Study on Adsorption Characteristics of Ethanol onto Activated Carbons: Effect of Surface Treatment

Uddin, MD Kutub

https://doi.org/10.15017/1470620
Study on Adsorption Characteristics of Ethanol onto Activated Carbons
- Effect of Surface Treatment -

MD Kutub Uddin

Kyushu University, Japan
Department of Energy and Environmental Engineering
Interdisciplinary Graduate School of Engineering Sciences

June 2014
Study on Adsorption Characteristics of Ethanol onto Activated Carbons
- Effect of Surface Treatment -

MD Kutub Uddin

A Thesis Submitted
For the Degree of Doctor of Philosophy

Department of Energy and Environmental Engineering
Kyushu University, Japan
June 2014
Acknowledgement

I would like to express my deepest sense of gratitude and indebtedness to my supervisors, Professor Shigeru Koyama, Professor Bidyut Baran Saha and Associate Professor Takahiko Miyazaki for their invaluable guidance and inspiration throughout my entire research work and most importantly their understanding and patience during the difficult period of this research work.

I am also indebted to Dr. Ibrahim I. El-Sharkawy for his valuable assistance and providing me the opportunity to discuss technical results of this work any time.

For this dissertation I would like to thank Professor Shigeru Koyama, Professor Bidyut Baran Saha, Professor Yasuyuki Takata and Associate Professor Takahiko Miyazaki in taking time to examine the manuscript in spite of their busy academic schedule.

I also wish to express thanks to all of my present and former lab mates, in particular Dr. Naoya Makimoto, Mr. Yutaro Terao and Mr. Hayato Imamura for their help and cooperation. I want to express my heartiest gratitude and thanks to all of the laboratory members for their warm relationship and kind cooperation.

I wish to express my sincere appreciation of the funding provided by the Japanese Government and the study leave approved by Jagannath University, Bangladesh. I consider myself fortunate to have enjoyed the opportunity of working in this laboratory.

Last but not least, I wish to thank my beloved wife, Ms. Kaniz Mantasa, my son, Mstr. Kashif Rayan, for the understanding, quiet patience and encouragement during my study. I also wish to thank my parents for their faith in me.

MD Kutub Uddin
Kyushu University
June 2014
Contents

Summary ........................................................................................................................................ iv

List of Figures ........................................................................................................................... vi

List of Tables ............................................................................................................................ x

Chapter 1. Introduction ............................................................................................................... 1

  1.1 Principle of Adsorption ...................................................................................................... 1
    1.1.1 Adsorption Equilibrium .......................................................................................... 3
    1.1.2 Adsorption Kinetics ............................................................................................... 5
  1.2 Adsorption Cooling System .............................................................................................. 7
  1.3 Selection of Adsorbent and Refrigerant pair ..................................................................... 8
    1.3.1 Choice of Adsorbent ............................................................................................... 9
    1.3.2 Choice of Refrigerant .............................................................................................. 10
  1.4 Review of Adsorbent/Refrigerant Pairs and Adsorption Cooling and
      Heat Pump Systems ........................................................................................................... 13
    1.4.1 Review of Adsorbent/Refrigerant Pairs .................................................................. 13
      1.4.1.1 Silica gel/Water Pair ....................................................................................... 14
      1.4.1.2 Zeolite/Water Pair ......................................................................................... 15
      1.4.1.3 Activated Carbon/Ammonia Pair .................................................................. 16
      1.4.1.4 Activated Carbon/Methanol Pair ................................................................ 17
      1.4.1.5 Activated Carbon/Ethanol Pair .................................................................... 17
    1.4.2 Review on the Development of Adsorption Cooling and Heat Pump
      Systems ............................................................................................................................... 18
      1.4.2.1 Basic Adsorption Refrigeration Cycle ........................................................... 18
      1.4.2.2 Advanced Adsorption Refrigeration Cycle ..................................................... 20
      1.4.2.3 Hybrid Adsorption Cooling System ............................................................... 27
  1.5 Objective and Scopes of the Present Thesis ...................................................................... 28
  1.6 Thesis Outline .................................................................................................................. 29
  1.7 References ......................................................................................................................... 31

2.1 Introduction ............................................................................................................... 38
2.2 Experimental Apparatus and Method ................................................................. 40
   2.2.1 Adsorbent Materials ......................................................................................... 40
   2.2.2 Refrigerants ........................................................................................................ 43
   2.2.3 Instrumentation .................................................................................................. 44
   2.2.4 Procedure ............................................................................................................ 46
   2.2.5 Uncertainty Analysis ......................................................................................... 47
2.3 Adsorption Isotherm Correlation ........................................................................... 47
2.4 Results and Discussion ......................................................................................... 48
2.5 Nomenclature .......................................................................................................... 61
2.6 Conclusion ............................................................................................................... 61
2.7 References ............................................................................................................... 62

Chapter 3. Adsorption Kinetics of Ethanol onto Parent and Surface Treated
Activated Carbon Powders ............................................................................................ 65
3.1 Introduction ............................................................................................................... 65
3.2 Experimental ............................................................................................................ 67
   3.2.1 Materials ............................................................................................................... 67
   3.2.2 Particle Size Distribution .................................................................................... 68
   3.2.3 Kinetics Data Collection ..................................................................................... 71
   3.2.4 Uncertainty Analysis .......................................................................................... 71
3.3 Mathematical Modeling .......................................................................................... 72
3.4 Data Analysis ........................................................................................................... 73
3.5 Nomenclature .......................................................................................................... 86
3.6 Conclusion ............................................................................................................... 87
3.7 Reference ................................................................................................................. 87

Chapter 4. Isosteric heat of Adsorption Extracted from Adsorption
Equilibrium Data .......................................................................................................... 90
4.1 Introduction ............................................................................................................... 90
4.2 Clausious Clapeyron Equation ............................................................................... 91
4.3 Proposed Correlation .............................................................................................. 92
4.4 Results and Discussion ......................................................................................... 94
4.5 Nomenclature .......................................................................................................... 102
4.6 Conclusion ............................................................................................................... 102
4.7 Reference ................................................................................................................. 103
Chapter 5. Specific Heat Capacity of Adsorbents ................................................. 105
  5.1 Introduction ................................................................................................. 105
  5.2 Experimental .............................................................................................. 107
    5.2.1 Materials ............................................................................................ 107
    5.2.2 Experimental Apparatus ................................................................. 109
    5.2.3 Experimental Procedure ................................................................. 110
  5.3 Theoretical Derivation of DSC Measurement ........................................... 111
  5.4 Data Reduction .......................................................................................... 116
  5.5 Results and Discussion ............................................................................. 118
  5.6 Nomenclature ............................................................................................ 125
  5.7 Conclusion .................................................................................................. 126
  5.8 References .................................................................................................. 126

Chapter 6. Thermodynamic Analysis of Adsorption Cooling Cycle ..................... 129
  6.1 Introduction .................................................................................................. 129
  6.2 Equilibrium Model .................................................................................... 131
    6.2.1 Analytical Expression ....................................................................... 131
    6.2.2 Thermodynamic Cycle ..................................................................... 134
    6.2.3 Effect of Operating Temperatures ................................................... 139
  6.3 Nomenclature ............................................................................................. 146
  6.4 Conclusion .................................................................................................. 147
  6.5 References .................................................................................................. 148

Chapter 7. General Conclusions .......................................................................... 152
  7.1 Future Work ................................................................................................ 154

Appendices ......................................................................................................... 155
  Appendix A2: Buoyancy Correction ................................................................. 157
  Appendix B: Isotherm of Maxsorb III/R32 and ACF/R32 Pairs ....................... 160
  Appendix C: Fraunhofer diffraction Theory and Mie Scattering Theory ......... 161
  Appendix D: A Case Study for Adsorption-Compression Hybrid System ........ 165
Summary

Adsorption refrigeration and heat pump systems powered by waste heat sources utilizing environment friendly adsorbent and refrigerant pairs received great attention in the past few decades. The main feature of these systems are; the ability to operate by low temperature heat source typically below 100ºC that would be abundantly available from industrial waste heat or solar energy, almost no electricity usage, no movable parts and simple in operation.

Among the adsorbents studied so far, highly porous activated carbon powders have been proven to be efficient adsorbents for adsorption cooling and heat pump application. Due to higher surface area and pore volume, it exhibits higher uptake and faster kinetics compared to granular type of activated carbon when operates with environmental friendly alcohols such as ethanol. Ethanol is a non-toxic substance and it has relatively higher vapor pressure even at a low temperature levels. Despite the perceived suitability of activated carbon powder/ethanol pairs, there is a dearth of adsorption characteristics (e.g. adsorption isotherms, kinetics, isosteric heat), specific heat capacity and design data for cooling/heat pump systems hitherto in the literature.

From the above perspective, the objectives of this thesis is to gather the adsorption characteristics and design data for parent and surface treated activated carbon/ethanol pairs considering the suitable working conditions for adsorption cooling and heat pump system.

The adsorption kinetics of ethanol onto the adsorbents, namely parent Maxsorb III, H₂ treated Maxsorb III and KOH-H₂ treated Maxsorb III is studied by using a magnetic suspension adsorption measurement unit (MSB-VG-S2). Experiments have been conducted across assorted adsorption temperatures that are useful for the operation of adsorption chiller.

The Fickian diffusion model is used to estimate the adsorption kinetics of the studied
adsorbent/refrigerant pairs considering the spherical shape of adsorbent particle. The proposed technique to evaluate the diffusion time constant avoids the uncertainties in adsorption uptake measurement in the early adsorption stage. Moreover, this technique helps to overcome the effects of heat generation at early stage of adsorption. Using the equilibrium adsorption data, a non-dimensional empirical correlation of the isosteric heat of adsorption has been proposed which is found to be a function of concentration and adsorbent temperature.

The specific heat capacity of parent and surface treated Maxsorb III along with commonly used adsorbent has been measured using a differential scanning calorimeter (DSC) for the temperature range suitable in adsorption chiller operation.

A theoretical analysis of an equilibrium adsorption cooling cycle comprising the assorted adsorbent/refrigerant pairs is presented using a time-independent model. The comparisons of specific cooling capacities under various regeneration and evaporation temperatures are presented. The proposed adsorbent/refrigerant pairs are capable to deliver cooling load below 0°C.

In this work, among the studied pairs, H₂-treated Maxsorb III/ethanol pair possesses the highest adsorption equilibrium uptake. However, the diffusion time constant of KOH-H₂-treated Maxsorb III is found to be significantly higher than that of other two studied pairs.

A brief performance analysis of an adsorption-compression hybrid system has also been presented. Parent Maxsorb III/ethanol is taken as a working pair in the adsorption cycle of the hybrid system. The proposed hybrid system can contribute up to 30% energy saving as compared to mechanical compression system.
# List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fig. 1.1</td>
<td>Adsorbate in porous material during adsorption</td>
<td>2</td>
</tr>
<tr>
<td>Fig. 1.2</td>
<td>Potential energy involve during adsorption</td>
<td>2</td>
</tr>
<tr>
<td>Fig. 1.3</td>
<td>Adsorbed phase and gas phase of adsorbate</td>
<td>4</td>
</tr>
<tr>
<td>Fig. 1.4</td>
<td>The IUPAC classification of adsorption isotherm for solid/gas equilibrium (1985, 1994)</td>
<td>5</td>
</tr>
<tr>
<td>Fig. 1.5</td>
<td>Schematic diagram of adsorption cooling system</td>
<td>8</td>
</tr>
<tr>
<td>Fig. 1.6</td>
<td>Basic adsorption refrigeration cycle using conceptual Dühring diagram</td>
<td>19</td>
</tr>
<tr>
<td>Fig. 1.7</td>
<td>Schematic diagram of three-bed silica gel adsorption chillers (Saha et al. 2006)</td>
<td>21</td>
</tr>
<tr>
<td>Fig. 1.8</td>
<td>Photograph of the three-bed experimental device (Uyun et al. 2009)</td>
<td>21</td>
</tr>
<tr>
<td>Fig. 1.9</td>
<td>Schematic diagram of the multi-bed adsorption chiller (Saha et al. 2003)...</td>
<td>23</td>
</tr>
<tr>
<td>Fig. 1.10</td>
<td>The schematic of the dual evaporator type three bed adsorption chiller (Miyazaki et al. 2010)</td>
<td>23</td>
</tr>
<tr>
<td>Fig. 1.11</td>
<td>Schematic of a re-heat two-stage adsorption chiller (Saha et al. 2001, Khan et al. 2007)</td>
<td>25</td>
</tr>
<tr>
<td>Fig. 1.12</td>
<td>Conceptual Dühring diagram for both the conventional and two stage cycle (Saha et al. 2001)</td>
<td>25</td>
</tr>
<tr>
<td>Fig. 1.13</td>
<td>Schematic of three-stage chiller without mass recovery scheme (Saha et al. 1995b, Khan et al. 2008)</td>
<td>26</td>
</tr>
<tr>
<td>Fig. 1.14</td>
<td>Conceptual Dühring diagram of the advanced adsorption chiller in dual-mode operations (Saha et al. 2003)</td>
<td>26</td>
</tr>
<tr>
<td>Fig. 1.15</td>
<td>Three adsorber cascading cycle (arrows represent heat flows) (Douss and Meunier, 1989)</td>
<td>28</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fig. 2.1</td>
<td>SEM pictures of the studied adsorbents (a) Parent Maxsorb III, (b) H₂ treated Maxsorb III and (c) KOH-H₂ treated Maxsorb III</td>
<td>42</td>
</tr>
<tr>
<td>Fig. 2.2(a)</td>
<td>Pictorial view of experimental apparatus</td>
<td>44</td>
</tr>
<tr>
<td>Fig. 2.2(b)</td>
<td>Schematic diagram of experimental apparatus</td>
<td>45</td>
</tr>
<tr>
<td>Fig. 2.3(a)</td>
<td>Linear fitting of D-A equation for parent Maxsorb III/ethanol pair</td>
<td>50</td>
</tr>
<tr>
<td>Fig. 2.3(b)</td>
<td>Linear fitting of D-A equation for KOH-H₂ treated Maxsorb III/ethanol pair</td>
<td>51</td>
</tr>
<tr>
<td>Fig. 2.3(c)</td>
<td>Linear fitting of D-R equation for H₂ treated Maxsorb III/ethanol pair</td>
<td>51</td>
</tr>
<tr>
<td>Fig. 2.4(a)</td>
<td>Adsorption equilibrium of parent Maxsorb III/ethanol pair</td>
<td>52</td>
</tr>
<tr>
<td>Fig. 2.4(b)</td>
<td>Adsorption equilibrium of KOH-H₂ treated Maxsorb III/ethanol pair</td>
<td>52</td>
</tr>
<tr>
<td>Fig. 2.4(c)</td>
<td>Adsorption equilibrium of H₂-treated Maxsorb III/ethanol pair</td>
<td>53</td>
</tr>
</tbody>
</table>
List of Figures (Contd..)

Fig. 2.5(a) Plot of fractional uptake versus adsorption potential for parent Maxsorb III/ethanol pair ................................................................. 54
Fig. 2.5(b) Plot of fractional uptake versus adsorption potential for KOH-H₂ treated Maxsorb III/ethanol pair ................................................................. 54
Fig. 2.5(c) Plot of fractional uptake versus adsorption potential for H₂ treated Maxsorb III/ethanol pair ................................................................. 55
Fig. 2.6(a) Plot of the adsorption potential versus relative pressure for parent Maxsorb III/ethanol pair ................................................................. 56
Fig. 2.6(b) Plot of the adsorption potential versus relative pressure for KOH-H₂ treated Maxsorb III/ethanol pair ................................................................. 56
Fig. 2.6(c) Plot of the adsorption potential versus relative pressure for H₂ treated Maxsorb III/ethanol pair ................................................................. 57
Fig. 2.7(a) Linear fitting of D-A equation for parent Maxsorb III/ethanol (95%) pair... 58
Fig. 2.8(a) Adsorption isotherms of parent Maxsorb III/ethanol (95%) pair ............ 59
Fig. 2.8(b) Adsorption isotherms of KOH-H₂ treated Maxsorb III/ethanol (95%) pair.. 59
Fig. 2.8(c) Adsorption isotherms of H₂ treated Maxsorb III/ethanol (95%) pair ...... 60

Fig. 3.1(a) A pictorial view of laser diffraction particle size analyzer .................. 69
Fig. 3.1(b) Particle size distribution for a sample of parent Maxsorb III ............... 69
Fig. 3.1(c) Particle size distribution for a sample of KOH-H₂ treated Maxsorb III .... 70
Fig. 3.1(d) Particle size distribution for a sample of H₂ treated Maxsorb III ........... 70
Fig. 3.2(a) Temporal histories of adsorption uptake and pressure of Maxsorb III/ethanol pair at adsorption temperature 30°C ........................................ 74
Fig. 3.2(b) Temporal histories of adsorption uptake and pressure of Maxsorb III/ethanol pair at adsorption temperature 70 °C ................................. 74
Fig. 3.3 Temporal histories of adsorption uptake and pressure of KOH-H₂-treated Maxsorb III/ethanol pair at adsorption temperature 30°C ................... 75
Fig. 3.4 Temporal histories of adsorption uptake and pressure of H₂-treated Maxsorb III/ethanol pair at adsorption temperature 30°C ......................... 75
Fig. 3.5(a) Plot of ln(1-F) versus adsorption time for Maxsorb III/ethanol pair at 30°C adsorption temperature and evaporator pressure of 3.34 kPa .......... 78
Fig. 3.5(b) Plot of ln(1-F) versus adsorption time for Maxsorb III/ethanol pair at 70°C adsorption temperature and evaporator pressure of 11.26 kPa .... 78
Fig. 3.6 Plot of ln(1-F) versus adsorption time for KOH-H₂-treated Maxsorb III/ethanol pair at 30°C adsorption temperature and evaporator pressure of 2.27 kPa ................................................. 79
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fig. 3.7</td>
<td>Plot of $ln(1-F)$ versus adsorption time for $H_2$-treated Maxsorb III/ethanol pair at 30°C adsorption temperature and evaporator pressure of 3.36 kPa…</td>
</tr>
<tr>
<td>Fig. 3.8(a)</td>
<td>Fractional uptake versus time for Maxsorb III/ethanol pair at adsorption temperature 30°C, 50°C and 70°C (symbols present experiments and lines present FD model)…</td>
</tr>
<tr>
<td>Fig. 3.8(b)</td>
<td>Fractional uptake versus time for KOH-$H_2$ treated Maxsorb III/ethanol pair at adsorption temperature 30°C, 50°C and 70°C (symbols present experiments and lines present FD model)…</td>
</tr>
<tr>
<td>Fig. 3.8(c)</td>
<td>Fractional uptake versus time for $H_2$-treated Maxsorb III/ethanol pair at adsorption temperature 30°C, 50°C and 70°C (symbols present experiments and lines present FD model)…</td>
</tr>
<tr>
<td>Fig. 3.9</td>
<td>Plot of diffusion time constant versus equilibrium pressure for assorted pairs at 50 °C (error bars present 5%)…</td>
</tr>
<tr>
<td>Fig. 3.10</td>
<td>Arrhenius plot of the assorted pairs…</td>
</tr>
<tr>
<td>Fig. 3.11</td>
<td>Uptake for different diffusion time constant…</td>
</tr>
<tr>
<td>Fig. 3.12</td>
<td>Variation of the SCE with diffusion time constant…</td>
</tr>
<tr>
<td>Fig. 4.1(a)</td>
<td>Plot of $ln(P)$ vs $1/T$ at different uptake range for Maxsorb III/ethanol pair…</td>
</tr>
<tr>
<td>Fig. 4.1(b)</td>
<td>Plot of $ln(P)$ vs $1/T$ at different uptake range for KOH-$H_2$ treated Maxsorb III/ethanol pair…</td>
</tr>
<tr>
<td>Fig. 4.1(c)</td>
<td>Plot of $ln(P)$ vs $1/T$ at different uptake range for $H_2$ treated Maxsorb III/ethanol pair…</td>
</tr>
<tr>
<td>Fig. 4.2(a)</td>
<td>Isosteric heat of adsorption of ethanol onto Maxsorb III/ethanol pair…</td>
</tr>
<tr>
<td>Fig. 4.2(b)</td>
<td>Isosteric heat of adsorption of ethanol onto KOH-$H_2$ treated Maxsorb III/ethanol pair…</td>
</tr>
<tr>
<td>Fig. 4.2(c)</td>
<td>Isosteric heat of adsorption of ethanol onto $H_2$ treated Maxsorb III/ethanol pair…</td>
</tr>
<tr>
<td>Fig. 4.3(a)</td>
<td>Plot of $ln(P)$ vs $1/T$ at different uptake range for KOH-$H_2$ treated Maxsorb III/ethanol (95%) pair…</td>
</tr>
<tr>
<td>Fig. 4.3(b)</td>
<td>Plot of $ln(P)$ vs $1/T$ at different uptake range for $H_2$ treated Maxsorb III/ethanol (95%) pair…</td>
</tr>
<tr>
<td>Fig. 4.4(a)</td>
<td>Isosteric heat of adsorption of ethanol onto Maxsorb III/ethanol (95%) pair…</td>
</tr>
<tr>
<td>Fig. 4.4(b)</td>
<td>Isosteric heat of adsorption of ethanol onto KOH-$H_2$ treated Maxsorb III/ethanol (95%) pair…</td>
</tr>
<tr>
<td>Fig. 4.5</td>
<td>Percentage of deviation of isosteric heat from its average value for Maxsorb III/ethanol pair…</td>
</tr>
</tbody>
</table>
List of Figures (Contd..)

| Fig. 5.1 | Photograph of the DSC experiment | 109 |
| Fig.5.2 | Schematic diagram of the DSC experimental set up | 110 |
| Fig. 5.3 | Electrical network analogous to DSC heat flow | 112 |
| Fig. 5.4 | Illustration of heat capacity calculation by DSC | 117 |
| Fig. 5.5 | Results of DSC measurements for the reference material (sapphire) | 118 |
| Fig. 5.6(a) | Comparison of heat flow of parent Maxsorb III, H₂ treated Maxsorb III and KOH-H₂ treated Maxsorb III | 120 |
| Fig. 5.6(b) | Comparison of specific heat capacity of parent Maxsorb III, H₂ treated Maxsorb III and KOH-H₂ treated Maxsorb III | 120 |
| Fig. 5.7 | Comparison of specific heat capacity of new types of Maxsorb III | 121 |
| Fig. 5.8(a) | Comparison of heat flow of silica gel based adsorbents | 121 |
| Fig. 5.8(b) | Comparison of specific heat capacity of silica gel based adsorbents | 122 |
| Fig. 5.9 | Comparison of specific heat capacity of MOF-101 and Kupfer-BTC | 122 |
| Fig. 5.10 | Comparison of specific heat capacity of expanded graphite materials | 123 |
| Fig. 6.1(a) | Adsorption isotherms of Maxsorb III/ethanol as predicted by equilibrium isotherm equation | 132 |
| Fig. 6.1(b) | Adsorption isotherms of H₂ treated Maxsorb III/ethanol as predicted by equilibrium isotherm equation | 133 |
| Fig. 6.1(c) | Adsorption isotherms of KOH-H₂ treated Maxsorb III/ethanol pair as predicted by equilibrium isotherm equation | 133 |
| Fig. 6.2 | Schematic diagram of ideal adsorption cooling system | 135 |
| Fig.6.3 (a) | P-T-W diagram of Maxsorb III/ethanol | 136 |
| Fig.6.3(b) | P-T-W diagram of H₂ treated Maxsorb III/ethanol | 136 |
| Fig.6.3(c): | P-T-W diagram of KOH-H₂ treated Maxsorb III/ethanol pairs | 137 |
| Fig.6.4(a) | Effect of desorption temperature on specific cooling effect (SCE) at evaporation temperature -5 °C | 140 |
| Fig. 6.4(b) | Effect of desorption temperature on specific cooling effect (SCE) at evaporation temperature 10 °C | 141 |
| Fig. 6.5 | Effect of desorption temperature on Coefficient of performance (COP) | 141 |
| Fig.6.6 | Variation of COP with specific heat capacity | 142 |
| Fig.6.7 | Uptake for different diffusion time constant following FD equation | 145 |
| Fig.6.8 | Variation of the SCE with diffusion time constant using different ΔW | 146 |
List of Tables

Table 1.1  Summary physical, safety and environmental data for some refrigerants (sorted by ASHRAE Standard 34 designation) (Calm and Hourahan, 2001)........................................................................................................ 9
Table 1.2  Basic types of adsorbents (Dabrowski, 2001)........................................ 11

Table 2.1  Thermophysical properties of parent and surface treated Maxsorb III (Kil et al. 2013)........................................................................................................ 41
Table 2.2  Elemental composition of parent, KOH-H₂ and H₂ treated Maxsorb III (Kil et al. 2013)........................................................................................................ 42
Table 2.3  Composition of ethanol (95%)................................................................... 43
Table 2.4  Isotherm parameters of assorted adsorbent/refrigerant pairs................. 50
Table 2.5  Adsorption parameters of assorted adsorbent/refrigerant (ethanol 95%) pairs........................................................................................................ 60

Table 3.1  Kinetic measurements of parent Maxsorb III/ethanol pair..................... 83
Table 3.2  Kinetic measurements of KOH-H₂ treated Maxsorb III/ethanol pair........ 84
Table 3.3  Kinetic measurements of H₂-treated Maxsorb III/ethanol pair................. 85
Table 3.4  Parameters of Arrhenius equation of studied adsorbent/refrigerant pairs... 86

Table 5.1  Adsorbent materials used in the experiment.......................................... 108
Table 5.1  Specific heat capacity of adsorbent materials.......................................... 124

Table 6.1  Adsorption uptake and cycle performance of the assorted adsorbents using ethanol for ice making applications; adsorption and evaporation temperatures are 30 and -5°C............................................................... 143
Table 6.2  Adsorption uptake and cycle performance of the assorted adsorbents using ethanol for air-conditioning applications; adsorption and evaporation temperatures are 30 and 10°C............................................................... 144
Adsorption refrigeration systems use solid sorption material such as silica gel, zeolite and activated carbon with suitable refrigerant to produce cooling effect. These systems are attracting increasing attention because they can be driven by low-grade thermal energy and use refrigerants having zero ozone depletion potential and low global warming potential. The adsorption refrigeration system has several advantages compared to the absorption refrigeration system and the vapor compression refrigeration system in terms of energy use, operating temperature, moving parts and environment safety etc.

1.1 Principle of Adsorption

Adsorption phenomenon has been known for long time and the study did exist for separation, purification, and heat-powered refrigeration technologies. The heart of an adsorption process is usually a porous solid medium which provides a very large surface area and large pore volumes and therefore large adsorptive capacity (Duong, 1998). The surface of the solid material is usually unsaturated and unbalanced. When surface is brought into contact with gas, there is an interaction between the unbalanced molecular forces at the surface and the gas molecular forces. That is because; solid surface tends to satisfy these residual forces by attracting and retaining on its surface the molecules, atoms, or ions of the gas. This results in a greater concentration of the gas or liquid in the near vicinity of the solid surface than in the bulk gas or vapor phase, despite the nature of the gas or vapor. The process by which this surface excess is caused is called adsorption (Bansal and Goyal, 2005).
The adsorption process may occur in two ways; physisorption, and chemisorption, depending on the constraining force during the adsorption. In the physisorption process, the adsorbate molecules are attracted to the adsorbent surface by the weak van der Waals force which are similar to the molecular forces of cohesion and are involved in the condensation of vapors into liquids. There are not any changes in the chemical composition of the adsorption pair (see Fig.1.1). The adsorbed molecules can be released by applying heat which usually does
not exceed 80 kJ/mol. Physical adsorbents can adsorb consecutive layers of the adsorbate gas and the thickness of the adsorbed phase is multilayer. The chemisorption process involves valence forces arising from sharing of electrons between the adsorbent and the adsorbate atoms. This results in a chemical reaction and forming a complex surface compound. The forces of these formed bonds are much stronger than the Van der Waals force in the physisorption (see Fig. 1.2). As a consequence, much more heat of adsorption is required to release the adsorbate, up to 800 kJ/mol. It should be mentioned that the adsorptive action is physical for almost all of solid adsorbents which are commonly used in adsorption cooling systems.

