residence times</td>
<td>127</td>
</tr>
<tr>
<td>Table 4-7:</td>
<td>Diffractograms of rice husk ash samples from thermal treatment of water-washed rice husk* in</td>
<td></td>
</tr>
</tbody>
</table>
the muffle furnace at different temperatures and residence times

Table 4-8: Diffractograms of rice husk ash samples from thermal treatment of water-washed rice husk in the muffle furnace at 900°C for different residence times

Table 4-9: Fluidisation properties of rice husk, rice husk char, rice husk ash and silica sand samples

Table 4-10: Screening of commercial silica sand* size for experimental study of rice husk combustion in fluidised bed combustor systems

Table 4-11: Mixing behaviours of rice husk in the 80-mm inner diameter fluidised bed column at different fluidising velocities (sand size = 250 – 595 μm, static bed height = 0.5 Dc, mass fraction of rice husk in sand bed = 10 wt%)

Table 4-12: Mixing behaviours of rice husk in the 80-mm inner diameter fluidised bed column at different static bed heights (sand size = 250 – 595 μm, fluidising velocity = 4 Umf, mass fraction of rice husk in sand bed = 10 wt%)

Table 4-13: Fly ash samples from the combustion of rice husk in the 80-mm inner diameter fluidised bed combustor with a bed of 595 – 841 μm sand (fluidising velocity = 3 – 5 Umf, static bed height = 0.5 Dc, primary air factor ≈ 1.0)

Table 4-14: Ash samples from the combustion of rice husk in the 80-mm inner diameter fluidised bed combustor with a bed of 250 – 595 μm sand (fluidising velocity = 3 – 5 Umf, static bed height = 0.5 Dc, primary air factor ≈ 1.0)

Table 4-15: Ash samples from the combustion of rice husk in the 80-mm inner diameter fluidised bed combustor
at different fluidising velocities (sand size = 250 – 595 μm, static bed height = 0.5 $D_c$, primary air factor ≈ 1.0)

Table 4-16: Diffractograms of fly ash samples from the combustion of rice husk in the 210-mm inner diameter fluidised bed at different fluidising velocities (sand size = 250 – 595 μm, static bed height = 0.5 $D_c$, primary air factor ≈ 1.0)

Table 4-17: Products and diffractograms of fly ash sample after sand de-contamination stage

Table 4-18: Ash samples from the combustion of rice husk in the 210-mm inner diameter fluidised bed combustor at different fluidising velocities (sand size = 250 – 595 μm, static bed height = 0.5 $D_c$, primary air factor ≈ 1.0)

Table 4-19: Diffractograms of fly ash samples from the combustion of rice husk in the 210-mm inner diameter fluidised bed at different static bed heights (sand size = 250 – 595 μm, fluidising velocity ≈ 3 $U_{mf}$, primary air factor ≈ 1.0)

Table 4-20: Fly ash samples from the combustion of rice husk in the 210-mm inner diameter fluidised bed at different static bed heights (sand size = 250 – 595 μm, fluidising velocity ≈ 3 $U_{mf}$, primary air factor ≈ 1.0)

Table 4-21: Diffractograms of fly and bottom ashes from the combustion of rice husk in the 80-mm inner diameter fluidised bed at different bed temperatures (sand size = 250 – 595 μm, static bed height = 0.5 $D_c$, fluidising velocity ≈ 4 $U_{mf}$, primary air factor ≈ 1.0)

Table 4-22: Diffractograms of ash samples from the combustion of rice husk in the 210-mm inner
diameter fluidised bed combustor at different freeboard temperatures (sand size = 250 – 595 μm, static bed height = 0.5 Dc, fluidising velocity = 4 – 5 Umf, primary air factor ≈ 1.0, oxygen level in cyclone ≥ 6 vol%)

Table 4-23: Ash samples from the combustion of rice husk in the 210-mm inner diameter fluidised bed at different freeboard temperatures (sand size = 250 – 595 μm, static bed height = 0.5 Dc, fluidising velocity = 4 – 5 Umf, primary air factor ≈ 1.0, oxygen level in cyclone ≥ 6 vol%)

Table 4-24: Diffractograms of fly ash samples from the combustion of rice husk in the non-insulated and insulated 210-mm inner diameter fluidised bed combustors (sand size = 250 – 595 μm, static bed height = 0.5 Dc, fluidising velocity ≈ 3 Umf, primary air factor ≈ 1.5)

Table 4-25: Ash samples from thermal treatment of raw, water-washed and acid-leached rice husk

Table 4-26: Effect of alkali metals removal from rice husk on the bed temperatures during combustion of rice husk in the 210-mm inner diameter fluidised bed (primary stage combustion) (sand size = 250 – 595 μm, static bed height = 0.5 Dc, fluidising velocity ≈ 3 Umf, primary air factor ≈ 1.2)

Table 4-27: Physical appearances of the raw and water-washed rice husk samples

Table 4-28: Diffractograms of ash samples from the combustion of raw and water-washed rice husk in the 210-mm inner diameter fluidised bed combustor (effect of alkali metals removal on combustion efficiency in the primary stage) (sand
Table 4-29: Ash samples from the combustion of raw and water-washed rice husk in the 210-mm inner diameter fluidised bed combustor (effect of alkali metals removal on combustion efficiency in the primary stage) (sand size = 250 – 595 μm, static bed height = 0.5 Dc, fluidising velocity ≈ 3 U_{mf}, primary air factor ≈ 1.2).

