STUDY OF ACTIVATED CARBON/METHANOL ADSORPTION REFRIGERATION TUBE AND SYSTEM INTEGRATION

BY

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A THESIS SUBMITTED IN FULFILMENT OF THE REQUIREMENT FOR THE DEGREE OF MASTER OF ENGINEERING SCIENCE

AT

SCHOOL OF MECHANICAL ENGINEERING
THE UNIVERSITY OF ADELAIDE

JANUARY 2011
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# Table of Contents

Table of Contents                                                                                                    i
List of Tables                                                                                                        v
List of Figures                                                                                                       vi
Abstract                                                                                                               x
Acknowledgements                                                                                                      xii
Nomenclature                                                                                                          xiii

1 INTRODUCTION ........................................................................................................................................ 1

1.1 Introductory Background ..................................................................................................................... 1

1.2 Research Aims .................................................................................................................................. 3

1.3 Scope and Limitations ......................................................................................................................... 3

2 LITERATURE REVIEW .......................................................................................................................... 5

2.1 Introduction ................................................................................................................................... 5

2.2 Working Pairs .................................................................................................................................. 6

2.3 Thermodynamic Cycles ..................................................................................................................... 7

2.3.1 Basic Cycle ................................................................................................................................. 7

2.3.2 Heat Recovery Cycle .................................................................................................................. 8

2.3.3 Mass Recovery Cycle ................................................................................................................ 10

2.3.4 Cascading Cycle ....................................................................................................................... 12

2.3.5 Other Advanced Cycles ............................................................................................................. 13

2.4 Generator and ART’s Structures ...................................................................................................... 14

2.5 Mathematical Model ......................................................................................................................... 17

2.5.1 Heat Transfer Model .................................................................................................................. 17

2.5.2 Mass Transfer Model ................................................................................................................ 18

2.5.3 Adsorption Model ..................................................................................................................... 19
2.6 Adsorption Refrigeration Systems ................................................................. 20
  2.6.1 Intermittent System .............................................................. 20
  2.6.2 Traditional Continuous System ............................................. 21
  2.6.3 Modular Continuous System ................................................. 23
2.7 Research Objectives ............................................................................. 24
2.8 Thesis Outline ...................................................................................... 25

3 STUDY OF ADSORPTIVE PROPERTIES ......................................................... 27
  3.1 Introduction ...................................................................................... 27
  3.2 Theoretical Considerations ................................................................ 29
    3.2.1 Adsorption Equations ............................................................ 29
    3.2.2 Clausius-Clapeyron Equation ................................................. 31
    3.2.3 Thermodynamic Analysis ...................................................... 33
  3.3 Testing of Adsorptive Properties ....................................................... 36
    3.3.1 Testing Setup ....................................................................... 37
    3.3.2 Testing Procedures ............................................................. 39
    3.3.3 Determination of the Parameters ......................................... 40
  3.4 Discussion ......................................................................................... 42
    3.4.1 Format Agreement Comparison ............................................. 42
    3.4.2 Format Impact on $Q_c$ ........................................................ 46
    3.4.3 Format Impact on COP ......................................................... 48
    3.4.4 Sensitivities of the Parameters ............................................. 50
  3.5 Conclusions ....................................................................................... 54

4 PHYSICAL AND MATHEMATICAL MODELS ............................................... 55
  4.1 Introduction ...................................................................................... 55
  4.2 Physical Model ................................................................................ 56
    4.2.1 ART Configuration .............................................................. 56
    4.2.2 Working Principle of the ART .............................................. 57
    4.2.3 Mechanism of the Model ...................................................... 58
4.3 Mathematical Model ........................................................................................................ 61
  4.3.1 Modeling Assumptions ............................................................................................. 61
  4.3.2 Governing Equations .............................................................................................. 62
  4.3.3 Boundary Conditions .............................................................................................. 65
4.4 Numerical Solution ........................................................................................................ 68
  4.4.1 Introduction ............................................................................................................... 68
  4.4.2 Domain Meshing ...................................................................................................... 69
  4.4.3 Domain Equations ................................................................................................... 70
  4.4.4 Boundary Conditions .............................................................................................. 70
5 EXPERIMENTAL VALIDATION ...................................................................................... 71
  5.1 Introduction .................................................................................................................. 71
  5.2 Experimental Apparatus .............................................................................................. 71
    5.2.1 Generator ............................................................................................................... 71
    5.2.2 Condenser .............................................................................................................. 73
    5.2.3 Evaporator ............................................................................................................ 74
    5.2.4 Heat Source .......................................................................................................... 75
    5.2.5 Temperature Sensor .............................................................................................. 76
    5.2.6 Data Logger ........................................................................................................... 76
    5.2.7 Pressure Gauge .................................................................................................... 77
  5.3 Analysis of Experimental Errors .................................................................................. 77
    5.3.1 Measuring Instruments Errors .............................................................................. 77
    5.3.2 Data Acquisition Errors ....................................................................................... 78
    5.3.3 Other Errors ......................................................................................................... 78
    5.3.4 Summary of Errors .............................................................................................. 79
  5.4 Experimentation ............................................................................................................ 79
    5.4.1 Experimental System ............................................................................................ 79
    5.4.2 Experiment Conditions ......................................................................................... 80
    5.4.3 Testing Procedures ............................................................................................... 82
  5.5 Model Validation ......................................................................................................... 83
5.5.1 System Pressure ................................................................. 83
5.5.2 Solid Phase Temperature .................................................. 85
5.5.3 Fluid Phase Temperature ................................................... 87
5.5.4 Sorption Amount ............................................................. 88
5.6 Discussion of Concentration Migration .................................... 89
5.7 Conclusions ........................................................................ 91

6 PARAMETRIC ANALYSIS ............................................................. 93
  6.1 Introduction ...................................................................... 93
  6.2 Non-equilibrium Adsorption Effects .................................... 95
  6.3 Parameter Effects on Cycle Time .......................................... 96
  6.4 Parameter Effects on COP .................................................. 97
  6.5 Parameter Effects on SCP .................................................. 98
  6.6 Cycle Time Optimisation .................................................... 99
  6.7 Conclusions ...................................................................... 100

7 ANALYSIS OF POTENTIAL APPLICATION .................................. 101
  7.1 Introduction ...................................................................... 101
  7.2 System Integration Solution ............................................... 102
    7.2.1 General Integration Strategy .......................................... 102
    7.2.2 Introduction to Components .......................................... 102
    7.2.3 Home Application ..................................................... 105
    7.2.4 Commercial Application ............................................. 106
  7.3 Economics Analysis .......................................................... 106
  7.4 Conclusion and Recommendation ....................................... 109

8 CONCLUSIONS ........................................................................ 110

APPENDICES .............................................................................. 113
  Appendix A Thesis Assessment Details ..................................... 113
  Appendix B Publications Arising From This Work ..................... 114
  Appendix C Experimental Data ................................................ 115

BIBLIOGRAPHY ........................................................................ 128
List of Tables

Table 3.1  Parameters of each sample in different adsorption equations.............. 42
Table 3.2  Parameters in $Q_r$ calculation .................................................................. 48
Table 5.1  Operating parameters of the experiment..................................................... 80
Table 5.2  Thermophysical properties of the working pair.......................................... 81
Table 5.3  Geometrical dimensions of the adsorber....................................................... 81
Table 7.1  The estimated cost of the initial capital investment of one ARTs module.......................................................... 107
Table 7.2  Assumed usage information for home and commercial users .............. 107
List of Figures

Figure 2.1 Clapeyron diagram of an ideal basic adsorption refrigeration cycle........8
Figure 2.2 Schematic diagram of an external heat recovery cycle with identical adsorbents.................................................................9
Figure 2.3 Diagram of a pressure driven mass recovery cycle ..................11
Figure 2.4 Temperature driven mass recovery cycle. Redrawn from Uyun et al. (2009).................................................................12
Figure 2.5 Schematic of a cascading cycle ........................................13
Figure 2.6 Configuration of a centre-heated generator. Summarised structure with structures proposed by Marletta et al. (2002), Leong and Liu (2006), Maggion et al. (2006). ......................................................15
Figure 2.7 Configuration of an external-heated generator. Summarised structure with structures proposed by Hu (1996), Dai and Sumathy (2003), Cortés et al. (2009), Fadar et al. (2009). ......................................................16
Figure 2.8 Configuration of an ART. Redrawn from Critoph (2001), Wu et al. (2009). .................................................................17
Figure 2.9 Schematics of a solar ice maker. From Jing and Execll (1994).......21
Figure 2.10 Two-bed adsorption chiller. From Xia et al. (2008). ................22
Figure 2.11 Three bed adsorption chiller. From Miyazaki et al. (2010). ........22
Figure 2.12 Modular rotary refrigeration system. From Critoph (2001). ........23
Figure 2.13 Multi-tube adsorption system. From Wang and Zhang (2009). ....24
Figure 3.1 P-T-x diagram of an ideal basic adsorption refrigeration cycle....34
Figure 3.2 Schematic diagram of the testing system.................................37
Figure 3.3 Photograph of the testing system ........................................38
Figure 3.4 Comparison of experimental data and fitted isosteric lines, 207C ....43
Figure 3.5  Comparison of experimental data and fitted isosteric lines, 207EA ...... 44
Figure 3.6  Comparison of experimental data and fitted isosteric lines, WS-480 .... 45
Figure 3.7  Refrigeration output $Q$ vs heat source temperature $T$ calculated with Langmuir format, Freundlich format and D-A format respectively ................................................................. 47
Figure 3.8  Refrigeration COP vs heat source temperature $T$ calculated with Langmuir format, Freundlich format and D-A format respectively .................................................................................. 49
Figure 3.9  Impact on $Q$, and COP caused by error of parameters $K'$ and $Q_{\pi}$ in Langmuir equation: (a) $Q$, (b) COP ................................................................. 51
Figure 3.10 Impact on $Q$, and COP caused by error of parameters $x_{i}$ and $n$ in Freundlich equation: (a) $Q$, (b) COP ................................................................. 52
Figure 3.11 Impact on $Q$, and COP caused by error of parameters $x_{i}$, $n$ and D in D-A equation: (a) $Q$, (b) COP ................................................................. 53
Figure 4.1  Overview and cross-section of the proposed ART ...................................... 57
Figure 4.2  Claperyon diagram of an ideal adsorption refrigeration cycle of an ART .............................................................................................................. 59
Figure 4.3  A rending of the pore-level transport, reaction, and phase change In porous media. Figure from Kavinay (1955). ........................................ 59
Figure 4.4  Schematics of convective heat transfer in adsorbent bed .............. 60
Figure 4.5  Diagram of meshing mechanism .............................................................. 70
Figure 4.6  Diagram of 1-D meshing of computational domain ............................ 70
Figure 5.1  Overview of the testing system ................................................................. 72
Figure 5.2  Detailed cross-section of the generator showing the arrangement of temperaturer sensors ................................................................. 73
Figure 5.3  Detailed cross-section of the condenser subassembly showing the arrangement of temperature sensor and pressure gauge .............. 74
Figure 5.4  Schematic diagram of the evaporator ..................................................... 75
Figure 5.5  Schematic diagram of an assembled feedthrough with a
thermocouple ............................................................................................................. 76

Figure 5.6 Photograph of the experiment system ................................................. 79

Figure 5.7 Comparison of numerical and experimental results of the
system pressure variation in process 1-2-3 ......................................................... 84

Figure 5.8 Comparison of numerical and experimental results of the
system pressure variation in process 3-4-1 ......................................................... 84

Figure 5.9 Comparison of numerical and experimental results: adsorbent
temperature development at selected radial positions in process
1-2-3 ...................................................................................................................... 86

Figure 5.10 Comparison of experimental and numerical results: adsorbent
temperature development at selected radial positions in process
3-4-5 ...................................................................................................................... 87

Figure 5.11 Comparison of numerical results of gas temperature development
at r=55mm and the gas temperature measured at radial position
r=53mm .............................................................................................................. 88

Figure 5.12 Comparison of numerical and experimental results of the
dynamic desorption amount ........................................................................... 88

Figure 5.13 Comparison of numerical and experimental results of the
dynamic adsorption amount ........................................................................... 89

Figure 5.14 Numerical results of adsorbate concentration variation at selected
radial positions in the first 1200s of process 1-2-3 ................................. 90

Figure 5.15 Numerical results of adsorbate concentration variation at selected
radial positions in the first 1200s of process 3-4-1 ................................. 91

Figure 6.1 Effect of evaporating temperature requirement to running cycle .... 94

Figure 6.2 A case of adsorbent temperature development during
process 1-2-3 ...................................................................................................... 95

Figure 6.3 A case of adsorbate concentration development during
process 1-2-3 ...................................................................................................... 95

Figure 6.4 Effects of diameter and evaporating temperature on ICT .............. 97

viii
Figure 6.5  Effects of diameter and evaporating temperature on COP ................. 97
Figure 6.6  Effects of diameter and evaporating temperature on SCP .................. 98
Figure 6.7  Effects of cycle time on SCP and COP ........................................ 99
Figure 7.1  System integration strategy using single ART .................................. 102
Figure 7.2  Schematic diagram of a single ART .............................................. 103
Figure 7.3  Schematic diagram of an ARTs Unit .............................................. 103
Figure 7.4  Schematic diagram of an ARTs Module ........................................ 104
Figure 7.5  Schematic diagram of an ARTs Module showing heat exchange
            system ............................................................................................. 105
Figure 7.6  Schematic diagram of an ARTs Module serving as a normal
            air-conditioner .................................................................................. 105
Figure 7.7  Total cost versus use time employing ARTs system and traditional
            air-conditioning system, respectively. ................................................ 108
Abstract

Solid adsorption refrigeration systems are attracting much research interest because they have numerous advantages, such as using low grade thermal energy and being environment friendly. In recent decades many efforts have been put into developing various prototypes. The adsorption refrigeration tube (ART) is one such development. Through better system integration, a module consisting of a number of individually working ARTs can achieve significant refrigeration capacity, which may solve the vacuum leaking problem that besets large adsorption systems.

In order to propose a feasible ART, this thesis undertakes a study of adsorptive properties of three types of activated carbon/methanol working pairs and modelling of the adsorption refrigeration cycle.

In this examination of adsorptive properties, three activated carbon samples, Calgon 207C, 207EA and WS-480, were used to test and determine their pressure-temperature-concentration ($P - T - x$) relationship with methanol as the adsorbate. Based on the experimental data, three adsorption state equations, Langmuir equation, Freundlich equation and Dubinin-Astakov (D-A) equation, were compared in terms of their agreement with experimental data and their format impact on calculating coefficient of performance (COP) and refrigeration output ($Q_r$), if one of the formats was used for presenting experimental data. Moreover, a sensitivity analysis was conducted to reveal the parameters’ sensitivity to calculation of COP and $Q_r$. It was found in this study that the D-A equation is the best state equation for presenting the adsorptive properties of the tested activated carbon/methanol working pairs in terms of the best agreement of $P - T - x$ correlation and least sensitivities to parameters’ errors.
A 1-D dynamic model was established and validated experimentally, in which a local non-equilibrium treatment and dynamic boundary condition were introduced to the mathematical model. Regarding thermal non-equilibrium treatment, the temperatures of the local solid phase (activated carbon and adsorbed methanol) and local fluid phase were treated separately. Due to this non-equilibrium treatment, i.e. a two temperature treatment, convective heat transfer within the transport pores of activated carbon can be considered in the mathematical model. Moreover, a mathematically defined function was introduced to present the transient pressure process at the beginning of an adsorption process. Using this function, the temperature jump phenomenon can be well predicted by the mathematical model.

After the mathematical model had been established and validated, a parametric analysis was conducted using the mathematical model. The effects of the cylindrical activated carbon column’s diameter and evaporating temperature on cycle time, COP and specific cooling power (SCP) were examined. Furthermore, a case study of cycle time optimisation was conducted.

Finally, based on the parametric analysis, a practical solution using integrated groups of individual ART was proposed for home or domestic application. A preliminary economics analysis was also conducted to evaluate the potential of this application.
Acknowledgements

I would like to thank the people and organisations that provided me with invaluable contributions and ultimately helped to bring this project to a successful conclusion.

My most sincere gratitude goes to my supervisors, Associate Professor Eric Hu and Dr Antoni Blazewicz, for their tremendous efforts in making the research a great success. My principal supervisor, Associate Professor Eric Hu, provided me with tremendous support, not only technical support but also personal assistance. Without his kind help, it was not possible to complete this project efficiently.

A special thank you goes to Professor Wang R.Z. (Shanghai Jiao Tong University) for granting access to the relevant laboratory which experiments regarding adsorptive properties could be conducted.

I would also like to thank the staff in the workshops at the School of Mechanical Engineering and School of Electrical Engineering, the University of Adelaide, for constructing the test rig required for this project. In particular my thanks go to Richard Patemen, Dr Michael Riese and Lydia Zhang.