1.1.1 Adsorption Equilibrium

When a solid surface is exposed to a gas, the molecules of the gas strike the surface of the solid. Some of these striking molecules stick to the solid surface and become adsorbed, while some others rebound back. The rate of adsorption is large at the beginning because the whole surface is bare. It continues to decrease as more and more of the solid surface becomes covered by the adsorbate molecules. However, the rate of desorption increases because desorption takes place from the covered surface. Figure 1.3 shows gas molecules in adsorbed phase (blue color) and desorbed phase (golden color). The equilibrium is reached when the rate of adsorption is equal to the rate of desorption. At this point, the gas-solid system is said to be in adsorption dynamic equilibrium because the number of molecules sticking to the surface is equal to the number of molecules rebounding from the surface (Bansal and Goyal 2005).
In equilibrium state, the amount of adsorbate uptake per kg of adsorbent, $W \text{[kg/kg]}$, is called adsorption equilibrium capacity or equilibrium uptake. Adsorption equilibrium capacity, $W$, depends on the equilibrium pressure, $P$, the adsorbent temperature, $T$, and the nature of gas-solid system, thus it may be written as (Rouquerol et al. 1999),

$$W = f \left( P, T, \text{system type} \right)$$  \hspace{1cm} (1.1)

The form of the Eq.(1.1) may be complex and $f$ is usually determined experimentally. There is no simple quantitative theory for predicting adsorption isotherms in detail from known parameters. However, most of the gas and/or vapor adsorption isotherms can be categorized by means of IUPAC classification scheme which has six types of isotherm for solid/gas equilibrium as shown in Fig. 1.4. It is based on earlier classification by Brunauer (1945) which had five types of isotherm. Isotherms of type I are generally true for microporous adsorbents for subcritical and supercritical conditions. Type II is observed in adsorbents having a wide range of pore sizes, with either mono or multi-molecular adsorption layers. Adsorption of benzene vapor on graphitized carbon represents an example of this type of isotherms. Type III is uncommon and they include capillary condensation in addition to the multi-molecular adsorption layer. Adsorption of bromine on silica gel is an example of this
type of isotherms. Isotherms of type IV involve formation of two surface layers on the adsorbents having pore size much larger than the molecule diameter of the adsorbate. Isotherms of type V are observed on the adsorbents involving large forces produced by intermolecular attraction such as adsorption of phosphorus on NaX. Type VI, which was not included in the Brunauer classification, illustrates that the adsorption isotherms can have one or more steps (Adamson 1976).

Fig. 1.4: The IUPAC classification of adsorption isotherm for solid/gas equilibrium (IUPAC recommendations, 1985, 1994).

1.1.2 Adsorption Kinetics

In practical adsorption applications, especially in adsorption cooling/heat pump systems, the maximum adsorption capacity of the adsorbent cannot be fully utilized. This is because it takes a long time to reach the equilibrium state. In order to estimate practical or dynamic adsorption capacity, adsorption kinetics should be conducted. The central problem in the
designing of adsorption systems is the unavailability of accurate adsorption kinetics. Without an accurate knowledge about adsorption kinetics, it is impossible to design or to analyze the performance of adsorption systems. The well-known Linear driving force (LDF) model proposed by Glueckauf, E. (1955) is widely used to simulate the dynamic behavior of adsorption chillers and to predict the system performance. Adsorption rate of the adsorbent/adsorbate pair can be estimated by using the classical LDF model (Eq. (1.2) - Eq. (1.4)) below;

\[
\left( \frac{dw}{dt} \right)_{LDF} = K(W - w)
\]  

\[K = \frac{F_0 D_s}{R_p^2} \]  

\[D_s = D_{so} \exp \left( \frac{-E_a}{R_g T} \right)\]

In these equations, \(W\) is the equilibrium adsorption capacity of adsorbate per kg of adsorbent, \(w\) is the instantaneous adsorption capacity (uptake) and the left hand side of the Eq.(1.2) represents the adsorption/desorption rates and \(K\) is the particle mass transfer coefficient. \(D_s\) stand for the surface diffusivity and \(R_p\) is the adsorbent particle radius. \(F_0\) is a geometric parameter that depends on the adsorbent particle shape and it is equal to 15 for spherical adsorbent particles (El-Sharkawy, 2011), \(E_a\) is the activation energy. High accuracy experimental measurements are required to estimate the numerical value of the parameters in above equations.
1.2 Adsorption Cooling System

Cooling technology, based on the principle of adsorption, got consideration attention in last few decades in view of pressing need for combating ozone layer depletion and global warming problems. Adsorption systems use natural refrigerants rather than chlorofluorocarbons (CFCs) or hydro-chlorofluorocarbons (HFCs). These systems provide an alternative to conventional vapor compression and absorption systems. Adsorption systems have some other distinct advantages like, their simple control, the low operation and maintenance costs, the absence of vibration problems as a result of the absence of moving parts other than magnetic valves and the very long lifetime. The lower driving temperatures of heat source that can be used make these systems more attractive. Adsorption systems can be powered by heat sources with temperature as low as 50 ºC (Saha and Kashiwagi, 1997). Due to the fact that adsorption refrigeration systems use solid adsorbent, they are suitable for conditions with serious vibration, such as in fishing boats and locomotives compared to the absorption systems.

Figure 1.5 shows schematic diagram of basic adsorption cooling system. The adsorbent containing the refrigerant is heated (by the solar collectors or waste heat) and the adsorbed refrigerant is expelled as vapour and condenses in the condenser. The condensed refrigerant is then transfer to the evaporator via expansion valve, leading to a lower pressure area. The refrigerant evaporates in the evaporator, taking up the heat from the chilled water and finally adsorbed in cooled adsorbent part. The adsorption heat is evacuated by the cool water. For continuous cooling production two sorption bed is used in this diagram.
Though there are lots of advantages of adsorption cooling systems but still there are some drawbacks which are the requirements of special design to maintain high vacuum, the large volume and weight relative to traditional refrigeration systems. The reason which limits the extensive application of this technology is the low specific cooling power (SCP) and the low coefficient of performance (COP) compared to absorption and vapor compression systems.

1.3 Selection of Adsorbent and Refrigerant Pair

The adsorption characteristics of a certain pairs depend on the nature of the adsorbent, the nature of the adsorbate, the reactivity of the surface, the surface area, and the temperature and pressure of adsorption. The performance of the adsorption cooling system also depends on the selection of working pairs. The choice criterion of refrigerant and adsorbent depends on a number of important requirements (Critoph 1996; Alghoul et al. 2007; ASHRAE hand book 2009, Wang et al. 2010; Hassan and Mohamad 2012). Sections 1.3.1. and 1.3.2 include some of criterion to select the adsorbent and refrigerant.
1.3.1 Choice of Adsorbent

The important considerations influencing the choice of a suitable adsorbent are:

- Adsorption of large amount of the adsorbate under low temperature conditions to yield good coefficient of performance (COP).
- Desorption of most of the adsorbate when exposed to thermal energy (waste heat or solar heat).
- Wide concentration change in a small change of temperature.
- Reversibility of adsorption process for many cycles.
- Possession of high latent heat of adsorption compared to sensible heat.
- High packing density and thermal conductivity.
- Non-toxic and non-corrosive.
- Low cost and widely available.

Table 1.2 Basic types of adsorbents (Dabrowski, 2001).

<table>
<thead>
<tr>
<th>Carbon Adsorbents</th>
<th>Mineral Adsorbents</th>
<th>Other Adsorbents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbon powders</td>
<td>Silica gels</td>
<td>Synthetic polymers</td>
</tr>
<tr>
<td>Activated carbon fibers</td>
<td>Activated alumina</td>
<td>Composite adsorbents:</td>
</tr>
<tr>
<td>Molecular carbon sives</td>
<td>Oxides of metals</td>
<td>Complex mineral-carbons,</td>
</tr>
<tr>
<td>Mesocarbon microbeads</td>
<td>Metal chlorides</td>
<td>X-elutrilithe; X=Zn, Ca</td>
</tr>
<tr>
<td>Fullerenes</td>
<td>Hydroxides of metals</td>
<td>Expanded graphite</td>
</tr>
<tr>
<td>Heterofullerenes</td>
<td>Zeolites</td>
<td></td>
</tr>
<tr>
<td>Carbonaceous nanomaterial</td>
<td>Clay minerals</td>
<td>Mixed sorbents</td>
</tr>
<tr>
<td>Surface treated activated</td>
<td>Porous clay hetero-structures</td>
<td>MOF (metal organic framework) (Henninger et al. 2010, Rezk et al. 2013)</td>
</tr>
<tr>
<td>carbon (Kil et al. 2013)</td>
<td>(PCHs)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pillared clays</td>
<td></td>
</tr>
</tbody>
</table>
1.3.2 Choice of Refrigerant

The important considerations influencing the choice of a suitable refrigerant are:

- The refrigerant latent heat should be high, so the circulation rate of the refrigerant and adsorbent can be minimized.
- Small molecular size to enable it to be adsorbed into the adsorbent.
- The refrigerant/adsorbent pair should not form a solid phase over the expected range of composition and temperature to which it will be subjected.
- The refrigerant should be much more volatile than the adsorbent so the two can be separated easily without the need to a rectifier.
- The adsorbent should have a strong affinity for the refrigerant under conditions in which adsorption takes place. Strong affinity allows less adsorbent to be circulated for the same refrigeration effect, reducing sensible heat losses, and allows a smaller liquid heat exchanger.
- Moderate operating pressure is required. High pressure requires heavy-walled equipment, and significant electrical power may be needed to pump fluids from the low-pressure side to the high pressure side. Low pressure requires large-volume equipment and special means of reducing pressure drop in the refrigerant vapor paths.
- Thermally stable with the adsorbent at the cycle operating temperatures ranges.
- Non-toxic, non-corrosive and non-flammable.
- Low global warming potential (GWP) and low ozone depletion potential (ODP).
Table 1.1 Summary physical, safety and environmental data for some refrigerants (sorted by ASHRAE Standard 34 designation) (Calm and Hourahan, 2001).

<table>
<thead>
<tr>
<th>Compositonal group</th>
<th>Refrigerants</th>
<th>Chemical formula</th>
<th>NBP (°C)</th>
<th>$P_c$ (MPa)</th>
<th>Safety group</th>
<th>ODP</th>
<th>GWP</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFCs</td>
<td>R-11</td>
<td>CCl$_3$F</td>
<td>23.7</td>
<td>4.41</td>
<td>A1</td>
<td>1</td>
<td>4600</td>
</tr>
<tr>
<td></td>
<td>R-12</td>
<td>CCl$_2$F$_2$</td>
<td>-29.8</td>
<td>4.14</td>
<td>A1</td>
<td>0.82</td>
<td>10600</td>
</tr>
<tr>
<td></td>
<td>R113</td>
<td>CCl$_2$FCCIF$_2$</td>
<td>47.6</td>
<td>3.39</td>
<td>A1</td>
<td>0.9</td>
<td>6000</td>
</tr>
<tr>
<td></td>
<td>R114</td>
<td>CCIF$_2$CCIF$_2$</td>
<td>3.6</td>
<td>3.26</td>
<td>A1</td>
<td>0.85</td>
<td>9800</td>
</tr>
<tr>
<td></td>
<td>R115</td>
<td>CCIF$_2$CF$_3$</td>
<td>-38.9</td>
<td>3.12</td>
<td>A1</td>
<td>0.4</td>
<td>7200</td>
</tr>
<tr>
<td>HCFCs</td>
<td>R-22</td>
<td>CHClF$_2$</td>
<td>-40.8</td>
<td>4.99</td>
<td>A1</td>
<td>0.34</td>
<td>1700</td>
</tr>
<tr>
<td></td>
<td>R-123</td>
<td>CHCl$_2$CF$_3$</td>
<td>27.8</td>
<td>3.66</td>
<td>B1</td>
<td>0.012</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td>R-124</td>
<td>CHClFCCF$_3$</td>
<td>-12</td>
<td>3.62</td>
<td>A1</td>
<td>0.026</td>
<td>620</td>
</tr>
<tr>
<td></td>
<td>R-141b</td>
<td>CH$_3$CCl$_2$F</td>
<td>32</td>
<td>4.25</td>
<td>A1</td>
<td>0.086</td>
<td>700</td>
</tr>
<tr>
<td></td>
<td>R-142b</td>
<td>CH$_3$CClF$_2$</td>
<td>-9</td>
<td>4.12</td>
<td>A2</td>
<td>0.043</td>
<td>2400</td>
</tr>
<tr>
<td>HFCs</td>
<td>R-23</td>
<td>CHF$_3$</td>
<td>-82.1</td>
<td>4.84</td>
<td>A1</td>
<td>0.034</td>
<td>1700</td>
</tr>
<tr>
<td></td>
<td>R-32</td>
<td>CH$_2$F$_2$</td>
<td>-51.7</td>
<td>5.8</td>
<td>A2</td>
<td>0.00</td>
<td>550</td>
</tr>
<tr>
<td></td>
<td>R-125</td>
<td>CHF$_2$CF$_3$</td>
<td>-48.1</td>
<td>3.63</td>
<td>A1</td>
<td>0.00</td>
<td>3400</td>
</tr>
<tr>
<td></td>
<td>R-134a</td>
<td>CH$_2$FCF$_3$</td>
<td>-26.1</td>
<td>4.06</td>
<td>A1</td>
<td>0.00</td>
<td>1300</td>
</tr>
<tr>
<td></td>
<td>R-143a</td>
<td>CH$_3$CF$_3$</td>
<td>-47.2</td>
<td>3.78</td>
<td>A2</td>
<td>0.00</td>
<td>4300</td>
</tr>
<tr>
<td></td>
<td>R-152a</td>
<td>CH$_3$CHF$_2$</td>
<td>-24</td>
<td>4.52</td>
<td>A2</td>
<td>0.00</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td>R-227ea</td>
<td>CF$_3$CHFCF$_3$</td>
<td>-15.6</td>
<td>2.98</td>
<td>B1r</td>
<td>0.00</td>
<td>3500</td>
</tr>
<tr>
<td></td>
<td>R-236fa</td>
<td>CF$_3$CH$_2$CF$_3$</td>
<td>-1.4</td>
<td>3.2</td>
<td>A1</td>
<td>0.00</td>
<td>9400</td>
</tr>
<tr>
<td></td>
<td>R-245fa</td>
<td>CHF$_2$CH$_2$CF$_3$</td>
<td>15.1</td>
<td>4.43</td>
<td>B1r</td>
<td>0.00</td>
<td>950</td>
</tr>
<tr>
<td>Compositional group</td>
<td>Refrigerants</td>
<td>Chemical formula</td>
<td>NBP (°C)</td>
<td>( P_c ) (MPa)</td>
<td>Safety group</td>
<td>ODP</td>
<td>GWP</td>
</tr>
<tr>
<td>---------------------</td>
<td>--------------</td>
<td>------------------</td>
<td>----------</td>
<td>----------------</td>
<td>--------------</td>
<td>-----</td>
<td>------</td>
</tr>
<tr>
<td>Natural refrigerant</td>
<td>R-290</td>
<td>( \text{CH}_3\text{CH}_2\text{CH}_3 )</td>
<td>-42.2</td>
<td>4.25</td>
<td>A3</td>
<td>0.00</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Propane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R-600</td>
<td>R-600</td>
<td>( \text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_3 )</td>
<td>-0.5</td>
<td>3.8</td>
<td>A3</td>
<td>0.00</td>
<td>~20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H₃- butane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R-600a</td>
<td>R-600a</td>
<td>( \text{CH}((\text{CH}_3))_2\text{-CH}_3 )</td>
<td>-11.7</td>
<td>3.64</td>
<td>A3</td>
<td>0.00</td>
<td>~20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>n-butane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R-717</td>
<td>NH₃- ammonia</td>
<td>-33.3</td>
<td>11.34</td>
<td>0.00</td>
<td>B2</td>
<td></td>
<td>&lt;1</td>
</tr>
<tr>
<td>R-718</td>
<td>H₂O- water</td>
<td>100</td>
<td>22.06</td>
<td>0.00</td>
<td>A1</td>
<td></td>
<td>&lt;1</td>
</tr>
<tr>
<td>R-729</td>
<td>Air</td>
<td>-194.4</td>
<td>3.77</td>
<td>0.00</td>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>R-744</td>
<td>CO₂- carbon</td>
<td>-78.4</td>
<td>7.38</td>
<td>0.00</td>
<td>A1</td>
<td></td>
<td>1</td>
</tr>
</tbody>
</table>

NBP= normal boiling point; \( P_c \)=critical pressure; Letter A, B indicates relative toxicity followed by number (1, 2, 3) that indicates relative flammability, e.g. A1 means lower toxicity and no flame propagation; ODP=ozone depletion potential (modeled relative to R11); GWP= global warming potential (for 100 yr integration relative to CO₂)
1.4 Review of Adsorbent/Refrigerant Pairs and Adsorption Cooling and Heat Pump Systems

There have been considerable efforts over the past few decades to use adsorption principle for cooling and heat pump applications. But still refrigeration and heat pump system using solid/vapor adsorption systems are rarely seen in the market. Promising recent developments have been made in Japan, Europe and the United States for the use of porous metal hybrids and composite adsorbents (Srivastava and Eames, 1998).

Extensive studies have been conducted to investigate the performance of adsorption cooling and heat pump systems considering various types of adsorbent/refrigerant pairs. In the following subsection a brief review of adsorbent/refrigerant pairs which are commonly used in adsorption cooling/heat pump applications is given. A review on the advanced adsorption cooling systems is also given in the following subsections. Advanced cooling systems are designed either to enhance the performance of the basic systems or to use low temperature grade heat source. Regenerative systems aim to achieve the former target and multi stage systems are designed to achieve the later. However, as this field has become so large and there is a huge number of works, it can not be concluded entirely in this chapter.

1.4.1 Adsorbent/Refrigerant Pairs for Adsorption Cooling Applications

Working pairs are the crucial parts in the adsorption refrigeration system. Actually there are no working pairs to completely meet the requirements mentioned in the previous adsorbent and refrigerant selection sections. But there are many commonly used working pairs which closely meet these requirements will be discussed in this section.
1.4.1.1 Silica gel/Water Pair

The silica gel is a type of amorphous synthetic silica. It is a rigid, continuous net of colloidal silica, connected to very small grains of hydrated SiO$_4$. The pore diameters of common silica gel are 2, 3 nm (A type) and 0.7 nm (B type), and the specific surface area is about 100-1000 m$^2$/g (Wang et al. 2010).

Adsorption refrigeration systems using silica gel/water pair were investigated mainly in Japan in the 1980s due to its suitability for low grade heat source. Sakoda and Suzuki (1984) proposed a transient simulation model using silica gel/water pair for solar powered adsorption cooling cycle. The authors (Sakoda and Suzuki, 1986) also analyzed solar-driven adsorption refrigeration system. They reported that a COP of 0.2 can be achieved using solar collector with dimensions of 500×500×50 mm and 1kg silica gel. Saha et al. (1995) analytically investigated the effects of operating conditions on the cooling capacity and COP of a silica gel/water based adsorption chiller and found hot water temperature 50 °C is only viable when cooling water temperature of less than 25 °C. Boelman et al. (1995) was continued to study parametrically the influence of thermal capacitance and heat exchanger UA-values on cooling capacity for the silica gel-water system. A lumped transient model and distributed transient model of a two-bed adsorption cooling system using silica gel-water pair were investigated by Chua et al. (1999, 2004); and found good agreement between the prediction and experimental data. Saha et al. (1997, 2003) developed and analyzed multi-stage adsorption cooling cycles using silica gel/water pair and found the optimum COP values at driving source temperatures between 50 and 55 °C in three-stage mode and between 80 and 85 °C in single stage multi-bed mode.
1.4.1.2 Zeolite/Water Pair

Zeolite is a type of alumina silicate crystal composed of alkali or alkali soil. The porosity of the alumina silicate skeletal is between 0.2 and 0.5 nm. There are about 40 types of natural zeolites, and the main types for adsorption refrigeration are chabazite, sodium–chabazite, cowlesite and faujasite. About 150 types of zeolites can be artificially synthesized, and they are named by one letter or a group of letters, such as type A, type X, type Y, type ZSM, etc. Artificially synthesized zeolite molecular sieves have micropores with uniform size, and different sizes can be obtained by different manufacturing methods. 4A, 5A, 10X and 13X zeolite molecular sieves are the main types used for adsorption refrigeration (Askalany et al. 2013).

A zeolite/water system for solar air-conditioning and refrigeration applications was investigated nearly four decades back (Tchernev 1979). Wang et al. (2006) investigated design and performance prediction of a novel zeolite/water adsorption air conditioner. The conditioner supplied 8-12 °C chilled water for the fan coil when it was driven by 350-450 °C exhaust gas. The designed refrigerating power and COP were 5 kW and 0.25 respectively. The refrigerating power of the machine was up to 10kW with an evaporating temperature of 6.5 °C. The cycle time was 1320 s and the SCP reached to 200 W/kg. Vasta et al. (2012) developed a mobile adsorption air conditioner employing zeolite/water pair. By using a double adsorption bed, the COP of the system was about 0.4 whereas the SCP was about 600 W/kg. Zhang (2000) presented a prototype of an adsorption cooling system driven by waste heat from a diesel engine, using zeolite/water pair. It is reported that the proposed system can achieve a specific cooling power (SCP) and COP of 2.57 W/kg and 0.38 respectively. Sward et al. (2000) presented a model for a thermal wave adsorption heat pump cycle using NaX zeolite/water pair to examine the cycle performance. It is reported that the COP was as high as 1.2 at heat source, condenser and evaporator temperatures of 120, 30 and -15°C.
respectively. Li et al. (2014) investigated the performance of a zeolite FAM Z01/water pair adsorption chiller and found the optimum COP at hot water temperature of around 65ºC.

### 1.4.1.3 Activated Carbon/Ammonia Pair

Activated carbons are made by pyrolyzing and carbonizing source materials, such as coal, lignite, wood, nutshell sand synthetic polymers, at high temperatures (700-800 ºC). Activated carbons are available in many forms including powders, micro-porous, granulated, molecular sieves and carbon fibers (Srivastava and Eames, 1998). Ammonia has a relatively high latent heat of about 1365 kJ/kg at 30 ºC and the maximum adsorption quantity in activated carbon is 0.29 kg/kg (Wang et al. 2006), but it has the disadvantage of toxicity and corrosive. The heat of adsorption for carbon-ammonia pair is in range of 2000-2700 kJ/kg (Srivastava and Eames, 1998). Tamainot-Telto and Criptoph (2003) studied the adsorption refrigerator using monolithic carbon-ammonia pair. The results demonstrated that the maximum specific cooling power (SCP) and the COP were 60 W/kg and 0.12, respectively. Tamainot-Telto et al. (2009) investigated carbon/ammonia pairs for adsorption refrigeration applications. The simulation was done for 26 various AC/ammonia pairs with three cycles (single bed, two-bed and infinite number of beds) and with a driving temperature varied from 80 to 200ºC. Considering a two-bed cycle, the best thermal performances based on power density were obtained with the monolithic carbon, with a driving temperature of 100ºC; the cooling production was about 66 MJ/m³ (COP=0.45) and 151 MJ/m³ (COP=0.61) for ice-making and air-conditioning respectively. Critoph and Metcalf (2004) reached to 0.35 COP and 2000 W/kg SCP with a plate type generator at 200 ºC driving temperature and 15 ºC evaporation temperatures. The minimum cycle time was 1200 s. Metcalf et al. (2012), studied the optimal cycle selection in carbon/ammonia adsorption cycles. Using AC/ammonia they achieved cooling COP of about 0.4 at about 200 W/kg SCP in modeling results.
1.4.1.4 Activated Carbon/Methanol Pair

AC/methanol is one of the most common working pair due to the large adsorption quantity and lower adsorption heat, which is about 1800-2000 kJ/kg. However, AC/methanol has the disadvantage of operating under sub-atmospheric pressure (Srivastava and Eames 1998). However, the methanol decomposes at 120 °C and aluminum alloys were found to have a stronger catalytic effect on the decomposition reaction than copper (HU Eric, 1998).

The research on this pair started in Europe since 1980. Pons and Guilleminot (1986) studied an AC/methanol system for ice production using renewable energy. Douss and Meunier (1988) investigated the possibility of using active carbon of type AC135 along with methanol as a working fluid for refrigeration application. It is reported that for an evaporating temperature lift equal to 25 °C, the experimental COP of the intermediate cycle reached 0.5 with regeneration temperature difference equal to 65 °C. Critoph (1988) studied the possibility of using activated charcoal with different types of refrigerants working at sub-atmospheric and super-atmospheric pressures. Anyanwu and Ezekwe (2001) and Wang et al. (2003) also conducted studies on various adsorption systems using the same adsorbent/adsorbate pair. El-Sharkawy et al. (2009) investigated the isothermal characteristics of methanol on two specimen of ACs: Maxsorb III and Tsurumi activated charcoal. The Dubinin-Radushkevich (D-R) equation is used to correlate the adsorption isotherms of the two assorted pairs. Experiment results show the superiority of Maxsorb III/methanol pair over Tsurumi activated carbon/methanol pair.

1.4.4.5 Activated Carbon/Ethanol

Saha et al. (2007a, 2007b) studied an innovative adsorption chiller employs pitch based ACF of type A-20 as adsorbent which is a fibrous adsorbent having the advantages of fast adsorption rate, high porosity and ease of handling when compared with granular adsorbents
and powdered adsorbents. Ethanol is used as refrigerant as it has no harm to environment, it
is a non-toxic substance, moreover, ethanol has comparatively higher vapor pressure even at
low temperature. This innovative system utilizes effectively low-temperature waste heat
sources of temperature between 60 and 95 ºC along with a coolant at 30 ºC. The COP reached
to about 0.6 with a cycle time of 600-700s.

El-Sharkawy et al. (2008) experimentally investigated the AC/ethanol pair for solar powered
adsorption cooling application. They used a highly porous activated carbon, named Maxsorb
III, and found the maximum adsorption capacity of Maxsorb III was 1.2 kg/kg for ethanol
adsorption. Theoretical calculations showed that, the Maxsorb III/ethanol adsorption cycle
can achieve a specific cooling effect of about 420 kJ/kg at an evaporator temperature of 7ºC
along with a heat source of temperature 80 ºC. And at evaporation temperature of 15 ºC the
COP of an ideal system was about 0.8.

1.4.2 Review the Development of Adsorption Cooling and Heat Pump
Systems

Extensive works have been conducted to investigate the performance of adsorption
cooling/heat pump systems. Advanced cycles are generally designed to enhance the
performance of conventional cycles in terms of cooling load and/or the COP. These cycles
can also be operated with a low grade heat source which is impossible with the basic cycle.

1.4.2.1 Basic Adsorption Refrigeration Cycle

The basic adsorption refrigeration cycle (Fig. 1.6) consists of two isosters, having constant
adsorbed phase concentration and two isobars corresponding to condenser and evaporator
pressure. Due to heating by some external source, temperature as well as pressure of the
adsorber system increases (process b to c) till it reaches condenser pressure. Desorption takes
place at condenser pressure; desorbed refrigerant gets condensed by rejecting heat to a sink (process c to d). The refrigerant liquid goes to evaporator via a pressure reducing valve. Cooled by some external fluid, pressure and temperature of the adsorber system decreases (process d to a) till it reaches evaporator pressure, saturation vapor pressure of the refrigerant at the evaporator temperature. Boiling of the refrigerant, latent heat being supplied by the cooling load, takes place with vapor uptake at the adsorber (process a to b), completing the cycle.

Basic cycle is simple and reliable; however it suffers from the problem of low efficiency; for single bed basic cycle, cold production is also intermittent. Hence different modified cycles are being tried to improve the efficiency and practicability of the basic cycle. These include multi stage cycle, heat recovery cycle, heat and mass recovery cycle, thermal wave cycle, forced convective thermal wave cycle, cascade cycle and multi-bed cycle etc.

Fig. 1.6: Basic adsorption refrigeration cycle using conceptual Dühring diagram.
1.4.2.2 Advanced Adsorption Refrigeration Cycle

Few cycles are proposed to utilize relatively low temperature heat source. Though silica gel/water adsorption chiller (Saha et al. 1995) can be operated by the heat source of temperature below 100 °C using cooling source of temperature 30 °C, the utilization of near environment temperature (below 60 °C ) heat source such as waste heat or solar heat is still facing technical hurdles.