Table 4-30: Silica structures of ash samples from the combustion of raw and water-washed rice husk in the 210-mm inner diameter fluidised bed (effect of alkali metals removal on combustion efficiency in the secondary stage) (sand size = 250 – 595 μm, static bed height = 0.5 Dc, fluidising velocity ≈ 3 U_{mf}, primary air factor ≈ 1.2, oxygen level in cyclone = 6 – 12 vol%).

Table 4-31: Ash samples from the combustion of raw and water-washed rice husk in the 210-mm inner diameter fluidised bed (effect of alkali metals removal on combustion efficiency in the secondary stage) (sand size = 250 – 595 μm, static bed height = 0.5 Dc, fluidising velocity ≈ 3 U_{mf}, primary air factor ≈ 1.2, oxygen level in cyclone = 6 – 12 vol%).

Table 4-32: Comparisons of ash samples before and after loss on ignition tests (ash from combustion of raw rice husk in the 210-mm inner diameter fluidised bed at different freeboard temperatures; sand size = 250 – 595 μm, static bed height = 0.5 Dc, fluidising velocity ≈ 3 U_{mf}, primary air factor ≈ 1.2, oxygen level in cyclone = 6 – 12 vol%).
Table 4-33: Diffractograms of fly and bottom ashes from the combustion of rice husk in the 210-mm inner diameter fluidised bed at different primary air factors (sand size = 250 – 595 μm, static bed height = 0.5 D_c, fluidising velocity = 5 – 6 U_{mf})

Table 4-34: Ash samples from the combustion of rice husk in the 210-mm inner diameter fluidised bed at different primary air factors (sand size = 250 – 595 μm, static bed height = 0.5 D_c, fluidising velocity = 5 – 6 U_{mf})

Table 4-35: Ash samples from the combustion of rice husk in the 210-mm inner diameter fluidised bed at different primary-to-secondary air ratios (sand size = 250 – 595 μm, static bed height = 0.5 D_c, fluidising velocity = 5.7 U_{mf}, primary air factor = 0.65)

Table 4-36: Ash samples from the combustion of rice husk in the 210-mm inner diameter fluidised bed combustor at different primary-to-secondary air ratios (sand size = 250 – 595 μm, static bed height = 0.5 D_c, fluidising velocity = 5.7 U_{mf}, primary air factor = 0.65)

Table 4-37: Diffractograms of fly ash samples from the combustion of rice husk in the 210-mm inner diameter fluidised bed at different pneumatic air feeding velocities (sand size = 250 – 595 μm, static bed height = 0.5 D_c, fluidising velocity ≈ 3 U_{mf}, primary air factor ≈ 1.5)

Table 4-38: Fly ash samples from the combustion of rice husk in the 210-mm inner diameter fluidised bed at different pneumatic air feeding velocities (sand size = 250 – 595 μm, static bed height = 0.5 D_c, fluidising velocity ≈ 3 U_{mf}, primary air factor ≈ 1.5)
Table 4-39: Rice husk samples used for the combustion of water-washed rice husk at different moisture contents in the 210-mm inner diameter fluidised bed combustor

Table 4-40: Diffractograms of ash samples from the combustion of water-washed rice husk at different moisture contents in the 210-mm inner diameter fluidised bed combustor (sand size = 250 – 595 μm, static bed height = 0.5 D_c, fluidising velocity ≈ 3 U_{mf}, primary air factor ≈ 1.2)

Table 4-41: Ash samples from the combustion of water-washed rice husk at different moisture contents in the 210-mm inner diameter fluidised bed combustor (sand size = 250 – 595 μm, static bed height = 0.5 D_c, fluidising velocity ≈ 3 U_{mf}, primary air factor ≈ 1.2)

Table 4-42: Heat capacities of materials used in the experimental study

Table 4-43: Comparisons of silica structures of ash samples from the combustion of rice husk in the 210-mm inner diameter fluidised bed with different feeding methods (sand size = 250 – 595 μm, static bed height = 0.5 D_c, fluidising velocity ≈ 3 U_{mf}, primary air factor ≈ 1.2)

Table 4-44: Ash samples from the combustion of rice husk in the 210-mm inner diameter fluidised bed with different feeding methods (sand size = 250 – 595 μm, static bed height = 0.5 D_c, fluidising velocity ≈ 3 U_{mf}, primary air factor ≈ 1.2)

Table 4-45: Comparisons of physical appearances of different particles from the combustion of rice husk in fluidised bed combustor

Table 4-46: Expected trajectories of particles in the computational fluid dynamics (CFD) model of rice
husk combustion in the 210-mm inner diameter fluidised bed combustor with different feeding methods

Table 4-47: Diffractograms of ash samples from the combustion of rice husk in the 210-mm inner diameter fluidised bed with inclined, tangential feeding port at different fluidising velocities (sand size = 250 – 595 μm, static bed height = 0.5 Dc, primary air factor ≈ 1.2)