An additional mention goes to Ms Karen Adams and Mr Phillips Thomas for their kind help in article manuscript and thesis editing.

Last but not least, I would like to thank my parents. My parents, Mr Zhenggui ZHAO and Mrs Baofen CHEN, deserve the highest level of respect for their selfless support and encouragement of me along my journey towards success.
### Nomenclature

#### Abbreviation

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>D-A</td>
<td>Dubinin-Astakhov</td>
</tr>
<tr>
<td>ART</td>
<td>Adsorption Refrigeration Tube</td>
</tr>
<tr>
<td>ARTs</td>
<td>Adsorption Refrigeration Tubes</td>
</tr>
<tr>
<td>COP</td>
<td>Coefficient of Performance</td>
</tr>
<tr>
<td>SCP</td>
<td>Specific Cooling Power</td>
</tr>
<tr>
<td>H-R</td>
<td>Heat Recovery</td>
</tr>
<tr>
<td>M-R</td>
<td>Mass Recovery</td>
</tr>
<tr>
<td>WBA</td>
<td>Water Bath A</td>
</tr>
<tr>
<td>WBB</td>
<td>Water Bath B</td>
</tr>
</tbody>
</table>

#### Notation

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
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<tbody>
<tr>
<td>$A_0$</td>
<td>Specific surface area of adsorbent</td>
<td>1/m</td>
</tr>
<tr>
<td>$C$</td>
<td>Gas density</td>
<td>mol/m$^3$</td>
</tr>
<tr>
<td>$D$</td>
<td>Parameter in D-A equation</td>
<td></td>
</tr>
<tr>
<td>$D_{cb}$</td>
<td>Effective diffusion coefficient of adsorbent bed</td>
<td>m$^2$/s</td>
</tr>
<tr>
<td>$d_h$</td>
<td>Hydraulic diameter of transport pores</td>
<td>m</td>
</tr>
<tr>
<td>$h_0$</td>
<td>Specific enthalpy</td>
<td>J/kg</td>
</tr>
<tr>
<td>$h$</td>
<td>Heat transfer coefficient</td>
<td>W/m$^2$K</td>
</tr>
<tr>
<td>$H$</td>
<td>Enthalpy</td>
<td>J</td>
</tr>
<tr>
<td>$L_0$</td>
<td>Latent heat of vaporization</td>
<td>kJ/kg</td>
</tr>
<tr>
<td>$L$</td>
<td>Physical length of component</td>
<td>m</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td>Unit</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td>------</td>
</tr>
<tr>
<td>$M_0$</td>
<td>Molar mass</td>
<td>kg/mol</td>
</tr>
<tr>
<td>$M$</td>
<td>Mass</td>
<td>kg</td>
</tr>
<tr>
<td>$P$</td>
<td>Pressure</td>
<td>bar</td>
</tr>
<tr>
<td>$Q$</td>
<td>Heat flow</td>
<td>W</td>
</tr>
<tr>
<td>$Q_{st}$</td>
<td>Adsorption heat, a constant in Langmuir</td>
<td>J/kg</td>
</tr>
<tr>
<td>$R_i$</td>
<td>Inside radius of carbon column</td>
<td>m</td>
</tr>
<tr>
<td>$R_o$</td>
<td>Outside radius of carbon column</td>
<td>m</td>
</tr>
<tr>
<td>$R$</td>
<td>Universal gas constant</td>
<td>J/mol K</td>
</tr>
<tr>
<td>$R_o$</td>
<td>Specific gas constant of methanol</td>
<td>J/kg K</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
<td>K or °C</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
<td>s</td>
</tr>
<tr>
<td>$x$</td>
<td>Adsorbate concentration</td>
<td>kg/kg</td>
</tr>
<tr>
<td>$x_0$</td>
<td>A constant in D-A equation or Freundlich</td>
<td>kg/kg</td>
</tr>
<tr>
<td>$n$</td>
<td>A constant in D-A equation or Freundlich</td>
<td></td>
</tr>
<tr>
<td>$K'_o$</td>
<td>The adsorption constant in Langmuir equation</td>
<td></td>
</tr>
<tr>
<td>$K$</td>
<td>Permeability of porous adsorbent bed</td>
<td>m²</td>
</tr>
<tr>
<td>$c$</td>
<td>Specific heat capacity</td>
<td>J/kg K</td>
</tr>
</tbody>
</table>

**Greek Symbols**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
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<tbody>
<tr>
<td>$\rho$</td>
<td>Density</td>
<td>Kg/m³</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Thermal conductivity</td>
<td>W/m K</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Effective porosity</td>
<td></td>
</tr>
<tr>
<td>$\mu$</td>
<td>Dynamic viscosity</td>
<td>Pa s</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Coefficient reflecting the transient pressure</td>
<td>1/s</td>
</tr>
</tbody>
</table>
Subscripts

$s$  Solid phase
$f$  Fluid phase
$g$  Gas phase
$l$  Liquid phase
$hw$  Hot water (simulated heat source)
$cw$  Cool water (simulated heat sink)
$e$  Evaporating status or evaporator
$c$  Condensing status or condenser
$sat$  Saturation status
$tra$  Transient process
$ini$  Initial status
$in$  Internal
$ex$  External
$eq$  Equilibrium status
$ge$  Generator
$r$  Refrigeration or refrigerant (methanol)
$ac$  Activated carbon
$max$  Maximum value
$min$  Minimum value
$1,2,3,4,3',4'$  Status of relevant processes
CHAPTER 1

INTRODUCTION

1.1 Introductory Background

With the growth in people’s living standards, the demand for a comfortable indoor environment has increased. Consequently, there has been a significant increase in electricity consumption in heating, ventilation, and air conditioning (HVAC). With regard to air conditioning, in both the domestic (i.e. household) and commercial sector, demand for electricity is boosting the pressure for more electricity to be supplied, especially in peak time. Refrigerants in traditional refrigeration systems contain Chlorofluorocarbons (CFCs) and Hydrochlorofluorocarbons (HCFCs), which can act as catalytic agents and accelerate the depletion of the Earth’s ozone layer. Therefore, an alternative solution to current refrigeration technology is required.

A technology known as solar powered solid adsorption refrigeration has aroused extensive interest since the 1990s because it has numerous advantages, such as being energy free, noise free and environmentally-friendly. In recent decades, research into solar powered adsorption refrigeration has been conducted extensively, which concerned developing new working pairs, proposing advanced thermal cycles, and designing prototypes. Thanks to these efforts, one critical evaluation criterion - coefficient of performance (COP) - has been improved significantly. However, due to the increasing complexity of advanced cycles (e.g. cycles with heat and mass recovery) and natural feature of solar power, these sorts of systems face two major
limitations, namely the lack of working reliability due to the issue of long-term vacuum keeping and paucity of a reliable heat source in poor weather conditions.

To address the above two limitations, this thesis examines the waste heat-driven modular adsorption refrigeration system. Compared to solar energy, waste heat from power station and various processes of manufacturing, can be controlled in terms of amount and supply time and enable the adsorption refrigeration system to operate more cycles per day. Furthermore a modular designed system may greatly improve the system’s reliability since each sub-system works independently.

Adsorption refrigeration tube (ART) is a sub-system that can work independently and it was initially proposed by Tamainot-Telto and Critoph (2003). Through systematic integration, a module having multiple ARTs can achieve a significant refrigeration capacity. In recent years, research into ART technology tried different working pairs, modifying ART’s configuration, modelling the refrigeration cycle, and proposing modular integration solutions. Studies in working pairs have identified typical adsorbent/adsorbate combinations for different application purposes, such as activated carbon/methanol, activated carbon/ammonia, silica gel/water, zeolite/water, etc. Investigations into ART’s configuration modification and multi-ART system integration have been initiated and two typical modular systems were proposed. Research into modelling of the refrigeration cycle, especially that based on cylindrical generators, was conducted intensively. In terms of dynamic models, four categories of mathematical models, i.e. uniform temperature-uniform pressure, uniform temperature-non-uniform pressure, non-uniform temperature-uniform pressure, and non-uniform temperature-non-uniform pressure were proposed and investigated.

Although ART has been extensively studied from configuration to working pair and refrigeration cycle modelling, current investigations have not proposed a comprehensively experimental validated dynamic model that takes into account of convective heat transfer within an adsorbent bed. Moreover, the adsorptive properties of new adsorbents available on the market should be examined for their potential
application. In addition, the ART’s configuration and system integration solution can be further improved.

1.2 Research Aims

The aims of this research are as follows:

(a) To understand the adsorptive properties of activated carbon and methanol, and how they are linked to basic adsorption refrigeration.

(b) To understand the dynamic behaviour of the adsorption refrigeration processes by establishing a validated dynamic model.

(c) To optimise the structure and operating parameters of the ART and then design an ART system by integrating a number of individual ARTs.

1.3 Scope and Limitations

The dynamic model developed in this research is a 1-D dynamic model of the carbon/methanol ART with a cylindrical generator design. This is not only the configuration of the ART proposed in this thesis; it is also how other complex generators are typically structured. After comprehensive experimental validation, the model can be used for complex adsorption refrigeration systems having cylindrical generators since the non-equilibrium adsorption, heat transfer resistances and mass transfer resistances are comprehensively taken into account.

Three types of activated carbon with methanol as the adsorbate were tested and the study of adsorptive properties aims at to provide design calculation guidance.

The ART experimental rig built serves mainly to validate the mathematical model. The optimal or best configuration is only studied numerically with the validated model.
The modular system proposed by integrating multi-ARTs is not tested with a practical prototype. Although the influence of real applications will be taken into account in system modelling and performance simulation, the results may still possess certain deviations from practical application.
CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Research regarding solid adsorption refrigeration technology has mainly focused on five themes: studying new working pairs, proposing advanced thermodynamic cycles, establishing more accurate mathematical models, modifying generator structures, and developing refrigeration systems. These five topics are essential and significant for both developing a conventional adsorption refrigeration system and ART-based modular adsorption refrigeration system. In order to propose an ART-based modular adsorption refrigeration system and more importantly to establish a dynamic model that is not only applicable for ART but also accurate and able to provide thermal performance prediction for those conventional systems working with advanced thermal cycles, a comprehensive literature review of what has been done is presented in this chapter.

In this literature review of working pairs, conventional common combinations of adsorbent/adsorbate are discussed in detail while composite adsorbents are briefly covered. The purpose of this section of the literature review is to identify appropriate categories of working pairs for a low grade heat-driven adsorption refrigeration system.
Chapter 2  Literature Review

The thermodynamic cycle and generator structure are reviewed to identify the dominant cycle mechanism and the typical generator structures which will be the physical of the mathematical model that is developed in this study.

Finally, the literature review of the mathematical model aims to locate gaps in the knowledge so that a model can be established that has universal application. Adsorption refrigeration systems are reviewed so that their potential improvement is emphasised.

2.2 Working Pairs

Working pairs are the essential and critical element in adsorption refrigeration systems. The requirements for appropriate working pairs and status of current research into this topic were reviewed by Wang et al. (2009). Two aspects were reviewed: firstly, refrigeration performance requirements; and secondly, basic natural property requirements. In regard to the former requirements, a refrigerant should have large latent heat of vaporisation and little adsorption heat so that a high COP can be achieved, while an adsorbent should have significant and varied adsorption capacity that corresponds with temperature change, in order to generate high specific cooling power (SCP). Ideally with regard to requirements for natural properties, being environmental friendly, appropriate working pressure and temperature, and having thermal stability are aimed for.

In investigations of common working pairs, numerous adsorbent/adsorbate combinations have been applied and compared. Most research has been done using activated carbon/methanol, activated carbon/ammonia, zeolite/water, silica gel/methanol, silica gel/water as working pairs. Various comparative studies were conducted by Critoph (1988), San and Lin (2008) and Wang et al. (2009). According to these comparative studies, activated carbon/methanol and silica gel/water have been recognised as two appropriate working pairs in the application of a low-temperature driven system, because both of these two working pairs can normally be driven by a low temperature heat source (below 100°C), while a working pair with zeolite normally needs the temperature of a heat source to be 200°C.
Some physical methods were employed to improve and change the working pairs’ properties so they worked better. Tamainot-Telto and Critoph (2000) investigated the thermophysical properties of monolithic carbon that is manufactured by compressing and firing solid carbon with an organic binder. Three critical parameters of the monolithic carbon were significantly improved: max concentration increased from 0.29 to 0.36 kg/kg; thermal conductivity rose from 0.16 to 0.60 W/mK; and density increased by 50% to 750 kg/m³.

Research into composite working pairs mainly focuses on improving thermal conductivity and enhancing the adsorption capacity of adsorbents. Currently, there are two main ways to produce composite adsorbents, namely simple mixture and impregnation.

The first method is simply the process of mixing the chemical adsorbent and porous physical adsorbent. The chemical adsorbent is applied as an impregnated salt while the physical adsorbent is added as a host matrix to form an internal porous structure and enhance thermal conductivity.

The second method is known as impregnation in which a compound adsorbent is extracted from a mixed solution, whereby both the physical adsorbent (additive) and chemical adsorbent are dissolved and mixed in a solution. In order to further increase the thermal conductivity and physical density, a composite adsorbent that is made using the above two methods can be compressed to form adsorbent blocks, known collectively as solidified composite adsorbent.

### 2.3 Thermodynamic Cycles

#### 2.3.1 Basic Cycle

An idealised basic adsorption refrigeration cycle normally includes four processes, these being isosteric heating (1→2), isobaric desorption-condensation (2→3), isosteric cooling (3→4), and isobaric adsorption-evaporation (4→1) (see Figure 2.1). The specific descriptions are as follows. In the first half of the cycle, i.e. processes 1→2→3, the generator is heated up using an external heat source that can be derived
from solar power or waste heat. During this process, the trapped refrigerant is gradually and continuously desorbed from the adsorbent and then the gaseous refrigerant flows to the condenser and is condensed there. The condensed liquid refrigerant flows to the evaporator for the following evaporation. When the generator reaches its peak temperature, this process is completed and then the generator is cooled down to initiate the second half of the cycle (i.e. processes $3\to 4 \to 1$). As soon as the system pressure drops due to the gaseous adsorbate being readsorbed, the refrigerant evaporates to output the refrigeration benefit. The evaporated gaseous refrigerant is readSORbed by the adsorbent bed and the adsorption heat is removed by using an external heat sink.

![Clapeyron diagram of an ideal basic adsorption refrigeration cycle.](image)

**Figure 2.1** Clapeyron diagram of an ideal basic adsorption refrigeration cycle.

### 2.3.2 Heat Recovery Cycle

Heat recovery is an effective and technically feasible strategy that can be applied to an adsorption refrigeration system to significantly improve thermal performance. Currently, heat recovery cycles can be classified into external heat recovery cycle and internal heat recovery according to their different mechanisms.

The first category which is called the external heat recovery cycle can be achieved by employing two or more adsorbers which work out of phase. Heat released in the desorption process from one adsorber can be used to heat up another adsorber, which
occurs in isosteric heating and isobaric desorption processes. Figure 2.2 is a schematic diagram showing a two-adsorber heat recovered cycle, in which two identical adsorbers (i.e. adsorbers A and B) operate out of half a cycle, i.e. cycle \( A_1 \rightarrow A_2 \rightarrow A_3 \rightarrow A_4 \rightarrow A_1 \) and cycle \( B_3 \rightarrow B_4 \rightarrow B_1 \rightarrow B_2 \rightarrow B_3 \). Within such a heat recovery system, part of the heat released in process \( B_3 \rightarrow B_4 \rightarrow B_{eq} \) is used to heat up another adsorber from status \( A_1 \) to \( A_{eq} \) through an external heat transfer fluid, which normally generates a pre-heating process. This sort of heat recovery cycle could improve the COP considerably by as much as 25% compared to a basic adsorption refrigeration cycle, which has been reported by Qu et al. (2001) and Wang (2001).

![Figure 2.2 Schematic diagram of an external heat recovery cycle with identical adsorbents.](image_url)

The second category of heat recovery cycle is called internal heat recovery cycle which is normally based on thermochemical effect. A double-effect thermochemical sorption and a triple-effect thermochemical sorption was conceptually studied by Li et al. (2009). A COP as high as 146%-200% compared to a conventional refrigeration cycle can be expected using the triple-effect thermochemical sorption cycle. Li et al. (2008b) conducted experimental study of heat pipe type internal heat recovery and pointed out that the COP can be improved more than 23% at the given operating conditions.
2.3.3 Mass Recovery Cycle

Mass recovery cycle is another advanced and feasible cycle that may lead to better thermal performance. The general principle of a mass recovery cycle is utilising the mass concentration difference within two different adsorbent beds. The mass recovery process is achieved by interconnecting the two adsorbent beds. Based on this fundamental principle, several advanced mass recovery cycles have been proposed and studied, leading to the cycles being classified into two categories, namely pressure driven mass recovery cycles and temperature driven mass recovery cycles.