In another endeavor, Saha et al. (2003) have investigated the three bed non-regenerative adsorption chillers from the perspectives of smoothen the delivered chilled water temperature. Figure 1.7 depicts the schematic diagram of the proposed system. The 3-bed system comprises with an evaporator, a condenser and three sorption elements (adsorber/desorber heat exchangers). In the system operation, there is a time lag between each sorption element and hence at least one of the sorption elements is in adsorption mode during the cycle operation. This makes it possible to have a uniform chilled water outlet temperature. Chua et al. (2001) reported that the four-bed chiller can produce 70 % more cooling capacity than the conventional two bed chiller.

Uyun et al. (2009) experimentally investigated a three-bed adsorption chiller (Fig. 1.8) employing mass recovery cycle. The authors found the higher COP and SCP values specially for heat source temperature below 75 °C from the conventional single-stage adsorption chiller and found similar results with the conventional four bed adsorption cycle proposed by Ng et al. (2006).
Chapter 1

Introduction

Fig. 1.7: Schematic diagram of three-bed silica gel adsorption chillers (Saha et al. 2006).

Fig. 1.8: Photograph of the three-bed experimental device (Uyun et al. 2009).
Chua et al. (2001) have analytically investigated a multi-bed regenerative adsorption chiller. The regenerative chiller improves significantly the waste heat recovery efficiency. However, the chiller is operational with driving source temperature above 60 °C in combination with a coolant at 30 °C.

Saha et al. (2003) made an interesting study of a dual mode, multistage, multi-bed regenerative adsorption system (Fig. 1.9), which could operate with heat source temperature ranging from 40 to 95 °C. In one operational mode, it worked as a single stage multi bed chiller when the driving source temperature was from 60 to 95 °C. For a heating source temperature less than 60 °C, the chiller worked as a three stage adsorption chiller and could operate up to 40 °C of driving source temperature. Multi staging helped the chiller to exploit near ambient source temperature with a regenerating temperature lift of as low as 10 °C, while multi bed operation at higher source temperature yielded high performance with reduced fluctuation in condenser and evaporator temperatures. Authors have commented that with this very low driving source temperature in combination with a coolant at 30 °C, no other cycle except an advanced adsorption cycle with staged regeneration will be operational.

Miyazaki et al. (2010) proposed an innovative waste heat driven dual evaporator type three-bed adsorption chiller (Fig. 1.10) and predicted that both SCC and COP of the system could be increased by 50% and by 70%, respectively than the two bed single stage adsorption chiller.
Fig. 1.9: Schematic diagram of the multi-bed adsorption chiller (Saha et al. 2003).

Fig. 1.10: The schematic of the dual evaporator type three bed adsorption chiller (Miyazaki et al. 2010).
Saha et al. (2000, 2001) proposed two-stage chiller and driving heat source temperature was validated by experiment. In this cycle, the evaporation temperature lifts between evaporator and condenser is divided into two smaller lifts. The refrigerant pressure thus rises into two progressive steps from the evaporator to an intermediate pressure and from the intermediate pressure to the condenser pressure (see Fig. 1.12). This makes it possible to use a low temperature heat source such as solar energy. A two-stage silica gel-water adsorption refrigeration cycle can exploit the heat source of temperature around 60 °C with the cooling source at 30 °C. The coefficient of performance (COP) of a two-stage adsorption refrigeration cycle, however, is quiet low. Moreover, both the COP and cooling capacity of a two-stage chiller are extremely sensitive to the driving heat source temperature.

A novel adsorption chiller, namely, ‘Reheat two-stage’ chiller using silica gel/water is introduced by Alam et al. (2007) and Khan et al. (2006, 2007) and shown that the chiller is able to exploit the heat source of temperature 50-90°C and can produce effective cooling. They also found that the chiller performance increases significantly in the range of silica gel mass from 4 to 20 kg.

To utilize such a low temperature heat source, Saha et al. (1995b) launched a three-stage silica gel/water adsorption chiller (Fig. 1.13). The chiller was able to produce effective cooling by utilizing the heat source temperature 50 °C with cooling source temperature 30 °C. Saha et al (2003) also investigated the performance of a dual mode, three stage, non-regenerative, and six-bed, regenerative silica gel/water chiller, which can be driven by low temperature waste heat or renewable energy sources in a wide range; between 40 and 95 °C.
Fig. 1.11: Schematic of a re-heat two-stage adsorption chiller (Saha et al. 2001, Khan et al. 2007).

Fig. 1.12: Conceptual Dühring diagram for both the conventional and two stage cycle (Saha et al. 2001).
**Fig. 1.13:** Schematic of three-stage chiller without mass recovery scheme (Saha et al. 1995b, Khan et al. 2008).

**Fig. 1.14:** Conceptual Dühring diagram of the advanced adsorption chiller in dual-mode operations (Saha et al. 2003).
1.4.2.3 Hybrid adsorption cooling System

Hybrid adsorption cooling system is a mixture of different techniques in one system to improve its efficiency. This mixture could be by using different cooling technologies like a compression cycle with the adsorption cycle. It also could be in the application of the system like using the waste heat of the adsorption cooling system as a heat source for some domestic applications. And it could be in heat source like using solar energy with an electrical heater to drive the adsorption cooling system. The hybrid adsorption systems will be divided into three branches. First according to cooling technologies, second according to its employment and finally according to the heat source (Ahmed et al. 2012).

Cascading cycles (Fig. 1.15) utilize different working temperatures of adsorbent-adsorbate pairs. Douss and Meunier (1989) did work on a cascading adsorptive heat pump. An activated carbon/methanol intermittent cycle was topped by a two adsorber zeolite/water cycle. Driving heat was supplied by a boiler to zeolite adsorbers while activated carbon adsorber was heated by heat recovered from zeolite adsorber under adsorption. Evaporators of both basic cycles operated at the same temperature. A cooling COP of 1.06 could be achieved, which was much more than the COP of an intermittent cycle or the COP of a two adsorber zeolite/water cycle under similar operating conditions. COP of the cascading cycle was found to be very sensitive to the evaporating temperature lift and advantage of the cascading cycle depended on it. For a temperature lift of 45 °C or more, cascading was not advantageous. As the evaporating temperature lift became lower, higher was the gain in COP of the cascading cycle.
Wang et al. (2000) developed one hybrid system consisting of solar water heater and adsorption ice maker. The system could provide 60 kg of hot water at 90 °C and 10 kg of ice daily with a vacuum heat pipe type solar collector area of 2 m². The authors remarked that other than solar energy this system could very well operate with waste heat like exhaust gases of an automobile, etc. Banker et al. (2008) studied the performance of mechanical and adsorption hybrid compression refrigeration cycles using HFC 134a. The study found almost 40% energy saving potential by carrying out a part of the compression in a thermal compressor.

1.5 Objective and Scopes of the Present Thesis

The main objective of this work is to develop adsorption cooling systems which have the capability of utilizing low grade thermal energy, including heat from solar hot water, industrial waste heat and geothermal sources. The aim of this thesis is to investigate, both experimentally and thermodynamically the utilization of parent and surface treated activated carbon/ethanol pairs. The surface treated adsorbent/refrigerant pair may contribute in reduction of adsorbent mass thus results in compactness of the system and also improve the
performance of the system. The scopes of the present thesis are:

1. To measure the adsorption isotherms of environment friendly refrigerant ethanol onto the surface treated activated carbon, namely H₂ treated Maxsorb III and KOH-H₂ treated Maxsorb III using magnetic suspension adsorption measuring unit.
2. To measure the adsorption kinetics of ethanol onto surface treated activated carbon considering a suitable operating condition for adsorption chiller. To use Fickian diffusion (FD) model for measuring the adsorption rate of assorted adsorbent refrigerant pairs.
3. To provide a new correlation of isosteric heat of adsorption as a function of adsorbent temperature and adsorbate concentration. Verify the proposed relation by the experimental data.
4. To investigate the performance of adsorption refrigeration cycles using parent and surface treated Maxsorb III and ethanol pairs employing a time-independent mathematical model.
5. To measure the specific heat capacity of adsorbent material using differential scanning calorimeter (DSC).
6. To analyze the performance of adsorption-compression hybrid refrigeration systems with two different cycle configurations, namely cascade type and subcool type.

1.6 Thesis Outline

This thesis consists of seven chapters which describe the experiments and theory to achieve the research objectives. Following are the brief description of the contents of each chapter.

Chapter 1 provides a scientific background about the adsorption phenomenon and the
classifications of sorption systems. The theory of operation of the basic adsorption cooling cycle is also discussed in this chapter. A literature review on adsorbent/refrigerant pairs and systems which are commonly used in adsorption cooling and heat pump systems are presented therein. The research objective and scope has also been enumerated in this chapter.

Chapter 2 describes the experimental methods, apparatus and procedures in determining the adsorption equilibria of the parent and surface treated Maxsorb III and ethanol pairs. The isotherm data are measured using a gravimetric method at temperatures and pressures ranges corresponding to the working conditions of adsorption cooling cycles. Experimental data have been analyzed and fitted using Dubinin Radushkevich (D-R) and Dubinin-Astakhov (D-A) equations.

Chapter 3 presents experimental and theoretical studies on the adsorption kinetics of ethanol onto parent and surface treated Maxsorb III. Experiments have been carried out at different adsorption temperatures ranging from 30 to 70 °C and relative pressure up to 0.9., which are suitable for adsorption chiller design. The mass of ethanol adsorbed onto parent and treated Maxsorb III is measured by magnetic suspension adsorption measuring unit under a controlled pressure and temperature environment. The measured uptake mass is logged with a time interval of 0.1 second making a continuous change of ethanol uptake with time. The experimental data are regressed with expression derived from the Fickian diffusion (FD) model.

In Chapter 4, a simplified method for isosteric heat of adoption is proposed using the D-A isotherm model and the Van’t Hoff equation. In the proposed correlation, isosteric heat is found to be a function of the refrigerant concentration and adsorbent temperature and it is expected that it will be useful for designing adsorption cooling and heat pump systems.

Chapter 5 deals with the specific heat capacity measurement of the parent and surface treated
Maxsorb III along with other currently used adsorbents using a differential scanning calorimeter (DSC). The temperature range is used from 30 to 150 °C. These data are also essential for accurate system design.

Chapter 6 presents thermodynamic analysis of adsorption refrigeration cycles using parent and surface treated Maxsorb III and ethanol pairs employing a time-independent mathematical model. The study considers the refrigeration and air-conditioning application of adsorption systems.

In a case study, the performance of adsorption-compression hybrid refrigeration systems with two different cycle configurations, namely cascade type and subcool type have been analyze and presented in Appendix D. Parent Maxsorb III/ethanol pair is used in the adsorption cycle of the hybrid system.

The conclusions of the work are presented in Chapter 7 which highlights the practicality of choosing the pairs of surface treated activated carbon/ethanol for adsorption cooling and heat pump systems and the contribution of the author.

### 1.7 References


Chapter 1

Introduction


refrigeration cycle, Energy, **Vol. 22 (4)**, p.437-447.


54. Tamainot-Telto Z, Critoph R.E. 2003, Advanced solid sorption air conditioning modules


Chapter 2

Adsorption Equilibrium of Activated Carbon Powder/Ethanol Pairs

Adsorption isotherms describe the equilibrium uptake at a given pressure and adsorption temperature. It is the equilibrium relationship between the concentration in the fluid phase and the concentration in the adsorbent particle at a given temperature. The adsorption characteristics of a certain pairs depend on the nature of the adsorbate, the nature of the adsorbent, the reactivity of the surface, the surface area, and the pressure and temperature of adsorption.

An experimental approach to determine the adsorption isotherm data of ethanol onto parent and surface treated activated carbon powder are presented in this Chapter. Experimental data are correlated with popular Dubinin-Radushkevich (D-R) and Dubinin-Astakhov (D-A) isotherm models. Measurements cover the useful operation range of adsorption chiller.

2.1 Introduction

Adsorption characteristic of adsorbent/refrigerant pairs in terms of adsorption isotherm is essential for the optimum design and development of adsorption cooling and heat pump systems. Extensive studies have been conducted to investigate the performance of adsorption/cooling and heat pump system considering various adsorbent/refrigerant pairs which are discussed in Chapter 1 (Section 1.4). However, few works have been conducted to measure the adsorption equilibrium data.

The key information to design the thermally driven system is the adsorption characteristics of
adsorbent/refrigerant pair which is measured experimentally. Chua et al. (2002) measured the adsorption characteristic of silica gel/water system at temperature range from 25 to 65 °C and pressure 0.5 to 7 kPa. Esteves et al. (2008) measured adsorption isotherm of natural gas and biogas components on activated carbon over the pressure and temperature ranges of 0-9 MPa and 0-52 ºC, respectively. El-Sharkawy et al. (2006) measured the adsorption characteristics of activated carbon fibers/ethanol pair at evaporation temperature 10 and 15°C with varying adsorption temperatures from 11 to 60 ºC. Saha et al. (2009) measured the adsorption characteristics and heat of adsorption of activated carbon/R-134a pair at temperature range of 5-70 ºC and pressure up to 1.2 MPa.

On the other hand, the accuracy of adsorption equilibrium data depends on the method and the design of measurement system. The most common techniques used for measuring adsorption isotherms are; (i) gravimetric method using thermogravimetric analyzer (TGA) unit (El-Sharkawy et al. 2008, Sheikh et al. 1996, Himeno et al. 2005, Alcaniz-Monge et al. 1997, Salem et al. 1998, Agnihotri et al. 2005) or magnetic suspension balance (MSB) (Hornbostel et al. 2013, Saha et al. 2012, Henninger et al. 2010) (ii) chromatographic method (Glueckauf and Coats 1947), (iii) constant volume variable pressure (CVVP) method (Loh et al. 2010, Saha et al. 2011) (iv) measuring the liquid refrigerant level at evaporator side (El-Sharkawy et al. 2006, 2009), and (v) desorption method (Saha et al. 2007).

However, it is proven that the gravimetric method employing TGA or the magnetic suspension balance provides high accuracy of adsorption equilibrium and kinetic measurements. El-Sharkawy et al. (2008) measured the adsorption equilibrium of ethanol onto activated carbon powder, namely Maxsorb III, for solar powered adsorption cooling applications using a TGA unit of type Chan-2121coupled with a controlled temperature evaporator. Experimental results showed that Maxsorb III can adsorb up to 1.2 kg of ethanol per kg of adsorbent. Hornbostel et al. (2013) studied the characteristics of carbon sorbent for
Chapter 2 Adsorption equilibrium of activated carbon/ethanol pairs

CO₂ capture using a temperature programmed TGA. Saha et al. (2012) studied the adsorption characteristics of R134a onto activated carbons using Rubotherm ISOSORP 2000 within evaporation temperatures between -20 and 40 °C and adsorption temperatures ranges from 30 to 80°C for refrigeration and cooling applications.

In this Chapter, the adsorption characteristics of environment friendly refrigerant ethanol onto activated carbon powder, namely (i) parent Maxsorb III, (ii) KOH-H₂ treated Maxsorb III, and (iii) H₂ treated Maxsorb III are measured using an automated controlled magnetic suspension adsorption measurement unit of type MSB-VG-S2 within evaporation temperature ranges between -14 and 77°C and adsorption temperature from 20 to 80°C.

2.2 Experimental

2.2.1 Adsorbent Materials

Adsorbents used in the present chapter are highly porous activated carbon, namely parent Maxsorb III, H₂ treated Maxsorb III and KOH-H₂ treated Maxsorb III. The sample, H₂ treated Maxsorb III is prepared by placing parent Maxsorb III in a reduction environmental condition (Ar/H₂=8/2 (v/v)) at a temperature 600 °C for 24 h. To prepare the KOH-H₂ treated Maxsorb III, potassium hydroxide (KOH) treatment was applied to H₂ treated Maxsorb III at different weight ratios and the mixture is heat treated at temperature 600 - 750 °C for 1h under nitrogen flow and finally washed with HCl to adjust the pH value of about 7 (Kil et al. 2013). Figure 2.1 shows the SEM pictures of the studied adsorbents whilst their elemental compositions are summarized in Table 2.2. The particle size distribution of the assorted adsorbents has been measured by and presented in Chapter 3. It can be seen from Table 2.2 that the parent Maxsorb III contains 0.13% of ash and 4.35% of oxygen whilst the H₂ treated Maxsorb III
and KOH-H$_2$ treated Maxsorb III having no ash and the oxygen contents varies between 1.75 and 10.46%, respectively. It is worthy to mention that, for polar molecules such as ethanol, surface functional groups should have a strong influence on the adsorption behaviors. Therefore, the main intention for the treatment is to clarify such influence by changing oxygen contents of activated carbon with maintaining similar thermo-physical properties (specific surface area, pore volume, and pore size) as much as possible (see Table 2.1).

**Table 2.1** Thermophysical properties of parent and surface treated Maxsorb III

(Kil et al. 2013)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area [m$^2$/g]</th>
<th>Micropore volume [cm$^3$/g]</th>
<th>Average pore width [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parent Maxsorb III</td>
<td>3045</td>
<td>1.70</td>
<td>1.12</td>
</tr>
<tr>
<td>KOH-H$_2$-Maxsorb III</td>
<td>2992</td>
<td>1.65</td>
<td>1.11</td>
</tr>
<tr>
<td>H$_2$-Maxsorb III</td>
<td>3029</td>
<td>1.73</td>
<td>1.15</td>
</tr>
</tbody>
</table>
Table 2.2 Elemental composition of parent Maxsorb III, KOH-H$_2$ and H$_2$ treated Maxsorb III (Kil et al. 2013)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elemental composition</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C [%]</td>
<td>H [%]</td>
<td>N [%]</td>
<td>O [%]</td>
<td>(diff.) O/C [%]</td>
<td>Ash [%]</td>
</tr>
<tr>
<td>Parent Maxsorb III</td>
<td>95.13</td>
<td>0.14</td>
<td>0.25</td>
<td>4.35</td>
<td>0.034</td>
<td>0.13</td>
</tr>
<tr>
<td>KOH-H$_2$-Maxsorb III</td>
<td>89.15</td>
<td>0.27</td>
<td>0.08</td>
<td>10.46</td>
<td>0.088</td>
<td>-</td>
</tr>
<tr>
<td>H$_2$-Maxsorb III</td>
<td>97.91</td>
<td>0.22</td>
<td>0.12</td>
<td>1.75</td>
<td>0.013</td>
<td>-</td>
</tr>
</tbody>
</table>

Fig. 2.1: SEM pictures of the studied adsorbents (a) Parent Maxsorb III, (b) H$_2$ treated Maxsorb III and (c) KOH-H$_2$ treated Maxsorb III.
Chapter 2

Adsorption equilibrium of activated carbon/ethanol pairs

2.2.2 Refrigerants

The refrigerant used in this study is ethanol of 99.5% purity, supplied by Osaka Kishida Chemical Co., Ltd., Japan. Another type of ethanol (95%) supplied by Wako Pure Chemical Industry Ltd., Japan is briefly presented at the end of this Chapter. The latter type of ethanol is tested by the same company and its compositions are furnished in Table 2.3. As the assorted ethanol (95%) has few percentages of other components, it is considered to behave like a pseudo pure component at the evaporator temperature.

Table 2.3 Composition of ethanol (95%).

<table>
<thead>
<tr>
<th>Component</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>94.8-95.8 vol.%</td>
</tr>
<tr>
<td>Density (20 ºC)</td>
<td>0.808-0.812 g/ml</td>
</tr>
<tr>
<td>Residue after evaporation</td>
<td>Max. 0.001% (mass/mass)</td>
</tr>
<tr>
<td>Acidity (as CH₃COOH)</td>
<td>Max. 0.002% (mass/mass)</td>
</tr>
<tr>
<td>Alkalinity (as NH₃)</td>
<td>Max. 1 ppm (mass/mass)</td>
</tr>
<tr>
<td>Heavy metals (as Pb)</td>
<td>Max. 1ppm (mass/mass)</td>
</tr>
<tr>
<td>Aldehydes &amp; ketones (as CH₃COCH₃)</td>
<td>Max. 0.001% (mass/mass)</td>
</tr>
<tr>
<td>1-butanol [CH₃(CH₂)₂CH₂OH] (GC)</td>
<td>Max. 0.005% (mass/mass)</td>
</tr>
<tr>
<td>1-propanol [CH₃CH₂CH₂OH] (GC)</td>
<td>Max. 0.005% (mass/mass)</td>
</tr>
<tr>
<td>2-propanol [(CH₃)₂CHOH] (GC)</td>
<td>Max. 0.01% (mass/mass)</td>
</tr>
<tr>
<td>Methanol [CH₃OH] (GC)</td>
<td>Max. 0.02% (mass/mass)</td>
</tr>
<tr>
<td>3-methyl-1-butanol [(CH₃)₂CHCH₂CH₂OH] (GC)</td>
<td>Max. 0.004% (mass/mass)</td>
</tr>
</tbody>
</table>
2.2.3 Instrumentation

Figures 2.2(a) and (b) show the pictorial view and the schematic of the experimental apparatus, respectively, which consists mainly of the magnetic suspension adsorption measurement unit, ultrahigh vacuum system, a controlled temperature evaporator, isothermal circulation oil bath that controls adsorption and evaporation temperature, and isothermal air bath to avoid condensation through connecting tubes. The suspension balance system makes it possible to weigh samples contactless instead of direct contact between the measuring cell and the weighing instrument. The suspension magnet consists of a permanent magnet, a sensor core and electronic control unit (www.rubotherm.com). It should be highlighted that buoyancy effect on the measurements is considered automatically by the system. The diaphragm pump, rotary pump and turbo molecular pump work sequentially to reach the ultrahigh vacuum condition (less than 3×10^{-5} Pa). All the valves of the system are functioned automatically using N\(_2\) gas following the provided setting condition. The measurement data are recorded continuously. The temperatures and pressure in the evaporator, sorption cell and connecting tubes are measured with platinum thermocouples and high accuracy absolute pressure gauges, respectively.

---

**Fig.2.2 (a)**: Pictorial view of the experimental set up.

**Fig. 2.2 (b):** Schematic diagram of experimental apparatus.
2.2.4 Procedure

The magnetic suspension adsorption measurement unit was used to measure the adsorption characteristics of ethanol adsorption onto adsorbents within evaporation temperature ranges from -14 to 77 °C and adsorption temperature between 20 and 80 °C. Experiments have been conducted using the multi-step technique where adsorption temperature is kept constant and evaporator temperature increased step by step until reaching a relative pressure of about 0.9. Experimental procedure for each isotherm measurement can be explained as follows;

(i) An adsorbent sample of 77 mg is placed in the sample basket and placed into the measuring chamber of the magnetic suspension balance unit.

(ii) firstly, the sorbent sample is heated at 120 °C using sheathed heater for about 4 hours in a vacuum condition of about 3×10^{-5} Pa to remove any adsorbed gas on the sample. After that, the sorbent is cooled down to the set adsorption temperature where the system considered the buoyancy effect of the measurements,

(iii) valve between evaporator and adsorption chamber is then opened to allow ethanol vapor to flow towards adsorbent sample. After that, adsorption process starts where adsorption uptake is continuously measured using the magnetic suspension balance until reaching the equilibrium conditions corresponding to the set relative pressure,

(iv) valve between evaporator and adsorption chamber is closed and evaporator temperature increased to prepare for the next relative pressure step,

(v) Process (ii) and (iii) are repeated for each relative pressure

To avoid condensation, the piping system was always kept at 20 °C higher than the saturation temperature of the vapor, which was achieved by isotherm air bath around the piping system.
2.2.5 Uncertainty Analysis

In the TGA apparatus, the weight of sample has been measured directly by a magnetic suspension balance with resolution 1μg for measuring scale around 10g. The reproducibility (standard deviations) is ±1μg if the sample mass is around 5g. The adsorbent mass used in this study is around 60-80 mg. And the ethanol uptake is found little bit higher than the sample mass. In this case the relative error is always less than 0.001% so the experimental error bars could not be visible in isotherm figures.

2.3 Adsorption Isotherm Correlation

The Dubinin-Radushkevich (D-R) and Dubinin-Astakhov (D-A) (Dubinin 1961, Dubinin and Astakhov 1971) equation is widely accepted for adsorption equilibrium of gases and vapors onto microporous adsorbents. The D-R and D-A adsorption isotherm model, Eq. (2.1) and Eq.(2.2), respectively, are used to fit the measured adsorption equilibrium uptake for ethanol onto parent Maxsorb III, KOH-H₂ treated Maxsorb III and H₂ treated Maxsorb III.

\[
W = W_0 \exp \left( -\frac{A}{E} \right)^2
\]  
(2.1)

\[
W = W'_0 \exp \left( -\frac{A}{E} \right)^n
\]  
(2.2)

Where \( A \) is the adsorption potential, defined as the molar energy required for the isentropic compression of the adsorbed species to the saturation pressure, that can be estimated using Eq. (2.3):

\[
A = R T_g \ln \left( \frac{P_s}{P} \right)
\]  
(2.3)
Linearization of Eq. (2.2) yields equation (2.4) below;

\[
\ln W = \ln W_0 - \frac{1}{E^n} \left[ RT \ln \left( \frac{P_s}{P} \right) \right]^n \quad (2.4)
\]

Where \( W \) stands for the equilibrium uptake [kg/kg] of the adsorbent/refrigerant pair, \( W_0 \) defines the maximum adsorption capacity [kg/kg] and \( E \) is the adsorption characteristic energy [kJ/kg] which measure the adsorption strength between adsorbent and adsorbate and can be evaluated experimentally. The exponential parameter \( n \) gives the best fitting of \( \ln(W) \) versus \( A^n \). In Eq. (2.3), \( T \) is the adsorption temperature [K], \( P_s \) defines the saturation pressure of refrigerant at adsorption temperature [kPa] whilst \( P \) is the equilibrium pressure [kPa].

### 2.4 Results and Discussion

Figures 2.3(a), (b) and (c) show the plots of \( \ln(W) \) versus \( A^n \) of ethanol adsorption onto parent Maxsorb III, KOH-H\(_2\) treated Maxsorb III and H\(_2\) treated Maxsorb III using Eq.(2.4), respectively. Employing this equation, one can estimate adsorption isotherm parameters in terms of \( n, W_0, E \) of the assorted pairs. At \( n=2 \) Eq.(2.4) reduced to D-R equation. Their numerical values are furnished in Table 2.4.

Plots of equilibrium adsorption uptake versus equilibrium pressure of parent Maxsorb III/ethanol, KOH-H\(_2\) treated Maxsorb III/ethanol and H\(_2\)-treated Maxsorb III/ethanol pairs are presented in Figs. 2.4(a), (b) and (c), respectively. The Dubinin-Astakhov equation (Eq. 2.2) is used to fit adsorption isotherms of parent Maxsorb III/ethanol and KOH-H\(_2\) treated Maxsorb III/ethanol pairs whilst the Dubinin-Raduskevich equation (Eq. 2.1) is found to be more suitable for fitting of adsorption uptake of H\(_2\)-treated Maxsorb III/ethanol pair. Isotherm parameters of the assorted adsorbent/refrigerant pairs are estimated as described by
El-Sharkawy et al. (2006). Numerical values of these parameters are furnished in Table 2.4.

Figures 2.4(a), (b) and (c) demonstrate a good agreement between the measured value and the predicted value using the theoretical (D-A) and (D-R) adsorption isotherm model. The behavior of these graphs is typical to type I adsorption isotherm in the International Union of Pure and Applied Chemistry (IUPAC) classification (Brunauer et al. 1940), which describe monolayer adsorption mechanisms exhibited by microporous adsorbents.

One can notice from Table 2.4 that H₂ treated Maxsorb III has the highest maximum adsorption uptake (Wₒ), followed by parent Maxsorb III and the lowest value is found to be corresponding to KOH-H₂ treated Maxsorb III. This order agrees with the order of micro-pore volume of the assorted adsorbents keeping in mind that all adsorbents have nearly the same surface area (see Table 2.1). It is also worthy to mention that the numerical value of adsorption characteristics E of parent Maxsorb III/ethanol pair is slightly higher than that presented by El-Sharkawy et al. (2008). This is because, in the present study, adsorption uptake is measured at different evaporation pressures at each isotherm where the relative pressure varies between 0.1 to about 0.8 employing the multi-step technique whilst adsorption uptake measured in the previous study was conducted at a single evaporation pressure.
Table 2.4 Isotherm parameters of assorted adsorbent/refrigerant pairs.