Table 4-48: Ash samples from the combustion of rice husk in the 210-mm inner diameter fluidised bed with inclined, tangential feeding port at different fluidising velocities (sand size = 250 – 595 μm, static bed height = 0.5 Dc, primary air factor ≈ 1.2)

Table 5-1: Trajectories and mass loss history of burning rice husk particles with different sizes in the fluidised bed combustor model (⌀500mm × 5250mm)

Table 5-2: Histograms for residence time distribution from computational fluid dynamics (CFD) modelling of burning rice husk particles in the 210-mm inner diameter fluidised bed combustor

Table 5-3: Trajectories and residence times of burning rice husk particles in the 210-mm inner diameter fluidised bed combustor from CFD modelling

Table 5-4: Computational fluid dynamics (CFD) modelling results on the trajectories and residence times of particles during the combustion of rice husk in the 210-mm inner diameter fluidised bed combustor with inclined feeding port (Model FM-A)

Table 5-5: Computational fluid dynamics (CFD) modelling results on the trajectories and residence times of particles during the combustion of rice husk in the
210-mm inner diameter fluidised bed combustor
with inclined, tangential feeding port (Model FM-B)

Table 5-6: Trajectories and residence times of fly ash particles in Model FM-A (inclined feeding method)

Table 5-7: Trajectories and residence times of fly ash particles in Model FM-B (inclined, tangential feeding method)

Table 5-8: Trajectories of fly ash particles in Model FM-B (inclined, tangential feeding) when the tangential feeding velocity was reduced by half (from 1.1 m/s to 0.55 m/s)

Table 5-9: Mass loss history of burning rice husk particles in Model FM-A (inclined feeding method)

Table 5-10: Mass loss history of burning rice husk particles in Model FM-B (inclined, tangential feeding method)

Table 5-11: Trajectories and residence times of bottom ash particles in Model FM-A (inclined feeding method)

Table 5-12: Trajectories and residence times of bottom ash particles in Model FM-B (inclined, tangential feeding method)
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>FIGURE</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1-1:</td>
<td>Power generation potential from rice husk mills</td>
<td>8</td>
</tr>
<tr>
<td>Figure 2-1:</td>
<td>Diffractogram of fresh rice husk (taken from Liou, 2004)</td>
<td>40</td>
</tr>
<tr>
<td>Figure 2-2:</td>
<td>Diffractogram of crystallised rice husk ash showing characteristic crystal peak of cristobalite at 20 angle of 21.93° (rice husk sample fired at 1000°C at different time intervals) (Ibrahim and Helmy, 1981)</td>
<td>41</td>
</tr>
<tr>
<td>Figure 2-3:</td>
<td>Effect of secondary airflow on the temperature distribution in the firebrick-insulated fluidised bed combustor during the combustion of rice husk (Chen et al., 1998)</td>
<td>59</td>
</tr>
<tr>
<td>Figure 2-4:</td>
<td>Chart for transport disengaging height (TDH) estimation of fine particle (Geldart A) beds (Zenz and Weil, 1958)</td>
<td>63</td>
</tr>
<tr>
<td>Figure 3-1:</td>
<td>Adiabatic flame temperatures from combustion of rice husk sample at different air factors computed using the FLAME programme code</td>
<td>69</td>
</tr>
<tr>
<td>Figure 3-2:</td>
<td>Particle size distribution of silica sand samples used in the experimental study</td>
<td>70</td>
</tr>
<tr>
<td>Figure 3-3:</td>
<td>Bed particles used in the combustion of rice husk in fluidised bed</td>
<td>71</td>
</tr>
<tr>
<td>Figure 3-4:</td>
<td>Boat-like shape of whole rice husk</td>
<td>71</td>
</tr>
<tr>
<td>Figure 3-5:</td>
<td>Diffractogram of fresh rice husk sample</td>
<td>72</td>
</tr>
</tbody>
</table>
Figure 3-6: Diffractogram of amorphous rice husk ash (from thermal treatment of rice husk in muffle furnace at 600°C and 1 hour) 73
Figure 3-7: Diffractogram of crystallised rice husk ash (exposure to temperature of 725°C for 10 hours in a muffle furnace) 73
Figure 3-8: Diffractogram of fresh silica sand 74
Figure 3-9: Diffractogram of used silica sand (from fluidised bed after combustion of rice husk) 74
Figure 3-10: Experimental setup of the 80-mm inner diameter Perspex fluidised bed for investigation of fluidisation and mixing behaviours of rice husk 77
Figure 3-11: Behavioural changes of bed with gas velocity in a conventional fluidised bed (Howard, 1989) 78
Figure 3-12: Pressure drop versus gas velocity plot for increasing and decreasing gas flow 79
Figure 3-13: Determination of terminal velocity from the plot of pressure drop versus fluidisation velocity (Hao et al., 1995) 79
Figure 3-14: Positions of thermocouples (T1 – T6), feeding port and viewing port at the 210-mm inner diameter fluidised bed combustor 86
Figure 3-15: Overall schematic diagram of the 210-mm inner diameter fluidised bed combustor system 87
Figure 3-16: Algorithm for the solution of a non-adiabatic two-mixture-fraction case in pre-PDF and FLUENT 105
Figure 3-17: Size distribution of elutriated sand particles during the combustion of rice husk in the 210-mm inner diameter fluidised bed (bed sand size 250 – 595 μm) 107
Figure 3-18: Three-dimensional computational grid of the fluidised bed combustor model 107
Figure 3-19: Three-dimensional computational grid of the 210-mm inner diameter fluidised bed combustor