Pressure driven mass recovery cycle is the one initially proposed, in which mass recovery is achieved by interconnecting two identical adsorbent beds where one is in a high pressure stage and the other experiences low pressure. The vapour (gaseous refrigerant) within the high pressure adsorbent bed moves to the one at a relatively low pressure so that the mass variation of refrigerant is enlarged. This helps to enhance refrigeration power. Figure 2.3 illustrates the mechanism of an ideal pressure driven mass recovery. When adsorber A completes the process of heating-desorption, its temperature and pressure are at $T_{A3}$ and $P_e$. In the meantime, adsorber B completes the process of cooling-adsorption and consequently its temperature and pressure are at $T_{B1}$ and $P_e$. This point in the process connects adsorber A and B, and enables them to reach an equilibrium pressure $P_m$. As a result, adsorber A reaches the status $A_m$ while adsorber B reaches $B_m$. If the heat recovery technique is incorporated during this step, adsorber A will develop along $A_m - A_x - A_{eq}$ and correspondingly B will develop along $B_m - B_{2} - B_{eq}$. Using this mass recovery approach, adsorbate concentration variation will be increased by $X_4 - X_{eq}$, which will contribute to greater refrigeration capacity. According to Sumathy et al. (2003), this mass recovery approach can improve refrigeration capacity by more than 10% without reducing the COP. Moreover, the introduced heat recovery process can cover approximately 35% of the total energy used by each adsorbent bed, Sumathy et al. (2003).
Temperature driven mass recovery cycle has been recently proposed by Uyun et al. (2009), in which mass recovery is achieved by heating up and cooling down corresponding adsorbent beds to generate adsorption and desorption simultaneously (see Figure 2.4). This mass recovery cycle needs three adsorbers - two adsorbers working in a relative broad pressure range while the other works within a narrow pressure range. The adsorbers working within a broad pressure range are named High Adsorbers (HA) and the adsorber working within a narrow pressure range is named Low Adsorber (LA). In this heat recovery approach, two High Adsorbers, i.e. HA1 and HA2, go through five steps in each cycle, namely desorption (1-2), pre-cooling (2-3), adsorption (3-4), mass recovery with cooling (4-5), and pre-heating (5-1). In the meantime, the Low Adsorber, i.e. LA, needs to experience three processes in a cycle: desorption/mass recovery with heating (4-6), pre-cooling (6-7), and adsorption (7-4). A numerical simulation conducted by Uyun et al. (2009) found that this mass recovery approach can produce the highest SCP value compared to other traditional mass recovery cycles.
2.3.4 Cascading Cycle

Cascading cycle was initially proposed by Douss et al. (1988) who aimed to utilise the inherent heat difference among a set of particularly selected working pairs operating with different driven temperatures requirements. Figure 2.5 illustrates the mechanism of the cascading cycle, which is based on heat recovery reclaiming sensible heat and adsorption heat rejected from cooling-adsorption process of the top-level cycle to drive the sub-cycle. Theoretical calculation and experimental results have proved that this kind of cycle mechanism can generate remarkable improvement in COP. Meunier (1985) has shown that a theoretical COP of 1.85 can be expected when employing infinite sub-cycles and ideal heat recovery, while a recent numerical study conducted by Liu and Leong (2006) also obtained a COP of 1.3 using a twin adsorber (zeolite-water) as a top-level cycle; the other adsorber (silica gel-water) severed as a sub-level cycle. According to Douss and Meunier (1989), experimental results also obtained a value of 1.06.

However, the cascading cycle has a poor SCP compared to other cycle types. Furthermore, this cycle normally needs a heat source with a relatively high
2.3.5 Other Advanced Cycles

Thermal wave cycle was initially proposed by Shelton et al. (1989) and this cycle aimed to achieve heat recovery between adsorption heat and desorption heat of two adsorbent beds by circulating heat transfer fluid through the adsorbent beds. A typical thermal wave system consists of seven components: two adsorbers (adsorber A and adsorber B), a heat source, a cooling source, a condenser, an evaporator and a reversible circulating pump. In the first half circle of this system, the heat transfer fluid flows through adsorber A, circulating pump, heat source, adsorber B and cooling source in sequence, in which the heat transfer fluid cools down and heats up the corresponding adsorbent respectively. The heat transfer fluid continues circulating until the adsorbents complete their desorption and adsorption processes. The second half circle is simply the process of reversing the circulation direction of the heat transfer fluid. A COP of approximately 1.2 was obtained in a numerical study conducted by Ben Amar et al. (1996). However, this cycle still faces a major challenge if one expects to achieve an excellent COP in practical application. Specifically the adsorbent’s thermal conductivity has to be improved significantly.
Sun et al. (1997) pointed out that the thermal conductivity must be more than five W/mK to accelerate the heat transfer process in the adsorbent bed to minimise the time required for heat transfer, which reduces the proportion of energy consumed by the circulating pump. However, when the thermal conductivity is enhanced by consolidating the adsorbent, the mass transfer property will decline as well, which in turn leads the thermal wave cycle working poorly because the great mass transfer resistance results in a smaller cycled net mass quantity of the adsorbate. Therefore, this is a contradiction that limits the performance of this cycle.

In order to tackle this contradiction, Critoph (1996) proposed another modified cycle called the convective thermal wave cycle. In this cycle, the poor heat transfer within the adsorbent was solved by circulating external pre-heated or pre-cooled refrigerant through the adsorbent bed to heat up or cool down the adsorbent directly, in which the high internal heat exchange surfaces between refrigerant and adsorbent particle enhance the heat transfer. Critoph (1996) claimed that a simulated COP of approximately 1.2 occurred when evaporating temperature and condensing temperature were at 10°C and 30°C respectively. However, the simplified simulation does not take in account the energy consumed by the circulation pump, which in fact is a critical parameter that is affected by a few factors, i.e. mass transfer resistance, velocity of circulating refrigerant, density of refrigerant, etc. A recent study by Tierney (2008) dealt with these issues and he studied the feasibility of this cycle in detail, including considering the efficiency of a circulation pump. Unfortunately, the results showed that the pumping power is unacceptable unless the COP and SCP are as low as 0.27 and 1 W/kg respectively. In other words, the cycle may not work better when pumping power is given serious consideration.

### 2.4 Generator and ART’s Structures

The generator is a key component of an adsorption refrigeration system. Cylindrical shaped generators are the dominant structures that have been employed in experimental and numerical studies, for example Hu (1996), Marletta et al. (2002), Dai and Sumathy (2003), Leong and Liu (2006), Maggio et al. (2006), Cortés et al. (2009), Fadar et al. (2009). Furthermore, finned tube and heat-transfer coil are
typically used in generator design aiming at improving heat transfer, for instance Zhang et al. (2002), Wang et al. (2004), Al Mers et al. (2006), Li et al. (2008a).

Various cylindrical based generators have been proposed and studied, which can be summarily classified into two categories according to different heating mechanisms, i.e. centre-heated generator and external-heated generator (see Figures 2.6 and 2.7).

Figure 2.6 illustrates the schematics for a type of centre-heated generator investigated by Marletta et al. (2002), Leong and Liu (2006), Maggio et al. (2006). In this configuration, the adsorbent typically is packed around the heat-exchange tube using a metal mesh, enabling heat transfer fluid (heating/cooling fluid) to flow through the centre tube to heat up or cool down the adsorbent bed. Refrigerant vapor can flow between the condenser/evaporator and the adsorbent bed via the mass transfer channel.

![Image of a centre-heated generator](image)

Figure 2.6 Configuration of a centre-heated generator. Summarised structure with structures proposed by Marletta et al. (2002), Leong and Liu (2006), Maggio et al. (2006).

Figure 2.7 illustrates a type of external-heated generator examined by Hu (1996), Dai and Sumathy (2003), Cortés et al. (2009), Fadar et al. (2009). In this configuration,
the adsorbent is packed inside the centre tube and the centre tube can be heated up or cooled down through external heat transfer fluid. Similarly, refrigerant vapor can flow between the condenser/evaporator and the adsorbent bed via the mass transfer channel. Compared to the centre-heated generator, this kind of external-heated generator can be modified into a solar radiation powered generator by removing the water jacket.

Figure 2.7 Configuration of an external-heated generator. Summarised structure with structures proposed by Hu (1996), Dai and Sumathy (2003), Cortés et al. (2009), Fadar et al. (2009).

The generator’s structure of an ART usually applies the external-heated style because it has easy manufacturing, bed packing and modular integration properties. Figure 2.8 shows a typical ART’s structure as proposed by Critoph (2001), Wu et al. (2009), where a generator and integrated condenser/evaporator are featured. In this kind of structure, the adsorbent is packed or made in situ between the metal tube and the metal mesh. An adiabatic section is usually added between the generator and the evaporator/condenser to reduce heat losses. Fins can be added to the adsorbent bed and evaporator/condenser to improve heat transfer performance. This improved configuration has been proposed by Wang and Zhang (2009) and Tamainot-Telto and Critoph (2003).


Figure 2.8 Configuration of an ART. Redrawn from Critoph (2001), Wu et al. (2009).

2.5 Mathematical Model

Various mathematical models for solid adsorption refrigeration systems were proposed, especially based on the cylindrical generator as the typical configuration, for both the ART and the basic structure of other complicated generators. Since solid adsorption refrigeration is basically an adsorption phenomenon involving heat and mass transfer processes, the modelling work mainly includes establishing heat transfer model, mass transfer model and adsorption model.

2.5.1 Heat Transfer Model

Treatment of heat transfer model in modelling of adsorption refrigeration system includes two streams, i.e. uniform temperature and non-uniform temperature.

Khattab (2006), Wang and Zhang (2009) established models based on the assumption of uniform temperature in order to study the thermal performance of ART. However, this kind of temperature treatment is not able to examine the temperature profile within the adsorbent bed. Since typical adsorbents, such as activated carbon, silica gel and zeolite have very poor heat conductivity, temperature difference within an adsorbent bed can be fairly significant, especially when the adsorbent bed is “thick” or the system is rapidly cycled.

Compared to uniform-temperature treatment, non-uniform temperature treatment is employed by major models, such as those proposed by Marletta et al. (2002), Leong
and Liu (2006), Cortés et al. (2009). This kind of model is able to study the detailed temperature profile within the adsorbent bed. However, these non-uniform temperature-based models did not examine the effect of temperature profile on the system performance, but instead studied system performance using an average bed temperature. Therefore, the effect of uneven temperature profile on the system refrigeration performance is still unknown.

On the other hand, as assumption of local thermal equilibrium that is adopted by almost all existing models lacks sufficient experimental validation, e.g. Hu (1996), Marletta et al. (2002), Cortés et al. (2009). In circumstances where there is fast desorption heat sink and adsorption heat generation, local thermal non-equilibrium between solid adsorbent and gaseous adsorbate can be employed to develop a more accurate model.

### 2.5.2 Mass Transfer Model

The mechanism of mass transfer within an adsorbent bed is normally considered to be the pressure gradient causing mass flow. Hence, mass transfer resistance is considered using the non-uniform pressure model while the uniform pressure model does not take the mass transfer resistance into account.

Hu (1996), Khattab (2006), Fadar et al. (2009) established uniform pressure-based models to study solar powered adsorption refrigeration systems. In a solar powered, daily-cycled adsorption refrigeration system, mass transfer resistance may be neglected since the sorption process lasts for a long time. However, for a multi-cycled system, the effect of mass transfer resistance may be significant. Li and Wu (2009) investigated a multi-cycled system using a uniform pressure model. Maximum errors are 9.9% and 10.8% from cooling capacity and COP respectively. However, the proportion of errors caused due to uniform pressure assumption is not clear. Wang and Zhang (2009) also modelled an ART using uniform pressure. Unfortunately, the model lacks experimental validation.

On the other hand, non-uniform pressure assumption has been adopted in other models, such as Marletta et al. (2002), Dai and Sumathy (2003), Liu and Leong
(2005), Leong and Liu (2006), Maggio et al. (2006). However, these models did not examine the adsorbent temperature profile and its development. In numerical studies conducted by Marletta et al. (2002), Maggio et al. (2006), average temperature development of adsorbent bed and system pressure variation were predicted. Unfortunately, part of the predicted results, i.e. prediction of the adsorption process, does not match the experimental results observed in our lab. The adsorbent temperature and system pressure should demonstrate sudden jumps after the adsorption process has been initiated.

In fact, when the evaporator is connected to the generator to initiate the adsorption process, the system pressure would jump to condensing pressure \( p_c \) and in the meantime intense adsorption would lead to a temperature jump in adsorbent bed. The temperature jump was also experimentally observed by Li et al. (2002) while the system jump has not been identified previously in numerical or experimental studies.

### 2.5.3 Adsorption Model

Equilibrium-based adsorption models and non-equilibrium-based adsorption models are the two streams used when an adsorption refrigeration cycle is being mathematically modelled.

In equilibrium-based adsorption models, Dubinin-Astakov (D-A), Langmuir equation and Freundlich equation are typically employed in various mathematical models, e.g. Hu and Exell (1994), Gupta et al. (2008). Compared to equilibrium-based adsorption equations, non-equilibrium adsorption models, i.e. linear driving force (LDF) based models have become increasingly dominant, e.g. Marletta et al. (2002), Maggio et al. (2006), Yang (2009). Wang and Wang (2005) compared the refrigeration COP using the equilibrium adsorption model and non-equilibrium adsorption model respectively. They pointed out that the COP based on the non-equilibrium adsorption model is much lower than that calculated using the equilibrium adsorption model, especially when the cycle time is short.
2.6 Adsorption Refrigeration Systems

Numerous adsorption refrigeration systems have been proposed, including solar powered intermittent system, traditional multi-bed continuous system and modular continuous system integrated with individual ARTs.

2.6.1 Intermittent System

Solar powered adsorption refrigeration system is a typical intermittent system and it was proposed and intensively studied during the 1990s. This solar powered system aimed to provide small-scale refrigeration for special applications (e.g. keeping vaccines) in rural areas. Hu and Exell (1994) and Hu (1996) studied a valve controlled and non-valve controlled solar powered ice maker (schematics shown in Figure 2.9). Hu (1996) pointed out that the ideal constant evaporating pressure can be achieved in a non-valve controlled system. In other words, more effective refrigeration can be lost if the system runs without a control valve. Li et al. (2002) and Li et al. (2004) investigated a similar structural prototype focusing on improving refrigeration performance. Stainless steel fins were added into the adsorbent bed to improve heat transfer. A COP of about 0.12 was achieved to their experimental studies. Boubakri et al. (1992), Buchter et al. (2003), Hildbrand et al. (2004) conducted studies based on this kind of prototype and investigated the effect of “bad” weather conditions. Hildbrand et al. (2004) demonstrated that the prototype is almost able to maintain a temperature of freezing water for three days in “bad” weather conditions.
Figure 2.9 Schematics of a solar ice maker. From Hu and Exell (1994).

2.6.2 Traditional Continuous System

Continuous adsorption refrigeration system is normally achieved through a multi-bed operation. Two-bed (Liu et al. (2005), Xia et al. (2008)), three-bed (Uyun et al. (2009), Miyazaki et al. (2010)), and four-bed (Alam et al. (2004), Akahira et al. (2005)) systems have been numerically and experimentally studied. Figure 2.10 is a schematic diagram showing a two-bed adsorption chiller recently developed by Xia et al. (2008). A maximal COP of 0.432 was achieved using this prototype assisted by the mass recovery process which enhanced the COP by as much as 32%. The discontinuity of the chilled water output occupied approximately 20% of each cycle. In a recent study of a three-bed system conducted by Miyazaki et al. (2010), the system diagram shown in Figure 2.11, shows that refrigeration discontinuity was reduced to about 10% of each cycle and in the meantime the refrigeration COP was improved by 75% at 80°C heat source. Regarding the four-bed system, numerical studies of Alam et al. (2004) concluded that thermal performance, including refrigeration COP and refrigeration effect, had not significantly improved.
Figure 2.10 Two-bed adsorption chiller. From Xia et al. (2008).

Figure 2.11 Three-bed adsorption chiller. From Miyazaki et al. (2010)
2.6.3 Modular Continuous System

Modular system refers to the system built with individual ARTs. The major advantage of this kind of system is that the working reliability of the system can be greatly improved since each individual ART works independently. Even when one or several ARTs within the system are out of order, the system is still able to work, except part of refrigeration capacity is lost. Two typical modular systems proposed by Critoph (2001) and Wang and Zhang (2009) are shown in Figure 2.12 and Figure 2.13 respectively. Critoph (2001) conducted a parametric study on the prototype and revealed that an increase in the number of ARTs could enhance the refrigeration COP while affecting the SCP negatively. In the multi-tube system proposed by Wang and Zhang (2009), two sub-adsorbers (i.e. adsorber A and adsorber B) could achieve external heat recovery. The reported COP is as high as 0.5 at the given operating condition when the heat recovery process is employed.