<table>
<thead>
<tr>
<th>Adsorbent/refrigerant pair</th>
<th>$W_0$ [kg kg$^{-1}$]</th>
<th>$n$ [-]</th>
<th>$E$ [kJ kg$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parent Maxsorb III/ethanol</td>
<td>1.2</td>
<td>1.8</td>
<td>139.5</td>
</tr>
<tr>
<td>KOH-H$_2$ treated Maxsorb III/ethanol</td>
<td>1.0</td>
<td>1.9</td>
<td>152</td>
</tr>
<tr>
<td>H$_2$ treated Maxsorb III/ethanol</td>
<td>1.23</td>
<td>2</td>
<td>138</td>
</tr>
</tbody>
</table>

Fig. 2.3(a): Linear fitting of D-A equation for parent Maxsorb III/ethanol pair.
Fig. 2.3(b): Linear fitting of D-A equation for KOH-H$_2$ treated Maxsorb III/ethanol pair.

Fig. 2.3(c): Linear fitting of D-R equation for H$_2$ treated Maxsorb III/ethanol pair.
Chapter 2  
**Adsorption equilibrium of activated carbon/ethanol pairs**

**Fig. 2.4(a):** Adsorption equilibrium of parent Maxsorb III/ethanol pair.

**Fig. 2.4(b):** Adsorption equilibrium of KOH-H$_2$ treated Maxsorb III/ethanol pair.
Fig. 2.4(c): Adsorption equilibrium of H$_2$-treated Maxsorb III/ethanol pair.

Figures 2.5(a), (b) and (c) show the plots of fractional uptake versus adsorption potential for parent Maxsorb III/ethanol, KOH-H$_2$ treated Maxsorb III/ethanol and H$_2$ treated Maxsorb III/ethanol pairs. These figures show that characteristic energy is temperature-independent and the adsorption proceeds according to the respected isotherm model. On the basis of the adsorption characteristic curve, the adsorption isotherm for any temperature can be drawn (Esteves et al. 2008).
Fig. 2.5(a): Plot of fractional uptake versus adsorption potential for parent Maxsorb III/ethanol pair.

Fig. 2.5(b): Plot of fractional uptake versus adsorption potential for KOH-H₂ treated Maxsorb III/ethanol pair.
Fig. 2.5(c): Plot of fractional uptake versus adsorption potential for H₂ treated Maxsorb III/ethanol pair.

Plots of the adsorption potential versus the relative pressure are shown in Figs. 2.6(a), (b) and (c). It is shown from these figures that at low relative pressure the adsorption potential is quite high, while it is low for high relative pressure which means that at higher relative pressure less molar work is required for adsorption via micropore filling when the gas is approaching the vapor pressure.
Chapter 2  
Adsorption equilibrium of activated carbon/ethanol pairs

Fig. 2.6(a): Plot of the adsorption potential versus relative pressure for parent Maxsorb III/ethanol pair.

Fig. 2.6(b): Plot of the adsorption potential versus relative pressure for KOH-H₂ treated Maxsorb III/ethanol pair.
Fig. 2.6(c): Plot of the adsorption potential versus relative pressure for \( \text{H}_2 \) treated Maxsorb III/ethanol pair.

Figures 2.7 show the plots of \( \ln(W) \) versus \( A^n \) of ethanol adsorption onto Maxsorb III using the D-A equation. But this time the commercially available refrigerant ethanol of 95\% purity is used. Employing D-A equation, Eq. (2.4), adsorption isotherm parameters in terms of \( n, W_0, E \) of the assorted pairs are estimated and their numerical values are furnished in Table 2.5.

Experiment results show that the numerical value of \( W_0 \) using less purity ethanol is slightly higher than that of high purity ethanol (Table 2.4 and Table 2.5). However, there is chance of non-condensable gases present in the less purity ethanol. So, this study focused to use only the high purity ethanol for adsorption cooling/heat pump application.
Fig. 2.7(a): Linear fitting of D-A equation for parent Maxsorb III/ethanol (95%) pair.

Figures 2.8(a), (b) and (c) demonstrate a good agreement between the measured value and the predicted value using the theoretical (D-A) adsorption isotherm model. It can also be seen from Figs. 2.8(a), (b) and (c) that, the adsorption capacity of H₂ treated Maxsorb III is slightly higher than that of Maxsorb III whilst the KOH-H₂ treated Maxsorb III possesses the lowest adsorption capacity. This order agrees with the order of the micropores volume of the studied adsorbents as shown in Table 2.1.
Adsorption equilibrium of activated carbon/ethanol pairs

**Fig. 2.8(a):** Adsorption isotherms of parent Maxsorb III/ethanol (95%) pair.

**Fig. 2.8(b):** Adsorption isotherms of KOH-H$_2$ treated Maxsorb III/ethanol (95%) pair.
Fig. 2.8(c): Adsorption isotherms of H$_2$ treated Maxsorb III/ethanol (95%) pair.

Table 2.5 Adsorption parameters of assorted adsorbent/refrigerant (ethanol 95%) pairs.

<table>
<thead>
<tr>
<th>Adsorbent/refrigerant pair</th>
<th>$W_0$ [kg/kg]</th>
<th>$n$ [-]</th>
<th>$E$ [kJ/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maxsorb III</td>
<td>1.24</td>
<td>1.9</td>
<td>114.28</td>
</tr>
<tr>
<td>KOH-H$_2$ treated Maxsorb III</td>
<td>1.09</td>
<td>1.6</td>
<td>115.7</td>
</tr>
<tr>
<td>H$_2$ treated Maxsorb III</td>
<td>1.25</td>
<td>1.9</td>
<td>103.8</td>
</tr>
</tbody>
</table>
2.5 Nomenclature

\begin{align*}
A & \quad \text{adsorption potential, kJ/kmol} \\
E & \quad \text{adsorption characteristic parameter, J/mol} \\
n & \quad \text{exponent fitting parameter used in the D-A equation} \\
P & \quad \text{equilibrium pressure of refrigerant, kPa} \\
P_S & \quad \text{saturation pressure of refrigerant at adsorption temperature, kPa} \\
Q_s & \quad \text{isosteric heat of adsorption, kJ/kg} \\
R & \quad \text{universal gas constant, J/mol K} \\
T & \quad \text{temperature, K} \\
W & \quad \text{equilibrium uptake, kg/kg} \\
W_0 & \quad \text{maximum adsorption capacity, kg/kg}
\end{align*}

2.6 Conclusion

Adsorption isotherms of parent Maxsorb III/ethanol, KOH-H\(_2\) treated Maxsorb III/ethanol and H\(_2\) treated Maxsorb III/ethanol pairs have been experimentally measured using magnetic suspension adsorption measurement unit. Experiments have been conducted within evaporation temperature ranges from -14 to 77 °C and adsorption temperature between 20 and 80 °C. The data have been correlated using the Dubinin-Radushkevich and Dubinin-Astakhov isotherm model. Experimental results show that, adsorption capacity of H\(_2\) treated Maxsorb III/ethanol is slightly higher than that of Maxsorb III/ethanol pair whilst the KOH-H\(_2\) treated Maxsorb III possesses the lowest adsorption capacity. However, KOH-H\(_2\) treated Maxsorb III/ethanol pair shows significantly higher adsorption kinetics compared to the other pairs which is described in Chapter 3.
2.7 References


11. El-Sharkawy, I. I., Uddin, K., Miyazaki, T., Saha, B. B., Koyama, S., Miyawaki, J., Yoon,


Chapter 3

Adsorption Kinetics of Ethanol onto Parent and Surface Treated Activated Carbon Powder

In this chapter, both experimental and theoretical studies have been conducted on the adsorption kinetics of ethanol onto parent and surface treated activated carbons, namely parent Maxsorb III, H₂ treated Maxsorb III and KOH-H₂ treated Maxsorb III. Experiments have been conducted across assorted adsorption temperatures ranges from 30 to 70 ºC which are useful for the operation of adsorption chillers. The kinetic data for each isotherm is measured accurately using magnetic suspension balance adsorption measurement unit from which the diffusion time constant and consequently, the overall mass transfer coefficient could be evaluated. The proposed concentration profile removes the restrictions between the overall mass transfer coefficient and the diffusion time constant. Guided by the experimental measurements, the surface diffusion is also estimated and is found that it follows the classical Arrhenius law within the experimental temperature range.

3.1 Introduction

Design of efficient adsorption cooling systems requires accurate information about adsorption characteristics of adsorbent/refrigerant pairs. Among these characteristics, adsorption isotherms and kinetics play essential rules on the system design and performance optimization. Extensive research efforts have been conducted to investigate adsorption isotherms of various adsorbent/refrigerant pairs which are explained in Chapter 2. Adsorption kinetics has also been addressed by a notable number of researchers, following
are some representative examples: Aristov et al. (2006a) measured adsorption kinetics of water vapor on loose grains of Fuji Davison RD silica gel using TG differential method. Experiments have conducted within a temperature range of 29 to 64 °C and a pressure range from 6.5 to 34 mbar. Adsorption kinetics of water onto composite material (CaCl₂ confined to mesoporous silica named SWS-1L) has also been investigated using a CAHN microbalance under isothermal conditions at constant pressure (Aristov et al. 2006b). Three different grain sizes of SWS-1L have been tested and results showed a remarkable enhancement in adsorption rate with the decrease in particle size. El-Sharkawy et al. (2006) investigated adsorption kinetics of activated carbon fiber/ethanol pair by gravimetric method using TGA (CAHN TG 2121) unit. The authors proposed a new concentration profile that removes the restrictions between the overall mass transfer coefficient and the diffusion time constant and the model has been validated experimentally. Adsorption kinetics of ammonia onto composite adsorbent material (BaCl₂ impregnated into a vermiculite matrix) has been investigated under isothermal conditions and in a laboratory scale system (Zhong et al. 2009). Veselovskaya et al. (2010) measured adsorption kinetics of the same pairs under conditions more close to the real conditions of adsorption chillers. The authors reported that this material can provide a COP as high as 0.54 ± 0.01 and SCP ranging from 300 to 680 W/kg using heat source temperatures between 80 and 90 °C. Dawoud and Aristov (2003) measured adsorption kinetics of water vapor sorption on mesoporous silica gel, alumina, microporous silica gel and two composites, namely SWS-1L and SWS-1A. These composite materials are formed by impregnating CaCl₂ into mesoporous silica gel and alumina, respectively. The authors reported that there is an increase of about two to three times in the differential water loading on the SWS-composites compared to the host materials. However, the kinetics of water sorption into the host matrices is faster than that into the studied two SWS-composites. Aristov (2012) discussed principles of creating database of adsorbents promising for adsorptive transformation of heat. The proposed database considered the main
Chapter 3

Adsorption kinetics

adsorbent properties and addresses the issues of their measurement and calculation. The study also presented a tentative list of promising adsorbent-adsorbate pairs. Other studies dealing with adsorption kinetics can be found elsewhere (El-Sharkawy, 2011; Rezk et al. 2012; Saha et al. 2006; Habib et al. 2010; Dawoud, 2013).

The present Chapter deals with experimental investigation of adsorption kinetics of ethanol onto three types of adsorbents namely: parent Maxsorb III, KOH-H$_2$ treated Maxsorb III and H$_2$ treated Maxsorb III. Experimental measurements have been conducted using a magnetic suspension balance. Experiments have been conducted across assorted adsorption temperature that is useful for the operation of adsorption chillers. The adsorption kinetics is correlated using the Fickian diffusion model.

3.2 Experimental

3.2.1 Materials

The adsorbents used in the present study are; (i) Parent Maxsorb III which is a highly porous activated carbon powder provided by Kansai Coke & Chemicals Co. Ltd., Japan (ii) KOH-H$_2$ surface treated Maxsorb III and (iii) H$_2$-surafce treated Maxsorb III. Activated carbon powders (ACPs) have been proven to be efficient adsorbents for adsorption cooling and heat pump application. However there is a lack of information about its adsorption behavior with polar molecules (e.g. ethanol) because ACPs usually possess nonpolar (or less polar) surfaces due to the high-temperature conditions of their manufacture. Accordingly, many researchers have been trying to introduce polar surface functional groups such as C=O, –OH, –COOH and –SO$_3$H onto carbon surfaces, by various methods. The surface treatment procedure of the samples used in this study has been described in reference (Kil et al. 2013).

Thermo-physical properties and elemental composition of assorted adsorbents are given in Table 2.1 (Chapter 2). It can be seen from Table 2.1 that, there is no significant change in
both surface area and average pore width. However, H₂-treated Maxsorb III possesses the highest micropore volume followed by parent Maxsorb III than KOH-H₂- treated Maxsorb III. As can also be seen from Table 2.1, oxygen contents increases significantly for KOH-H₂ treated Maxsorb III whilst H₂ treated Maxsorb III has the lowest oxygen content among assorted adsorbents which indicates the formation of surface functional group. Ethanol of 99.5 % purity supplied by Osaka Kishida Chemical Co., Ltd is used as adsorbate in the present study.

### 3.2.2 Particle Size Distribution

The particle size distribution is measured using a Laser Diffraction Particle Size Analyzer, SALD-2300, supplied by Shimadzu Corporation, Japan. Pictorial view of the apparatus is shown in Fig. 3.1(a). Particle size distribution is calculated using the light intensity distribution pattern of scattered light that is generated from sample particles when laser irradiates them. The adsorbent sample is mixed with distilled water in the dissipation bath of SALD-2300; it is then circulated through the flow cell in the measuring unit where it is irradiated with a laser beam. The SALD analyzer works based on Fraunhofer diffraction theory and Mie scattering theory. The Fraunhofer diffraction gives good approximation for large size particle (particle diameter > 10 λ (wavelength of light used)) and for small scattering angle ( < 30° ). Whereas the Mie scattering gives good approximation for the smaller size of particle (< 10 λ) and various scattering angle. Theoretical analysis of Fraunhofer diffraction and Mie scattering theory along with mean diameter calibration are presented in Appendix C. Figures 3.1(b)-(d) shows the particle size distributions of parent Maxsorb III, KOH-H₂ treated Maxsorb III and H₂ treated Maxsorb III. It can be seen that the percentage of cumulative normalized particle amount reaches a value of 50% at particle diameters of 105, 100 and 107 μm for parent Maxsorb III, KOH-H₂ treated Maxsorb III and H₂ treated Maxsorb III, respectively.
**Fig. 3.1(a):** A pictorial view of laser diffraction particle size analyzer.

**Fig. 3.1(b):** Particle size distribution for a sample of parent Maxsorb III.
Fig. 3.1(c): Particle size distribution for a sample of KOH-H$_2$ treated Maxsorb III.

Fig. 3.1(d): Particle size distribution for a sample of H$_2$ treated Maxsorb III.
3.2.3 Kinetics Data Collection

Adsorption kinetics of assorted adsorbent/refrigerant pairs are measured gravimetrically using magnetic suspension adsorption measurement unit (Rubotherm of type MSB-VG-S2) supplied by BEL Japan, Inc. Figure 2.2 (Chapter 2) shows the schematic diagram of the magnetic suspension adsorption measurement unit. Experimental procedure can be explained briefly as follows;

(1) Sample of 77 mg is placed uniformly to make a thin layer into the sample basket and placed into the measuring chamber,

(2) The sample is regenerated at 120 °C under vacuum conditions for about 4 hours,

(3) The measuring chamber is cooled down to adsorption temperature and connected to the evaporator chamber. Adsorption process is then carried out where adsorbent mass is recorded continuously until reaches to the adsorption equilibrium conditions.

(4) Evaporator is then disconnected from the adsorption chamber until reaching next measuring step.

(5) Steps (2) and (3) are repeated for other sets of adsorption temperatures.

It is worthy to mention that the instantaneous measurement of adsorbent sample is used to investigate adsorption kinetics.

3.2.4 Uncertainty Analysis

In the magnetic suspension adsorption measurement unit, the weight of sample has been measured directly by a magnetic suspension balance with resolution 1μg. The reproducibility (standard deviations) defined by the manufacturer is ±1μg even for the case of sample mass 5g. But in the present experiment, adsorbent mass is used only around 50-77 mg. The ethanol uptake is found little bit higher than the sample mass. So the relative error is always less than 0.001%. In this small error, the experimental error bars could not be visible in temporal history figures.
3.3 Mathematical Modeling

The Fickian diffusion model is used to estimate the adsorptions kinetics of assorted adsorbent/refrigerant pairs. Considering a spherical adsorbent particle shape, adsorption rate can be estimated using the diffusion equation (Eq. 3.1) as follows (Ruthven, 1984);

\[
\frac{\partial w}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 D \frac{\partial w}{\partial r} \right) \quad (3.1a)
\]

For constant diffusivity Eq.3.1a simplifies to

\[
\frac{\partial w}{\partial t} = D \left( \frac{\partial^2 w}{\partial r^2} + \frac{2}{r} \frac{\partial w}{\partial r} \right) \quad (3.1b)
\]

Where \( D \) is the intracrystalline diffusivity and \( w(r, t) \) is the adsorbed phase concentration. Even if the diffusivity is concentration dependent, the assumption of a constant diffusivity is still an acceptable approximation provided that the uptake curve is measured over a small differential change in adsorbed phase concentration. If the uptake of sorbate by the adsorbent is small relative to the total quantity of sorbate introduced into the system, the ambient sorbate concentration will remain essentially constant following the initial step change, and the appropriate initial and boundary conditions are;

\[
w(r, 0) = w_{in}, \quad w(r, t) = W, \quad \left( \frac{\partial w}{\partial r} \right) = 0
\]

The solution for the uptake curve in Eq.3.1 is then given by the familiar expression (Eq.3.2) below (Crank, 1956);

\[
F = \frac{w - w_m}{W - w_{in}} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left( -\frac{n^2 \pi^2 D t}{R_p^2} \right) \quad (3.2)
\]

where \( R_p \) is the particle radius of adsorbent.
The expression given in Eq. (3.2) converges rapidly in the long time region since the higher terms of the summation become vanishingly small (Ruthven, 1984). Equation (3.2) can be then simplified to Eq. (3.3) at longer times:

\[
F = \frac{w - w_{in}}{W - w_{in}} = 1 - \frac{6}{\pi^2} \exp\left(-\frac{\pi^2Dt}{R_p^2}\right)
\]  

(3.3)

The linearization of Eq. (3.3) gives;

\[
\ln(1 - F) = \ln\left(\frac{6}{\pi^2}\right) - \pi^2\left(\frac{D}{R_p^2}\right) t
\]  

(3.4)

The plots of \(\ln(1-F)\) versus time should be linear with slope \(-\pi^2D/R_p^2\) and intercept \(\ln\left(\frac{6}{\pi^2}\right)\). Such plot provides a simple method of both checking the conformity and experimental uptake curve with the diffusion equation and determining the diffusion time constant \((D/R_p^2)\) (Ruthven, 1984, 1992; Rutherford and Coons, 2003, 2004).

### 3.4 Data Analysis

Temporal histories of adsorption uptake and pressure of parent Maxsorb III/ethanol pair for adsorption temperatures of 30 and 70 °C are shown in Figs. 3.2(a) and 3.2(b), respectively. At each adsorption step, adsorption uptake increases continuously until reaches the equilibrium condition corresponding to adsorption temperature and evaporator pressure. Similar plots of adsorption uptake and pressure versus time at adsorption temperature of 30 °C for both KOH-H\(_2\) treated Maxsorb III/ethanol and H\(_2\)-treated Maxsorb III/ethanol pairs are depicted in Figs. 3.3 and 3.4, respectively.
Chapter 3

Adsorption kinetics

Fig. 3.2(a): Temporal histories of adsorption uptake and pressure of Maxsorb III/ethanol pair at adsorption temperature 30°C.

Fig. 3.2(b): Temporal histories of adsorption uptake and pressure of Maxsorb III/ethanol pair at adsorption temperature 70°C.
**Fig. 3.3:** Temporal histories of adsorption uptake and pressure of KOH-H₂-treated Maxsorb III/ethanol pair at adsorption temperature 30°C.

**Fig. 3.4:** Temporal histories of adsorption uptake and pressure of H₂-treated Maxsorb III/ethanol pair at adsorption temperature 30°C.
Figures 3.5(a) and (b) show plots of $\ln(1-F)$ versus time for parent Maxsorb III/ethanol pair at adsorption temperatures of 30 and 70 °C and certain evaporation pressures. It can be seen that the diffusional time constant can be estimated with high accuracy. It is also worth mentioning that, evaluation of $(D/R_p^2)$ using this technique avoids the uncertainties in adsorption uptake measurements in the early stage of adsorption. Moreover, this technique helps to overcome the effects of generation of heat of adsorption at early stage of adsorption.

The same plots for KOH-H$_2$ treated Maxsorb III/ethanol and H$_2$ treated Maxsorb III/ethanol pairs at 30 °C adsorption temperature are shown in Fig. 3.6 and Fig. 3.7, respectively. Experimental fractional uptake and that predicted using the Fickian diffusion model for parent Maxsorb III/ethanol, KOH-H$_2$ treated Maxsorb III/ethanol and H$_2$ treated Maxsorb III/ethanol pairs are shown in Figs. 3.8(a)-(c).

Diffusion time constant at each pressure step for parent Maxsorb III/ethanol, KOH-H$_2$ treated Maxsorb III/ethanol and H$_2$ treated Maxsorb III/ethanol pairs are presented, respectively, in Tables 3.1, 3.2 and 3.3. It can be seen that the diffusion time constant of KOH-H$_2$ treated Maxsorb III/ethanol pair is higher than that of the other two studied pairs which leads to a faster adsorption kinetics. This can be explained as follows, the polar ethanol molecules is quickly attached and adsorbed by the functionalities nearby the surface through hydrogen bonds, which causes faster adsorption rate. Figure 3.9 shows plots of diffusion time constant versus equilibrium pressure for the assorted pairs at adsorption temperature of 50 °C. It can be seen that the diffusion time constant of the studied pairs is high at the low equilibrium pressure. However, it decreases to reach a minimal value at pressure around 3 kPa and then slightly increases with relatively higher pressures. The same trend is also observed by some other researchers for other adsorbent/refrigerant pairs (Aristov et al. 2006b).

The average values of diffusion adsorption kinetics at each temperature is calculated and a
plot of $\ln(D/R_p^2)$ versus the inverse of adsorption temperature $(1/T)$ is shown in Fig. 3.10 for all three studied pairs. It can be seen from Fig. 3.10 that the relationship between $\ln(D/R_p^2)$ and $(1/T)$ follows the usual trend of classical Arrhenius equation (Eq. 3.5).

$$D = D_0 \exp \left( \frac{-E_a}{R_g T} \right)$$  \hspace{1cm} (3.5)

Dividing both sides of Eq. (3.5) by $R_p^2$, the linearization of this equation gives;

$$\ln \left( \frac{D}{R_p^2} \right) = -\ln \left( \frac{D_0}{R_p^2} \right) - \left( \frac{E_a}{R_g} \right) \left( \frac{1}{T} \right)$$  \hspace{1cm} (3.6)

Numerical values of the pre-exponential constant ($D_0/R_p^2$) and activation energy ($E_a$) of assorted pairs are furnished in Table 3.4. It can be observed from Table 3.4 that the KOH-H$_2$ treated Maxsorb III/ethanol pair has the highest activation energy among the three studied pairs. This is might be due to the hydrogen bonds that formed between polar ethanol molecules and the functionalities nearby the adsorbent surface. It can be seen from Figs. 3.1(b)-(d) that parent Maxsorb III, KOH-H$_2$ treated and H$_2$ treated Maxsorb III have a wide range of particle size distributions. The large particle size might control adsorption kinetics at the last stage of adsorption time where the linear tail on Figs. 3.5(a)-3.7 is observed. Therefore, using the average value of the relatively larger size particles to estimate the numerical values of $D_0$ of the assorted pairs might be a justified assumption. A detailed study of adsorption kinetics using a narrow range of particle size will be considered in another study.
Fig. 3.5(a): Plot of $\ln(1-F)$ versus adsorption time for Maxsorb III/ethanol pair at 30°C adsorption temperature and evaporator pressure of 3.34 kPa.

Fig. 3.5(b): Plot of $\ln(1-F)$ versus adsorption time for Maxsorb III/ethanol pair at 70°C adsorption temperature and evaporator pressure of 11.26 kPa.
**Fig. 3.6:** Plot of \( \ln(1-F) \) versus adsorption time for KOH-H\(_2\)-treated Maxsorb III/ethanol pair at 30°C adsorption temperature and evaporator pressure of 2.27 kPa.

**Fig. 3.7:** Plot of \( \ln(1-F) \) versus adsorption time for H\(_2\)-treated Maxsorb III/ethanol pair at 30°C adsorption temperature and evaporator pressure of 3.36 kPa.
Fig. 3.8(a): Fractional uptake verses time for Maxsorb III/ethanol pair at adsorption temperature 30°C, 50°C and 70°C (symbols present experiments and lines present FD model).

Fig. 3.8(b): Fractional uptake verses time for KOH-H₂ treated Maxsorb III/ethanol pair at adsorption temperature 30°C, 50°C and 70°C (symbols present experiments and lines present FD model).
Fig. 3.8(c): Fractional uptake versus time for H\textsubscript{2}-treated Maxsorb III/ethanol pair at adsorption temperature 30\degree C, 50\degree C and 70\degree C (symbols present experiments and lines present FD model).

Fig. 3.9: Plot of diffusion time constant versus equilibrium pressure for assorted pairs at 50 \degree C (error bars present 5\%).
Fig. 3.10: Arrhenius plot of the assorted pairs.
Table 3.1 Kinetic measurements of parent Maxsorb III/ethanol pair.

<table>
<thead>
<tr>
<th>$T_{\text{ads}}$, [°C]</th>
<th>Equilibrium Pressure, [kPa]</th>
<th>$D/R_p^2$, [s$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>30.2</td>
<td>2.3</td>
<td>$2.54 \times 10^{-4}$</td>
</tr>
<tr>
<td>3.3</td>
<td></td>
<td>$2.84 \times 10^{-4}$</td>
</tr>
<tr>
<td>39.9</td>
<td>1.8</td>
<td>$2.94 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>2.8</td>
<td>$2.43 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>3.8</td>
<td>$2.94 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>5.6</td>
<td>$3.45 \times 10^{-4}$</td>
</tr>
<tr>
<td>49.7</td>
<td>1.6</td>
<td>$4.06 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>3.2</td>
<td>$2.74 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>4.6</td>
<td>$3.14 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>6.3</td>
<td>$3.35 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>8.0</td>
<td>$3.45 \times 10^{-4}$</td>
</tr>
<tr>
<td>60.0</td>
<td>4.9</td>
<td>$4.06 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>$3.55 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>$3.8 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>12.6</td>
<td>$4.06 \times 10^{-4}$</td>
</tr>
<tr>
<td>69.9</td>
<td>8.0</td>
<td>$4.67 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>11.3</td>
<td>$4.26 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>15.7</td>
<td>$4.06 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>19.4</td>
<td>$4.06 \times 10^{-4}$</td>
</tr>
</tbody>
</table>
Table 3.2 Kinetic measurements of KOH-H₂ treated Maxsorb III/ethanol pair.

<table>
<thead>
<tr>
<th>( T_{ads} ) [^\circ C]</th>
<th>Equilibrium Pressure, ([kPa])</th>
<th>( D/R_p^2 ) [[s^{-1}]]</th>
</tr>
</thead>
<tbody>
<tr>
<td>30.0</td>
<td>2.3</td>
<td>2.43 \times 10^{-4}</td>
</tr>
<tr>
<td></td>
<td>3.3</td>
<td>3.14 \times 10^{-4}</td>
</tr>
<tr>
<td>49.9</td>
<td>1.6</td>
<td>4.26 \times 10^{-4}</td>
</tr>
<tr>
<td></td>
<td>3.1</td>
<td>3.35 \times 10^{-4}</td>
</tr>
<tr>
<td></td>
<td>4.6</td>
<td>3.35 \times 10^{-4}</td>
</tr>
<tr>
<td></td>
<td>6.3</td>
<td>3.85 \times 10^{-4}</td>
</tr>
<tr>
<td>70.0</td>
<td>3.8</td>
<td>6.09 \times 10^{-4}</td>
</tr>
<tr>
<td></td>
<td>8.1</td>
<td>5.17 \times 10^{-4}</td>
</tr>
<tr>
<td></td>
<td>11.5</td>
<td>4.67 \times 10^{-4}</td>
</tr>
<tr>
<td></td>
<td>16.0</td>
<td>4.67 \times 10^{-4}</td>
</tr>
</tbody>
</table>
Table 3.3 Kinetic measurements of H$_2$-treated Maxsorb III/ethanol pair.