Figure 3-20: Three-dimensional computational grid of the 210-mm inner diameter fluidised bed combustor with inclined feeding port (Model FM-A)

Figure 3-21: Three-dimensional computational grid of the 210-mm inner diameter fluidised bed combustor with inclined, tangential feeding port (Model FM-B)

Figure 4-1: Experimental values of velocities range for the fluidising state of rice husk, rice husk char, rice husk ash and sand samples

Figure 4-2: Real-time temperature profiles during combustion of rice husk in the 210-mm inner diameter fluidised bed at 3.3 $U_{mf}$

Figure 4-3: Real-time temperature profiles during combustion of rice husk in the 210-mm inner diameter fluidised bed at 2.5 $U_{mf}$ and 1.5 $U_{mf}$

Figure 4-4: Residual carbon contents in fly ash samples from the combustion of rice husk in the 210-mm inner diameter fluidised bed at different fluidising velocities (sand size = 250 – 595 μm, static bed height = 0.5 $D_c$, primary air factor ≈ 1.0)

Figure 4-5: Estimated bubble size just before eruption at the bed surface and bubble rise velocity at different static bed heights in the 210-mm inner diameter fluidised bed combustor (sand size = 250 – 595 μm, fluidising velocity = 3 $U_{mf}$)

Figure 4-6: Real-time temperature profiles during the combustion of rice husk in the 210-mm inner diameter fluidised bed combustor with sand static bed height of 0.25 $D_c$ (sand size = 250 – 595 μm, fluidising velocity ≈ 3 $U_{mf}$, primary air factor ≈ 1.0)
Figure 4-7: Real-time temperature profiles during the combustion of rice husk in the 210-mm inner diameter fluidised bed combustor with sand static bed height of 0.5 Dc (sand size = 250 – 595 μm, fluidising velocity ≈ 3 Umf, primary air factor ≈ 1.0)

Figure 4-8: Real-time temperature profiles during the combustion of rice husk in the 210-mm inner diameter fluidised bed combustor with sand static bed heights of 0.625 Dc and 0.75 Dc (sand size = 250 – 595 μm, fluidising velocity ≈ 3 Umf, primary air factor ≈ 1.0)

Figure 4-9: Temperature profiles during the combustion of rice husk in the 210-mm inner diameter fluidised bed combustor at different static bed heights (sand size = 250 – 595 μm, fluidising velocity ≈ 3 Umf, primary air factor ≈ 1.0)

Figure 4-10: Effect of static bed height on the bed temperature and residual carbon content in fly ash during combustion of rice husk in the 210-mm inner diameter fluidised bed combustor (sand size = 250 – 595 μm, fluidising velocity ≈ 3 Umf, primary air factor ≈ 1.0)

Figure 4-11: Residual carbon contents in ash samples from the combustion of rice husk in the 80-mm inner diameter fluidised bed at different bed temperatures (sand size = 250 – 595 μm, fluidising velocity ≈ 4 Umf, primary air factor ≈ 1.0)

Figure 4-12: Exact locations of thermocouples and secondary burners at the 210-mm inner diameter fluidised bed combustor column

Figure 4-13: Statistical analysis on the bed temperatures (T1) during combustion of rice husk in the 210-mm inner diameter fluidised bed at different freeboard
temperatures (sand size = 250 – 595 μm, static bed height = 0.5 Dc, fluidising velocity = 4 – 5 Umf, primary air factor ≈ 1.0, oxygen level in cyclone ≥ 6 vol%)

Figure 4-14: Statistical analysis on the freeboard temperatures (T3 – T6) during combustion of rice husk in the 210-mm inner diameter fluidised bed – Lower freeboard temperature range (400 – 600°C) (sand size = 250 – 595 μm, static bed height = 0.5 Dc, fluidising velocity = 4 – 5 Umf, primary air factor ≈ 1.0, oxygen level in cyclone ≥ 6 vol%)

Figure 4-15: Statistical analysis on the freeboard temperatures (T3 – T6) during combustion of rice husk in the 210-mm inner diameter fluidised bed – Higher freeboard temperature range (600 – 700°C) (sand size = 250 – 595 μm, static bed height = 0.5 Dc, fluidising velocity = 4 – 5 Umf, primary air factor ≈ 1.0, oxygen level in cyclone ≥ 6 vol%)

Figure 4-16: Comparisons of residual carbon contents in ash samples from the combustion of rice husk in the 210-mm inner diameter fluidised bed at different freeboard temperatures (sand size = 250 – 595 μm, static bed height = 0.5 Dc, fluidising velocity = 4 – 5 Umf, primary air factor ≈ 1.0, oxygen level in cyclone ≥ 6 vol%)