![Diagram of Modular rotary refrigeration system](image)

Figure 2.12 Modular rotary refrigeration system. Redrawn from Critoph (2001).
2.7 Research Objectives

The literature review has shown that most research into adsorption refrigeration tends to focus on complicated systems that work with increasingly complex heat recovery, mass recovery and other innovative approaches. On the other hand, less research has been conducted on simple systems, such as systems based on ARTs. This project aims to develop an ARTs-based modular system that is reliable and has the potential for large scale commercial application.

This project will mainly address a gap in the mathematical modelling regarding the adsorption refrigeration cycle. A literature review of current progress in mathematical modelling and advanced adsorption refrigeration systems indicates that local thermal equilibrium assumption between solid phase and fluid phase is no
longer accurate enough for recently proposed systems that incorporate internal heat and mass recovery processes.

The specific objectives are identified to address the gaps in knowledge in existing areas, and these objectives are:

(1) to compare three adsorption equations (i.e. D-A equation, Langmuir equation and Freundlich equation) so that the most appropriate isothermal form for presenting the activated carbon-methanol adsorptive properties can be identified.

(2) to propose a physically modified ART where the evaporating pressure can be controlled in order to achieve higher single tube COP.

(3) to establish a mathematical model based on the local thermal non-equilibrium assumption and the transient evaporating pressure.

(4) to validate the mathematical model experimentally and to conduct parametric study using the validated model.

(5) to propose a modular system design based on the modified ART.

2.8 Thesis Outline

Chapter 1 introduces the research background and general research aims of this project. The scope and limitations are also presented.

Chapter 2 presents the literature review regarding solid physical adsorption refrigeration, including working pair, thermodynamic cycle, generator and ART’s structure, mathematical model and adsorption refrigeration system. This is followed by an outline of specific research objectives and how the thesis is structured.

Chapter 3 assesses the adsorptive properties of three activated carbon samples using isosteric-based testing method. Moreover, three typical isothermal formats, i.e. D-A equation, Langmuir equation and Freundlich equation, are compared in terms of their agreement with experimental data and the parameters’ sensitivity to thermal
performance calculation are investigated. In this chapter, D-A equation is selected for presenting the adsorptive properties for tested activated carbon-methanol working pair and the activated carbon sample WS-480 is selected for experiments due to its sensitive adsorption performance within a narrow temperature variation.

Chapter 4 comprises the physical and mathematical models of the ART. Regarding the physical model, an ideal conceptual design of the ART is presented. For the mathematical model, a dynamic model is developed. The dynamic model is established using a two-temperature treatment (i.e. local thermal non-equilibrium) and self-defined transient pressure process, which is the core outcome of this project. The dynamic model can be used to examine the detailed thermal parameters within the ART, such as adsorbent temperature profile, adsorbate concentration profile, dynamic sorption amount, etc. A numerical solution regarding the dynamic model is also presented.

Chapter 5 presents an experimental validation of the established dynamic model. Firstly, test rig and experimental errors are illustrated and discussed. Furthermore, the results of numerical simulations of a typical operating condition are compared with the experimental data in terms of solid phase temperature development, fluid phase temperature development, system pressure variation and dynamic sorption amount. An interesting finding regarding adsorbate migration is also discussed in this chapter.

Chapter 6 is a parametric study using the validated model. Effects of a major operating parameters (i.e. evaporating temperature) and the diameter of the generator on three significant system evaluation criteria (i.e. COP, SCP and cycle time) are studied and summarised.

Chapter 7 presents a case study incorporating a conceptual modular adsorption refrigeration system that is designed with a group of individual ARTs. Economics analysis is also conducted in this chapter.

Chapter 8 presents the overall conclusion of the present thesis.
CHAPTER 3

STUDY OF ADSORPTIVE PROPERTIES

3.1 Introduction

When designing an adsorption refrigeration system, the selection of a working pair (i.e., adsorbent and adsorbate) is crucial since the system’s thermal performance largely depends on the adsorptive properties of the working pair employed. Obtaining accurate adsorptive property data of the working pair and choosing a suitable adsorption equation are essential for good design and predicting how well such a system performs. Measuring and determining a pair’s adsorptive property is normally determining the correlations of the adsorbent and adsorbate using a pressure-temperature-concentration (i.e. $P-T-x$) relationship.

Traditionally, the adsorptive property of an adsorbent and an adsorbate pair is normally determined experimentally using adsorption equilibrium tests. Adsorption equilibrium is usually tested with isotherm and isobar methods (see Hu and Exell (1993), Ng et al. (2001)). However, both methods are not efficient and precise enough since experiments normally are conducted at a series of constant temperatures or pressures which may not cover the entire temperature and pressure range of sorption to be utilised directly. The isosteric-based method conducted by Xia et al. (2008) could directly test typical isosteric lines within the range to be used in a real adsorption refrigeration cycle. Therefore the isosteric-based method is a very convenient and efficient approach for obtaining the adsorptive property of a working pair when a real-life adsorption refrigeration cycle is to be designed.
However, once the experimental data for equilibrium tests had been obtained, processing them into which adsorption equations is still a question. In the area of adsorption equation, the Langmuir and Freundlich equations as well as the D-A equation are the classic ones in which the experimental data is fitted. The Freundlich equation was proposed as an empirical equation and currently is widely used in adsorption equilibrium modelling regarding solid adsorption systems, e.g. Alam et al. (2000), Gupta et al. (2008). Compared to the Freundlich equation, the Langmuir equation is a semi-empirical formula in which the monolayer surface adsorption assumption was introduced and is now widely employed in solid adsorption chiller and desalination systems, e.g. Liu and Leong (2005). The D-A equation, was proposed based on carbonaceous substance and volume filling theory (Dabrowski (2001)), and is currently the most dominant adsorption equation used for carbonaceous adsorbent adsorption systems, e.g. Hu and Exell (1994), Critoph and Metcalf (2004), Fadar et al. (2009). Compared to the Freundlich and Langmuir equations, in which each has two parameters that need to be determined experimentally, the D-A equation has three parameters, possibly contributing to a better agreement with experimental data due to the stronger adjustment.

In this chapter, experimental studies of the adsorptive properties of three activated carbon samples (i.e., 207C, 207EA and WS-480, sourced from Calgon Carbon Corporation) using methanol as the adsorbate are presented. Experimental data were fitted into all three isotherm formats (i.e., Langmuir, Freundlich and D-A equations) so their agreement could be compared. The COP calculation based on each format was conducted to reveal any differences if the same activated carbon and methanol were used as a working pair in a practical adsorption refrigeration cycle. Furthermore, the sensitivities of error of each format’s parameters to calculating thermal performance (i.e. refrigeration output $Q$, and COP) were studied.
3.2 Theoretical Considerations

3.2.1 Adsorption Equations

Adsorptive property of a physical adsorption is usually described using three parameters, namely adsorbate concentration ($x$), adsorbent temperature ($T$) and adsorption pressure ($P$). For an equilibrium adsorption, the concentration is a function of adsorbent temperature and adsorption pressure, which can be expressed mathematically as:

$$x = f(T, P)$$  \hfill (3.1)

To determine the adsorptive property of a working pair (i.e. adsorbent/adsorbate), one of these three parameters is usually fixed and the correlation between another two parameters can then be obtained experimentally.

The three prevailing adsorption equations are Langmuir equation, Freundlich equation and D-A equation. All these equations describe equilibrium adsorption through the three parameters, i.e. $P, T, x$.

(1) Langmuir Equation

Langmuir equation was proposed based on uniform surface adsorption assumption and merely deemed one monolayer adsorption generated on a uniform surface. One practical working form of Langmuir equation can be expressed as follows (Ng et al. (2001)):

$$x = P \cdot K'_0 \exp\left(\frac{Q_a}{R_a T}\right)$$  \hfill (3.2)

where:

$x$ is the concentration of adsorbed adsorbate (kg/kg);

$P$ is adsorption pressure (Pa);

$K'_0$ is the adsorption constant (1/Pa);

$Q_a$ is adsorption heat (kJ/kg);
$R_0$ is specific gas constant (J/kg K);

$T$ is the temperature of adsorbent (K); and

$K_0^f$ and $Q_{st}$ are two parameters that can be determined experimentally.

(2) Freundlich Equation

Freundlich equation is an empirical equation and exhibits considerable accuracy in describing physical adsorption within the range where adsorbate concentration is relatively high. For solid-vapor adsorption, Freundlich equation can be given as:

$$x = x_0 \left( \frac{P}{P_{sat}} \right)^{1/n} \quad (3.3)$$

where:

$x$ is the concentration of adsorbed adsorbate (kg/kg);

$x_0$ is theoretical maximum adsorption capacity (kg/kg);

$P_{sat}$ is saturation pressure at adsorbent temperature (Pa);

$P$ is system adsorption pressure (Pa); and

$x_0$ and $n$ are two parameters that can be determined experimentally.

(3) D-A Equation

D-A equation was proposed based on carbonaceous substances and modified from Dubinin-Radushkevich (D-R) equation which established volume filling theory. Compared to Langmuir and Freundlich equations, D-A equation is more popular for physical micropores adsorption and its format is given below (Hu and Exell (1993)):

$$x = x_0 \exp(-D(T \ln \frac{P_{sat}}{P})^n) \quad (3.4)$$

where:

$x$ is the concentration of adsorbed adsorbate (kg/kg);

$P$ is adsorption pressure (Pa);

$x_0$ is theoretical maximum adsorption capacity (kg/kg);
$T$ is the temperature of adsorbent (K);

$D$ is a constant that depends on the adsorbent microstructure;

$n$ is a parameter introduced to achieve a better fit with experimental data; and

$x_0, D$ and $n$ are normally determined using experiments.

### 3.2.2 Clausius-Claperyon Equation

Ideal sorption (desorption and adsorption) is considered to be a phase transformation process between vapour phase and liquid phase at constant pressure. The latent heat of the phase transformation of desorption or adsorption process can be described with a Claperyon equation as follows:

\[
\frac{dP}{dT} = \frac{\left(h^{(\beta)}_b - h^{(\alpha)}_b\right)}{T(v^{(\beta)} - v^{(\alpha)})}
\] (3.5)

Where: the superscripts $(\alpha)$ and $(\beta)$ represent the coexisting phase vapour and liquid; and symbols $h$ and $v$ represent the specific enthalpy and specific volume. Since the pressure of the system is relatively low, the volume of vapour is far bigger than that of liquid refrigerant trapped by the adsorbent. Therefore, the volume of the liquid is negligible and the volume of the vapour can be described using the ideal gas law (Eq 3.6). Here superscript symbols “$s$” and “$m$” represent saturated liquid phase and saturated gaseous phase respectively. Symbol $H$ is used to represent latent enthalpy of the phase transformation. The Claperyon equation can be simplified into Eq 3.7.

\[
v^s P = R_0 T
\] (3.6)

where:

$P$ is absolute pressure (Pa);

$v^s$ is specific volume of vapour (m$^3$ kg$^{-1}$);

$T$ is temperature (K); and

$R_0$ is the specific gas constant of methanol (J kg$^{-1}$ K$^{-1}$).
\[ \frac{dP}{dT} = \frac{h'' - h'}{T(v'' - v')} = \frac{H}{T(v'' - v')} \approx \frac{H}{Tv''} = \frac{PH}{R_0 T^2} \] (3.7)

Or

\[ \frac{d(\ln P)}{d(-1/T)} = \frac{H}{R} \] (3.8)

When temperature variation is not significant, the value of \( H \) may be recognised as a fixed value. The value of \( H \) can be obtained by integrating Eq 3.8. Thus the expression of \( H \) can be written as Eq 3.9 by integrating the above differential equation from the initial phase to another phase (superscripts 1 and 2 denote the initial phase and second phase respectively). For the desorption process, the value of \( H \) is a negative value calculated from the following equation indicating that the desorption process is in fact a heat absorption process.

\[ H = R_0 \cdot \frac{T_1 T_2}{T_1^2 - T_2^2} \cdot \ln \frac{P^2}{P_i^2} \] (3.9)

In an ideal adsorption refrigeration cycle (shown in Figure 2.1), desorption heat can be calculated from the above equation by substituting corresponding threshold values, specifically point 1 and point 2 together with corresponding pressure \( P_e \) and \( P_c \). Therefore, the expression of desorption heat at an isosteric line can be given in Eq 3.10:

\[ H_{d1} = R_0 \cdot \frac{T_1 T_2}{T_1 - T_2} \cdot \ln \frac{P}{P_e} \] (3.10)

Similarly, desorption heat on another isosteric line (from point 3 to point 4) can be written as Eq 3.11 by substituting corresponding values of point 3 and point 4:

\[ H_{d2} = R_0 \cdot \frac{T_3 T_4}{T_3 - T_4} \cdot \ln \frac{P}{P_e} \] (3.11)

Therefore, the average heat of desorption can be calculated by averaging two extreme values of the desorption heat as follows:
\[ H_d = \frac{(H_{d1} + H_{d2})}{2} \] (3.12)

Regarding the adsorption heat, this is basically a reverse process and can be calculated using the above equations as well.

### 3.2.3 Thermodynamic Analysis

In order to study the impact of firstly different adsorption equations and secondly, that of their parameters’ errors on thermodynamic calculation, a brief static thermodynamic analysis of a typical ideal adsorption refrigeration cycle is presented. With the adsorptive property of the working pairs determined using the \( P-T-x \) relationship-based adsorption equations (Langmuir, Freundlich and D-A equations), static thermodynamic analysis can be conducted as follows.

Figure 3.1 illustrates an ideal adsorption refrigeration cycle presented in a \( P-T-x \) diagram. For a given working condition, the ideal cycle in a \( P-T-x \) diagram has a fixed shape. Position of point 1 is determined by the evaporating pressure and cooling source temperature (\( T_i \) is the minimum temperature of the generator, i.e. carbon). Point 2 depends on the condensing pressure or temperature while point 3 is determined by the highest temperature of heat source. Finally the position of point 4 depends on evaporating pressure.

The calculations of two significant evaluation criteria of an adsorption refrigeration system, i.e. refrigeration output \( Q_r \) and refrigeration COP, can be achieved with the following static analysis.
Figure 3.1  \( P - T - x \) diagram of an ideal basic adsorption refrigeration cycle.

**Process 1: isosteric heating (1→2)**

Within this process, heat is supplied to heat up adsorbent (activated carbon) together with adsorbate that was trapped in the micropores of activated carbon particles. Concentration of methanol in the carbon in this process remains unchanged. When energy losses in heat transfer and heat supplied to the metal tube are not taken into account, energy input in this process can be calculated by Eq 3.13.

\[
Q_{1-2} = (c_{ac}M_{ac} + c_rM_{ri})(T_2 - T_1)
\]

(3.13)

where:

- \( Q_{1-2} \) is heat supplied to heat up activated carbon and methanol from point 1 to point 2;
- \( c_{ac} \) and \( c_r \) represent heat capacities of activated carbon and refrigerant respectively;
- \( M_{ac} \) and \( M_{ri} \) are mass of activated carbon and refrigerant adsorbed \( (M_{ri} = x_iM_{ac}) \) respectively; and \( T_1, T_2 \) are temperatures of adsorbent and adsorbate at point 1 and point 2.
**Chapter 3  Study of Adsorptive Properties**

**Process 2: isobaric desorption (2→3)**

The heat supplied in this process is used to heat up activated carbon and desorb the methanol. Therefore, concentration of methanol in carbon is no longer a constant in this process, but decreases with heating. In other words, in this process, heat supplied does not only increase the generator’s temperature, but also drives desorption of methanol out of carbon as desorption heat. Energy input can be calculated using Eq 3.14.

\[
Q_{2\rightarrow3} = (c_{aw}M_{aw} + c_r\overline{M}_r)(T_2 - T_3) + \Delta xM_{aw}H_d
\]  

(3.14)

where:

- \(Q_{2\rightarrow3}\) is heat supplied to heat up activated carbon and methanol, leading to desorption; \(\overline{M}_r\) is the average mass of methanol, which can be evaluated approximately using \(\overline{M}_r = (M_{r2} + M_{r3})/2\); \(T_2, T_3\) are temperatures of point 2 and point 3; \(\Delta x\) is concentration variation that is calculated by \(\Delta x = x_2 - x_3\); and \(H_d\) is desorption heat calculated by using Eq 3.9 to Eq 3.12, or usually \(H_d\) is treated as a constant for a given pair.