<table>
<thead>
<tr>
<th>$T_{ads}$ [°C]</th>
<th>Equilibrium Pressure, kPa</th>
<th>$D/R_p^2$ [s$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>30.0</td>
<td>2.3</td>
<td>$2.03 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>3.4</td>
<td>$2.54 \times 10^{-4}$</td>
</tr>
<tr>
<td>50.0</td>
<td>1.6</td>
<td>$3.04 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>3.1</td>
<td>$2.43 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>4.6</td>
<td>$2.43 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>6.3</td>
<td>$2.43 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>7.9</td>
<td>$2.84 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>9.4</td>
<td>$3.04 \times 10^{-4}$</td>
</tr>
<tr>
<td>69.2</td>
<td>3.8</td>
<td>$3.55 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>7.9</td>
<td>$3.55 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>11.2</td>
<td>$3.14 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>15.5</td>
<td>$3.04 \times 10^{-4}$</td>
</tr>
</tbody>
</table>
Table 3.4 Parameters of Arrhenius equation of studied adsorbent/refrigerant pairs.

<table>
<thead>
<tr>
<th>Adsorbent/refrigerant pair</th>
<th>$D_{so}/R_p^2$ [s$^{-1}$]</th>
<th>$E_a$ [kJ kg$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parent Maxsorb III/ethanol</td>
<td>1.61x10$^{-2}$</td>
<td>234.5</td>
</tr>
<tr>
<td>KOH-H$_2$ treated Maxsorb III/ethanol</td>
<td>5.32x10$^{-2}$</td>
<td>300</td>
</tr>
<tr>
<td>H$_2$ treated Maxsorb III/ethanol</td>
<td>4.53x10$^{-3}$</td>
<td>171</td>
</tr>
</tbody>
</table>

3.5 Nomenclature

$D$  diffusivity (m$^2$ s$^{-1}$)  
$D_{so}$  pre-exponential constant (m$^2$ s$^{-1}$)  
$E_a$  activation energy (kJ kg$^{-1}$)  
$F$  fractional uptake (-)  
$R_g$  gas constant (kJ kg$^{-1}$ K$^{-1}$)  
$R_p$  particle radius (µm)  
$T$  temperature (K)  
$t$  time (s)  
$W$  equilibrium adsorption uptake (kg kg$^{-1}$)  
$w$  instantaneous adsorption uptake (kg kg$^{-1}$)  
$w_{in}$  initial uptake (kg kg$^{-1}$)
3.5 Conclusion

Adsorption kinetics of parent Maxsorb III/ethanol, KOH-H₂ treated Maxsorb III/ethanol and H₂ treated Maxsorb III pairs have been measured experimentally using a magnetic suspension adsorption measurement unit. The Dubinin-Astakhov (D-A) and the Dubinin-Radushkevich (D-R) equations are used to fit the equilibrium uptake (see Chapter 2) whilst adsorption kinetics is presented by the Fickian diffusion model. It is found that, the Fickian diffusion model can fairly present adsorption kinetics of assorted adsorbent/refrigerant pairs. Adsorption kinetics of ethanol onto KOH-H₂ treated Maxsorb III is faster than other two studied adsorbents. Data extracted from the present study are essential in designing high performance thermally powered adsorption chiller and heat pump systems.

3.6 References


Chapter 4

Isosteric Heat of Adsorption

Extracted from Adsorption Equilibrium Data

The isosteric heat of adsorption is a specific property of an adsorbent and adsorbate combination. It is defined as the difference between the activation energy for adsorption and desorption which also represent the strength of adsorbate-adsorbent interaction (Szekely et al. 1976). It is a major contributor to the heating inventories of adsorption refrigeration and gas storage systems. Adsorption equilibrium data has been presented in Chapter 2 using Dubinin-Radushkevich (D-A) and Dubinin-Astakhov (D-A) equation. In the present chapter, a correlation is proposed to describe the concentration dependence isosteric heat of adsorption which is derived from the D-A equation along with Van’t Hoff equation.

4.1 Introduction

In the design of systems involving adsorption of a gaseous medium by a solid sorbent, the heat of adsorption is a property to be considered (Hartzog and Sircar, 1995). In an adsorption refrigerator, when the working fluid is adsorbed by a solid adsorbent in a thermal compressor, the heat of adsorption has to be removed using heat sink. Similarly, when the gas is desorbed at a higher temperature and pressure there is a need to add the heat of adsorption. Thus, one has to consider the variation of the heat of adsorption as a function of loading, which in turn depends on the pressure and temperature at which adsorption/desorption occurs (Prasad et al. 1999, Chua et al. 2003).
Isosteric heat of adsorption ($Q_{st}$) is traditionally expressed as a function of concentration as its dependence on temperature is relatively weak (Prasad et al. 1999, Akkimaradi et al. 2001). Quantification of $Q_{st}$ is very important for kinetic studies of adsorption process because the heat released upon adsorption is partially adsorbed by the adsorbent which causes a rise in adsorbent temperature and thus influences the rate of adsorption (Agnihotri et al. 2005). The isosteric heat of adsorption is hard to be measured experimentally. Differences between the various types of heats are of the order of $RT$, which is small or negligible for chemisorption but as much as 10% of the heat of physisorption. Thus for physisorption it is important to specify exactly which type of heat is being measured and how it is measured (Dunne et al. 1996).

The isosteric heat is also essential parameter for designing the adsorption cooling and heat pump systems precisely. This chapter presents the measurement technique of isosteric heat of adsorption of Maxsorb III/ethanol, KOH-H$_2$ treated Maxsorb III/ethanol and H$_2$ treated Maxsorb III/ethanol pairs using Clausius-Clapeyron equation and proposed correlation.

### 4.2 Clausius-Clapeyron Equation

The heat release during the adsorption process due to the change in energy level of the adsorbate molecules is known as the heat of adsorption and the Clausius - Clapeyron equation has long been used for evaluation of heat of adsorption from the adsorption uptake data assuming ideal gas-phase behavior of the adsorbate molecules in their gaseous phase (Al-Muhtaseb and Ritter 1999).

$$\frac{-Q_{st(CC)}}{R} \frac{M}{T} = \frac{\partial \ln P}{\partial \left( \frac{1}{T} \right)} \quad (4.1a)$$
For the present purpose, it is more useful to take advantages of logarithmic mathematics to write the Clausius - Clapeyron equation as follows

\[
\ln P = -\frac{Q_{st}(CC)}{RT} \frac{M}{C} + C \tag{4.1b}
\]

\(Q_{st}\) is the isosteric heat of adsorption [kJ/kg] which is a negative quantity because of exothermic adsorption process. \(R\) is the universal gas constant [kJ/kmol·K], \(M\) is molar constant [kg/kmol], \(P\) is the equilibrium pressure [kPa]. \(T\) is the adsorption temperature [K].

The standard procedure for evaluation of isosteric heat of adsorption is to plot the isosters on \(\ln P\ vs \frac{1}{T}\) plane. Normally, a constancy of slope is observed at temperatures well over the critical point of the adsorbate and it does not warrant bringing the \(Q_{st}\) in the temperature dependence.

### 4.2.1 Correlation Proposed for Isosteric Heat of Adsorption

Heats of adsorption published in the literature are often showing a big difference which means a dearth of theoretical formulation that could accurately represent the value in a wide range of uptake. There are some correlations to calculate the isosteric heat of adsorption.

Chakraborty et al. (2006) described a thermodynamic framework to derive an expression for isosteric heat of adsorption which is then verified with experimental data. El-Sharkawy et al. (2007) proposed a non-dimensional empirical correlation for isosteric heat of adsorption on carbon based adsorbents. Shen et al. (2000) presented a comparative study among some experimental techniques for measuring the isosteric heat of adsorption. Hill (1949) defined various types of heats of adsorption corresponding to different experimental procedures.

The wide range of isosteric heat for adsorbate/adsorbent pairs are dependent on the selected isotherm equation used in modeling the adsorbed phase. In this study a simplified method for
isosteric heat of adoption is proposed using the D-A isotherm model along with Van’t Hoff equation (Do, D.D. 1998). Starting with the D-A equation, isosteric heat of adsorption equation can be derived as follows;

\[
\ln \left( \frac{W}{W_0} \right) = - \left( \frac{RT}{E} \ln \left( \frac{P}{P_s} \right) \right)^n
\]

(4.2)

Rearranging Eq. (4.2), one can write;

\[
\ln \left( \frac{P}{P_s} \right) = \frac{E}{RT} \left\{ - \ln \left( \frac{W}{W_0} \right) \right\}^{1/n}
\]

(4.3)

Therefore;

\[
P = P_s \exp \left[ \frac{E}{RT} \left\{ - \ln \left( \frac{W}{W_0} \right) \right\}^{1/n} \right]
\]

(4.4)

or \( \ln P = \ln(P_s) - \frac{E}{RT} \left\{ - \ln \left( \frac{W}{W_0} \right) \right\}^{1/n} \)

(4.5)

Differentiating equation (8) with respect to 1/T, one can get

\[
\frac{\partial \ln P}{\partial T} = \frac{\partial}{\partial T} \ln(P_s) + \frac{E}{RT^2} \left\{ - \ln \left( \frac{W}{W_0} \right) \right\}^{1/n}
\]

(4.6)

Substituting for isosteric heat of adsorption which is defined by Van’t Hoff equation

\[
- \frac{Q_{st}}{RT^2} = \frac{\partial}{\partial T} \ln(P_s) + \frac{E}{RT^2} \left\{ - \ln \left( \frac{W}{W_0} \right) \right\}^{1/n}
\]

(4.7)

\[
- Q_{st} = RT^2 \frac{\partial}{\partial T} \ln(P_s) + E \left\{ - \ln \left( \frac{W}{W_0} \right) \right\}^{1/n}
\]

(4.8)

The \( Q_{st} \) estimated using Eq. (4.8) is in (kJ/kmol), however, in this study \( Q_{st} \) is presented in (kJ/kg) using the molecular weight of the refrigerant.
4.3 Results and Discussion

The isosteric heat of adsorption is calculated using the Clausius-Clapeyron equation by means of equilibrium adsorption data which are shown in Figs. 4.1(a), (b) and (c). Data presented in these figures are generated from direct pressure and temperature measurements during adsorption. All experimental data yielded straight lines with regression coefficients >99.9%. The slopes of the line yield the value of \(-Q_{st}/R\). The average values of isosteric heats of adsorption for Maxsorb III, KOH-H\(_2\) treated Maxsorb III and H\(_2\) treated Maxsorb III with ethanol pairs are found to be 1070, 1065 and 1104 kJ/kg, respectively.

Fig. 4.1(a): Plot of \(\ln(P)\) vs. \(1/T\) at different uptake range for parent Maxsorb III/ethanol pair.
Fig. 4.1(b): Plot of \( \ln(P) \) vs \( 1/T \) at different uptake range for KOH-H\(_2\) treated Maxsorb III/ethanol pair.

Fig. 4.1(c): Plot of \( \ln(P) \) vs \( 1/T \) at different uptake range for H\(_2\) treated Maxsorb III/ethanol pair.
Figures 4.2(a), (b) and (c) show the concentration dependance of isosteric heat of adsorption at constant temperature using Eq. (4.8) for parent Maxsrob III/ethanol, KOH-H$_2$ treated Maxsorb III/ethanol and H$_2$-treated Maxsorb III/ethanol pair, respectively. It can be seen from Figures 4.2(a), (b) and (c) that the isosteric heat of adsorption decreases with increasing adsorbate uptake which reveals the heterogenous adsorbents characteristics with a wide range of gas-solid interaction energies (Dunne et al.1996). As the molecules first penetrate into the narrower micropores, which results in a stronger interaction between adsorbate and assorted adsorbents. This implies a higher value of isosteric heat of adsorption at the beginning of the adsorption. After that molecules are gradually accumulated in larger pores, which means the adsorption affinity becomes weaker in higher uptake region. Therefore the graph shows a monotonic decrease of isosteric heat of adsorption as a function of loading and finally the value approaches towards the latent heat of evaporation ($h_{fg}$) of the refrigerant.

As can be noticed from Figs. 4.2(a), (b) and (c) that the isosteric heat using Clausius-Clapeyron equation gives constant value, however, the proposed correlation show the declining trend of isosteric heat with higher loading. The proposed correlation also validated with experimental data. It is anticipated, for accurate system analysis, one should use the proposed correlation.
Fig. 4.2(a): Isosteric heat of adsorption of ethanol onto parent Maxsorb III/ethanol pair.

Fig. 4.2(b): Isosteric heat of adsorption of ethanol onto KOH-H₂ treated Maxsorb III/ethanol pair.
Chapter 4  

Isosteric heat of adsorption

The isosteric heat of adsorption for parent and surface treated Maxsorb III/ethanol (95%) has also been presented in this Chapter. Figures 4.3(a) and (b) follow the similar technique to determine the isosteric heat of KOH-H₂-Maxsorb III and H₂-treated Maxsorb III with ethanol (95%) pair, respectively. The concentration dependence of isosteric heat for the similar pairs also presented in Figures 4.4(a) and (b) respectively. The average values of isosteric heats of adsorption for Maxsorb III, KOH-H₂ treated Maxsorb III and H₂ treated Maxsorb III with less pure ethanol (95%) pairs are found to be 1002, 1063 and 926 kJ/kg, respectively.

It can be seen from the following figures that the less purity ethanol also follows almost identical trend like high purity ethanol. But this study focused to use high purity ethanol for adsorption cooling and heat pump system.
Fig. 4.3(a): Plot of $\ln(P)$ vs $1/T$ at different uptake range for KOH-H$_2$ treated Maxsorb III/ethanol (95%) pair.

Fig. 4.3(b): Plot of $\ln(P)$ vs $1/T$ at different uptake range for H$_2$ treated Maxsorb III/ethanol (95%) pair.
**Fig. 4.4(a)**: Isosteric heat of adsorption of ethanol onto Maxsorb III/ethanol (95%) pair.

**Fig. 4.4(b)**: Isosteric heat of adsorption of ethanol onto KOH-H$_2$ treated Maxsorb III/ethanol (95%) pair.
Figure 4.5 shows the percentage of deviation of isosteric heat values from its average value for Maxsorb III/ethanol pair. The isosteric heat data are calculated using Eq. (4.8) for adsorption temperatures of 30, 50 and 70 °C. The deviation is found to be within ±10% over the whole range of fractional uptake. It can be noted here that one should consider the isosteric heat data as a function of fractional uptake for evaluating the adsorption system performance precisely.
4.4 Nomenclature

\( A \)  adsorption potential, kJ/kmol

\( E \)  adsorption characteristic parameter, kJ/kmol

\( n \)  exponent fitting parameter used in the D-A equation

\( P \)  equilibrium pressure of refrigerant, kPa

\( P_s \)  saturation pressure of refrigerant at adsorption temperature, kPa

\( Q_{st} \)  isosteric heat of adsorption, kJ/kg.

\( R \)  universal gas constant, kJ/mol·K

\( T \)  temperature, K

\( W \)  equilibrium uptake, kg/kg

\( W_0 \)  maximum adsorption capacity, kg/kg

4.5 Conclusion

The isosteric heats of adsorption of assorted adsorbent/refrigerant pairs are evaluated from the experiment data using Clausius-Clapeyron equations, which appears to be well interpreted from the derivation of the D-A equations. It is found that, the heats of adsorption following Clausius-Clapeyron equation of ethanol onto parent Maxsorb III, KOH-H\(_2\) treated Maxsorb III and H\(_2\) treated Maxsorb III is found to be 1070, 1065 and 1104 kJ/kg, respectively. The concentration dependence isosteric heat of adsorption using the proposed correlation is also presented for the assorted adsorbent/refrigerant pairs.
Chapter 4  Isosteric heat of adsorption

4.6 References


10. Hill, T. L., 1949, Statistical mechanics of adsorption. V. Thermodynamics and heat of
Chapter 4  Isosteric heat of adsorption


Chapter 5

Specific Heat Capacity of Adsorbents

The aim of this Chapter is experimentally investigate the specific heat capacity of parent and surface treated Maxsorb III along with some other adsorbent materials commonly used in adsorption systems. The measurements have been conducted between temperature range of 30 and 150 °C employing a heat flux type differential scanning calorimeter (DSC). This temperature range is suitable for the design of adsorption cooling and heat pump systems.

5.1 Introduction

Specific heat capacity \((c_p)\) is a material property describing the energy required to induce a certain change in the temperature of a unit mass of the material. It is the basic data in chemistry and engineering, from which many other thermodynamic parameters such as enthalpy and entropy can be calculated. It significantly affects the system performance of adsorption cooling system in which a porous material is used as adsorbent. The amount of heat transferred in this process is proportional to the temperature difference between the objects and the heat capacity of the object. Many researchers used the fixed value of specific heat of adsorbent when simulating the adsorption processes to investigate the system performance but actually the specific heat capacity is a function of temperature. For example, Boelmant et al. (1995) used the specific heat capacity of silica gel is 924 J/kg·K which is found in Chihara et al. (1983), to investigate the COP of adsorption refrigeration cycle using silica gel/water pair. Jribi et al. (2014) used the specific heat capacity of Maxsorb III is 1375 J/kg·K to simulate of an activated carbon/CO\(_2\) based four bed adsorption cooling system. Askalani et al (2013) used specific heat capacity of granular activated carbon is 930 J/kg·K
Chapter 5

Specific heat capacity of adsorbents

during performance evaluation of adsorption cooling system employing granular activated carbon/R134a pair. Chan et al. (2012) used the specific heat capacity of zeolite 13X/CaCl₂ composite is 836 J/kg·K to predict the performance of the system. There have been no details analysis of specific heat capacity of currently used adsorbent material is available in open literature.

The specific heat capacity of a material can be calculated by using different methods. Jian et al. (2011) determined the heat capacities and thermodynamic properties of MOFs materials using temperature modulated differential scanning calorimetry (TMDSC). Dachs et al. (2011) experimentally studied heat capacity of mg-sized powder samples at low temperature using quantum design physical properties measurement system (PPMS) and proposed a factor to adjust the data with DSC. Czerniecka et al. (2013) measured the heat capacities of poly (3-hydroxybutyrate) using PPMS, TDMS and DSC over the temperature range of 1 to 460 K. Wang et al. (2005) measured the heat capacities and thermodynamic properties of 2-(Chloromethylthio) benzothiazole by an adiabatic calorimeter in the temperature range between 80 and 250 K and showed the deviation of measurement data with standard material α-Al₂O₃. Gӧbel et al. (2013) explained a laser flash calorimetry (LFC) method to measure specific heat capacity of BK7 glass at low temperature and the experimental calibration was done by using the standard specimen α-Al₂O₃. Cao et al. (1997) investigated the methodology of heat capacity determination using MDSC. Authors used indium as a sample and suggested that multiple run of the experiment is necessary to precisely measure the specific heat.

Differential scanning calorimetry is a powerful technique to measure accurately the specific heat capacity of milligram level sample. It measures the required differential heat energy to keep the sample and reference channels at a same temperature. Watson et al. (1964) described the advantages of DSC over the conventional thermal analysis system. Ramakumar et al. (2001) and Saxena et al. (2002) investigated the procedures for measuring heat capacity of
disk type and powder type samples using DSC and analyzed the effect of sample mass and rate of heating. Danley (2003) developed a new measuring technique for using DSC which reduced instrument baseline defects resulting from imbalances using comprehensive heat flow measurement equations. Heat capacities of \( \text{RCO}_3 \) were calculated by Patil et al. (2007) using DSC in the temperature range 450 to 780 K to know the nature of phase transitions of the compounds. Kousksou et al. (2011) found the effect of heating rate and sample geometry on the apparent specific heat capacity measurement using DSC. Mu & Walton (2011) studied the heat capacity and thermal stability of MOF materials using thermal gravimetric analyzer coupled with DSC technique in the temperature range from 0 to 200 ºC. However, no heat capacity data are available in open literature for parent and surface treated Maxsorb III and many other recently developed adsorbents. In the present study, a heat flux type differential scanning calorimeter is used to investigate the specific heat capacity of parent Maxsorb III, \( \text{H}_2 \) treated Maxsorb III and \( \text{KOH-H}_2 \) treated Maxsorb III along with other commonly used adsorbents.

5.2 Experimental

5.2.1 Materials

Several types of adsorbent materials are studied in this Chapter, such as parent and surface treated Maxsorb III, three types of silica gel, two types of expanded graphite and two types of metal organic framework (MOF). Some available information about the samples is given in Table 5.1.
### Table 5.1 Adsorbent Materials used in the experiment

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Sample type</th>
<th>Supplier/ Source</th>
<th>$D_{50}$ ($\mu$m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maxsorb III</td>
<td>Carbon based powder</td>
<td>Kansai Coke &amp; Chemicals Co. Ltd., Japan</td>
<td>105</td>
</tr>
<tr>
<td>H$_2$ treated Maxsorb III</td>
<td>Surface treated</td>
<td>Materials Chemistry &amp; Eng. Kyushu University</td>
<td>107</td>
</tr>
<tr>
<td>KOH-H$_2$ treated Maxsorb III</td>
<td>Surface treated</td>
<td>Materials Chemistry &amp; Eng. Kyushu University</td>
<td>100</td>
</tr>
<tr>
<td>MSC-30</td>
<td>Carbon based powder</td>
<td>Kansai Coke &amp; Chemicals Co. Ltd., Japan</td>
<td>77</td>
</tr>
<tr>
<td>MSC-30</td>
<td>Carbon based powder</td>
<td>Kansai Coke &amp; Chemicals Co. Ltd., Japan</td>
<td>12.9</td>
</tr>
<tr>
<td>MSA-20</td>
<td>Carbon based powder</td>
<td>Kansai Coke &amp; Chemicals Co. Ltd., Japan</td>
<td>5.4</td>
</tr>
<tr>
<td>MIL-101Cr</td>
<td>MOF powder</td>
<td>Fraunhofer Lab. Germany</td>
<td>100</td>
</tr>
<tr>
<td>Kupfer-BTC</td>
<td>MOF powder</td>
<td>Fraunhofer Lab. Germany</td>
<td></td>
</tr>
<tr>
<td>RD Silica gel</td>
<td>Spherical</td>
<td>Fuji Silysia Chem. Ltd. Japan</td>
<td>~2000</td>
</tr>
<tr>
<td>RD silica gel</td>
<td>Granular</td>
<td></td>
<td>~900</td>
</tr>
<tr>
<td>RD silica gel</td>
<td>Powder</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Expanded graphite</td>
<td>Powder</td>
<td>Ito Graphite Co., Ltd., Japan</td>
<td>6.58</td>
</tr>
<tr>
<td>Expanded graphite</td>
<td>Powder</td>
<td>Ito Graphite Co., Ltd., Japan</td>
<td>13.37</td>
</tr>
</tbody>
</table>
5.2.2 Experimental Apparatus

The pictorial view of the experiment apparatus are shown in Fig. 5.1. It is a heat flux type Differential Scanning Calorimeter of type DSC-60 coupled with thermal analysis workstation, provided by Shimadzu Corporation, Japan. This model can achieve a peak height with higher sensitivity and a noise level less than 1 μW. The temperature program speed can be used between 0.1 °C/hour and 99.9 °C/min. The schematic diagram of the differential scanning calorimeter is show in Fig.5.2. It is designed in such way that the sample and reference calorimeters are independent. The main body of the sensor is constantan and consists of thick flat base to hold the sample and reference pans. A thin chromel disk is welded to the underside of each platform and functions as an area thermocouple junction to reduce the variations of contact sensitivity between sensor and pans. All the pans are made of aluminum and nearly identical weight and size. Signals from both sensors provide information to the computer via the workstation. This allows it to regulate the temperature and provide an accurate heating rate to the sample and reference section. A microbalance of model AND BM-22 which has an accuracy of ±1 μg is used to measure the sample and Al crucible weight.

![Fig. 5.1: Photograph of the DSC experiment](image)
5.2.3 Experimental Procedure

Firstly, the sample was dried in an oven at 120 °C for 6 hours to eliminate any adsorbed gases on the sample. The weight of an empty crucible was measured using a microbalance. Adsorbent sample of 15 mg was placed in the crucible and took the weight of crucible and sample together from where the true sample weight was measured. As all of the samples are powder and granular form, maximum care was taken to ensure that proper thermal contact was established between the sample and the supporting Al crucible. For calibration, experiments were carried out with standard sapphire (α-Al₂O₃) sample with known specific heat and weight.

For each type of sample the following three steps of measurements are done in multiple times.
Chapter 5  
Specific heat capacity of adsorbents

(1) Blank measurement was done putting an empty sample crucible and an empty reference crucible in designated position $T_s$ and $T_r$, respectively, shown in Fig. 5.2.

(2) Reference measurement was done putting reference material $\alpha$-$\text{Al}_2\text{O}_3$, with known specific heat capacity and mass ($m_0$) in the sample crucible shown in position $T_s$ in Fig. 5.2.

(3) Sample measurement was done with replacing reference material into sample material in the sample crucible with known mass ($m$) in position $T_s$, shown in Fig. 5.2.

A three-segment temperature program was used in every time. The first segment was isothermal for duration of 10 min at the initial temperature. Second segment was started from the initial temperature and went to the final temperature at a heating rate of 10 °C/min. The final segment was also isothermal for 10 min at the final temperature. The temperature range used in the experiment was between 30 and 150 °C considering the working range of adsorption cooling and heat pump system. Same temperature range and heating protocol was maintained for all samples.

In order to maintain dry and inert atmosphere $\text{N}_2$ gas was pumped to the sample area during experiment. This gas helps to sweep away any off gases that might be released when the sample is heated. The typical flow rate of nitrogen was around 50 ml/min.

5.3  Theoretical Derivation of DSC Measurement

A mathematical model is used to determine the relationship between the measured temperatures and heat flow based on the lumped heat capacity method where a thermal system is represented by thermal resistance and heat capacities. Figure 5.3 shows an equivalent circuit that can be used to represent the heat flow measurement.
Here the subscripts $s$ and $r$ present the sample and reference parts of the calorimeter. The temperatures $T_s$ and $T_r$ are measured for sample and reference calorimeters where $T_0$ is the temperature of the enclosure. $q_s$ is the heat flow to the sample section where $q_r$ is the heat flow to the reference section. In Fig. 5.3, portion below the broken line represents the DSC while portion above the line represents the sample and pans and contact resistance.

A heat balance equation can be derived in terms of temperatures $T_s$, $T_r$, $T_0$ and thermal parameters $R_s$, $C_s$, $R_r$, $C_r$:

$$
\dot{q}_s = \frac{T_0 - T_s}{R_s} - C_s \frac{dT_s}{dt} \quad (5.1)
$$

$$
\dot{q}_r = \frac{T_0 - T_r}{R_r} - C_r \frac{dT_r}{dt} \quad (5.2)
$$

The temperature difference between the sample and reference heat flow is
Chapter 5

Specific heat capacity of adsorbents

\[ \dot{q} = \dot{q}_s - \dot{q}_r = \frac{T_0 - T_s}{R_s} - C_s \frac{dT_s}{dt} - \frac{T_0 - T_r}{R_r} + C_r \frac{dT_r}{dt} \]  \hspace{1cm} (5.3)

Substitute with two measured differential temperatures \( \Delta T = T_s - T_r \) and \( \Delta T_0 = T_0 - T_s \)

\[ \dot{q} = \frac{\Delta T}{R_r} + \Delta T_0 \left[ \frac{1}{R_s} - \frac{1}{R_r} \right] + \frac{dT_s}{dt} \left[ C_r - C_s \right] - C_r \left[ \frac{dT_s}{dt} - \frac{dT_r}{dt} \right] \]  \hspace{1cm} (5.4)

In DSC the measured signal is the difference in temperatures of the sample and the reference positions of the sensor.