Figure 4-17: Real-time temperature profiles during combustion of rice husk in the non-insulated 210-mm inner diameter fluidised bed combustor system (Case Study HL1) (sand size = 250 – 595 μm, static bed height = 0.5 Dc, fluidising velocity ≈ 3 Umf, primary air factor ≈ 1.5)

Figure 4-18: Real-time temperature profiles during combustion of rice husk in an insulated 210-mm inner diameter
fluidised bed combustor system (Case Study HL2)
(sand size = 250 – 595 μm, static bed height = 0.5
Dc, fluidising velocity ≈ 3 Umf, primary air factor ≈ 1.5)

Figure 4-19: Average combustor temperatures during
combustion of rice husk in the non-insulated and
insulated 210-mm inner diameter fluidised bed
combustors (sand size = 250 – 595 μm, static bed
height = 0.5 Dc, fluidising velocity ≈ 3 Umf, primary
air factor ≈ 1.5)

Figure 4-20: Fly ash samples from the combustion of rice husk
in the non-insulated and insulated 210-mm inner
diameter fluidised bed combustors (sand size = 250
– 595 μm, static bed height = 0.5 Dc, fluidising
velocity ≈ 3 Umf, primary air factor ≈ 1.5)

Figure 4-21: Real-time temperature profile during combustion of
raw rice husk in the 210-mm inner diameter
fluidised bed combustor (sand size = 250 – 595 μm,
static bed height = 0.5 Dc, fluidising velocity ≈ 3
Umf, primary air factor ≈ 1.2, oxygen level in
cyclone = 6 – 12 vol%)

Figure 4-22: Real-time temperature profile during combustion of
water-washed rice husk in the 210-mm inner
diameter fluidised bed combustor (sand size = 250
– 595 μm, static bed height = 0.5 Dc, fluidising
velocity ≈ 3 Umf, primary air factor ≈ 1.2, freeboard
temperatures (T4 – T6) = 700 – 900°C, oxygen
level in cyclone = 6 – 12 vol%)

Figure 4-23: Comparisons of average bed temperatures during
combustion of rice husk in the 210-mm inner
diameter fluidised bed at different primary air
factors (sand size = 250 – 595 μm, static bed height
= 0.5 Dc, fluidising velocity = 5 – 6 Umf)
Figure 4-24: Residual carbon contents of ash samples from the combustion of rice husk in the 210-mm inner diameter fluidised bed at different primary air factors (sand size = 250 – 595 μm, static bed height = 0.5 Dc, fluidising velocity = 5 – 6 Umf) 224

Figure 4-25: Average combustor temperatures during combustion of rice husk in the 210-mm inner diameter fluidised bed at different primary-to-secondary air ratios (sand size = 250 – 595 μm, static bed height = 0.5 Dc, fluidising velocity = 5.7 Umf, primary air factor = 0.65) 227

Figure 4-26: Temperature profiles during the combustion of rice husk in a non-insulated combustor (Armesto et al., 2002) 228

Figure 4-27: Temperature profile along the 210-mm inner diameter fluidised bed combustor during combustion of rice husk at different pneumatic air feeding velocities (sand size = 250 – 595 μm, static bed height = 0.5 Dc, fluidising velocity ≈ 3 Umf, primary air factor ≈ 1.5) 233

Figure 4-28: Average bed temperatures and residual carbon contents in ash samples from the combustion of rice husk in the 210-mm inner diameter fluidised bed at different pneumatic air feeding velocities (sand size = 250 – 595 μm, static bed height = 0.5 Dc, fluidising velocity ≈ 3 Umf, primary air factor ≈ 1.5) 238

Figure 4-29: Total air velocity at the freeboard region of the fluidised bed combustor at different pneumatic air feeding velocities 238

Figure 4-30: Comparisons of bed temperatures during combustion of water-washed rice husk at different moisture contents in the 210-mm inner diameter
fluidised bed combustor (sand size = 250 – 595 μm, static bed height = 0.5 Dc, fluidising velocity ≈ 3 \( U_{mf} \), primary air factor ≈ 1.2)

Figure 4-31: Comparisons of residual carbon contents of ash samples from the combustion of water-washed rice husk at different moisture contents in the 210-mm inner diameter fluidised bed combustor (sand size = 250 – 595 μm, static bed height = 0.5 Dc, fluidising velocity ≈ 3 \( U_{mf} \), primary air factor ≈ 1.2)

Figure 4-32: Real-time temperature profiles during combustion of rice husk in the 210-mm inner diameter fluidised bed combustor with inclined feeding port (Case Study FM1) (sand size = 250 – 595 μm, static bed height = 0.5 Dc, fluidising velocity ≈ 3 \( U_{mf} \), primary air factor ≈ 1.2)

Figure 4-33: Real-time temperature profiles during combustion of rice husk in the 210-mm inner diameter fluidised bed combustor with inclined, tangential feeding port (Case Study FM2) (sand size = 250 – 595 μm, static bed height = 0.5 Dc, fluidising velocity ≈ 3 \( U_{mf} \), primary air factor ≈ 1.2)