**Process 3: isosteric cooling (3→4)**

From point 3 to point 4 the process is called isosteric cooling because the generator is isolated, in which adsorbent is cooled down by a cooling source (ambient air or water from cooling tower). In the meantime, system pressure drops due to micro-adsorption resulting from the adsorbent’s temperature decline. In this process, sensible heat is removed by an external cooling source and energy balance can be expressed as Eq 3.15.

\[
Q_{3\rightarrow4} = (c_{aw}M_{aw} + c_rM_{r4})(T_3 - T_4)
\]  

(3.15)

where: \(Q_{3\rightarrow4}\) is heat removed from the adsorbent and adsorbate by external cooling source; and \(T_3\) and \(T_4\) are temperatures of adsorbent at point 3 and point 4.
Process 4: isobaric adsorption (4→1)

Once the system pressure drops to the designed evaporating pressure, the evaporator is connected to the generator to initiate the adsorption process in which refrigeration effect is generated. Refrigeration output can be approximately calculated using Eq 3.16, in which the first term in the right hand of the equation represents the gross refrigeration capacity while the second term represents the refrigeration power loss due to its self-cooling from condensing temperature to evaporating temperature.

\[ Q_r = \Delta M_c L_0 - c_s \Delta M_s (T_y - T_d) \]  

(3.16)

where:

- \( Q_r \) is refrigeration output;
- \( L_0 \) is latent heat of vaporisation of refrigerant (treated as a constant in ideal case analysis);
- \( \Delta M_s \) is mass of liquid refrigerant that equates to \( M_{s2} - M_{s3} \);
- \( T_y, T_d \) are the values of condensing temperature and evaporation temperature respectively.

With above analysis, for an ideal cycle, the refrigeration COP of the cycle can be evaluated using Eq 3.17.

\[ \text{COP} = \frac{Q_r}{(Q_{12} + Q_{23})} \]  

(3.17)

3.3 Testing of Adsorptive Properties

As stated previously, the isosteric method was used to determine the adsorptive properties of three working pairs. The principle of the isosteric method is fixing concentration and then measuring corresponding adsorption pressure and adsorbent temperature, which can be expressed in a generic form as \( P = f(T) \). Once a number of pressures and temperatures were obtained under a range of concentrations, the adsorptive property of the tested working pair can be determined using an equation fitting technique.
3.3.1 Testing Setup

The experimental rig was located in the lab of the Institute of Refrigeration and Cryogenics at Shanghai Jiao Tong University (SJTU), China. Gravimetric method was applied in the test. Figure 3.2 is a schematic diagram showing the testing system while a photograph of the testing apparatus is shown in Figure 3.3.

![Testing Setup Diagram](image)

**Figure 3.2 Schematic diagram of the testing system.**

The main components and functions of the testing setup are as follows:

1. Stainless steel generator: Adsorbent container that is immersed in thermostatic bath to control the adsorbent’s temperature.
2. Integrated evaporator and condenser: Liquid adsorbate container that is immersed in thermostatic bath to control the evaporation temperature.
Figure 3.3 Photograph of the testing system.

3. Thermostatic bath: Used to control the temperature of both the generator and evaporator from 0°C to 100°C.
4. Vacuum valve: Used to cut off or connect different sections of the system.
5. Vacuum flange: Used for quick connection.
6. Pressure transducer: Used to measure the pressure of generator or the whole system within a range from 0 to 50 kPa at a precision of 50 Pa.
7. Temperature sensors (PT1000): Used to measure the temperature of adsorbent.
8. Heating wire: Used to heat the tubes directly connected to the generator and keep its temperature the same as the generator to avoid condensation inside the tube. A matched power governor is used to control the heating power of the heating wire.
9. Vacuum pump: Used to vacuum the system.
10. Electronic balance: Used to weight the mass of generator with a precision of 0.01g.
11. Data logger: Records pressure and temperature.
3.3.2 Testing Procedures

Prior to testing, the system vacuum condition was checked by vacuuming the system and kept for 24 hours during which no leaking was observed. Moreover, samples to be tested were placed in an oven at 110°C for 24 hours to dry. The stainless steel generator without flange and bolts was weighted first and record the mass as $M_1$. Then the testing procedures were conducted as follows.

1. Fill in the generator with dried activated carbon and weight the mass of generator to record as $M_2$. Then set up the testing system as Figure 3.1 illustrates.
2. Set the temperature of the water bath A ($T_{WBA}$) at about 100°C. Degas the generator continuously using vacuum pump, in which vacuum valves V1 and V2 open. The temperature of water bath A is set to a high temperature (i.e. 100°C) to achieve a better degas effect since the activated carbon has relatively low adsorption ability when its temperature is high.
3. Set the temperature of water bath B ($T_{WBB}$) at simulated evaporating temperature (i.e. $T_e$); keep the evaporator/condenser at the temperature for about 2 hours in order to close to the temperature set. Then close valve 1 to vacuum the evaporator/condenser for 20 seconds to make the methanol a little bit boiling to ensure the simulated evaporating pressure is reached.
4. Close valve V2 and open valve V1 to evacuate the generator to about 50 Pa. After that, close valve V3 and set the water bath A temperature to the simulated generator temperature (i.e. $T_{ge}$). The exact value of $T_{ge}$ is measured using a temperature sensor.
5. Open valve V1 and valve V2 for 12 hours to ensure the adsorbent bed reaching adsorption equilibrium.
6. Close valve V1 and turn on the heating wire to set its heating temperature 1°C higher than the temperature of the water bath for
heat transfer resistance consideration. When both the temperature and pressure within the generator are stable, record pressure and temperature.

7. Vary generator temperature ($T_{ge}$) through varying water bath A temperature and then record corresponding equilibrium pressure and temperature values after the generator reaches stability.

8. After measuring five sets of temperature ($T_{ge}$) and pressure ($P$), disconnect the system and dry the outside surface of the generator. Weight the mass and record as $M_3$. Thus the amount of methanol adsorbed is gained, equal to $M_3 - M_2$. Concentration can be calculated by $M_3 - M_2 / M_2 - M_1$.

9. Repeat step 3 to step 8 to obtain another isosteric line by setting an appropriate combination of $T_e$ and $T_{ge}$.

In the test, each sample was tested to obtain five isosteric lines that cover the concentration variation range in typical waste heat powered adsorption refrigeration system. Experimental data are attached in Appendix C. With the experimental data, the parameters in Langmuir, Freundlich and D-A equations can be determined respectively using a linear regression approach.

### 3.3.3 Determination of the Parameters

Experimental data were processed in the Matlab environment to determine the parameters of three adsorption formats respectively. For the Langmuir format, multiple linear regression technique was used to determine its coefficients while Curve Fitting of Matlab Toolbox was employed to determine coefficients in Freundlich and D-A formats.

(1) Langmuir Equation

In order to determine $K_0^l$ and $Q_{sl}$, the two parameters in the Langmuir equation/format (Eq 3.2), the experimental data was fitted into the Langmuir format
using a multiple linear regression approach. The Eq 3.2 is rewritten as Eq 3.18 and can then be mathematically expressed as Eq 3.19 for the purpose of explanation.

\[
\ln x = \ln K_0^{t} + \ln P + \frac{Q_{\text{sat}}}{R_0 T} (1 / R_0 T) \quad (3.18)
\]

\[
Y = a_0 + X_1 + a_i X_2 \quad (3.19)
\]

where: \( Y \) denotes the dependent variable \( \ln x \); \( a_0 \) and \( a_i \) represent \( \ln K_0^{t} \) and \( \frac{Q_{\text{sat}}}{R_0} \) respectively; and \( X_1 \) and \( X_2 \) represent experimental data \( \ln P \) and \( 1 / T \).

(2) Freundlich equation
In order to determine \( x_0 \) and \( n \), the two parameters in the Freundlich equation/format, the Freundlich format (i.e. Eq 3.3) can also be rewritten into a clear form for fitting:

\[
Y = x_0 \cdot X_1^{1/n} \quad (3.20)
\]

where: \( Y \) represents \( x \) in Freundlich equation; and \( X_1 \) represents \( P / P_{\text{sat}} \) which is treated as an independent variable.

(3) D-A equation
Similarly, D-A format (i.e. Eq 3.4) can be rewritten into the following form to determine the three parameters, i.e. \( x_0 \), \( D \) and \( n \).

\[
Y = x_0 \exp(-D \cdot X_1^n) \quad (3.21)
\]

where \( Y \) represents \( x \) while \( X_1 \) represents \( T \ln(P_{\text{sat}} / P) \).

In both the Freundlich and D-A equations, variable \( P_{\text{sat}} \) is the saturation pressure at the temperature \( T \) of the adsorbent, i.e. methanol. The correlation between \( P_{\text{sat}} \) (in bar) and \( T \) (in K) is given below, which is correlated in the pressure unit from initial correlation used by Khattab (2006).

\[
\ln P_{\text{sat}} = \ln(0.0013) + 18.587 - 3626.55 / (T - 34.29) \quad (3.22)
\]
Using multiple linear regression and simple curve fitting strategies, the parameters of each sample in three different formats were determined and shown in Table 3.1.

<table>
<thead>
<tr>
<th>Carbon Sample</th>
<th>Format</th>
<th>Fitted Parameters</th>
<th>r</th>
</tr>
</thead>
<tbody>
<tr>
<td>207C</td>
<td>Langmuir</td>
<td>$K_0^l = 5.68 \times 10^{-6}$</td>
<td>$Q_a = 1007.30$</td>
</tr>
<tr>
<td>207EA</td>
<td>Langmuir</td>
<td>$K_0^l = 7.12 \times 10^{-6}$</td>
<td>$Q_a = 1040.90$</td>
</tr>
<tr>
<td>WS-480</td>
<td>Langmuir</td>
<td>$K_0^l = 7.87 \times 10^{-7}$</td>
<td>$Q_a = 1196.30$</td>
</tr>
<tr>
<td>207C</td>
<td>Freundlich</td>
<td>$x_0 = 0.25$</td>
<td>$- \quad n = 1.65$</td>
</tr>
<tr>
<td>207EA</td>
<td>Freundlich</td>
<td>$x_0 = 0.54$</td>
<td>$- \quad n = 1.47$</td>
</tr>
<tr>
<td>WS-480</td>
<td>Freundlich</td>
<td>$x_0 = 0.43$</td>
<td>$- \quad n = 1.39$</td>
</tr>
<tr>
<td>207C</td>
<td>D-A</td>
<td>$x_0 = 0.15$</td>
<td>$D = 9.67 \times 10^{-6}$</td>
</tr>
<tr>
<td>207EA</td>
<td>D-A</td>
<td>$x_0 = 0.28$</td>
<td>$D = 8.45 \times 10^{-7}$</td>
</tr>
<tr>
<td>WS-480</td>
<td>D-A</td>
<td>$x_0 = 0.27$</td>
<td>$D = 9.08 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

### 3.4 Discussion

#### 3.4.1 Format Agreement Comparison

The values of $r$ in Table 3.1 indicate that D-A format (D-A equation) enjoys the best agreement with experimental data while Langmuir format has a relatively poor agreement. Figures 3.4 to 3.6 show the experimental data of each carbon sample presented in $P-T-x$ diagram based on three different adsorption equations. Corresponding theoretical isosteric lines plotted using the determined coefficients, which provide a clear view of how the three different adsorption equations agree.
Figure 3.4 Comparison of experimental data and fitted isosteric lines, 207C.
Figure 3.5 Comparison of experimental data and fitted isosteric lines, 207EA.
Figure 3.6 Comparison of experimental data and fitted isosteric lines, WS-480.
3.4.2 Format Impact on $Q_r$

Although the above results show that D-A equation (format) presents the adsorptive properties best in terms of experimental data agreement, all three formats apparently can present the adsorptive properties well because all the r-square of fitting are higher than 0.9 (see Table 3.1). The following section compares the estimated refrigeration performance, i.e. refrigeration output $Q_r$ when different formats are used.

Figure 3.7 shows the refrigeration output calculated with different adsorption equations on each sample when the condensing and evaporating temperatures are assumed to be 30°C and 0°C, respectively. Parameters used in the numerical calculation are listed in Table 3.2. The figures in Figure 3.7, i.e. Figure 3.7(a), Figure 3.7(b) and Figure 3.8(c) clearly show that refrigeration output $Q_r$ calculated from D-A format always achieve the highest values for each tested samples while that calculated from the Langmuir format always has the lowest values. In the typical working temperature range of a low-temperature powered adsorption system, for instance 85°C-100°C, the difference of $Q_r$ from D-A format and Freundlich format can be significant, almost reaching 200% in each sample at the temperature of 85°C. Therefore, from the perspective of design calculation, selecting which adsorption format to use needs to be done carefully.

A preliminary experiment was conducted using the activated carbon WS-480 to verify the above conclusion. The experiment was carried out with a constant heat source temperature of 85°C. Refrigeration COP was calculated based on the desorption amount achieved after reaching sorption equilibrium. The result proves that the D-A equation can provide more accurate results for simulation.
Figure 3.7 Refrigeration output $Q_r$ vs heat source temperature $T$ calculated with Langmuir format, Freundlich format and D-A format respectively.
Table 3.2 Parameters in $Q_r$ calculation

<table>
<thead>
<tr>
<th>Symbol $T_x (T_y)$</th>
<th>Value</th>
<th>Unit</th>
<th>Symbol $c_r$</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30</td>
<td>°C</td>
<td>$c_r$</td>
<td>2.53</td>
<td>kJ/kg K</td>
</tr>
<tr>
<td>$T_x (T_y)$</td>
<td>0</td>
<td>°C</td>
<td>$M_w$</td>
<td>1</td>
<td>kg</td>
</tr>
<tr>
<td>$L_0$</td>
<td>1120</td>
<td>kJ/kg</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 3.4.3 Format Impact on COP

The impact of using different formats on calculating COP was also examined.

Figure 3.8 illustrates the COP calculated using different adsorption equations for each sample. Equation 3.17 is used to calculate the COP. The operating and physical parameters in calculation are the same as that used in Table 3.2 above.

From Figure 3.8, it is not difficult to see the variation of calculated COP when using different isotherm formats. Generally the D-A format provides the highest COP values calculated for a given carbon samples. The difference among the COP values calculated at a given heat source temperature using different isotherm can be quite significant. For instance, there is an approximately 170% absolute difference between results from the D-A and Freundlich equations for the sample WS-480 in the typical working temperature range.

A COP calculation based on the experimental data of the desorption amount of activated carbon WS-480 is shown in Figure 3.8 (c), which can indicate that the D-A format is more accurate when calculating COP.

Besides difference in COP values, the minimum heating source temperature required to run the refrigeration cycle calculated from those three adsorption equations varies considerably. The minimum temperatures calculated from the D-A and Freundlich equations do not vary much for each tested carbon sample while those calculated from the Langmuir equation vary markedly for different carbon samples.
Figure 3.8 Refrigeration COP vs heat source temperature $T$ calculated with Langmuir format, Freundlich format and D-A format respectively.
3.4.4 Sensitivities of the Parameters

In practice, it is inevitable that some errors will occur during the experiment and fitting the experimental data to the isotherm equations, which leads to errors in the parameters being determined and then the errors concerning the calculation of cycle performance calculated. Therefore a sensitivity analysis of each parameter in the three isotherm equations was conducted to examine the errors’ influence on calculating the system COP and refrigeration capacity. The scenario is that activated carbon 207C and methanol operates as a working pair in a refrigeration system with a heating source at 100°C and cooling source at 30°C to generate an evaporating temperature of 0°C. Up to ±10% errors is assumed for each parameter which is caused by the experiment and data processing. Figure 3.9 to Figure 3.11 show the results of the sensitivity study.

Figure 3.9 shows that for the Langmuir equation, an error in the parameter $Q_u$ has a significant impact on refrigeration output and system COP while parameter $K_0'$ only has a relatively slight affection. When $K_0'$ has a 10% error, the impact on the values refrigeration output $Q_r$ or system COP is in the similar range, i.e. approximately 10% and 5% respectively. However, the impact of the error in $Q_u$ is very large. When the error in $Q_u$ is +1%, the variation of calculated refrigeration output $Q_r$ and COP is about 10% to 5%. If the error in $Q_u$ was up to 10%, variation in $Q_r$ could be as high as 340% while the variation in COP is about 55%. Moreover, a positive error in $Q_u$ could affect $Q_r$ more significantly compared to that caused by a negative error.
Figure 3.9 Impact on $Q_r$ and COP caused by error of parameters $K'_o$ and $Q_o$ in Langmuir equation: (a) $Q_r$, (b) COP.

For the Freundlich equation, errors in both the parameters (i.e. $x_o$ and $n$) apparently have little influence on the calculations of refrigeration output $Q_r$ and system COP as shown in Figure 3.10. Figure 3.10 shows that the calculated values of $Q_r$ and COP are less sensitive to parameter $n$ than to parameter $x_o$. 
Figure 3.10 Impact on $Q_r$ and COP caused by error of parameters $x_0$ and $n$ in Freundlich equation: (a) $Q_r$, (b) COP.

In the D-A equation, parameter $n$ is more sensitive to the calculations of $Q_r$ and COP as shown in Figure 3.11. A -10% error in the parameter $n$ could lead to about -48% and -34% deviations in refrigeration output $Q_r$ and system COP respectively. Figure 3.11 also shows that the calculated values of $Q_r$ and COP are less sensitive to errors of parameters $x_0$ and $D$. 
Figure 3.11 Impact on $Q_r$ and COP caused by error of parameters $x_0, n$ and D in D-A equation: (a) $Q_r$, (b) COP.
3.5 Conclusions

In this chapter, the isosteric-based adsorption equilibrium tests are presented, including experiments, adsorption equation fitting and comparison of the three adsorption equations.