In Eq. (5.4) the first term is equivalent to conventional DSC heat flow, the second and third terms reflect imbalances and heat capacities of the sample and reference with pan. The fourth term is a heat flow resulting from differences in heating rate between the sample and reference calorimeters. It is generally zero if there is no transition in the sample.

To calculate the actual heat flow to the sample \( (q_{sam}) \) the following steps can be made:

The heat capacity \( C_{ps} \) and \( C_{pr} \) represent the sample and reference pan, respectively. \( R_p \) represent the thermal contact resistance between the sensor and sample pan/reference pan.

The reference pan is assumed to be empty. The sample and reference pan temperatures are \( T_{ps} \) and \( T_{pr} \).

Substituting with differential temperatures \( \Delta T = T_s - T_r \) and \( \Delta T_0 = T_0 - T_s \), into Eqs. (5.1) and (5.2) to obtain the sample and reference heat flow measurement equations:

\[ \dot{q}_s = \frac{\Delta T_0}{R_s} - C_s \frac{dT_s}{dt} \]  \hspace{1cm} (5.5)

\[ \dot{q}_r = \frac{\Delta T_0 + \Delta T}{R_r} - C_r \left( \frac{dT_s}{dt} - \frac{d\Delta T}{dt} \right) \]  \hspace{1cm} (5.6)

The measured sample heat flow includes the sample and pan heat flow, likewise the measured reference heat flow is the sum of the pan and reference heat flows.
Chapter 5

Specific heat capacity of adsorbents

The objective of the measurement is to recover the actual sample heat flow $q_{sam}$. The measured sample heat flow is the sum of the sample and sample pan heat flows:

$$q_s = q_{sam} + m_{ps} c_{pan} \frac{dT_{ps}}{dt}$$  \hspace{1cm} (5.7)

$m_{ps}$ is the sample pan mass, $c_{pan}$ is the specific heat capacity of the pan material. The measured reference heat flow is just the pan heat flow because the reference pan was assumed to be empty:

$$q_r = m_{pr} c_{pan} \frac{dT_{pr}}{dt}$$  \hspace{1cm} (5.8)

$m_{pr}$ is the mass of reference pan. Use the reference heat flow equation to eliminate the pan specific heat capacity and solve for $q_{sam}$, giving:

$$c_{pan} = \frac{q_s - q_{sam}}{m_{ps} \frac{dT_{ps}}{dt}}$$  \hspace{1cm} (5.9)

From Eq. (5.7),

After putting the value of $c_{pan}$ in Eq. (5.8) one can get

$$q_{sam} = q_s - q_r \left[ m_{ps} \left( \frac{dT_{ps}}{dt} \right) - m_{pr} \left( \frac{dT_{pr}}{dt} \right) \right]$$  \hspace{1cm} (5.10)

This equation gives the actual sample heat flow and accounts for pan mass imbalances and heating rate differences between the sample and reference pans. The heating rate ratio accounts for the fact that during a DSC experiment the heating rates of the sample and reference pans may be different, e.g. during a transition. In conventional DSC, the heat flow measurement is in error because the reference pan does not always heat at the same rate as the sample pan. When the heating rate of the sample pan is higher or lower than the programmed heating rate, the reference heat flow off-setting the sample pan heat flow is too low or too high. The same comments apply to the sensor heat flow. The heat capacity terms in the heat flow measurement equations account for differences between the sample and reference sensor heating rates.
To use this heat flow measurement method, the sample and reference pan temperatures are needed. They are not measured directly but may be obtained from the measured quantities. Heat flow between the sample and reference pans and their sensors are given by:

\[ \dot{q}_s = \frac{T_s - T_{ps}}{R_p} \quad \dot{q}_r = \frac{T_r - T_{pr}}{R_p} \]  

which are solved to find the pan temperatures:

\[ T_{ps} = T_s - \dot{q}_s R_p \quad T_{pr} = T_r - \dot{q}_r R_p \]  

A model equation is used to calculate the contact resistance between the pan and sensor. It assumes that there are two parallel heat conduction paths between the pan and the sensor. One is solid conduction through the sensor and pan where they contact one another and the other is conduction through the gas layer between the pan and sensor. The solid conduction path consists of pan and sensor thermal resistances in series. The equation used for the contact resistance is:

\[ R_p = \frac{1}{\frac{1}{R_{pan}} + \frac{1}{R_{sen}} + \frac{1}{R_{gas}}} \]  

where subscripts pan, sen and gas indicate thermal resistances associated with the pan, the sensor and the purge gas. The component thermal resistances are calculated from:

\[ R = \frac{1}{\alpha k} \]  

where k is the thermal conductivity of the pan, sensor or purge gas and \( \alpha \) is a geometric factor for the pan, sensor or purge gas that is equivalent to the ratio of an area to a length. The geometric factors are dependent upon the pan and sensor shape. Typical values of the geometric factors are supplied in the instrument software for selected pan types.
5.4 Data Reduction

In Eq. (5.4), the fourth term is generally zero if there is no transition in the sample, the effect of second and third term can be minimized by proper calibration with standard reference sample with known specific heat.

For simplicity, the DSC output can be shown by Eq.(5.15)

\[
\dot{q} = -\frac{T_s - T_r}{R_r}
\]  

(5.15)

Here the temperature difference, \(T_s - T_r\), represents the output of the DSC, which is proportional to the difference in heat capacities between the sample and reference section (Fig.5.2). If we define DSC output is \(S\) and the proportionality constant is \(\kappa\), we can write

\[
C_s - C_r \propto -(T_s - T_r)
\]

\[
C_s - C_r = \kappa S
\]

(5.16)

After performing the blank, reference and sample measurement according to the procedure [1-3], the specific heat of the sample is analyzed. During the blank measurement, the sample side and reference side heat capacities are \(C_s^h\) and \(C_r^h\), respectively, which is only for empty crucible. If the specific heat capacities of the sample and reference material are defined \(c_{p,s}\) and \(c_{p,r}\), respectively, the following equations may be used to represent the measurement in the above three procedures (1, 2, 3)

(1) Blank measurement, \(\kappa S_1 = C_s^h - C_r^h\)

(5.17)

(2) Reference measurement, \(\kappa S_2 = (C_s^h + m_0 c_{p,r}) - C_r^h\)

(5.18)

(3) Sample measurement, \(\kappa S_3 = (C_s^h + m c_{p,s}) - C_r^h\)

(5.19)

Using the above three equations, the specific heat of the sample material can be calculated.
Chapter 5  
Specific heat capacity of adsorbents

\[
\frac{C_s^h + m c_{p,s}^h - C_r^h}{C_s^h + m_0 c_{p,s}^h - C_r^h} - \frac{C_s^h - C_r^h}{C_s^h - C_r^h} = \frac{\kappa S_3 - \kappa S_1}{\kappa S_2 - \kappa S_1}
\]  \quad (5.20)

\[
c_{p,s} = \frac{m_0 c_{p,r} \times S_3 - S_1}{m \times S_2 - S_1}
\]  \quad (5.21)

Since the specific heat capacity and mass of the reference material is known, the specific heat capacity of the sample can be determined on the basis of Eq. (5.21). A plot of DSC curve in this case appeared as shown in Fig. 5.4 using Eq. (5.17) to Eq. (5.19).

Fig. 5.4: Illustration of heat capacity calculation by DSC
5.4 Results and Discussion

To minimize the impact of heating rate and sample weight, many test measurements have been performed varying heating rate and sample weight. It is worthy to mention that the heating rate of 10°C/min and sample weight 15 mg provides the best result for the present DSC unit. So the specific heat capacity of the adsorbents presented here is investigated following the heating rate 10°C/min and sample weight 15 mg. The heat capacity measurements are carried out from 30 to 150°C. The measured values of specific heat capacities of some adsorbents are presented in Table 5.2.

The measured specific heat capacity for the reference material (sapphire) is plotted together with the standard value found in open literature with temperature which is shown in Fig. 5.5. It can be seen that the measured values of sapphire pleasantly matches with the value found in open literature over the whole temperature range and the deviation is within ±0.3%.

![Fig. 5.5: Results of DSC measurements for the reference material (sapphire)](image-url)
Figure 5.6(a) shows the DSC output data of reference material, parent and surface treated Maxsorb III where the secondary axis shows the temperature program followed by the control unit. Figure 5.6(b) shows the specific heat capacity of parent Maxsorb III, H$_2$ treated Maxsorb III and KOH-H$_2$ treated Maxsorb III with temperature. It can be found that KOH-H$_2$ treated Maxsorb III shows higher specific heat capacity than that of parent Maxsorb III and H$_2$ treated Maxsorb III whereas H$_2$ treated Maxsorb III shows the lowest value. It is also been seen that there is a broad bump at a temperature 50 to 60 °C for parent Maxsorb III and KOH-H$_2$ treated Maxsorb III. This anomaly might be because of the formation of surface functional group due to effect of surface treatment. The details of surface treatment and functional group formation can be found elsewhere (Kill et al. 2013, El-Sharkawy et al. 2014). This phenomenon also arises from the conflicting results between thermal expansion of rigid metal-oxygen clusters and thermal contraction of carbon-oxygen bonds due to transverse vibration of planar organic ligands (Zhou et al. 2008, Mu & Walton 2011). It should be mentioned that even though proper care was taken to ensure uniform spreading of the powder, it was not possible to realize close packing of the sample. The trapped air between the solid particles could result in variable heat flow into the sample resulting in larger uncertainties in the specific heat measurements (Ramkumar et al. 2001). The average value of specific heat capacity of parent Maxsorb III, H$_2$ treated Maxsorb III and KOH-H$_2$ treated Maxsorb III is found to be 0.94, 0.88 and 1.05 kJ/kg·K, respectively. The average value of activated carbon found by Xiao et al. (2012) is 0.98 kJ/kg·K considering the similar temperature range.

Similarly, Figs. 5.7(a) and (b) show the heat flow data and corresponding specific heat capacity of different silica gels. It is worth noting that the specific heat capacity curve indicates a thermal anomaly at ~120°C, which is due to the change of coordinated H$_2$O in the silica gels. Figures 5.8, 5.9 and 5.10 show the specific heat capacity of other three types of as received Maxsorb III, two types of MOFs, and two types of expanded graphite, respectively.
Fig. 5.6(a): Comparison of heat flow of parent Maxsorb III, H₂ treated Maxsorb III and KOH-H₂ treated Maxsorb III.

Fig. 5.6(b): Comparison of specific heat capacity of parent Maxsorb III,
H$_2$ treated Maxsorb III and KOH-H$_2$ treated Maxsorb III

**Fig. 5.7**: Comparison of specific heat capacity of new types of Maxsorb III

**Fig. 5.8(a)**: Comparison of heat flow of silica gel based adsorbents
Fig. 5.8(b): Comparison of specific heat capacity of silica gel based adsorbents

Fig. 5.9: Comparison of specific heat capacity of MOF-101 and Kupfer-BTC
Fig. 5.10: Comparison of specific heat capacity of expanded graphite materials.

As the measurement data is recorded in each second, so the huge number of data is presented here by a dash line.
Table 5.2 Specific heat capacity of adsorbent materials

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.834</td>
<td>0.813</td>
<td>0.869</td>
<td>0.975</td>
<td>0.835</td>
</tr>
<tr>
<td>40</td>
<td>0.962</td>
<td>0.86</td>
<td>1.02</td>
<td>1.143</td>
<td>0.929</td>
</tr>
<tr>
<td>50</td>
<td>1.053</td>
<td>0.841</td>
<td>1.153</td>
<td>1.256</td>
<td>0.971</td>
</tr>
<tr>
<td>60</td>
<td>1.054</td>
<td>0.823</td>
<td>1.209</td>
<td>1.417</td>
<td>1.035</td>
</tr>
<tr>
<td>70</td>
<td>0.992</td>
<td>0.818</td>
<td>1.172</td>
<td>1.639</td>
<td>1.136</td>
</tr>
<tr>
<td>80</td>
<td>0.925</td>
<td>0.822</td>
<td>1.087</td>
<td>1.896</td>
<td>1.283</td>
</tr>
<tr>
<td>90</td>
<td>0.883</td>
<td>0.833</td>
<td>1.011</td>
<td>2.152</td>
<td>1.478</td>
</tr>
<tr>
<td>100</td>
<td>0.861</td>
<td>0.848</td>
<td>0.969</td>
<td>2.39</td>
<td>1.707</td>
</tr>
<tr>
<td>110</td>
<td>0.858</td>
<td>0.866</td>
<td>0.951</td>
<td>2.626</td>
<td>1.941</td>
</tr>
<tr>
<td>120</td>
<td>0.863</td>
<td>0.884</td>
<td>0.953</td>
<td>2.866</td>
<td>2.129</td>
</tr>
<tr>
<td>130</td>
<td>0.875</td>
<td>0.907</td>
<td>0.961</td>
<td>3.06</td>
<td>2.208</td>
</tr>
<tr>
<td>140</td>
<td>0.884</td>
<td>0.926</td>
<td>0.969</td>
<td>3.12</td>
<td>2.138</td>
</tr>
</tbody>
</table>
5.6 Nomenclature

\( \alpha \) Geometrical factor of pan and sensor
\( C_s \) Thermal capacity of sample
\( C_r \) Thermal capacity of reference material
\( c_{\text{pan}} \) Specific heat of pan
\( c_{\text{sapph}} \) Specific heat of sapphire reference material
\( k \) Thermal conductivity
\( m_s \) Mass of sample
\( m_r \) Mass of reference material
\( m_{ps} \) Mass of sample pan
\( m_{pr} \) Mass of reference pan
\( q_s \) Heat flow to the sample and pan
\( q_r \) Heat flow to the reference and pan
\( q_{\text{sam}} \) Heat flow to the sample
\( R \) Thermal resistance
\( R_s \) Sensor thermal resistance for sample side
\( R_r \) Sensor thermal resistance for reference side
\( R_p \) Thermal resistance between pan and sensor
\( R_{\text{pan}} \) Contact resistance for the pan
\( R_{\text{sen}} \) Contact resistance for sensor
\( R_{\text{gas}} \) Thermal resistance for the purge gas
\( T_0 \) Temperature of the enclosure
\( T_r \) Temperature of the reference sensor
\( T_s \) Temperature of the sample sensor
\( T_{ps} \) Temperature of sample pan
\( T_{pr} \) Temperature of the reference pan
5.7 Conclusion

In this Chapter, specific heat capacities of parent and surface treated Maxsorb III along with other commonly used adsorbents are presented which is measured experimentally using a heat flux type DSC measurement technique. The temperature range used in each measurement is between 30 and 150 °C which is useful for the operation of adsorption chiller. These data are also essential for precise system design.

5.8 References


Chapter 5  

Specific heat capacity of adsorbents


Chapter 6

Thermodynamic Analysis of Adsorption Cooling Cycle

In this chapter, a thermodynamic analysis of an equilibrium adsorption cooling cycle using parent and surface treated Maxsorb III/ethanol pairs has been presented. The relationship between equilibrium pressure, adsorbent temperature and equilibrium adsorption capacity has been determined. The effect of operating condition in terms heat source and heat sink temperatures on the cycle performance are discussed using the assorted adsorbent/refrigerant pairs.

6.1 Introduction

Thermally driven adsorption refrigeration and heat pump systems got considerable attention nowadays due to its manufacturing simplicity and environment friendly adsorbent/refrigerant pairs. The research on this area intensified after the imposition of international restrictions on the production and use of CFCs (chlorofluoro-carbons) and HCFCs (hydrochlorofluoro-carbons), which are the commonly used refrigerants for cooling applications. These gases are identified as the major contributors to deplete the ozone layer around the globe (Miller, 1929; Aittomaki and Hakonen, 1986; Critoph, 1989; Meunier, 1993a; Cacciola and Restuccia, 1994). The adsorption cooling and heat pump systems could utilize low temperature waste heat or renewable energy sources. The working pairs of adsorption cooling and heat pump are mainly dominated by silica gel/water (Yanagi et al., 1992), zeolite/water (Rothmeyer et al. 1983; Solmuş et al. 2010), activated carbon/ammonia (Critoph, 1989), activated carbon/methanol (Wang et al., 2003) and activated carbon fiber
(ACF)/ammonia (Vasiliev et al., 2001) pairs.

Many researchers evaluated the performance of adsorption cooling and heat pump systems based on working pairs, system design and methodology. A transient simulation model for adsorption cooling system using silica gel/water pair powered by renewable energy was investigated (Sakoda and Suzuki, 1984). Saha et al. (1995) developed a cycle simulation program to investigate the influence of operating conditions on cooling output and COP of a sing-stage silica gel/water adsorption chiller and found hot water temperature 50ºC is only viable when cooling water temperature of less than 25ºC. Boelman et al. (1995) was continued to study parametrically the influence of thermal capacitance and heat exchanger UA-values on cooling capacity for the silica gel/water system. Saha et al. (2003) also evaluated the performance of low temperature waste heat driven multi-bed silica gel/water adsorption chiller and showed the system can work even if the heat source temperature is 60 ºC. Saha et al. (2007) presented the transient modelling for a two-bed, activated carbon fiber (ACF)/ethanol adsorption chiller using heat sources of temperature between 60 and 95 ºC along with a coolant at 30ºC. Miyazaki et al. (2010) evaluated the performance of innovative dual evaporator type three-bed adsorption chiller for cooling application and found significant improvement of system performance over two-bed single stage chiller. Uddin et al. (2013) analytically investigated the performance of an ideal adsorption-compression hybrid system and discussed the energy saving potential for the proposed system comparing the conventional system under same operating condition.

Water as refrigerant is commonly used effectively in the air-conditioning applications. However, for refrigeration applications that require relatively lower temperatures, methanol has been used before but reservations exist on its toxicity. On the other hand, the utilization of ethanol in adsorption cooling systems has couple of advantages, such as, ethanol is environmental friendly, non-toxic and it has a relatively high vapor pressure even at low
temperature levels and its low freezing temperature (Cui et al., 2005).

In the present chapter, the performance of time-independent adsorption refrigeration cycle using the using parent Maxsorb III/ethanol, H$_2$ treated Maxsorb III/ethanol and KOH-H$_2$ treated Maxsorb III/ethanol pairs have been investigated and compared with other adsorbent refrigerant pairs that available on the open literatures.

### 6.2 Equilibrium Model

Equilibrium model is a simplified model for the prediction of system performance using adsorption equilibrium data. An equilibrium model is presented here to calculate the adsorption cycle performance in terms of specific cooling capacity (SCE) and coefficient of performance (COP). Effect of operating temperatures such as regeneration and evaporator temperatures on the cycle performance is also introduced.

#### 6.1.1 Analytical Expression

The Dubinin - Radushkevich (D-R) and Dubinin - Astakhov (D-A) equations (Do 1998) are widely used to fit the equilibrium uptake data of vapors onto carbon based adsorbents. Eq. (6.1) and Eq. (6.2) represents the D-R and D-A equations, respectively.

\[
W = W_0 \exp \left( -\frac{A}{E} \right)^2
\]  
(6.1)

\[
W = W_0 \exp \left( -\frac{A}{E} \right)^n
\]  
(6.2)

Where $A$ is the adsorption potential that can be estimated as in Eq. (3):

\[
A = R_g T_{ad} \ln \left( \frac{P_{ad}}{P_{eva}} \right)
\]  
(6.3)
Here $W$ stands for the equilibrium uptake [kg/kg] for the adsorbent/refrigerant pair, $W_0$ defines the maximum adsorption capacity [kg/kg]. $E$ is the adsorption characteristic parameter [kJ/kg]. $T_{ad}$ is the adsorption temperature [K], $P_{ad}$ defines the saturation pressure [kPa] of refrigerant at adsorption temperature and $P_{eva}$ is the equilibrium pressure [kPa]. The exponential parameter $n$ gives the best fitting of $ln(W)$ versus $A^n$ plot. The numerical values of fitting parameters using the above correlations are furnished in Table 2.4 (Chapter 2).

Figures 6.1 (a)-(c) show the adsorption isotherms of Maxsorb III/ethanol, H$_2$-treated Maxsorb III/ethanol and KOH-H$_2$-treated Maxsorb III/ethanol pairs using the fitting parameters from Table 2.4 (Chapter 2), where ideal adsorption refrigeration cycles working at evaporation temperature -5°C adsorption temperature 30°C and desorption temperature 100°C have been superimposed.

![Fig. 6.1(a): Adsorption isotherms of Maxsorb III/ethanol as predicted by equilibrium isotherm equation.](image-url)
Fig. 6.1(b): Adsorption isotherms of H₂ treated Maxsorb III/ethanol as predicted by equilibrium isotherm equation.

Fig. 6.1(c): Adsorption isotherms of KOH-H₂ treated Maxsorb III/ethanol pair as predicted by equilibrium isotherm equation.
6.2.2 Thermodynamic Cycle

Figure 6.2 shows the schematic diagrams of a basic adsorption system. The system is mainly consists of an evaporator, a condenser and an adsorber/desorber heat exchangers (sorption element). The condenser and the evaporator are connected through a throttling valve or a bending capillary tube for maintaining the pressure difference. Here the basic cycle is assumed to be an ideal and as consequence, the pressure drops as well as the heat loss are neglected.

The P-T-W diagram shows the relationship between the equilibrium pressure, adsorbent temperature and adsorption capacity at equilibrium state conditions which makes it possible to estimate the performance of adsorption cycle. Figures 6.3(a)-6.3(c) show the P-T-W diagrams of Maxsorb III/ethanol, H₂ treated Maxsorb III/ethanol and KOH-H₂ treated Maxsorb III/ethanol pairs, respectively. The ideal cycle for the same adsorbent-refrigerant pair is super imposed therein. Each cycle consists of two isosteric and two isobaric processes.

In adsorption process (a→b), the pressure is kept constant at $P_{eva}$. The refrigerant vapor evaporates in the evaporator picking up its latent heat from the chilled water then, adsorbed by the adsorbent packed in the adsorber via the valve V1 (see Fig. 6.2). The refrigerant concentration in the adsorber increases from $W_{min}$ to $W_{max}$. In pre-heating (b→c) process, the sorption element is isolated and heated at constant concentration using a high temperature heat source and hence the pressure increases from $P_{eva}$ to $P_{con}$. 
In desorption process (c→d), the refrigerant regenerates and goes to the condenser via the valve V3 at pressure $P_{\text{con}}$. The refrigerant concentration on the sorption element decreases from $W_{\text{max}}$ to $W_{\text{min}}$. In the pre-cooling process (d→a), the adsorbent bed is cooled at constant concentration which makes the pressure decrease from $P_{\text{con}}$ to $P_{\text{eva}}$. 

**Fig. 6.2:** Schematic diagram of ideal adsorption cooling system.
Fig. 6.3 (a): P-T-W diagram of parent Maxsorb III/ethanol,

Fig. 6.3 (b): P-T-W diagram of H₂ treated Maxsorb III/ethanol
Fig. 6.3 (c): P-T-W diagram of KOH-H₂ treated Maxsorb III/ethanol pairs.

It can also be seen from Figs. 6.3(a)-6.3(c) that the concentration difference for H₂ treated Maxsorb III/ethanol pair is about 10% higher than parent Maxsorb III/ethanol pair and 19% higher than that of KOH-H₂ treated Maxsorb III/ethanol pair at the same operating condition, demonstrating the superiority in ice making applications. In addition to uptake difference, the adsorption kinetics of assorted working pair is another essential parameter that needed to be considered during making a dynamic simulation of adsorption system. The adsorption kinetics data for the assorted adsorbent/refrigerant pairs can be found elsewhere (El-Sharkawy et al., 2014).

The model described here is a thermodynamically equilibrium model. This means, all the thermal contributions are calculated based on heat and mass balance provided by the (P-T-W) diagrams.
Cooling effect can be estimated as given in Eq. (6.4),

\[ Q_C = M_s (W_{\text{max}} - W_{\text{min}}) \left[ \Delta h_{\text{eva}} - \int_{T_{\text{eva}}}^{T_{\text{ref}}} C_{p,\text{ref}} dT \right] \]  \hspace{1cm} (6.4)

Where \( M_s \) is the mass of the sample adsorbent, \( W_{\text{max}} \) and \( W_{\text{min}} \) is the maximum and minimum sorption uptake, respectively. \( \Delta h_{\text{eva}} \) is the vaporization enthalpy and \( C_{p,\text{ref}} \) is specific heat of refrigerant.

Desorption heat can be calculated as given in Eq. (6.5),

\[ Q_{\text{des}} = M_s Q_{\text{ad}} (W_{\text{max}} - W_{\text{min}}) \]  \hspace{1cm} (6.5)

\[ W_{\text{max}} = W_0 \exp \left[ - \left( \frac{RT_{\text{ad}} \ln \left( \frac{P_{\text{ad}}}{P_{\text{eva}}} \right)}{E} \right)^n \right] \]  \hspace{1cm} (6.6)

\[ W_{\text{min}} = W_0 \exp \left[ - \left( \frac{RT_{\text{des}} \ln \left( \frac{P_{\text{des}}}{P_{\text{eva}}} \right)}{E} \right)^n \right] \]  \hspace{1cm} (6.7)

Total sensible heat is the sum of sensible heat during pre-heating and desorption which is shown in Eq. (6.8)

\[ Q_{\text{sh}} = Q_{\text{sh,pr}} + Q_{\text{sh,des}} \]  \hspace{1cm} (6.8)

Sensible heat during pre-heating can be estimated as in Eq. (6.9),

\[ Q_{\text{sh,pr}} = M_s \int_{T_s}^{T_f} C_{p,\text{s}} dT + M_s W_{\text{max}} \int_{T_s}^{T_f} C_{p,\text{ref}} dT + M_{\text{bed}} \int_{T_s}^{T_f} C_{p,\text{bed}} dT \]  \hspace{1cm} (6.9)

Sensible heat during desorption can be estimated as in Eq. (6.10),

\[ Q_{\text{sh,des}} = M_s \int_{T_s}^{T_f} C_{p,\text{s}} dT + M_s \frac{W_{\text{max}} + W_{\text{min}}}{2} \int_{T_s}^{T_f} C_{p,\text{ref}} dT + M_{\text{bed}} \int_{T_s}^{T_f} C_{p,\text{bed}} dT \]  \hspace{1cm} (6.10)

For simplicity, the thermal capacity of the adsorption bed is considered two times that of
Chapter 6  
Thermodynamic analysis of adsorption cooling cycle

thermal capacity of the adsorbent. The specific cooling effect ($SCE$) and the coefficient of performance ($COP$) of the time independent ideal adsorption cycle is calculated using the following Eqs. (6.11) and (6.12), respectively:

$$SCE = (W_{\text{max}} - W_{\text{min}}) \left[ \Delta h_{\text{evu}} - \int_{T_{\text{ref}}}^{T_{\text{eva}}} C_p c_{\text{ref}} dT \right]$$  \hspace{1cm} (6.11) \\

$$COP = \frac{SCE}{Q_{\text{des}} + Q_{\text{sh}}}$$  \hspace{1cm} (6.12)

6.1.2 Effect of Operating Temperatures

Figures 6.4(a) and (b) Shows the variation of $SCE$ with desorption temperature for five different adsorbents/ethanol pairs at evaporation temperature -5 °C and 10 °C respectively, and adsorption temperature 30°C keeping in mind the application of ice making and air-conditioning applications. In both figures, the value of $SCE$ increases linearly with the increase of desorption temperature. This is due to the increase of concentration difference with increase of regeneration temperature at constant adsorption and evaporation temperature. It can be seen from both the Figs. 6.4(a) and (b) that the $SCE$ values for H$_2$ treated Maxsorb III is higher than the other studied working pairs. For the sake of comparison, the performance of adsorption cooling cycles employing four assorted pairs are furnished in Table 6.1(a) and Table 6.1(b) for evaporation temperature -5 °C and 10 °C, respectively. It is found that, at regeneration temperature 100°C along with adsorption and evaporation temperatures of 30 and -5°C, respectively, the H$_2$ treated Maxsorb III/ethanol pair achieves an $SCE$ as high as 374 [kJ/kg] whilst parent Maxsorb III/ethanol, KOH-H$_2$ treated Maxsorb III/ethanol and ACF A-20/ethanol pairs provide 90%, 81% and 64% of the $SCE$ value of H$_2$ treated Maxsorb III/ethanol pair, respectively. This is because the H$_2$ treated Maxsorb III/ethanol pair possess highest concentration difference ($W_{\text{max}} - W_{\text{min}}$) at the same operating conditions (see Table 6.2).
As for air-conditioning application where evaporation temperature is kept constant at 10°C, the values of *SCE* and *COP* at various regeneration temperatures of the assorted pairs are evaluated and furnished in Table 6.4(b). Theoretical calculations show that H₂ treated Maxsorb III/ethanol pair still possesses highest *SCE* among the other studied pairs. Moreover, the cycle could be driven by relatively lower regeneration temperatures to produce the similar cooling effect.