Figure 4-34: Average combustor temperatures during combustion of rice husk in the 210-mm inner diameter fluidised bed combustor utilising different feeding methods (sand size = 250 – 595 μm, static bed height = 0.5 Dc, fluidising velocity ≈ 3 \( U_{mf} \), primary air factor ≈ 1.2)

Figure 4-35: Histogram of particle size distribution for fly ash from the combustion of rice husk in the 210-mm inner diameter fluidised bed combustor with different feeding methods (sand size = 250 – 595 μm, static bed height = 0.5 Dc, fluidising velocity ≈ 3 \( U_{mf} \), primary air factor ≈ 1.2)
Figure 4-36: Histogram of particle size distribution for bottom ash from the combustion of rice husk in the 210-mm inner diameter fluidised bed combustor with different feeding methods (sand size = 250 – 595 μm, static bed height = 0.5 D_c, fluidising velocity ≈ 3 U_{mf}, primary air factor ≈ 1.2) 261

Figure 4-37: Average temperatures in the combustor during combustion of rice husk in the 210-mm inner diameter fluidised bed combustor with inclined, tangential feeding port at different fluidising velocities (sand size = 250 – 595 μm, static bed height = 0.5 D_c, primary air factor ≈ 1.2) 264

Figure 4-38: Comparisons of residual carbon contents in ash samples from the combustion of rice husk in the 210-mm inner diameter fluidised bed combustor with inclined tangential feeding port at different fluidising velocities (sand size = 250 – 595 μm, static bed height = 0.5 D_c, primary air factor ≈ 1.2) 269

Figure 4-39: Particle size distribution of fly ash samples from the combustion of rice husk in the 210-mm inner diameter fluidised bed combustor with inclined, tangential feeding at different fluidising velocities (sand size = 250 – 595 μm, static bed height = 0.5 D_c, primary air factor ≈ 1.2) 271

Figure 4-40: Particle size distribution of bottom ash samples from the combustion of rice husk in the 210-mm inner diameter fluidised bed combustor with inclined, tangential feeding at different fluidising velocities (sand size = 250 – 595 μm, static bed height = 0.5 D_c, primary air factor ≈ 1.2) 272

Figure 5-1: Trajectory of the 25 μm sand particle in the fluidised bed combustor model (Ø500mm × 5250mm) 278
Figure 5-2: Trajectory of the 50 μm sand particle in the fluidised bed combustor model (Ø500mm × 5250mm) 278
Figure 5-3: Trajectory of the 75 μm sand particle in the fluidised bed combustor model (Ø500mm × 5250mm) 279
Figure 5-4: Trajectory of the 100 μm sand particle in the fluidised bed combustor model (Ø500mm × 5250mm) 279
Figure 5-5: Trajectory of the 125 μm sand particle in the fluidised bed combustor model (Ø500mm × 5250mm) 280
Figure 5-6: Residence time of burning rice husk particles with different sizes in the fluidised bed model (Ø500mm × 5250mm) 283
Figure 5-7: Statistical analysis on the residence time distribution from computational fluid dynamics (CFD) modelling of burning rice husk particles in the 210-mm inner diameter fluidised bed combustor at different pneumatic air feeding velocities 285
Figure 5-8: Recirculating zone near the feeding port of the combustor in Model IV (pneumatic air feeding velocity = 1.36 m/s) 288
Figure 5-9: Absence of recirculating zones inside the fluidised bed combustor in Models I, II and III (pneumatic air feeding velocities of 0.42 – 0.85 m/s) 289
Figure 5-10: Char fraction of a burning rice husk particle in Model III (pneumatic air feeding velocity = 0.85 m/s) 291
Figure 5-11: Char fraction of a burning rice husk particle in Model IV (pneumatic air feeding velocity = 1.36 m/s) 291
Figure 5-12: Gas flow profile as indicated by trajectory of tracer particle in the 210-mm inner diameter fluidised bed with inclined feeding port (Model FM-A) 292

Figure 5-13: Gas flow profile inside in fluidised bed combustor with inclined feeding port (Model FM-A) 293

Figure 5-14: Gas flow profile as indicated by trajectory of tracer particle in the 210-mm inner diameter fluidised bed with inclined, tangential feeding port (Model FM-B) 293

Figure 5-15: Comparisons of residence time of fly ash of different sizes in Model FM-A (inclined feeding) and Model FM-B (inclined, tangential feeding) 302
LIST OF PLATES