The following conclusions can be drawn what this chapter has discussed:

(1) D-A equation is the most suitable format for presenting the adsorptive properties of the tested activated carbon/methanol working pairs in terms of its best agreement with experimental data. D-A format is selected as the adsorption state equation in the following study in this thesis.

(2) Langmuir equation is not suitable for presenting the adsorptive properties of the tested activated carbon/methanol working pair because it has the least agreement with experimental data. In addition, any error in the process of experiment and data processing would cause huge variation in the system performance calculations if the Langmuir format is used. No matter what working pair is used, much effort is necessary to determine the parameters accurately in Langmuir equation, especially the $Q_a$, otherwise the system performance calculations, such as silica gel water chillers, would suffer much.

(3) Carbon WS-480 is chosen to conduct experiments for its sensitive adsorption performance in a low temperature range (85°C-100°C). In other words, the high COP can be obtained via a low temperature heat source, as shown in Figure 3.8 (c).
CHAPTER 4

PHYSICAL AND MATHEMATICAL MODELS

4.1 Introduction

The typical physical structures of the core component (i.e. generator) of an adsorption refrigeration system and ART were summarised in section 2.4. The cylindrical generator is extensively applied in various adsorption refrigeration systems and devices, including traditional adsorption refrigeration systems and ART-based modular adsorption refrigeration systems. Therefore, physical refinement and mathematical modelling of a cylindrical shaped ART has a broad meaning.

The physical configuration of the ART in this study is developed based on a similar structure as proposed by Critoph (2001), Wang and Zhang (2009), Wu et al. (2009). A couple of modifications have been made to improve the performance of the ART. Firstly, a valve was added to control the evaporating pressure which can help improve the refrigeration COP. Secondly, the evaporator and condenser were separated to reduce heat loss.

Regarding the mathematical model, section 2.5 highlighted that no existing mathematical models have considered local thermal non-equilibrium together with the transient evaporating pressure process. Local thermal non-equilibrium between solid phase (adsorbent and adsorbed adsorbate) and fluid phase (gaseous adsorbate) may be significant in an adsorbent bed in that adsorption and desorption always
accompany fast huge heat sink and heat, Kavinany (1995). On the other hand, the transient pressure process at the beginning of the isobaric adsorption process should have a significant impact on adsorbent temperature development, which was experimentally identified previously by Li et al. (2002). However, to the best of this author’s knowledge, this process was neglected in all previous mathematical modelling.

To consider local thermal non-equilibrium and the effect of the transient pressure process, a two-temperature treatment of heat transfer and a mathematical definition of the transient pressure process are introduced when establishing the mathematical model. The model developed is able to provide better prediction of thermal performance for those adsorption systems run with rapid cycles and complex internal heat and mass recovery processes.

4.2 Physical Model

4.2.1 ART Configuration

The proposed ART is comprised of a generator, a condenser, an evaporator, insulation sectors, a circulation pipe, a water jacket and a control valve, as shown in Figure 4.1. Compared to the configurations proposed by Critoph (2001), Wu et al. (2009), this new structure has two major improvements. First, the condenser and evaporator are separated and located at two ends, which helps avoid heat loss and heat disturbances. Second, the control valve in the external circulation path can control evaporating pressure, which would enhance the production of useful refrigeration capacity.

In the generator, activated carbon can be produced in situ to reduce contact heat resistances. Normally, a perforated tube is placed centrally in the generator serving as a mass transfer channel and the activated carbon in the form of particles is filled in between the generator and the mass transfer channel. The diameter of the adsorbent bed (i.e. carbon column) is a crucial parameter that depends mainly on the request in cycle time.
Figure 4.1 Overview and cross-section of the proposed ART.

4.2.2 Working Principle of the ART

An idealised cycle within an ART contains four procedures: isosteric heating, isobaric desorption, isosteric cooling and isobaric adsorption (corresponding processes 1-2, 2-3, 3-4, 4-1, shown in Figure 4.2). The specific working processes of the ART are described below.

In process 1-2, the cycle starts from point 1, where adsorbate (methanol) is adsorbed in the adsorbent (carbon) at temperature $T_1$ and pressure $P_1$ (i.e. $P_c$). As the generator is heated up by circulating heat exchange fluid in the ART’s water jacket, the temperature and pressure increase along the isoster. In the meantime, the bulk concentration of the methanol in the adsorbent bed remains at $x_1$, until point 2 is reached.

Once the pressure reaches saturation pressure $P_2$ which is controlled by cooling water to the condenser, the cycle proceeds to process 2-3. In this process, methanol vapour is driven out of the carbon due to heating. Methanol vapor then travels
through the central tube to the condenser and condenses there. This desorption process is an isobar process, but the temperature of the generator, i.e. activated carbon and methanol adsorbed, keeps increasing until point 3 where the maximum cycle temperature is reached. During process 2-3, condensed methanol is collected in the evaporator (functioned as a receiver) and the bulk concentration of the methanol in the carbon decreases to its minimum $x_3$.

In process 3-4, the evaporator is isolated from the generator which is cooled along the isosteric line (i.e. at constant concentration $x_3$) to point 4 where the pressure reaches $P_e$ again. Once point is 4 reached, the evaporator is connected to the generator again to initiate the adsorption process, i.e. process 4-1.

In process 4-1, after the evaporator has been connected to the generator, the liquid methanol collected in the evaporator starts to evaporate and generate refrigeration power. However, this evaporation does not occur at the designed pressure immediately, but after a short period. The evaporated methanol returns to the generator via the circulation pipe to be re-adsorbed by the carbon. During this process, the sensible heat and the adsorption heat are removed by circulating cooling water in the water jacket. When this process is completed, the generator is re-stored to point 1.

In practical operation, process 1-2 and 2-3 have no apparent threshold, which can be deemed as the first half cycle (i.e. process 1-2-3). Similarly, processes 3-4 and 4-1 can be incorporated into the second half cycle (i.e. process 3-4-1), in which refrigeration is triggered.

### 4.2.3 Mechanism of the Model

Solid physical adsorption is a porous media involved process comprising heat transfer, mass transfer and physical adsorption. Figure 4.3 schematically illustrates the pore-level heat and mass transfer as well as phase change. In general, it is considered that gaseous species may be transported in the void space of a porous media, which accompanies the heat exchange and phase change.
Figure 4.2 Clapeyron diagram of an ideal adsorption refrigeration cycle of an ART

Figure 4.3 A rendering of the pore-level transport, reaction, and phase change in porous media. Derived from Kavinany (1995).

In this thesis, porous media activated carbon is believed to have three levels of pores, i.e. micropore, mesopore and macropore (Dubinin (1968)). Methanol vapor may be transported in transport pores (i.e. mesopores and macropores, see Dubinin (1968) ), which accompany the phenomena of heat exchange and sorption. Heat exchange at the pore-level is caused by conductive heat transfer between the fluid phase and solid phase. The adsorption and desorption accompany phase change, i.e. from gas to liquid and from liquid to gas respectively.
When an adsorbent bed is deemed to comprise uniform sized activated carbon particles, the thermodynamic mechanism of the entire bed can be simplified. Figure 4.4 schematically illustrates the thermodynamic process during the desorption process (i.e. process 2-3 illustrated in Figure 4.2). There are two kinds of convective heat transfer existing between methanol and carbon particles: interfacial \( (h_i) \) and external \( (h_e) \) convective heat transfers. The interfacial convection representing heat transfer mainly occurs due to methanol vapor moving through the internal transport pores of activated carbon particles, whereas external convection denotes the heat transfer happening at the external surfaces of activated carbon particles.

![Figure 4.4 Schematics of convective heat transfer in adsorbent bed.](image)

However, in a mathematical model, it is difficult to precisely consider both the convection mechanisms. This is because the exact proportion of methanol vapor that purely transfers among the gaps of particles and that which partly travels through transport pores and partly through gaps, is not known. In order to achieve a simplified and reasonable mathematical model, it is considered that the external convective heat transfer \( (h_e) \) is negligible. This simplification is justified because the convective heat transfer coefficients for the interfacial convection and the external convection are in the same order according to the experimental data compiled by Wakao and Kaguei (1982), while the effective heat transfer area
(specific surface area) of the interfacial convection is much larger than that of the external convection several orders. The specific surface area of activated carbon particles was evaluated with the data in Bansal et al. (1988).

Regarding mass transfer in the generator, the driving forces derive from two aspects: firstly, vapor temperature difference caused pressure gradient within the bed; and secondly, external fluid caused pressure gradient. Referring to Figure 4.2, during the process 1-2-3, methanol vapor and solid carbon are heated up from outside (i.e. Ro), resulting in the temperature difference of methanol vapor in the radial direction. The temperature difference results in the pressure gradient, further leading to convection. In other words, vapor methanol generally moves towards the inner positions.

On the other hand, in process 3-4-1, besides temperature difference caused pressure gradient, external fluid caused pressure gradient contributes to vapor movement as well. When the evaporator at condensing pressure is connected to the generator at point 4, the generator pressure jumps (from $P_1$ to $P_2$) and then takes some time to drop back to and remain at the constant designed $P_e$. Before the pressure reaches the stable value $P_e$ again, the pressure at the boundary $R_i$ is a transient value, resulting in vapor density at this boundary also having a transient value. This transient vapor density at the inner boundary, together with the existing density field (established in process 3-4) will lead to a further mass transfer.

4.3 Mathematical Model

4.3.1 Modeling Assumptions

Local thermal non-equilibrium between activated carbon and gaseous methanol is employed to establish convective heat transfer. Methanal vapor flows through transport pores within activated carbon particles. This part of the convective heat transfer (i.e. $h_m$) is taken into account in the modelling. The flows through the external surfaces of carbon particles, i.e. external convection $h_{eo}$ are neglected since the specific surface of particle external surface is rather small compared to that of transport pores.
Other assumptions are made as follows:

1. The activated carbon and adsorbed methanol (liquid state) are in local thermal equilibrium.
2. The gaseous methanol is assumed to be an ideal gas.
3. The thermal conductivities of the activated carbon and methanol are constant.
4. The size of transport pores of the activated carbon particles is assumed to be uniform.
5. The diameter of activated carbon particles is uniform.
6. Condensing pressure is constant.

4.3.2 Governing Equations

(1) Energy Transfer

The adsorption and desorption processes typically accompany apparent heat sink and generation in the solid adsorbent (activated carbon). In these circumstances, the assumption of local thermal equilibrium between solid phase and gaseous fluid (gaseous methanol) is not sufficient. Hence, local thermal non-equilibrium (i.e. the two-temperature treatment) is made to establish the following energy governing equations.

It is considered that heat conduction, interfacial convection, and internal heat source (or sink) contribute to heat transfer within the solid phase. For gaseous fluid, conduction and convection lead to heat transfer. Consequently, heat transfer equations for the solid phase and gaseous fluid can be written in Eq 4.1 and Eq 4.2, in cylindrical coordinates:

\[
(1 - \varepsilon)(\rho c)_s \frac{\partial T_s}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r}(\lambda_s r \frac{\partial T_s}{\partial r}) + A_h h_w (T_f - T_s) + \rho_s H \frac{\partial \chi}{\partial t} \quad (4.1)
\]

\[
\varepsilon(\rho c)_f \frac{\partial T_f}{\partial t} + \varepsilon(\rho c)_f \mathbf{v} \cdot (r \frac{\partial T_f}{\partial r}) = \frac{1}{r} \frac{\partial}{\partial r}(\lambda_f r \frac{\partial T_f}{\partial r}) + A_h h_w (T_s - T_f) \quad (4.2)
\]
where:

- $A_0$ is the specific surface area of the transport;
- $h_{in}$ is the interfacial convective heat transfer coefficient;
- $\mathbf{v}$ is the velocity of methanol vapour in transport pores;
- $T_s$ and $T_f$ are the temperature of solid phase and fluid phase respectively;
- $(\rho c)_s$ denotes the equivalent property of the solid phase, which equals to $\rho_w c_{aw} + \rho_f c_{pf}$;
- $(\rho c_p)_f$ denotes the property of the fluid phase, which equals to $\rho_c c_{pf}$;
- $\varepsilon$ is the effective porosity; and
- $H$ is the sorption heat, which is calculated using Eq 4.3:

$$H = AR_0 T_s / T_{sat} \tag{4.3}$$

where:

- $A$ is a constant, for methanol $A = 4666$;
- $R_0$ is the specific gas constant; and
- $T_{sat}$ is the saturation temperature corresponding to the local pressure.

(2) Mass Transfer

During the heating-desorption process (process 1-2-3), methanol vapor moves towards the mass transfer channel from the outer positions due to pressure gradient caused by temperature differences (i.e. gas density gradient). For the cooling-adsorption process (process 3-4-1), the mechanism of diffusion is different, not only the temperature differences causing density gradient, but also the external fluid (from the evaporator), resulting in convection. The latter factor, external pressure gradient, is presented through a transient boundary condition which will be introduced in the following section concerning boundary conditions.
The diffusion process within the bed can be described mathematically as:

$$\varepsilon \frac{\partial C}{\partial t} + (1 - \varepsilon) \cdot \rho_s \frac{\partial (x / M_o)}{\partial t} = \varepsilon \frac{1}{r} \frac{\partial}{\partial r} (D_{eb} r \frac{\partial C}{\partial r})$$

(4.4)

where:

$x$ is the concentration of adsorbed methanol (in micropores of the carbon);

$M_o$ is the molar mass of methanol;

$\varepsilon$ is the porosity of the carbon bed;

$D_{eb}$ is the effective diffusion coefficient;

$C$ is the local density of gaseous methanol; and

$\rho_s$ is the density of solid phase.

(3) Sorption Rate

Dubinin-Astakov equation (D-A) is employed as the adsorption state equation because of its good agreement with the adsorptive properties of the selected carbon WS-480. Moreover, the linear driving force (LDF) model is used to account for the non-equilibrium adsorption behaviour which is significant for the adsorption refrigeration system run with rapid cycles. Two equations are expressed as follows:

$$x_{eq} = x_0 \exp(-D(T_s \ln \frac{P_{sat}}{P})^\gamma)$$

(4.5)

$$\frac{\partial x}{\partial t} = \frac{15D_0}{R_p^2} \cdot \exp(-\frac{E_a}{RT_s}) \cdot (x_{eq} - x)$$

(4.6)

where:

$x_{eq}$ represents the equilibrium concentration at corresponding pressure and temperature; and $x$ denotes actual reached concentration; $15D_0 / R_p^2$ and $E_a / RT_s$ are coefficients.
(4) Darcy Law

Darcy law and a specifically modified permeability for packed bed, which is effective for the porosity between 0.35 and 0.67, are employed to describe the vapor velocity. This can be written as Eq 4.7 and Eq 4.8:

\[
v = -\frac{K}{\mu} \left( \frac{\partial P}{\partial r} \right)
\]  

(4.7)

\[
K = \frac{\varepsilon^{5.5}}{5.6} d_h^2
\]

(4.8)

It is worthy noting that \(d_h\) is not the physical diameter of the transport pores, but the hydraulic diameter which can be approximately calculated using \(d_h = 6 / A_g\), Kavinany (1995).

(5) Supplemental Equations

For methanol:

\[
\ln P_{sat} = 18.587 - 3626.55 / (T_f - 34.29)
\]  

(4.9)

\[
C = P / R_g T_f
\]  

(4.10)

4.3.3 Boundary Conditions

Boundary conditions of the present mathematical model refer to three parameters, \(T_s\), \(T_f\) and \(C\). Each parameter has two boundary conditions, at \(Ri\) and \(Ro\) respectively. The boundary condition of \(T_s\) at \(Ro\) applies Dirichlet boundary condition since the heat transfer resistance of a metal water jacket is negligible compared to the heat transfer resistance within the adsorbent bed. The heat conductivity of stainless steel is normally about 50 W/(m·K) while that of activated carbon usually is about 0.1-0.45 W/(m·K). On the other hand, the boundary condition of \(T_s\) at \(Ri\) applies adiabatic boundary condition during the process 1-2-3-4 of the refrigeration cycle while that over the process 4-1 uses Robin boundary condition. Similarly, \(T_f\) at
Ro applies Dirichlet boundary condition over the entire process while that at Ri employs adiabatic boundary condition and Robin boundary condition during the process 1-2-3-4 and process 4-1 respectively. For parameter C, boundary conditions at Ro apply mass isolation over the entire cycle while that at Ri adopt different boundary conditions according to different thermal processes. During the processes 1-2 and 3-4, boundary conditions at Ri apply mass isolation since it is assumed that the system only generates micro sorption phenomena during these two processes. Hence no mass (methanol vapor) flow into or out the adsorbent bed occurs. On the other hand, during the processes 3-4 and 4-1, boundary conditions at Ri use Dirichlet boundary condition. The value of C at boundary Ri is assumed to be equal to the density of methanol vapor in the condenser or evaporator.