It is worthy to note that, for a fixed temperature of both condenser and adsorption at 30 °C, the minimum required heat source temperature can be seen from Figs. 6.4(a) and (b) which are 71 and 52 °C corresponding to the evaporation temperatures of -5 and 10 °C, respectively, where there is no *SCE*.

![Graph](image)  

**Fig. 6.4(a):** Effect of desorption temperature on specific cooling effect (*SCE*) at evaporation temperature -5°C.
Fig. 6.4(b): Effect of desorption temperature on specific cooling effect (SCE) at evaporation temperature 10 °C

Fig. 6.5: Effect of desorption temperature on Coefficient of performance (COP).
Figure 6.5 shows the variation of coefficient of performance with desorption temperature at evaporation temperature -5 ºC. It can be noticed that the COP increases sharply only when the desorption temperature is below 50 ºC. After that there is no significant change in COP even though SCE increases. This is happened due to the requirement of heat input becomes significantly large when the temperature difference between heat source and heat sink becomes higher than 100 ºC. It can also be seen that the H2 treated Maxsorb III/ethanol pair possess highest COP in comparison with that other pairs. As for the ice making application where the evaporation temperature is kept constant at -5 ºC, the cycle should be driven by relatively higher regeneration temperature to produce sensible cooling production.

![Graph](image)

**Fig.6.6:** Variation of COP with specific heat capacity.

It can be seen from Fig.6.6 that the COP of the heat pump system decrease monotonically with the increase of specific heat capacity at constant temperature (T_{eva}= -5ºC, T_{ads}=30ºC, T_{des}=100ºC).
Table 6.1(a) Adsorption uptake and cycle performance of the assorted adsorbents using ethanol for ice making applications; adsorption and evaporation temperatures are 30 and -5 °C, respectively.

<table>
<thead>
<tr>
<th>Desorption temperature [°C]</th>
<th>Parent Maxsorb III</th>
<th>H₂ treated Maxsorb III</th>
<th>KOH-H₂ treated Maxsorb III</th>
<th>ACF A-20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wₘₐₓ [kg/kg]</td>
<td>0.543</td>
<td>0.561</td>
<td>0.516</td>
<td>0.363</td>
</tr>
<tr>
<td>Wₘᵋₐₜ [kg/kg]</td>
<td>0.254</td>
<td>0.235</td>
<td>0.261</td>
<td>0.152</td>
</tr>
<tr>
<td>SCE [kJ/kg]</td>
<td>251.2</td>
<td>283.7</td>
<td>222.0</td>
<td>183.7</td>
</tr>
<tr>
<td>COP [-]</td>
<td>0.447</td>
<td>0.468</td>
<td>0.427</td>
<td>0.448</td>
</tr>
</tbody>
</table>

| Wₘₐₓ [kg/kg]                | 0.543               | 0.561                  | 0.516                     | 0.363    |
| Wₘᵋₐₜ [kg/kg]              | 0.157               | 0.132                  | 0.168                     | 0.085    |
| SCE [kJ/kg]                 | 335.5               | 373.5                  | 303.2                     | 241.7    |
| COP [-]                     | 0.486               | 0.505                  | 0.471                     | 0.484    |

| Wₘₐₓ [kg/kg]                | 0.543               | 0.561                  | 0.516                     | 0.363    |
| Wₘᵋₐₜ [kg/kg]              | 0.092               | 0.068                  | 0.102                     | 0.044    |
| SCE [kJ/kg]                 | 391.9               | 428.9                  | 360.4                     | 277.5    |
| COP [-]                     | 0.501               | 0.516                  | 0.489                     | 0.495    |
Table 6.1(b) Adsorption uptake and cycle performance of the assorted adsorbents using ethanol for air-conditioning applications; adsorption and evaporation temperatures are 30 and 10°C, respectively.

<table>
<thead>
<tr>
<th>Desorption temperature [°C]</th>
<th>Maxsorb III</th>
<th>H₂ treated Maxsorb III</th>
<th>KOH-H₂ treated Maxsorb III</th>
<th>ACF A-20</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>W&lt;sub&gt;max&lt;/sub&gt; [kg/kg]</td>
<td>0.926</td>
<td>0.980</td>
<td>0.816</td>
</tr>
<tr>
<td></td>
<td>W&lt;sub&gt;min&lt;/sub&gt; [kg/kg]</td>
<td>0.76</td>
<td>0.804</td>
<td>0.691</td>
</tr>
<tr>
<td></td>
<td>SCE [kJ/kg]</td>
<td>147.2</td>
<td>156.6</td>
<td>110.8</td>
</tr>
<tr>
<td></td>
<td>COP [-]</td>
<td>0.364</td>
<td>0.361</td>
<td>0.328</td>
</tr>
<tr>
<td>70</td>
<td>W&lt;sub&gt;max&lt;/sub&gt; [kg/kg]</td>
<td>0.926</td>
<td>0.980</td>
<td>0.816</td>
</tr>
<tr>
<td></td>
<td>W&lt;sub&gt;min&lt;/sub&gt; [kg/kg]</td>
<td>0.561</td>
<td>0.582</td>
<td>0.531</td>
</tr>
<tr>
<td></td>
<td>SCE [kJ/kg]</td>
<td>323.9</td>
<td>354.0</td>
<td>252.7</td>
</tr>
<tr>
<td></td>
<td>COP [-]</td>
<td>0.479</td>
<td>0.479</td>
<td>0.449</td>
</tr>
<tr>
<td>80</td>
<td>W&lt;sub&gt;max&lt;/sub&gt; [kg/kg]</td>
<td>0.926</td>
<td>0.980</td>
<td>0.816</td>
</tr>
<tr>
<td></td>
<td>W&lt;sub&gt;min&lt;/sub&gt; [kg/kg]</td>
<td>0.389</td>
<td>0.386</td>
<td>0.384</td>
</tr>
<tr>
<td></td>
<td>SCE [kJ/kg]</td>
<td>476.8</td>
<td>527.9</td>
<td>383.8</td>
</tr>
<tr>
<td></td>
<td>COP [-]</td>
<td>0.526</td>
<td>0.526</td>
<td>0.502</td>
</tr>
</tbody>
</table>
The performance of adsorption heat pump system is strongly affected by the adsorption kinetics. Actually a dynamic mathematical model is required to analyze the effect of adsorption rate on system performance precisely. But in this chapter an equilibrium model is used to predict the effect of diffusion time constant on system performance. Figure 6.7 shows the uptake variation with time for different diffusion time constant, from where the effective sorption uptake ($\Delta W$) is calculated following same time interval ($\Delta t$). Figure 6.8 show the variation of SCE with different diffusion time constant putting corresponding $\Delta W$ in equilibrium model. It is found that the SCE increases sharply as the kinetics increases while keeping the other operation parameters constant ($T_{eva}=-5^\circ C$, $T_{ads}=30^\circ C$, $T_{des}=100^\circ C$). As the diffusion time constant for KOH-H$_2$ treated Maxsorb III is high among the studied pairs (see Chapter 3) which might give the higher system performance. Chahbani et al. (2002) shows the similar trend for the SCE and COP of the system with diffusion time constant.

![Figure 6.7: Uptake for different diffusion time constant following FD equation.](image-url)
Chapter 6  
Thermodynamic analysis of adsorption cooling cycle

Fig. 6.8: Variation of the SCE with diffusion time constant using different $\Delta W$.

6.6 Nomenclature

$A$  adsorption potential [kJ/kg]

$COP$ coefficient of performance

$C_{p,ref}$ specific heat of refrigerant [J/kg K]

$C_{p,s}$ specific heat of adsorbent [J/kg K]

$C_{p,bed}$ specific heat of bed [J/kg K]

$E$ adsorption characteristic parameter [kJ/kg]

$\Delta h_{eva}$ evaporation heat [J/kg]

$M_{bed}$ mass of bed [kg]

$M_s$ mass of adsorbent [kg]
The performance of an ideal adsorption cycle is analyzed using adsorption equilibriums data of Maxsorb III, H₂ treated Maxsorb III and KOH-H₂ treated Maxsorb III with ethanol pairs which are presented in Chapter 2. Thermodynamic analysis of assorted pairs show that the H₂ treated Maxsorb III/ethanol adsorption cycle can achieve a COP as high as 0.51 with an evaporation temperature -5°C, regeneration temperature 100 °C along with a coolant at 30 °C.
whereas the KOH-H$_2$ treated Maxsorb III/ethanol pair can achieve \textit{COP} about 0.47. The effect of adsorption kinetics on system performance is predicted at the end of this chapter where it is found the rapid increase of SCE with diffusion time constant. In chapter 2, it is shown that the adsorption kinetics of ethanol onto KOH-H$_2$ surface treated Maxsorb III is faster than other two studied pairs, so the use of kinetic data in system analysis might give the better performance for KOH-H$_2$ treated Maxsorb III than other two pairs.

6.8 References


21(4), 1350024, DOI: 10.1142/S2010132513500247


Chapter 7

General Conclusions

The primary objective of this work is to develop adsorption cooling systems which have the capability of utilizing low grade thermal energy, including heat from solar hot water, industrial waste heat and geothermal sources. To achieve this target the following studies have been conducted in chronological order:

1. A review of available literature with regard to the utilization of waste heat for adsorption cooling applications has been done to find the promising adsorbent/refrigerant pair.

2. Adsorption isotherms of environment friendly refrigerant ethanol onto the parent and surface treated activated carbon, namely Maxsorb III, H₂-treated Maxsorb III and KOH-H₂-treated Maxsorb III have been measured.

3. An experimental and theoretical study on the adsorption kinetics of assorted adsorbent/refrigerant pairs has been conducted.

4. Based on the experimental adsorption isotherms, isosteric heat of adsorption has been extracted.

5. The specific heat capacity of parent and surface treated Maxsorb III along with currently used adsorbent materials using differential scanning calorimeter (DSC) has been measured.

6. Having the experimental and theoretical knowledge, the time-independent single stage adsorption cooling system has been analyzed.

By conducting the above mentioned studies, the overall conclusions of the present thesis can be summarized as follows:
• Adsorption isotherms of parent Maxsorb III/ethanol, KOH-H₂ treated Maxsorb III/ethanol and H₂ treated Maxsorb III pairs have been measured experimentally using a magnetic suspension adsorption measurement unit. The Dubinin-Astakhov and the Dubinin–Radushkevich equations are used to fit the equilibrium uptake. Experimental results show that, the maximum adsorption capacity of H₂ treated Maxsorb III/ethanol pair is about 1.23 kg/kg whilst parent Maxsorb III/ethanol and KOH-H₂ treated Maxsorb III/ethanol has maximum adsorption capacities of 1.2 kg/kg and 1.01 kg/kg, respectively.

• The instantaneous measurement of adsorption data of assorted adsorbent/refrigerant pairs are measured gravimetrically using magnetic suspension adsorption measurement unit (Rubotherm of type MSB-VG-S2) to investigate adsorption kinetics. It is found that, the Fickian diffusion model can fairly present adsorption kinetics of assorted adsorbent/refrigerant pairs. Adsorption kinetics of ethanol onto KOH-H₂ treated Maxsorb III is found faster than other two studied adsorbents.

• The heat of adsorption of the assorted adsorbent/refrigerant pairs has been estimated by using Clausius-Clapeyron equation and a proposed correlation derived from D-A isotherm equation. The proposed correlation has been validated using experimental data.

• The specific heat capacity of adsorbent using differential scanning calorimeter (DSC) has been measured for the temperature range between 30 and 150 °C. It can be found that KOH-H₂ treated Maxsorb III shows higher specific heat capacity than that of parent Maxsorb III and H₂ treated Maxsorb III whereas H₂ treated Maxsorb III shows the lowest value. The broad bump at a temperature 50 to 60 °C for parent Maxsorb III and KOH-H₂ treated Maxsorb III might be due to the of surface functional group.
The performance of adsorption refrigeration cycles using assorted adsorbent/refrigerant pairs employing a time-independent mathematical model has been analyzed. Results showed that the H$_2$ treated Maxsorb III/ethanol pair has the potential to provide a higher adsorption cooling effect. The studied pairs can deliver significant cooling load even at -5 °C evaporation temperature. On the other hand, adsorption kinetics of ethanol onto KOH-H$_2$ treated Maxsorb III is significantly faster than other two studied adsorbents, which might give the better performance in dynamic simulation.

An adsorption-compression hybrid refrigeration systems having two different cycle configurations, namely cascade type and subcool type has also been presented. The hybrid system shows the capability to reduce work input for the mechanical compressor which results in energy saving potential up to 30%.

The findings of this thesis will contribute in the development of a new generation adsorption cooling and/or heat pump system.

7.1 Future Work

The author recommended further work in the following areas:

- Development of a simulation program based on 3D distributed model in order to
  (i) determine the local heat and mass transfer mechanism in adsorption/desorption bed,
  (ii) predict the system performance of adsorption cooling system using surface treated
    Maxsorb III/ethanol pairs.
- The effect of particle size on adsorption uptake and uptake rate are also recommended for
  further study.

The magnetic suspension balance, which is developed by RUBOTHERM, is based on the research of Ruhr University in the 1980s (Lösch 1987, Lösch et al. 1994, 1999). It is a weight change measurement system that is excellent in high-temperature & high-pressure resistance, since its weight measuring section (balance) is separated from the sample cell so that it is not exposed to the measurement atmosphere.

![Diagram of 3-position type magnetic suspension balance]

Fig. B1: 3-position type magnetic suspension balance

The 3-position type balance has 3 stages of this position: to correct the drift of the balance in the 1st stage (tare) (zero point, ZP), to measure the sample weight change in the 2nd stage (ZP → MP1), and to measure the density in the 3rd stage (MP1 → MP2).
(sorption) (measuring point, MP1), and to measure the fluid density by Archimedes' principle by lifting a titanium sinker of about 4.5 cm³ in the 3rd stage (density) (measuring point, MP2).

References:


**Appendix A2. Buoyancy Correction**

Buoyancy force correction is based on the Archimedes’ principle which stated that an object in fluid receives buoyancy that is equal to the gravity applied to the same volume of the fluid.

\[ F = \rho_{FL} g V \] \hspace{1cm} (A1)

Where, \( F \) expresses the buoyancy, \( \rho_{FL} \) expresses the fluid density, and \( g \) expresses the gravity. \( m_s \) is the true mass of the sinker, i.e., the mass of the sinker in the sample cell evacuated (not influenced by buoyancy). \( m_s^* \) is the apparent mass of the sinker, i.e., the mass of the sinker in the sample cell filled with fluid (influenced by buoyancy). \( V_s \) \((T, P)\) is the volume of the sinker, which depends on the temperature and pressure

Accordingly, the equation of the balance of the gravity and buoyancy applied to the sinker in fluid is expressed:

\[ m_s^* g = m_s g - F \] \hspace{1cm} (A2)

\[ m_s^* g = m_s g - \rho_{FL} g V_s(T, P) \] \hspace{1cm} (A3)

From equation (2), the density in fluid can be determined by the following equation.
When using the 3-position type magnetic suspension balance, the fluid density can be measured to an accuracy of ±0.02 kg/m$^3$. In addition, the software can calculate the fluid density by the equation of state of non-ideal gas using the 2\textsuperscript{nd} virial coefficient.

The volume of the sinker is changed by thermal expansion and compression due to temperature or pressure. This unit software corrects the volume change of the sinker due to temperature and/or pressure using the following equation of material mechanics, with reference to the volume at 20°C and 1 bar (already calibrated at the time of delivery: e.g., 13.852232 ± 0.0014 cm$^3$)

$$V_s(T, P) = V_s(T_0, P_0) \left[ 1 + 3. \frac{l(T) - l(T_0)}{l(T_0)} - 3. \frac{1-2\nu(T)}{E(T)} (P - P_0) \right]$$

$T_0 = 20°C$, $P_0$=1 bar, $E$: Young's modulus, $\nu$: Poisson's ratio $l$: Change in length due to temperature

Parameters for correcting the buoyancy used in this unit

- Sinker volume (atmospheric pressure, room temperature): 4.377 cm$^3$
- Sinker weight: 19.65132 g
- Hook section volume: 0.33525 cm$^3$
- Hook section weight: 2.65855 g
- Basket weight: 6.78475 g
- Stainless steel density: 7.98 g/cm$^3$
- Air density at the atmospheric pressure (standard atmosphere, altitude of approx. 300 m): 0.0012 g/cm$^3$
Appendix A

Total adsorption[g] = [MP1 − ZP]_{current} − [MP1 − ZP]_{after pretreatment} + MP1_{buoyancy} \quad (A6)

MP1_{buoyancy}[g] = \frac{MP1_{volume}[cm^3] + adsorbed \ phae \ volume[cm^3]}{\rho_{FL}} \quad (A7)

\rho_{FL} = \frac{MP2_{current}[g] − MP2_{vacuum}[g]}{sink \ ker \ volume[cm^3]} \quad (A8)
Appendix B. Adsorption Isotherm of R32 onto ACF and Maxsorb III

**Fig. A1.** Adsorption isotherm of Maxsorb III/R32 pair.

**Fig. A2.** Adsorption isotherm of ACF/R32 pair.

**Table C1** Isotherm fitting parameters of ACP and ACF/R32 pairs.

<table>
<thead>
<tr>
<th>Adsorption pair</th>
<th>$C_0$ [kg/kg]</th>
<th>$E$ [kJ/kg]</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>R32 ACP</td>
<td>1.514</td>
<td>92.17</td>
<td>1.32</td>
</tr>
<tr>
<td></td>
<td>1.014</td>
<td>104</td>
<td>1.32</td>
</tr>
</tbody>
</table>

Reference:
Appendix C. **Fraunhofer Diffraction and Mie Scattering Theory.**

The laser diffraction particle size analyzer is based on Fraunhofer diffraction theory and Mie scattering theory. Fraunhofer diffraction gives the good approximation over the Mie scattering theory for large size particle (particle size > 10\(\lambda\)) and smaller scattering angle ( < 30 degrees).

**Fraunhofer Diffraction Theory**

Consider a single particle illuminated by radiation with intensity \(I_0\) \((\text{W/m}^2)\). In all that follows the incident radiation has the form of an infinite plane wave. Practically this implies that the amplitude and phase must be sensibly constant across the particle.

![Fraunhofer diffraction phenomenon](image)

Fig.5 Fraunhofer diffraction phenomenon.

The total scattered power \(P_{\text{sca}}\) is proportional to \(I_0\), the constant having the dimensions of area, i.e.

\[
P_{\text{sca}} = C_{\text{sca}} I_0
\]

where \(C_{\text{sca}}\) is the scattering cross-section. Similarly, for absorption

Considering the electric and magnetic field of light wave, the energy flux of a scatter wave becomes
The scattered power is given by integration over a sphere at radius \( r \) as

\[
\mathcal{P}_{sca} = \frac{I_0}{k_0^2} \int_0^{2\pi} \int_0^\pi F(\theta, \phi) \sin \phi \, d\phi \, d\theta
\]

And the scattering cross-section is

\[
C_{sca} = \frac{I_0}{k_0^2} \int_0^{2\pi} \int_0^\pi F(\theta, \phi) \sin \phi \, d\phi \, d\theta
\]

The scattering intensity is noted that

\[
\zeta_{sca} = \frac{I_0}{k_0^2 r^2} F(\theta, \phi)
\]

The well-known approximation is valid for large obstacles and unpolarized light and scattering close to the forward direction. For a sphere, Hodkinson (1966) simplified the scattering intensity for Fraunhofer diffraction

\[
\zeta_{sca} = I_0 \frac{\pi^2 D^4}{16 \lambda^2} \left[ \frac{2J_1(x \sin \theta)}{x \sin \theta} \right]^2 \times \frac{1 + \cos^2 \theta}{2}
\]

Where \( D \) is the diameter of the particle and \( \lambda \) is the wavelength of light in the medium. \( \Theta \) is the scattering angle from the forwarded direction. It suggests that the shape of the scattering pattern depends only on size and is independent of refractive index. For transparent particle (refractive index is greater than 1.3) this equation shows some discrepancy. For non-absorbing particles of very low refractive index (<1:1) there is some error even for large particles. This is caused by transmission of the incident wave which interferes with that diffracted, leading to anomalous diffraction.

The diffraction approach also suggested that the cloud of irregular particles could be modelled as a cloud of spheres with size distribution equal to the probability distribution of radius for small height of irregularity. A diffraction approach to scattering by irregular crystals has been discussed by Muinonen (1989) where the diffraction part of the scattered...
intensity is approximated as

$$\zeta_{sca} = \int dyn(y) \frac{\pi y^2}{2} \left\{ y^2 \cos \theta \left[ \frac{2J_1(y \sin \theta)}{y \sin \theta} \right]^2 \theta(90 - \theta) + J_0(y)^2 + J_1(y)^2 \right\}$$

$$\int dyn(y) = 1$$

Where \( n \) is the normalized size parameter distribution for a projected area of the randomly oriented crystal and \( x \) is the mean projected area size parameter.

**Mie Scattering Theory**

Mie theory is best on the measurement of particle size specially when the particles are small (particle size \(< 10\lambda\)). The size distribution can be measured accurately with the Mie theory supposing that the refractive index of the particle is known.

According to the Mie theory, when a parallel light beam of light hits the spherical particles, if the incident light is unpolarized with intensity \( I_0 \), the scattering intensity is

$$\zeta_{sca} = \frac{\lambda^2 I_0}{4\pi^2 r^2} \left[ |s_1(\theta)|^2 + |s_2(\theta)|^2 \right]$$

where \( \lambda \) is the wavelength of the light, \( s_1 \) and \( s_2 \) are the amplitudes of the scattering field and are given by

$$s_1(\theta) = \sum_{n=1}^{\alpha} \frac{2n+1}{n(n+1)} (a_n \pi_n + b_n \tau_n)$$

$$s_2(\theta) = \sum_{n=1}^{\alpha} \frac{2n+1}{n(n+1)} (a_n \pi_n + b_n \tau_n)$$

where \( a_n \) and \( b_n \) are the Mie coefficients related to the Bessel and Hankel functions whose variables are the particle size parameter and the refractive index of the particle, \( \pi_n \) and \( \tau_n \) are the Mie angular functions.

The diffraction part of the scattered light can be expressed by the approximation
Appendix C

\[ z_{sca} = \frac{\lambda^2 I_0 \alpha^2}{8\pi^2 r^2} \frac{\theta}{\sin \theta} \left[ \frac{2J_1(\alpha \theta)}{\alpha \theta} \right]^2 \]

Where \( \alpha = \frac{\pi d}{\lambda} \) is the particle size parameter and \( d \) is the particle diameter.

**Calculation of Mean Diameter**

The mean diameter of particle is presented in the Laser Diffraction Particle Size Analyzer based on the log scale of particle diameter. The following technique is used:

Total measurement range is divided into number of small divisions and the diameter for respective division is defined.

- \( x_1 \): minimum diameter of measurement range
- \( x_2 \): maximum diameter of measurement range

And each division is expressed by \([x_i, x_{i+1}] \) \( (i = 1, 2, 3, ..., n) \)

The diameter for respective division is defined as follows;

\[ \frac{\log_{10} x_j + \log_{10} x_{j+1}}{2} \]

\( q_j \) \( (j = 1, 2, 3, ..., n) \) is normalized particle amount (=100%) at the division of \([x_i, x_{i+1}]\)

So, the mean diameter on log scale can be obtained using the following expression.

\[ \mu = \frac{1}{100} \sum_{j=1}^{n} q_j \left( \frac{\log_{10} x_j + \log_{10} x_{j+1}}{2} \right) \]
Appendix D: A Case Study for Adsorption-Compression Hybrid System

The performance of an adsorption-compression hybrid system is analyzed analytically with two different cycle configurations, cascade type and subcool type. The refrigerant examine for the mechanical compression cycle are R134a, R152a, R1234yf and R1234ze whereas ethanol is the refrigerant for the adsorption cycle. The main feature of the proposed system is the capability to significantly reduce work input for the mechanical compressor which results up to 30% energy saving potential depending on the selection of refrigerant and system configuration. Based on the thermodynamic properties and laws the study analyzed the effect of the major design parameters such as evaporation temperature, compressor discharge pressure and desorption temperature on the system performances.

D.1 Introduction

To address the challenges of global warming and ozone depletion issues together, the utilization of environmentally benign working fluids as well as the innovative thermodynamic system design is very important for refrigeration and air-conditioning technology. Vapor compression cycle is commonly used in refrigeration and air conditioning fields. Currently, different configurations of two-stage vapor compression cycles employing synthetic refrigerants are chosen for refrigeration and air conditioning applications (ASHRAE 1990). The two-stage vapor compression cycles are suited when the temperature difference between the heat rejection and refrigeration sides becomes relatively larger so that single-stage refrigeration system is not sufficient to maintain the temperature and pressure difference.

Generally, the high and low pressure sides of a two-stage refrigeration system are charged
with the same refrigerant, whereas in a cascade system the high and low temperature circuits are filled separately with assorted refrigerants. However, the disadvantage of the cascaded compression systems is the requirement of high electricity consumption due to the simultaneous operation of two compressors in two cycles.

To reduce electricity consumption, various thermally powered adsorption cycles have been investigated extensively employing several adsorbent-refrigerant pairs, such as silica gel-water (Boelman et al. 1995; Chakraborty et al. 2009) zeolite-water (Liu and Leong, 2005) activated carbon-carbon dioxide (Saha et al. 2011), and activated carbon-methane/R134a/R507A (Habib et al. 2010). El-Sharkawy et al. (2008) and Li et al. (2004) have been experimentally investigated the adsorption characteristics of activated carbon-ethanol pair for adsorption cooling applications. The electricity consumption of the above mentioned adsorption cycles are very small; however, the coefficient of performance ($COP$) values of these systems is poor.

To improve the $COP$ of the refrigeration cycle, extensive studies have been conducted on the single stage compression since 1930s (Karagoz et al. 2004; Arora and Kaushik 2008). These cycles are good in performance but not suitable in low-temperature applications. Accordingly, double stage compression (Rane and Radermacher 1993; Llopis et al. 2010) and cascade refrigeration systems have been analyzed employing R744/R717 (Getu and Bansal 2008; Lee et al. 2006; Messineo 2012), R507A/R23 (Parekh and Tailor 2012), R404a/R508b (Pyasi and Gupta 2011) as working fluids. Fernández-Seara et al. (2006) analyzed a compression-absorption cascade refrigeration system considering CO$_2$ and NH$_3$ as refrigerants in the compression stage and the NH$_3$-H$_2$O pair in the absorption stage, respectively. They evaluated the possibilities of powering the cascade refrigeration system by means of cogeneration system. These types of cascade refrigeration systems are suitable for industrial applications where low-temperature refrigeration system is required, but the
systems consume huge amount of electricity.

To minimize the utilization of electricity in refrigeration systems, the authors of the present study aim to investigate the performance of cascade type and sub-cool type hybrid refrigeration systems powered by low-grade waste heat from automobile engine. The proposed hybrid systems consist of two separate refrigeration cycles, one is adsorption cycle which is driven by the waste heat and the other is mechanical compression cycle which is driven by the electricity. So the system would decrease the electricity consumption compared to the two stages mechanical compression system, since it is required only one compressor at low temperature stage. The hybrid refrigeration cycles share a heat exchanger, which operates simultaneously as the condenser/subcooler of the compression cycle and as the evaporator of the adsorption cycle. Moreover, it could use environmentally friendly refrigerants such as hydrofluorocarbons (HFCs) in the mechanical compression stage and ethanol as a natural refrigerant in the adsorption system.