<table>
<thead>
<tr>
<th>PLATE</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plate 3-1:</td>
<td>The 80-mm inner diameter fluidised bed combustor system</td>
<td>82</td>
</tr>
<tr>
<td>Plate 3-2:</td>
<td>The 210-mm inner diameter fluidised bed combustor system (shown without insulation material)</td>
<td>88</td>
</tr>
<tr>
<td>Plate 4-1:</td>
<td>Ash product from burning raw rice husk inside the muffle furnace (650 – 750°C) after 10 minutes of combustion time</td>
<td>115</td>
</tr>
<tr>
<td>Plate 4-2:</td>
<td>Higher flaming times for a group of rice husk particles spread widely apart in the muffle furnace (650 – 750°C)</td>
<td>116</td>
</tr>
<tr>
<td>Plate 4-3:</td>
<td>Formation of dead zone at nearly two-third of the sand bed (595 – 841 μm) at fluidising velocity of 3 ( U_{mf} )</td>
<td>141</td>
</tr>
<tr>
<td>Plate 4-4:</td>
<td>Burning of rice husk was restricted to the top of the sand bed (595 – 841 μm) at fluidising velocity of 3 ( U_{mf} )</td>
<td>141</td>
</tr>
<tr>
<td>Plate 4-5:</td>
<td>Rapid accumulation of char and ash in the sand bed (595 – 841 μm) at fluidising velocity of 3 ( U_{mf} )</td>
<td>142</td>
</tr>
<tr>
<td>Plate 4-6:</td>
<td>Suspension burning of rice husk at fluidising velocity of 4 ( U_{mf} ) (sand size 595 – 841 μm)</td>
<td>143</td>
</tr>
<tr>
<td>Plate 4-7:</td>
<td>Suspension burning of rice husk at fluidising velocity of 5 ( U_{mf} ) (sand size 595 – 841 μm)</td>
<td>143</td>
</tr>
</tbody>
</table>
Plate 4-8: Good mixing during the combustion of rice husk (sand size 250 – 595 μm) at fluidising velocity of $3 U_{mf}$

Plate 4-9: Penetration of rice husk, char and ash into the sand bed during combustion (sand size 250 – 595 μm) at fluidising velocity of $3 U_{mf}$

Plate 4-10: Some degree of suspension burning during the combustion of rice husk (sand size 250 – 595 μm) at fluidising velocity of $4 U_{mf}$

Plate 4-11: Vigorous bed bubbling with good mixing of char and rice husk in the sand bed during the combustion of rice husk (sand size 250 – 595 μm) at fluidising velocity of $5 U_{mf}$

Plate 4-12: Residual bottom ash retained in the bed after the combustion of rice husk (sand size 250 – 595 μm) at fluidising velocity of $5 U_{mf}$

Plate 4-13: The inclined feeding port at the 210-mm inner diameter fluidised bed combustor

Plate 4-14: The inclined, tangential feeding port at the 210-mm inner diameter fluidised bed combustor
**LIST OF SYMBOLS**

\[ A \] - Area, (m²)

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

\[ C_{1e}, C_{2e} \] - Empirical constants, (\( C_{1e} = 1.42 \), \( C_{2e} = 1.68 \))

\[ C_d, C_g \] - 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 \( \left( = \frac{1}{\sum_{j=1}^{\infty} (\infty / d_{pi})} \right) \), (m)

\[ f \] - Mixture fraction, (dimensionless)

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

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

\[ f_c \] - Fractional conversion \( \left( = \frac{m}{m_{\text{initial}} - m_{\text{final}}} \right) \), (dimensionless)
\( F_D \) - Drag force, (N)
\( g \) - Gravitational acceleration, (= 9.81 m/s^2)
\( G_{\kappa} \) - Generation of turbulent kinetic energy, (m^2/s^2)
\( h_c \) - Natural or forced convection coefficient, [W/(m^2 \cdot K)]
\( h_r \) - Radiation heat transfer coefficient, [W/(m^2 \cdot K)]
\( H^* \) - Instantaneous enthalpy, (kJ/kg)
\( \Delta H_c \) - Heat of combustion of the fuel at reference temperature of 25°C, (J)
\( \hat{H}_i \) - Specific enthalpy of the \( i^{th} \) component at 25°C, [J/(kg \cdot K)]
\( H_s \) - Heat of vaporization of water, (J/mol)
\( k \) - Thermal conductivity, [W/(m \cdot 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)
\( \dot{m} \) - Instantaneous mass, (kg)
\( m_i \) - Local mass fraction, (dimensionless)
\( n \) - Number of mole, (kg-mol)
\( n_i \) - Mole of the \( i^{th} \) 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 \( \frac{\rho_f U d_p}{\mu_f} \), (dimensionless)

$S_m$ - Transfer of mass from reacting particles into gas phase, [kg/(m$^3 \cdot$ s)]

$T$ - Temperature, (K)

$T_{ad}$ - Adiabatic flame temperature, (K)

$t_{cross}$ - Particle eddy crossing time, (s)

$T_L$ - Fluid Lagrangian integral time \( T_L \approx 0.15 \frac{\kappa}{\varepsilon} \), (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