Mathematically, the boundary conditions can be expressed as follows.

For the thermal process $1-2-3$:

$$T_i \bigg|_{r=Ro,d_i<r<St_1} = T_f \bigg|_{r=Ro,d_i<r<St_1} = T_{ew} \quad (4.11)$$

$$\frac{\partial T_i}{\partial r} \bigg|_{r=Ri,d_i<r<St_3} = \frac{\partial T_f}{\partial r} \bigg|_{r=Ri,d_i<r<St_3} = 0 \quad (4.12)$$

$$\frac{\partial C}{\partial t} \bigg|_{r=Ro,d_i<r<St_3} = 0 \quad (4.13)$$

$$\frac{\partial C}{\partial t} \bigg|_{r=Ri,d_i<r<St_3} = 0 \quad (4.14)$$

$$C \bigg|_{r=Ri,d_i<r<St_3} = C_v \quad (4.15)$$

For the thermal process $3-4-1$:

$$T_i \bigg|_{r=Ro,d_i<r<St_3} = T_f \bigg|_{r=Ro,d_i<r<St_3} = T_{ew} \quad (4.16)$$
\[ \frac{\partial T_s}{\partial r} \bigg|_{r=R_0,s<r<s_l} = \frac{\partial T_f}{\partial r} \bigg|_{r=R_0,s<r<s_l} = 0 \]  \hspace{1cm} (4.17)

\[-\lambda_{eq} \frac{\partial T_s}{\partial r} \bigg|_{r=R_0,s<r<s_l} = h_i (T_s \bigg|_{r=R_0,s<r<s_l} - T_f \bigg|_{r=R_0,s<r<s_l}) \]  \hspace{1cm} (4.18)

\[ T_f \bigg|_{r=R_0,s<r<s_l} = T_{in} \]  \hspace{1cm} (4.19)

\[ \frac{\partial C}{\partial t} \bigg|_{r=R_0,s<r<s_l} = 0 \]  \hspace{1cm} (4.20)

\[ \frac{\partial C}{\partial t} \bigg|_{R_0,s<r<s_l} = 0 \]  \hspace{1cm} (4.21)

\[ C \bigg|_{R_0,s<r<s_l} = C_{in} \]  \hspace{1cm} (4.22)

In above boundary conditions, Eq 4.19 and Eq 4.22 represent the transient temperature and concentration of methanol from the evaporator after being connected to the generator. This transient process was neglected in almost all the models proposed by other researchers previously.

The temperature and density of methanol vapor from the evaporator are not constant, when the evaporator is just connected to the generator (at point 4). There is a process for the pressure to stabilise from \( P_t \) to \( P_c \), which results in a transient condition of vapor temperature and density. After this stage, the temperature and density of methanol vapor from the evaporator reach and remain at the stable values. To present this process, a concept of the transient system pressure (\( P_{na} \)) is introduced to reflect the corresponding transient vapor temperature (\( T_{na} \)) and density (\( C_{na} \)). The transient pressure (\( P_{na} \)) is defined as Eq 4.23:

\[ P_{na} = \frac{P - P_c}{1 + \alpha t} + P_c \]  \hspace{1cm} (4.23)
Where \( P_e \) and \( P_r \) denote the pressure in the evaporator at status point 3' and 4'(see Figure 4.2); \( t \) is time; and \( \alpha \) is a coefficient reflecting the time taken by the pressure to drop to \( P_r \) from \( P_e \).

Since the pressure falling-off process is relatively quick compared to the time taken for the entire adsorption process, \( \alpha \) is normally in the range \( 0 < \alpha \leq 1 \). This means that the bigger value \( \alpha \) is, the shorter time is needed for the evaporating pressure to drop. When \( \alpha = 1 \), the evaporating pressure falls to the designed evaporating pressure in dozens of seconds. The value of \( \alpha \) depends on the practical operating situation and system’s inner structure, which can be an empirical value and obtained experimentally.

Substituting Eq 4.23 into Eq 4.10, the correlation of the vapor transient temperature, density and pressure can be expressed as:

\[
C_{tr} = \frac{P_{tr}}{R_{tr}T_{tr}}
\]  
(4.24)

### 4.4 Numerical Solution

#### 4.4.1 Introduction

Previous mathematical models that comprise a set of second-order partial differential equations (PDEs) were usually solved using Tri-Diagonal Matrix Algorithm (TDMA) or Alternating-Direction Implicit (ADI) method. Leong and Liu (2006) solved a local thermal equilibrium-based model using TDMA. In their numerical solution, forward difference scheme and central difference scheme were employed in time and spatial discretisation respectively. Moreover, under-relaxation factors were employed to control convergence in the solution. On the other hand, ADI was used by Marletta et al. (2002), Maggio et al. (2006) to solve equation systems consisting of four second-order PDEs. In both these methods, time step and size step are crucial for computation accuracy and solving speed.

Although the TDMA and ADI methods are able to compute these previously proposed mathematical models, they are not effective and efficient for the model
proposed in this research. This is because one of the boundary conditions becomes
dynamic which would greatly increase the difficulty in solving the problem.

In order to solve the mathematical model effectively, software known as Comsol
Multiphysics was employed. This software is able to create a Multiphysics model in
which transient heat transfer equations, transient mass transfer equation as well as
adsorption equation can be solved as one fully coupled system. The solver is able to
choose and dynamic change time step automatically according to transient
convergence so that fast computing and convergence are achieved.

The numerical results can be then exported to Matlab as an M-file. Thus each
parameter of the multiphysics field, such as pressure, temperature and concentration
can be analysed using the solved multiphysics field.

4.4.2 Domain Meshing

Figure 4.5 illustrates the schematic diagram of meshing inside the adsorbent bed, i.e.
generator. The bed is divided into N layers and each layer has an even and enough
small thickness of \((R_o - R_i) / N\) within which the pressure and temperature can be
deemed uniform. In the computational domain, this cylindrically symmetrical
problem can be simplified into a radial 1-D problem. Figure 4.6 below shows the 1-D
meshing in the multiphysics model of Comsol Multiphysics. The symmetrical
computational domain can be generated by setting Independent variables in the Add
Geometry dialog box. The meshes can be created using the Free Mesh Parameters
dialog box. The number of layers, in other words, N depends on the real thickness of
the cylindrical adsorbent bed. Maggio et al. (2006) assumed a layer thickness of
0.3mm in a numerical study of a zeolite-water adsorption refrigeration cycle. In this
thesis the layer thickness is assumed to be 0.2mm in numerical solution.
4.4.3 Domain Equations

The governing equations of the model comprise four partial differential equations, i.e. Eq 4.1, Eq 4.2, Eq 4.4 and Eq 4.6, which were coupled in the Multiphysics Model using Conduction Model, Convection and Conduction Model, Diffusion Model and self-defined General Form PDE respectively.

4.4.4 Boundary Conditions

Mathematical expressions for the boundary conditions, i.e. Eq 4.11 to Eq 4.22 can be set up in Boundary Settings in governing equations’ corresponding models. The transient boundary condition of the diffusion equation, i.e. Eq 4.22, can be input by defining a function in Global Expressions and then invoking the function in the Boundary Settings dialogue box.
CHAPTER 5

EXPERIMENTAL VALIDATION

5.1 Introduction

This chapter presents the experimental validation of the model proposed in chapter 4. Figure 5.1 shows the overall test rig that includes generator, condenser, evaporator, heat sources, temperature sensors, pressure gauge, liquid level indicator, data acquisition system and external water system. In order to properly measure the temperature field of the adsorbent bed, the diameter of the cylindrical adsorbent bed was designed so that it was larger than the typical size of an ART’s generator. In this chapter, the design of each component of the test rig and the key features of the measuring apparatus is introduced (section 5.2). Then, the experimental uncertainties are analysed in section 5.3. In sections 5.4 and 5.5, the testing procedures and experimental validation are presented. In section 5.6, an interesting phenomenon of adsorbate migration is discussed.

5.2 Experimental Apparatus

5.2.1 Generator

The generator component includes a cylindrical adsorber, an integrated water jacket, mass and heat isolation covers, a porous tube and temperature sensors, shown in Figure 5.2. The adsorber jacket was made from 8” stainless steel tube and the wall of the tube was machined to 1mm to reduce heat transfer resistance and achieve good pressure-bearing. The mass and heat isolation covers were designed to restrict the
heat and mass transfer process occurring only in the radial direction. The inner and outer diameters of the adsorber (i.e. \( R_i \) and \( R_o \)) were carefully selected using the dynamic model in order to simulate a refrigeration cycle having a long cycle time, which can contribute to a better measuring accuracy. The upper and bottom covers were removable and could be tightly assembled to the adsorber jacket through bolting (sealing rubber was used to retain the vacuum). For measuring, four T-type thermocouples (i.e. TS1-TS4) were arranged in a radial direction.

Figure 5.1 Overview of the testing system.
Figure 5.2 Detailed cross-section of the generator showing the arrangement of temperature sensors.

5.2.2 Condenser

Figure 5.3 displays the cross-section of the condenser subassembly which consists of a stainless steel condenser and an acrylic water jacket. The designed bridging tube is not only for physical connection to the generator, but also serves as a convertor of the system status. When the system status proceeds to macro desorption (i.e. process 2-3 in Figure 4.2), methanol vapor goes to the condenser via the bridging tube and then condensed methanol liquid will only be able to flow to the evaporator due to the specific inner physical structure of the condenser. Conversely, when the system is in the macro adsorption process (i.e. process 4-1 in Figure 4.2), evaporated methanol vapor will travel to the adsorbent bed via the bridging tube. For measuring and indicating system status, a pressure gauge and thermocouple were arranged in this condenser. The thermocouple is able to measure both the gas temperature and liquid temperature using different operating approaches, which are illustrated in the experimental procedure section.

For the required area of the heat exchange surfaces of this condenser was calculated during the design phase. Assuming the generator contains a maximum amount of activated carbon WS-480 (equal to 3.2 kg) and the system runs with a 80%
theoretical maximum methanol concentration variation (i.e. $0.27 \times 0.8 \text{ kg/kg}$), then 0.69 kg methanol vapor need to be condensed, which means about total 760.38 kJ heat needs to be released over the desorption-condensing process. When the time needed for the desorption-condensing process is taken into account (at least eight hours), then the heat releasing rate of the condenser should reach 26.40 W. Assuming a three degree heat exchange temperature difference between external cooling water and inner methanol vapor, and assuming a 170 W/m²K natural convection heat exchange coefficient (Jing (1992)), the area of the heat exchange surfaces will be 0.052 m². Hence, the heat exchange surfaces of this condenser were made from a 5" stainless steel tube (serving as the side surface) and a flat stainless steel sheet (serving as the upper surface). The total effective heat exchange area of the side surface and the upper surface reaches 0.064 m², which satisfies the heat exchange requirement. During the experiment, the cooling water temperature can be adjusted to control the methanol condensing temperature. The real condensing temperature can be measured through the inserted thermocouple.

![Diagram of the condenser subassembly](image)

Figure 5.3 Detailed cross-section of the condenser subassembly showing the arrangement of temperature sensor and pressure gauge.

### 5.2.3 Evaporator

Figure 5.4 shows the schematic diagram of the evaporator which was designed as a slender shape to facilitate observation of the liquid level variation. The liquid level indicator was made from a 2mm thick tempered glass tube that can stand sudden
temperature variation and can bear one atmosphere pressure due to the vacuum requirement. The scale of the liquid level indicator was calibrated by filling water into the evaporator using a volume calibration syringe. The marked range of the liquid level indicator is 60-750 ml and the precision is 0.5mL. The start point is not from “0”ml since the small volume of the bottom area of the evaporator can contain a certain amount of liquid. The temperature sensor TS6 is arranged to measure the evaporating temperature inside the evaporator.

![Figure 5.4 Schematic diagram of the evaporator.](image)

### 5.2.4 Heat Source

Two water bathes were used as a simulated heat source and heat sink respectively. Water bath A (WBA) with a heating function (2500 W) severed as a simulated heat source. Water bath B (WBB) with a heating function (1000 W) and a cooling function (500 W) served as a simulated cooling source. The heating function of WBB can work independently to adjust the cooling power. When the heating function is turned off, the maximum cooling power of WBB, i.e. 500 W, is sufficient for the condenser according to the heat releasing rate of the condenser examined in section 5.2.2. On the other hand, the heating capacity of WBA is apparently sufficient as a heat source when assuming a COP of 0.1 for calculating the heating rate, which merely needs 264 W in the selected case analysed in section 5.2.2. Apart
from considering heating and cooling capacity, temperature precision can be controlled as well. It reaches 0.1 °C and it is sufficiently accurate for validating the present model.

### 5.2.5 Temperature Sensor

T-type thermocouple produced by TC Measurement & Control Pty Ltd was chosen to measure temperature, which has a tolerance of ±0.5°C in the range -40°C to +125°C. The diameter of the thermocouple selected is 1.5mm which enables it to provide certain stiffness for measuring location; the contact area is small which is helpful for better accuracy of measurement. Each thermocouple matched a feedthrough (including a cap, a follower, a sealant and a body) for sealing. Figure 5.5 illustrates an assembled feedthrough with a thermocouple. The sealant selected is made of Teflon and its diameter is 1.5mm, which can bear 150 bar pressure and is reliable for vacuum keeping in a carbon-methanol adsorption system.

![Figure 5.5 Schematic diagram of an assembled feedthrough with a thermocouple.](image)

### 5.2.6 Data logger

A data logger and assorted logging software were used to convert analogue signal from thermocouples to digital signal. The data logger package XSL-16 can be used for temperature data acquisition by choosing a corresponding working mode, which depends on the type of thermocouples to be worked with. The data logger was connected to a personal computer and the logging software can collect and display real-time data at a user-defined time interval. Prior to being used, each channel was calibrated using a Fluke 714 Thermocouple Calibrator. During the calibration, each
channel was given a series of standard analogue signals (correspond to known
temperature values) using the Fluke 714 Thermocouple Calibrator and then recording
the temperature values converted and displayed by the logging software. Comparing
the difference between each temperature point, the average drifts of each channel
were determined. By adjusting errors made by the data logger, each channel was
corrected before recording and displaying temperatures.

5.2.7 Pressure Gauge

A normal pressure gauge was selected for experiments, which has a working range in
vacuum -100 kPa to 0 kPa (one atmosphere) and the error is ±0.4 kPa. The pressure
gauge is mounted on top of the condenser and used to indicate the system pressure to
facilitate operating procedure during the experiments.

5.3 Analysis of Experimental Errors

In the following experimentation, errors arise from measuring instruments, data
acquisition and limitation of the experimental apparatus. The most significant
contributions arise from the experimental apparatus.

5.3.1 Measuring Instruments Errors

In the experiments, each thermocouples and the liquid level indicator were calibrated
before they were employed. The T-type thermocouples produced by TC
Measurement & Control Pty Ltd. performed fairly well, which have only a ±0.1°C
drift detected by the Fluke 9100S Calibrator. The scale of the liquid level indicator
was calibrated using a volume calibration syringe whose tolerance is 0.2 ml.
However, due to the inner side of the evaporator is not being polished; the inner wall
of the tube can suck a small amount of liquid during volume calibration, which leads
to certain errors. In order to minimise this calibration error, the volume calibrations
were repeated several times until the calibration finding for each time was stabilised.
The tolerance of the stabilised calibration result is 0.5 ml, which is acceptable for
validating the model in which the total liquid volume variation will be approximately
350–450 ml.
5.3.2 Data Acquisition Errors

Errors arise from data acquisition system are very small. The data logger and its logging software were calibrated using a Fluke 714 Thermocouple Calibrator and Fluke 9100S Calibrator. The drifts identified were corrected using the error adjust function of the data logger.

5.3.3 Other Errors

The most significant contributions resulted from limitations of the experimental apparatus.

Firstly, the pressure to be measured is the system pressure rather than the exact pressure at the inner boundary (i.e. at \( R_i \)) which is a pressure criterion used in numerical solutions. Theoretically, in thermal process 3-4 (see Figure 4.2), the dynamic pressure variation measured using the pressure gauge should lag behind that at the boundary \( R_i \), which will affect the timing needed to connect the evaporator to the generator to trigger thermal process 4-1. The timing may impact on the temperature development and profile within the adsorbent bed during the first stage of process 4-1. The impact will be examined and discussed in the following section.

Secondly, the desorption amount of refrigerant (liquid methanol) would be smaller than the true value due to the condensing issue. The tube connecting the evaporator and the condenser was not wrapped with heating wire. Therefore a tiny amount of methanol would condense and stick to the inside wall of the tube. In order to validate the mathematical model precisely in terms of sorption amount, the dynamic adsorption amount was measured, which was used as a better experimental result to validate the model’s prediction ability. The condensing issue can naturally be avoided in the adsorption process.