In the present study, two types of combined mechanical compression and adsorption cycles are proposed, which are the cascade type and the sub-cool type. The performances of the proposed hybrid refrigeration systems are evaluated based on the thermodynamic theoretical analysis. A computer program is developed to find the key design parameters and to investigate the effect of those parameters on the cooling capacity as well as the coefficient of performance (COP) of both cascade type and sub-cool type hybrid refrigeration systems.

**D.2 System Description**

**D.2.1 Cascade Type Hybrid Refrigeration System**

Figure D.1(a) shows the schematic diagram of a cascade type hybrid refrigeration system. This refrigeration system comprises two separate one-stage refrigeration cycles, namely, the adsorption cycle and the mechanical compression cycle, and each cycle is designed with
different refrigerant, best suited for the working conditions. In my study, four different HFCs are used one by one in mechanical cycle whereas ethanol is solely chosen in the adsorption cycle. Two cycles are thermally linked by an intermediate heat exchanger called cascade condenser, which acts as condenser for mechanical compression cycle and evaporator for adsorption cycle. Ethanol in the adsorption cycle works at sub-atmospheric pressure whereas HFCs in the mechanical compression cycle works above atmospheric pressure. Fig. D.1(a) illustrates that the evaporator of mechanical cycle absorbs heat from the refrigerated space and rejects heat into upper cycle through cascade condenser. The heat absorbed by the evaporator of the adsorption cycle is equal to the sum of the heat absorbed by the evaporator of mechanical cycle and work input to the compressor. The evaporated ethanol is led to the adsorption bed, where it gets adsorbed by the activated carbon. It is desorbed when the waste heat is supplied. The condenser in the adsorption cycle finally rejects heat to the environment.

**Fig. D.1(a):** Schematic diagram of the cascade type hybrid cooling system.
D.2.2 Subcool Type Hybrid Refrigeration System

Figure D.1(b) shows the schematic diagram of the subcool type cooling system, where the cascade condenser is replaced with the condenser and evaporative sub-cooler. The working principle for subcool type system is almost similar to the cascade type system. The difference is the introduction of a condenser in the mechanical cycle where the refrigerant at first cooled to the saturated liquid phase then it is sub-cooled by the evaporative subcooler. So the heat transfer in the evaporative subcooler is only the sensible heat of liquid refrigerant of the mechanical compression cycle, which is smaller than the heat transfer in the cascade condenser as shown in Fig. D.1(a).

Fig. D.1(b): Schematic diagram of the sub-cool type hybrid cooling system.
D.3 Refrigerants Selection

The refrigerants R1234yf, R1234ze, R152a and R134a are used at mechanical compression side, among these, first three have a very low global warming potential (GWP); 4, 9 and 140 respectively, in order to potentially replace R134a which has a GWP of 1300. On the other hand ethanol is selected for adsorption side as it has no ozone depletion potential (ODP) and GWP. It is worthy to mention here that all four refrigerants in the mechanical cycle work almost at the same pressure range. Some characteristic features of the refrigerants are summarized in Table D.1.

<table>
<thead>
<tr>
<th>Refrigerant name</th>
<th>R1234yf</th>
<th>R134a</th>
<th>R152a</th>
<th>R1234ze</th>
<th>Ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar mass [kg/kmol]</td>
<td>114.04</td>
<td>102.03</td>
<td>66.05</td>
<td>114.04</td>
<td>46.07</td>
</tr>
<tr>
<td>Boiling point at 1atm [ºC]</td>
<td>-29.45</td>
<td>-26.07</td>
<td>-24.02</td>
<td>-18.95</td>
<td>78.24</td>
</tr>
<tr>
<td>Critical temperature [ºC]</td>
<td>94.7</td>
<td>101.1</td>
<td>113.3</td>
<td>109.4</td>
<td>240.7</td>
</tr>
<tr>
<td>Critical pressure [MPa]</td>
<td>3.38</td>
<td>4.06</td>
<td>4.52</td>
<td>3.64</td>
<td>6.15</td>
</tr>
<tr>
<td>Latent heat of vaporization at 5ºC [kJ/kg]</td>
<td>160.02</td>
<td>194.74</td>
<td>301.94</td>
<td>180.88</td>
<td>939.91</td>
</tr>
<tr>
<td>ODP</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>GWP</td>
<td>4</td>
<td>1300</td>
<td>140</td>
<td>9</td>
<td>≈0</td>
</tr>
<tr>
<td>Safety group*</td>
<td>A2</td>
<td>A1</td>
<td>A2</td>
<td>A2</td>
<td>A3</td>
</tr>
</tbody>
</table>

*A1- lower toxicity, no flame propagation; A2- lower toxicity, moderate flammability, A3- lower toxicity, high flammability (ASHARE Stand 2010).
D.4 Analytical Expression

Thermodynamic analysis of the adsorption-compression hybrid refrigeration system is performed based on the following general assumptions which helped to simplify the mathematical program.

- The heat loss or gain and pressure drop in the connecting pipes are negligible.
- Isenthalpic expansion of refrigerant is considered in the expansion valves.
- The mechanical compressor is treated as isentropic.
- The refrigerants at the outlet of condensers are at saturated liquid state and those at the outlet of evaporators are at saturated vapor state.
- The change in kinetic and potential energy is negligible.

The thermophysical properties of the refrigerants specified in this paper were calculated using REFPROP (Lemmon et al. 2010), which has built-up property functions of many refrigerants. The first argument here for all built-in thermophysical property functions is the name of the substance. Then any set of valid arguments can be supplied owing to get desired thermodynamic functions.

In view of the schematic and state points of Figs. 6.5(a) and 6.5(b), the following sequences of equations are applied for the analysis. The cooling capacity of the evaporator for mechanical compression cycle is defined by:

\[
\dot{Q}_{eva,MC} = \dot{m}_{MC} \Delta h_{eva,MC}
\]  
(D.1)

Compressor power consumption for mechanical compression cycle:

\[
\dot{W}_{com} = \dot{m}_{MC} \Delta h_{com,MC}
\]  
(D.2)

Rate of heat transfer in the cascade condenser:

\[
\dot{Q}_{cas} = \dot{m}_{MC} \Delta h_{cond,MC} = \dot{m}_{AC} \Delta h_{eva,AC}
\]  
(D.3a)

Rate of heat transfer in the evaporative subcooler:
Appendix D

\[ \dot{Q}_{\text{eva,sub}} = \dot{m}_{MC} \Delta h_{\text{sub,MC}} = \dot{m}_{AC} \Delta h_{\text{eva,AC}} \]  

(D.3b)

Mass flow ratio for cascade type system:

\[ \gamma_{\text{cas}} = \frac{\dot{m}_{AC}}{\dot{m}_{MC}} = \frac{\Delta h_{\text{cond,MC}}}{\Delta h_{\text{eva,AC}}} \]  

(D.4a)

Mass flow ratio of subcool type system:

\[ \gamma_{\text{sub}} = \frac{\dot{m}_{AC}}{\dot{m}_{MC}} = \frac{\Delta h_{\text{sub,MC}}}{\Delta h_{\text{eva,AC}}} \]  

(D.4b)

The COP of the mechanical compression cycle is:

\[ \text{COP}_{\text{MC}} = \frac{\dot{Q}_{\text{eva,MC}}}{W_{\text{com}}} \]  

(D.5)

The specific cooling capacity: \( SCC = \frac{\dot{Q}_{\text{eva,MC}}}{M_s} \)  

(D.6)

The porous property of activated carbon, namely Maxsorb III, were measured by Saha et al. (2007), and it is found that Maxsorb III possesses a surface area of 3200 m\(^2\)/g and mean pore diameter 2.0 nm. Ethanol with a purity of 99.9% is used as refrigerant.

The Dubinin-Astakhov (D-A) equation is used to estimate the equilibrium uptake of ethanol gases onto Maxsorb III in the form which is given in Eq. (2.2) (Chapter 2).

According to I.I. El-Sharkawy et al. (2008), the exponential parameter \( n \) equals to 1.75 provided best fitting with experimental data, which yields the maximum adsorption capacity, \( W_0 \) and adsorption characteristics parameter, \( E \) is equal to 1.2 kg/kg and 120 kJ/kg, respectively, and isosteric heat of adsorption for the Maxsorb III-ethanol pair is found to be 1026 kJ/kg.

The amount of mass of adsorbents is calculated by the following equation:

\[ \dot{Q}_{\text{eva,AC}} = \frac{\Delta h_{\text{eva,AC}} M_s \Delta W}{t_{\text{cycle}} e_{\text{ads/des}}} \]  

(D.7)
Desorption heat: \( \dot{Q}_{dh} = M_s \dot{Q}_{ads} \Delta W \) \hfill (D.8)

Sensible heat is:

\[
\dot{Q}_{sh} = M_s C_{ads} \left[ 1 + \frac{W_{ref}}{C_{ads}} + \frac{(MC)_{bed}}{(MC)_{ads}} \right] \Delta T_{ad}
\] \hfill (D.9)

The COP of the adsorption cycle:

\[
COP_{AC} = \frac{\dot{Q}_{eva,AC}}{\dot{Q}_{sh} + \dot{Q}_{dh}}
\] \hfill (D.10)

The heat balance equations for cascade type and subcool type systems can be written as:

\[
\dot{Q}_{eva,MC} + W_{com} + \dot{Q}_{dh} = \dot{Q}_{ads} + \dot{Q}_{cond,AC}
\] \hfill (D.11a)

\[
\dot{Q}_{eva,MC} + W_{com} + \dot{Q}_{dh} = \dot{Q}_{cond,MC} + \dot{Q}_{ads} + \dot{Q}_{cond,AC}
\] \hfill (D.11b)

The energy savings is estimated:

\[
1 - \frac{COP_{conventional}}{COP_{MC,cascade\ subcool}}
\] \hfill (D.12)

Here \( COP_{conventional} \) stands for the coefficient of performance of conventional mechanical compression cycle which comprises with an evaporator, a compressor, a condenser and an expansion valve. The calculation of the thermodynamic state points and properties such as pressures, temperatures, entropies and enthalpies of the refrigerants for both systems are furnished in Table 6.3, where \( etha \) stand for ethanol and \( hfc \) stand for R134a or R152a or R1234yf or R1234ze refrigerants. The equations in Table 6.3 can be used for any other refrigerants under the same operating conditions.

The calculation described in Table D.2 have been implemented by simulation codes for the cascade and sub-cool type refrigeration systems developed on a programing tool, Mat lab. A flowchart of the simulation program is shown in Fig.D.2.
Fig. D.2: Flow chart of simulating program
Table D.2 Calculation of thermodynamic state points of cascade type and subcool type hybrid refrigeration systems.

<table>
<thead>
<tr>
<th>Mechanical cycle</th>
<th>Evaporator outlet</th>
<th>Mechanical Compressor outlet</th>
<th>Condenser outlet</th>
<th>Expansions on valve outlet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cascade type</td>
<td>( P_1 = f(hfc, T = T_E, Q = 1) )</td>
<td>( P_2 = P_{com} )</td>
<td>( P_3 = P_2 )</td>
<td>( P_4 = P_1 )</td>
</tr>
<tr>
<td></td>
<td>( T_1 = T_{eva} + T_{sup} )</td>
<td>( h_{i_2} = f(hfc, P = P_2, s = s_1) )</td>
<td>( T_3 = f(hfc, P = P_3, Q = 0) )</td>
<td>( T_4 = T_{eva} )</td>
</tr>
<tr>
<td></td>
<td>( h_1 = f(hfc, T = T_1, P = P_1) )</td>
<td>( h_2 = (h_{s_2} - h_1) / e_{com} + h_1 )</td>
<td>( h_3 = f(hfc, P = P_1, Q = 0) )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( s_1 = f(hfc, T = T_1, P = P_1) )</td>
<td>( T_2 = f(hfc, P = P_2, h = h_2) )</td>
<td>( h_4 = h_3 )</td>
<td></td>
</tr>
</tbody>
</table>

| Subcool type     | \( P_1 = f(hfc, T = T_E, Q = 1) \) | \( P_2 = P_{com} \) | \( P_3 = P_2 \) | \( P_4 = P_1 \) |
|                  | \( T_1 = T_{eva} + T_{sup} \) | \( h_{i_2} = f(hfc, P = P_2, s = s_1) \) | \( T_3 = T_{con} \) | \( T_4 = T_E \) |
|                  | \( h_1 = f(hfc, T = T_1, P = P_1) \) | \( h_2 = (h_{s_2} - h_1) / e_{com} + h_1 \) | \( T_{3, sub} = T_{con} - T_{sub} \) | \( h_4 = h_{1, sub} \) |
|                  | \( s_1 = f(hfc, T = T_1, P = P_1) \) | \( T_2 = f(hfc, P = P_2, h = h_2) \) | \( h_3 = f(hfc, P = P_1, Q = 0) \) |
|                  | \( h_{3, sub} = f(hfc, T = T_{3, sub}, P = P_3) \) |

**Thermal compressor**

- Cascade type
  - \( W_{max} = W_0 \exp \left[ - \frac{RT_{ad}}{E} \ln \left( \frac{P_{ad}}{P_{eva}} \right) \right] \)
  - \( T_6 = T_{con} \)
  - \( P_7 = P_5 \)

- \( T_{eva, AC} = T_3 - \Delta T \)

- Subcool type
  - \( W_{min} = W_0 \exp \left[ - \frac{RT_{dei}}{E} \ln \left( \frac{P_{ad}}{P_{eva}} \right) \right] \)
  - \( T_6 = T_{con} \)

- Adsorption cycle
  - \( \Delta W = W_{max} - W_{min} \)
  - \( h_6 = f(hfc, P = P_3, Q = 0) \)
  - \( h_7 = h_6 \)

- \( P_3 = f(etha, T = T_{eva, AC}, Q = 1) \)

- \( T_5 = T_{eva, AC} + T_{sup} \)

- \( h_3 = f(hfc, T = T_5, P = P_3) \)

Subscripts refer to the points indicated in Figs. D.1(a) and D.1(b).

175
Table D.3 Basic operating conditions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m_{MC}$</td>
<td>0.02 kg s$^{-1}$</td>
</tr>
<tr>
<td>Mechanical compression cycle</td>
<td></td>
</tr>
<tr>
<td>$P_{com}$</td>
<td>650 kPa</td>
</tr>
<tr>
<td>$T_{eva}$</td>
<td>5°C</td>
</tr>
<tr>
<td>$T_{sup}$</td>
<td>3°C</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>0.80</td>
</tr>
<tr>
<td>Adsorption cycle</td>
<td></td>
</tr>
<tr>
<td>$T_{cool}$</td>
<td>35°C</td>
</tr>
<tr>
<td>$T_{con}$</td>
<td>35°C</td>
</tr>
<tr>
<td>$T_{des}$</td>
<td>80°C</td>
</tr>
<tr>
<td>$t_{cycle}$</td>
<td>500 s</td>
</tr>
<tr>
<td>$\varepsilon_{ad}$</td>
<td>0.80</td>
</tr>
<tr>
<td>Subcool type system</td>
<td></td>
</tr>
<tr>
<td>$T_{sub}$</td>
<td>15°C</td>
</tr>
<tr>
<td>$P_{com}$</td>
<td>900 kPa</td>
</tr>
<tr>
<td>Temperature difference in cascade condenser</td>
<td>$\Delta T = 5°C$</td>
</tr>
</tbody>
</table>

D.5 Effect of Operating Condition

The authors have used system design parameters at different ranges to explain the influences of operating conditions on COP, specific cooling capacity (SCC) and mass flow ratios. The parameters include evaporation temperature, desorption temperature, compressor work, subcool temperature and temperature difference in cascade condenser.

In the cascade heat exchanger, the design parameter $\Delta T$ stands for the temperature difference between the condensation temperature in mechanical cycle and the evaporation temperature in the adsorption cycle while the subcool temperature, $T_{sub}$, shows how much the saturated liquid refrigerant is cooled below the condenser temperature.
D.5.1 Performance Analysis on the Cascade Type Hybrid Refrigeration System

D.5.1.1 Effect of the Design Parameters for the Mechanical Compression Cycle

Figure D.3 shows the results of the COP values of the compression and adsorption cycle with R1234yf, R134a, R152a and R1234ze as the refrigerant in the mechanical compression cycle and ethanol in the adsorption cycle varying the compressor pressure from 500 kPa to 800 kPa while keeping the remaining design parameters and operating conditions equal to the values indicated in Table D.3 (Saha et al. 2006; Saha et al. 2007). Here, it can be noticed that increase in compressor pressure caused simultaneously decrease in the COP_{MC} and increase in the COP_{AC}. The different COP values for different refrigerants mean the different volume flow rates at the compressor as well as different refrigeration effects produce by the respective refrigerant. The COP_{MC} decreased due to the higher input energy to raise the pressure as well as temperature of refrigerants in the compressor outlet (Fernández-Seara et al. 2006). R1234yf showed the highest COP_{MC} among the four studied refrigerants under the same system configuration because of its relatively higher vapor density. On the other hand, the COP_{AC} increased due to the higher evaporation temperature at adsorption cycle.

From Fig. D.4 it is shown that the required mass of Maxsorb III is reduced when the compressor pressure is increased in the mechanical cycle. R152a required the largest adsorbent mass whereas R1234ze resulted in the smallest adsorbent mass among the four refrigerants. The cooling load as well as work input for R152a was comparatively higher than other refrigerants, and therefore, the heat transfer by R152a in cascade condenser is also high. It is shown that the cascade system could work well with adsorbent mass less than 10 kg in combination with refrigerants besides R152a for the mechanical compression cycle.
Appendix D

Fig. D.3: Effect of compressor pressure on $COP_{MC}$ and $COP_{AC}$ in the mechanical cycle.

Fig. D.4: Effect of compressor pressure on mass of Maxsorb III.
Figure D.5(a) reveals that the $COP_{MC}$ would increase significantly when the evaporation temperature exceeded 10ºC despite that the cooling capacity is almost linear throughout the change of evaporation temperature -10ºC to 15ºC which is shown in Fig. D.5(b). Refrigerants R1234yf and R134a show good coefficient of performances at higher evaporation temperature although, in terms of cooling capacity, R152a is always better than other refrigerants we studied. As we increased evaporation temperature, the compressor required less amount of work to be done.

![Graph showing effect of evaporation temperature on COP](image)

**Fig. D.5(a):** Effect of evaporation temperature on $COP_{MC}$. 
Fig. D.5(b): Effect of evaporation temperature on cooling capacity in the mechanical compression cycle.

Fig. D.6: Effect of compressor pressure on mass flow ratio.
Figure D.6 shows the mass flow ratio \( \gamma_{\text{cas}} \) between the refrigerant flowed in the mechanical cycle and in the adsorption cycle. As the flow of refrigerant mass in mechanical cycle is kept constant at 0.02\text{kg s}^{-1} for all refrigerants so the ratio, \( \gamma_{\text{cas}} \), reflects the variation of ethanol mass flow in the adsorption cycle. Here the value of the ratio ranging from 0.16 to 0.32. The small value of the ratio is due to the high latent heat of vaporization of ethanol. Moreover, the low ethanol flow has positive consequences on the system safety, since it is a flammable substance.

**D.5.1.2 Effect of the Design Parameters for the Adsorption Cycle**

The desorption temperature found to be influential on the delivered cooling effect. As can be seen from Fig. D.7(a), the specific cooling capacity \( (SCC) \) of the system is increased with the rise of the desorption temperature because of lower amount of required adsorbent mass at higher desorption temperature. Fig. D.7(b) shows that the amount of required mass is almost constant after 70 °C, which resulted in the improvement of \( SCC \). The results also indicate that R1234ze would be advantageous in terms of compactness of the system because the specific cooling capacity for R1234ze shows higher value than that for the other assorted refrigerants.
Appendix D

Fig. D.7(a): The influence of desorption temperature on specific cooling capacity.

Fig. D.7(b): The influence of desorption temperature on mass of Maxsorb III.
Fig. D.8: Variation of $COP_{AC}$ with desorption temperature in the adsorption cycle.

Fig. D.8 shows the optimal value of $COP_{AC}$ as a function of desorption temperature. Results indicated that the system would achieve the highest $COP_{AC}$ with the desorption temperature between 75 and 85 °C irrespective of the refrigerant. With temperature higher than this range, the $COP_{AC}$ would moderately decrease, but the variation is not significant. This due to the constant amount of evaporation heat is exchanged in the cascade condenser.

**D.5.2 The Effect of the Interconnection Parameters**

Figure D.9(a) shows the effect of temperature difference ($\Delta T$) on $COP_{AC}$, while Fig. D.9(b) shows the effect of temperature difference ($\Delta T$) on SCC. It is evident from Figs. D.9(a) & D.9(b) that higher values of the temperature difference ($\Delta T$) caused the reduction of $COP_{AC}$ and SCC value of the system, which demonstrated the negative impact of system
Appendix D

performance. At higher $\Delta T$, higher irreversibility occurs in a heat transfer process. $\Delta T$ can be reduced by using larger heat exchangers. However it makes the refrigeration system bigger and more expensive.

![Fig. D.9(a): Effect of $\Delta T$ on $COP_{AC}$](image1)

![Fig. D.9(b): Effect of $\Delta T$ on SCC](image2)
D.5.3 Performance Analysis on the Subcool Type Hybrid Refrigeration System

Subcooling of liquid refrigerant is must for ensuring operational reliability for mechanical compression refrigeration system. During subcooling, the amount of heat withdrawn from the liquid refrigerant manifests itself as an increase on the refrigeration capacity of the system. The external subcool system which is independent of ambient temperature can control the possible targeted subcool temperature in the defined boundaries. Due to increase the subcooling temperature, the specific volume of refrigerant decreases during expansion, so at constant opening diameter of the valve, larger amount of refrigerant mass flow would be achieved and the capacity would increase additionally.

The mechanical cycle in subcool type system would work with relatively higher pressure range than that of the cascade type system to maintain the temperature of compressed refrigerant higher than the condenser temperature. So the added work done by the compressor reduces the $COP_{MC}$ of the subcool type system as shown in Fig. D.10. But when the subcooling is applied, the inlet enthalpy and the overall evaporation enthalpy increase, that leads to both refrigeration capacity and $COP_{MC}$ to increase which is shown in Figs. D.11(a) and 6.11(b), respectively. It is evident from Fig. D.11(a) that $COP_{AC}$ decreases with the increase in subcool temperature.

Figures D.12(a) and D.12(b) present the effect of subcool temperature on mass of Maxsorb III and $SCC$ of the system, respectively. The increased $T_{sub}$, means the higher heat transfer rate by the evaporative subcooler which causes in the increase of required mass. But the value of $SCC$ (shown in Fig. D.12 (b)) decreases sharply when $T_{sub}$ is below 10°C. The amount of mass required in the subcool type system is less than 5 kg which reduces the size and overall weight of the system.
**Fig. D.10:** Effect of compressor discharge pressure on $COP_{MC}$ for subcool type refrigeration system.

**Fig. D.11(a):** Variation of $COP_{MC}$ and $COP_{AC}$ with subcool temperature.
Fig. D.11(b): Variation of system cooling capacity with subcool temperature.

Fig. D.12(a): Effect of subcool temperature on mass of Maxsorb III.
D.5.3 Energy Saving Effect

The energy saving is calculated in terms of COP using Eq. (D.12) where the same boundary condition has applied for a single compression conventional system. It is found that the cascade type hybrid system can save energy up to 19% compared to the conventional system depending on the refrigerant used in the mechanical cycle (see Fig. D.13 (a)). This is due to the less work input in the mechanical compressor of the cascade type system. Here it is shown that R1234yf is the most energy efficient among the studied four refrigerants due to its relatively higher vapor pressure.

Energy saving for subcool type system is also estimated and it is shown in Fig. D.13(b). The subcool type system can save more energy than the cascade type system for all four refrigerants. The refrigerant R1234ze is found to be the most energy efficient for subcool type system.
The subcool type and cascade type system reduced the amount of required mass significantly. The subcool type system delivers cooling capacity up to 5.6 kW with adsorbent of 5 kg. Whereas, the cascade type system requires 10 kg of adsorbent to produce comparable amount of cooling capacity. It is noteworthy to mention here that the required adsorbent mass is about 100 kg in a single stage 2 bed adsorption only system to produce same amount of cooling effect. So the proposed system could be used as an automobile air conditioner.

Fig. D.13(a): Energy saving potential for cascade type system.

Fig. D.14(b): Energy saving potential for subcool type system.
Appendix D

D.7 Nomenclature

\( COP \)  
coefficient of performance

\( C \)  
specific heat \([\text{J/kg K}]\)

\( \varepsilon \)  
Efficiency

\( \gamma \)  
Mass flow ratio

\( \Delta h \)  
Specific enthalpy difference \([\text{kJ/kg}]\)

\( M_s \)  
Mass of adsorbent \([\text{kg}]\)

\( \dot{m} \)  
Rate of mass flow \([\text{kg/s}]\)

\( P_{\text{com}} \)  
desorption pressure \([\text{kPa}]\)

\( Q_{\text{des}} \)  
desorption Heat \([\text{J/kg}]\)

\( SCE \)  
specific cooling effect \([\text{J/kg}]\)

\( C_{\text{ads}} \)  
Specific heat of Maxsorb III \([\text{kJ/kg K}]\)

\( P \)  
Pressure \([\text{kPa}]\)

\( \dot{Q} \)  
Rate of heat transfer \([\text{kW}]\)

\( Q \)  
Quality of refrigerant (Dimensionless)

\( \Delta T_{\text{ad}} \)  
Temperature difference between adsorption and desorption \([\text{K}]\)

\( T \)  
Temperature \([\text{K}]\)

\( \Delta T \)  
Temperature difference in cascade condenser/evaporator, \([\text{K}]\)

\( t \)  
Time \([\text{s}]\)

\( \dot{W}_{\text{com}} \)  
Compressor power \([\text{kW}]\)

\( W \)  
equilibrium uptake \([\text{kg/kg}]\)

\( W_0 \)  
maximum adsorption capacity \([\text{kg/kg}]\)

\( W_{\text{max}} \)  
maximum uptake \([\text{kg/kg}]\)

\( W_{\text{min}} \)  
minimum uptake \([\text{kg/kg}]\)
ΔW  Difference in maximum and minimum uptake [kg/kg]

Subscripts

AC  Adsorption cycle
ads  Adsorption
bed  Adsorbent bed
cas  Cascade heat exchanger
com  Compressor
cond  Condensation
cool  Cooling of adsorption bed
des  Desorption
dh  Desorption heat
eva  Evaporator
MC  Mechanical compressor cycle
ref  Refrigerant
sh  Sensible heat
sub  Subcooling
Sup  Superheating

D.6 Conclusion
The study analyzed the performance of mechanical compression-adsorption hybrid system using R134a, R152a, R1234yf and R1234ze in mechanical cycle along with ethanol in adsorption cycle is analyzed. Based on the thermodynamic analysis of the main conclusions are as follows:

- The values of cooling capacity of the system vary from 2.7 kW to 5.6 kW depending of the used refrigerant and cycle configuration. R152a based cycle provides highest cooling capacity value which is followed by R134a, R1234ze and R1234yf.
• The variation of the COP in adsorption cycle is marginal with the change of refrigerants in mechanical compression cycle.
• Both COP and cooling capacity in mechanical compression cycle rise with the increase in evaporation temperature and subcool temperatures.
• The amount of required adsorbent mass is about 5 kg for delivered cooling capacity of 5.6kW when the system operates in subcooling mode.
• The cascade type and subcool type hybrid systems can save energy from 13% to 19% and 22% to 30%, respectively, depending on the refrigerant used in the mechanical cycle than the conventional mechanical compression system.
• The refrigerant subcooling effect demonstrates a reliable way of increasing cooling capacity, for example 1°C subcooling temperature causes in 1% improvement in cooling capacity.

D.7 References

1. ASHRAE Handbook, 1990, Refrigeration systems and applications, Atlanta, USA.
Appendix D


13. Lemmon, E.W., McLinden, M.O., Huber, M.L., 2010, Reference fluid thermodynamic and transport properties (Refprop) version 9, National institute of standards and technology (NIST), Physical and chemical properties division national institute of standards and technology.


Author’s Related Publications

Journal Publications


International Conferences


**Other Conferences**