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_\varepsilon$</td>
<td>Inverse effective Prandtl number for turbulent dissipation rate, (dimensionless)</td>
</tr>
<tr>
<td>$\alpha_\kappa$</td>
<td>Inverse effective Prandtl number for turbulent kinetic energy, (dimensionless)</td>
</tr>
<tr>
<td>$\alpha_s$</td>
<td>Swirl constant, (dimensionless)</td>
</tr>
<tr>
<td>$\delta$</td>
<td>Empirical constant, (dimensionless)</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Turbulent dissipation rate, (m$^2$/s$^3$)</td>
</tr>
<tr>
<td>$\xi$</td>
<td>Emissivity of the combustor surface, (dimensionless)</td>
</tr>
<tr>
<td>$\phi_i$</td>
<td>Instantaneous species concentration, density or temperature, (kmol/m$^3$, kg/m$^3$ or K)</td>
</tr>
<tr>
<td>$\phi_s$</td>
<td>Particle sphericity, (dimensionless)</td>
</tr>
<tr>
<td>$\varnothing$</td>
<td>Inner diameter of fluidised bed column, (m)</td>
</tr>
<tr>
<td>$\varsigma$</td>
<td>Normally distributed random number, (dimensionless)</td>
</tr>
<tr>
<td>$\Omega$</td>
<td>Swirl angular velocity, (rad/s)</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density, (kg/m$^3$)</td>
</tr>
<tr>
<td>$\sigma_i$</td>
<td>Constant in PDF equations (= 0.7), (dimensionless)</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Particle relaxation time (s)</td>
</tr>
<tr>
<td>$\tau_\varepsilon$</td>
<td>Characteristic lifetime of the eddy, (s)</td>
</tr>
<tr>
<td>$\tau_i$</td>
<td>Fraction of time that $f$ spends in the $\Delta f$ band, (s)</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Bragg angle in x-ray diffraction analysis, (°)</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>Turbulent kinetic energy, (m$^2$/s$^2$)</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Dynamic fluid viscosity, (kg/m-s)</td>
</tr>
</tbody>
</table>

Subscripts

<table>
<thead>
<tr>
<th>Subscript</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>Air</td>
</tr>
<tr>
<td>$feed$</td>
<td>Feed</td>
</tr>
<tr>
<td>$final$</td>
<td>Final</td>
</tr>
<tr>
<td>$fuel$</td>
<td>Fuel</td>
</tr>
<tr>
<td>$i$</td>
<td>i-direction or chemical species $i$</td>
</tr>
</tbody>
</table>
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 Heating Value
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
NOx - 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
# LIST OF APPENDICES

<table>
<thead>
<tr>
<th>APPENDIX</th>
<th>TITLE</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appendix A:</td>
<td>Estimation of Bubble Eruption Velocity</td>
<td>339</td>
</tr>
<tr>
<td>Appendix B:</td>
<td>Determination of Particle Sphericity ($\phi_s$)</td>
<td>340</td>
</tr>
<tr>
<td>Appendix C:</td>
<td>Properties of Rice Husk for its Definition as the Burning Fuel Particle in CFD Modelling (Input Data to Preprocessor PrePDF)</td>
<td>342</td>
</tr>
<tr>
<td>Appendix D:</td>
<td>Chart for Determining Sphericity ($\phi_s$) of Particles and Theoretical Equations for Estimating Minimum Fluidising Velocity ($U_{mf}$) and Terminal Velocity ($U_t$)</td>
<td>343</td>
</tr>
<tr>
<td>Appendix E:</td>
<td>Real-Time Temperature Profiles during Combustion of Rice Husk in the 210-mm Inner Diameter Fluidised Bed at Different Freeboard Temperatures</td>
<td>345</td>
</tr>
<tr>
<td>Appendix F:</td>
<td>Real-Time Temperature Profiles during Combustion of Raw and Water-Washed Rice Husk in the 210-mm Inner Diameter Fluidised Bed</td>
<td>347</td>
</tr>
<tr>
<td>Appendix G:</td>
<td>Mass Balance to Determine the Amount of Stoichiometric Air for Combustion of Rice Husk</td>
<td>348</td>
</tr>
<tr>
<td>Appendix H:</td>
<td>Real-Time Temperature Profiles during Combustion of Rice Husk at Different Pneumatic Air Feeding Velocities</td>
<td>349</td>
</tr>
<tr>
<td>Appendix I:</td>
<td>List of Publications</td>
<td>350</td>
</tr>
</tbody>
</table>
CHAPTER 1

INTRODUCTION

1.1 Introduction

The purpose of this research was to produce amorphous silica from 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, SiO₂) (Kaupp, 1984; Kapur, 1985; James and Rao, 1986) compared to other biomass materials, such as ash from sugarcane bagasse (57 – 73% SiO₂) (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 (SiO₂) 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°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 m²/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°C 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°C. 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 (CH₄), 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 CH₄ is some 25 times more potent as a greenhouse gas than carbon dioxide (CO₂), and since the two gases have similar atmospheric residence times, trading off CH₄ emissions for CO₂ 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 CH₄ and CO₂ 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 × 10⁹ 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.
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°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

<table>
<thead>
<tr>
<th>No.</th>
<th>Source/Reference</th>
<th>Price (per tonne)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>RM</td>
<td>USD</td>
</tr>
<tr>
<td>1</td>
<td>Torftech Application Description (August 2002)</td>
<td>1,140</td>
<td>300</td>
</tr>
<tr>
<td>2</td>
<td>The Hindu Newspaper (19th January 2003)</td>
<td>1,900 – 2,280</td>
<td>500 – 600</td>
</tr>
</tbody>
</table>

b) Fine Chemicals Industry

The emerging use of amorphous RHA is for the manufacture of water glass (sodium silicate or Na₂SiO₃), 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°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