Thirdly, the liquid level in the liquid level indicator was not stable during adsorption due to tiny bubbles evaporating from the inner wall of the evaporator which caused the liquid level to fluctuate. In the experiment, the liquid level was recorded when the liquid level was relatively stable.
5.3.4 Summary of Errors

As stated above, the maximum errors in the present experiments originated from the experimental apparatus. Although these errors are difficult to overcome, the experimental results are reliable and effective for validating the mathematical model for the purpose of predicting thermal performance.

5.4 Experimentation

5.4.1 Experiment System

A schematic diagram of the experiment system and each component of the experiment system are illustrated. Figure 5.6 is a photograph of the test rig.

Figure 5.6 Photograph of the experiment system.
The water bath WBB has a built-in pump used to pump cooling water to the condenser and generator via the external water system, according to specific requirements for different phases in experiment. For the water bath WBA not having a built-in water pump, an additional hot water pump was installed and used to pump hot water to the generator when required. The water jacket of the generator connects to the WBA and WBB, so heat transfer fluid to the generator can be shifted conveniently by controlling the external water system appropriately.

### 5.4.2 Experiment conditions

The experiment simulated an operating condition corresponding to a 10°C evaporating temperature requirement, a 25°C environment temperature and a 90°C heat source temperature. The activated carbon used was 2 kg for the consideration to achieve an appropriate sorption amount and “thickness” of the carbon column was carefully determined to simulate a refrigeration cycle with a long cycle time to minimise measuring errors. Relevant operating parameters, thermophysical properties of the working pair and the geometrical dimensions of the generator are listed in Table 5.1, Table 5.2 and Table 5.3, respectively.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{am}$</td>
<td>25</td>
<td>°C</td>
<td>Environment temperature</td>
</tr>
<tr>
<td>$T_{cw}$</td>
<td>25</td>
<td>°C</td>
<td>Simulated heat sink temperature</td>
</tr>
<tr>
<td>$T_{hv}$</td>
<td>90</td>
<td>°C</td>
<td>Simulated heat source temperature</td>
</tr>
<tr>
<td>$T_e$</td>
<td>10</td>
<td>°C</td>
<td>Required evaporating temperature</td>
</tr>
<tr>
<td>$P_e$</td>
<td>16.36</td>
<td>kPa</td>
<td>Corresponding evaporating pressure</td>
</tr>
<tr>
<td>$P_c$</td>
<td>7.14</td>
<td>kPa</td>
<td>Corresponding condensing pressure</td>
</tr>
</tbody>
</table>
### Table 5.2 Thermophysical properties of the working pair

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon bulk density</td>
<td>$\rho_{ac}$</td>
<td>420</td>
<td>kg m$^{-3}$</td>
</tr>
<tr>
<td>Methanol gas density</td>
<td>$\rho_g$</td>
<td>0.8</td>
<td>kg m$^{-3}$</td>
</tr>
<tr>
<td>Specific heat of solid carbon</td>
<td>$c_{ac}$</td>
<td>930</td>
<td>J kg$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>Specific heat of liquid methanol</td>
<td>$c_{pl}$</td>
<td>2530</td>
<td>J kg$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>Specific heat of gas methanol</td>
<td>$c_{pf}$</td>
<td>1370</td>
<td>J kg$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>Effective porosity</td>
<td>$\varepsilon$</td>
<td>0.65</td>
<td></td>
</tr>
<tr>
<td>Latent heat of methanol</td>
<td>$L_o$</td>
<td>1102</td>
<td>J kg$^{-1}$</td>
</tr>
<tr>
<td>Heat conductivity solid phase</td>
<td>$\lambda_s$</td>
<td>0.18</td>
<td>W m$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>Heat conductivity of fluid phase</td>
<td>$\lambda_f$</td>
<td>0.019</td>
<td>W m$^{-1}$ K$^{-1}$</td>
</tr>
</tbody>
</table>

### Table 5.3 Geometrical dimensions of the adsorber

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Dimensions</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outer diameter of the adsorber</td>
<td>$Ro$</td>
<td>105</td>
<td>mm</td>
</tr>
<tr>
<td>Inner diameter of the adsorber</td>
<td>$Ri$</td>
<td>55</td>
<td>mm</td>
</tr>
<tr>
<td>Location of temperature sensor 1</td>
<td>$r_1$</td>
<td>100</td>
<td>mm</td>
</tr>
<tr>
<td>Location of temperature sensor 2</td>
<td>$r_2$</td>
<td>80</td>
<td>mm</td>
</tr>
<tr>
<td>Location of temperature sensor 3</td>
<td>$r_3$</td>
<td>58</td>
<td>mm</td>
</tr>
<tr>
<td>Location of temperature sensor 4</td>
<td>$r_4$</td>
<td>53</td>
<td>mm</td>
</tr>
</tbody>
</table>
5.4.3 Testing Procedures

Experiments conducted incorporated three steps, these being: firstly, setting system status; secondary, conducting isosteric cooling and isobaric adsorption processes (i.e. process 3-4-1); and thirdly, conducting isosteric heating and isobaric desorption processes (i.e. process 1-2-3). Specific procedures of each step are illustrated as follows.

Step 1, setting system status:

(1) Evacuated the system and retained for 48 hours to ensure that the system can keep the vacuum well.

(2) Filled the generator with activated carbon; the amount filled in was $M_{ac}$.

(3) Heated and degassed the carbon bed simultaneously for twelve hours, and then isolated the generator by closing valve V2 (see Figure 5.1).

(4) Put methanol into the evaporator and maintained the evaporator at $T_y$. The amount in the evaporator is slightly higher than the amount $x_i \times M_{ac}$ to compensate for the loss during the vacuuming process.

(5) Charged methanol into the carbon bed. The amount charged is $x_3 \times M_{ac}$.

(6) Set the status of the generator to point 3 (see Figure 4.2) via circulating water (at $T_3 = T_{cw}$) in the water jacket until the carbon bed temperature reaches $T_3$ evenly.

Step 2, conducting the process 3-4-1:

(7) Circulated cooling water (i.e. at $T_{cw}$) to generate the isosteric cooling process, in which the generator was isolated from the evaporator.

(8) Recorded temperatures and pressures involved in this process.

(9) When the pressure reached the designed evaporating pressure, the evaporator was connected to the generator by turning on the valve V1.
(10) Recorded the amount of adsorption using the liquid level indicator of the evaporator, and kept recording temperatures and pressures.

Step 3, conducting the process 1-2-3:

(11) Circulated the cooling water for 24 hours so that the generator reached the status point 1, i.e. temperature and concentration tended to be distributed evenly.

(12) Shifted cooling water to hot water to initiate desorption-condensation processes, and in the meantime circulated cooling water in the water jacket of the condenser.

(13) Recorded temperatures, pressures, and the amount of desorbed methanol.

5.5 Model Validation

Experimental results are compared with the numerical solution to validate the proposed mathematical model. The numerical solution was solved under the simulated operating parameters, using the proposed mathematical model and the numerical approach introduced in section 4.3 and section 4.4. The mathematical model is comprehensively validated in terms of temperature development of solid phase and fluid phase, system pressure development and amount of dynamic sorption. Moreover, the predicted dynamic concentration variation is presented, in which an interesting concentration “centripetal migration” and “centripetal migration” are noted and discussed.

5.5.1 System Pressure

Figure 5.7 shows the comparison of pressure development between numerical results and experimental data. The predicted system pressure builds up slightly faster than the measured data. The reason is thought to be that the numerical results of system pressure are actually the calculated pressure at the inner boundary of the carbon bed while the pressure measuring point is on the top of the condenser (in Figure 5.6), thus there is a interval of time between the simulated results and the pressure gauge
measured data due to the vapour building up in the volume in the condenser and connected pipes.

![Graph showing pressure variation over time](image1)

**Figure 5.7** Comparison of numerical and experimental results for the system pressure variation in process 1-2-3.

![Graph showing pressure variation over time](image2)

**Figure 5.8** Comparison of numerical and experimental results for the system pressure variation in process 3-4-1.

Figure 5.8 shows the experimental data of system pressure during the process 3-4-1 and corresponding predicted pressure development with $\alpha=0.02$. Experimental data shows that system pressure experiences a sudden jump when the evaporator is just
connected to the generator, and then the system pressure drops and approaches the
designed evaporating pressure gradually. The parameter \( \alpha \) in the mathematical
definition of the transient pressure (i.e. Eq 4.23) was determined to be 0.02 for this
case by equation fitting technique using the experimental data. Using this transient
pressure definition (i.e. Eq 4.23), this transient pressure process can be well
presented, which was usually treated as a static evaporating pressure, such as studies
in Maggio et al. (2006) and Fadar et al. (2009).

5.5.2 Solid Phase Temperature

Figure 5.9 shows adsorbent (activated carbon) temperature histories measured at
three radial positions of the carbon bed and corresponding numerical simulation
results in the first half cycle, i.e. process 1-2-3. Figure 5.9 shows that the
experimental data agrees with the numerical results well for the entire process. In
addition, in Figure 5.9, two observations are worth noting. One is that the
temperature development is comprised of two stages, i.e. sharp climbing at the
beginning several minutes followed by the relatively gentle rise. The cause of this
phenomenon is thought to be that when the macro desorption starts, a considerable
part of input heat functions as desorption heat to desorb the methanol, rather than as
the sensible heat to increase the bed’s temperature. The other point is that the
temperatures of the two relative inner positions of the cylindrical carbon bed are
almost the same in the first ten minutes or so. This goes against the normal
perception that there should be a clear difference in the temperatures of these three
positions since heating time is short and the bed’s heat conductivity is poor. The
reason for this being so may be due to the local or micro methanol migration, i.e.
desorption and adsorption between carbon layers.
Figure 5.9 Comparison of experimental and numerical results:
adsorbent temperature development at selected radial positions in process 1-2-3.

Figure 5.10 shows measured temperature histories and simulated results (with α=0.02) of the carbon bed for process 3-4-1. The general development of temperature basically mirrors that shown in Figure 5.9. However, the temperature jump after status point 4 is notable, which is proportionally caused by the transient pressure process. When the evaporator is just connected to the generator, the gas density from the evaporator is much higher than that within the carbon bed, which results in convection caused by gas density. Due to this convection, adsorption in the bed is passively strengthened and therefore much adsorption heat is released leading to a temperature jump in the the local carbon. If the transient pressure was omitted, the temperature jump would not be well predicted, similar to numerical studies such as Maggio et al. (2006), Fadar et al. (2009), Marletta et al. (2002) and Hu (1996). The neglect of the transient pressure would also lead to a calculated time for process 4-1 being shorter than real, which introduces errors when calculating cycle time, especially for those systems run with frequent shifts among multi-beds.
Figure 5.10 Comparison of experimental and numerical results: adsorbent temperature development at selected radial positions in process 3-4-1.

5.5.3 Fluid Phase Temperature

In order to validate the two-temperature treatment used in the model, the temperature development of the fluid phase (gaseous methanol) needs to be validated experimentally as well. However, it is not practical to measure the gas temperature using inserted-type thermocouples like measuring carbon temperatures, since the temperature sensor would contact the solid phase. Therefore a temperature sensor is arranged very close (r4=53mm) to the inner boundary of the carbon column to measure the temperature, which is assumed to be equal to the gas temperature at the inner boundary (Ri=55mm) approximately. Figure 5.11 shows that the simulated fluid temperature development agrees with the measured data. According to Eichhorn and White (1952), the temperature difference between solid and gas phases is the same throughout the bed. Therefore, the temperature field of the gas phase in the bed is validated after the solid phase temperature and one point gas phase temperature is verified experimentally.
Figure 5.11 Comparison of numerical results of gas temperature development at 
r=55mm and the gas temperature measured at radial position r=53mm.

5.5.4 Sorption Amount

Figure 5.12 Comparison of numerical and experimental results of the dynamic desorption amount.

In terms of the amount of dynamic desorption, comparison of the experimental data and numerical result is shown in Figure 5.12. Unfortunately, the simulated outcome does not agree very well with the experimental data. One main factor that may result in this significant discrepancy is that part of the desorbed methanol condensed and
stuck to the inner surface of the condenser and the tube connecting to the evaporator, which causes the measured amount of desorbed methanol to be less than the theoretical value.

The amount of dynamic adsorption for process 4-1 is compared by evaluating experimental data and numerical results (Figure 5.13). This comparison shows that the experimental data have a much better agreement with the numerical result, comparing to desorption process 2-3, especially when the adsorption process takes more than four hours. The reason for this better agreement is that the condensing issue is avoided naturally in this part of the experiments. On the other hand, the larger error in the first four hours of the adsorption process may have resulted from the passive adsorption caused by transient pressure. This has not been well looked at in the static adsorption equation (D-A equation) and LDF model.

![Figure 5.13 Comparison of numerical and experimental results of the dynamic adsorption amount.](image)

**5.6 Discussion of Concentration Migration**

Figure 5.14 shows the numerical prediction of the methanol concentration variation at the three radial positions, which illustrates the micro concentration migration phenomenon mentioned above. Figure 5.14 indicates that there are two stages in the concentration development of three measured positions, in other words stage 1-2 and
stage 2-3. In stage 2-3, it is obvious that the concentrations at each position start to drop as the macro desorption process starts after the system pressure builds up to the condensing pressure. However, in stage 1-2, from the concentration variation at different radial positions, it can be seen that methanol migrates from the outer radial positions to the inner positions of the carbon bed. This phenomenon may be called “centripetal migration” or “heat pipe migration” of methanol. During this “centripetal migration”, desorbed methanol from the outer layers is re-adsorbed by the inner carbon layers. The adsorption heat enables the temperature of the inner layers in the carbon bed to increase, resulting in a similar rate of temperature increase for the outer and inner carbon layers.

![Graph](image)

**Figure 5.14** Numerical results of adsorbate concentration variation at selected radial positions in the first 1200s of process 1-2-3.

Like Figure 5.14, the phenomenon of methanol migration can also be found in process 3-4 (see Figure 5.15). However, in this latter process, the migration is not “centripetal” in its direction, but “centrifugal” instead.
Figure 5.15 Numerical results of adsorbate concentration variation at selected radial positions in the first 1200s of process 3-4-1.

5.7 Conclusions

The dynamic model based on the typical configuration of the generator of an adsorption refrigeration tube was established by taking into consideration of the local thermal non-equilibrium and transient pressure process. The model was numerically solved and experimentally validated. The numerical and experimental results obtained in the present study are summarised as follows:

(1) The simulation results of the model agree well with the experimental data in terms of adsorbent temperature development, system pressure variation, and the dynamic desorption/adsorption amount. The model can be used to simulate a system’s dynamic cycle since the non-equilibrium adsorption, heat transfer resistances and mass transfer resistances are considered comprehensively.

(2) The concept and mathematical definition of the transient pressure process (at the beginning of the macro adsorption process) is introduced and numerically solved in the model as a transient boundary condition in the diffusion equation. Using the transient boundary condition, the outstanding feature of the temperature development of the cycle (temperature jump of the bed) can be revealed, which would increase the accuracy of calculating the optimal cycle time.
(3) The temperature of gaseous fluid (methanol vapor) can be predicted due to the two-temperature treatment employed in the model. The fluid temperature prediction was validated experimentally in an approximation method. The two-temperature treatment provides better accuracy for predicting a system’s cycle time, which would be especially helpful for those systems having a frequent mass recovery process where the fluid’s (gaseous adsorbate) temperature may have a considerable impact on the adsorbent bed.

(4) The model is able to reveal the phenomenon of adsorbate migration during isosteric processes.
CHAPTER 6

PARAMETRIC ANALYSIS

6.1 Introduction

In adsorption refrigeration system, there are two categories of parameters having impacts on system performance, e.g. COP and SCP. The first category is normally termed operational parameters, which includes heat source temperature and heat sink temperature. The second category is termed designing parameters, and this incorporates evaporating temperature and geometrical sizes of adsorbent bed.

The effects of operational parameters on the adsorption refrigeration system’s thermal performance have been extensively discussed in other studies, such as Li and Wu (2009), Leong and Liu (2006), Fadar et al. (2009) and Yang (2009). In this chapter, the impact of the secondary parameters on system performance is studied using the dynamic model developed.

Specifically, for a waste heat powered ART, the impact on the thermal performance is derived mainly from two important designing parameters - the “thickness” of the adsorbent bed and evaporating temperature. The “thickness” of the cylindrical adsorbent bed of an ART obviously will have a significant impact on cycle time, COP and SCP, which are examined in this chapter. Apart from the impact of the geometric side, evaporating temperature also has a significant impact on system performance.

Figure 6.1 shows the running cycles if the evaporating temperature was set at different levels, which is determined by application requirements. When the
evaporating temperature is relatively high, the COP will also be high since a higher concentration variation of the adsorbate (refrigerant) can be achieved. On the other hand, when the evaporating temperature is relatively low, the COP will be low because the concentration variation will be low as well.

With regards to cycle time, a high evaporating temperature results in a higher concentration variation (see Figure 6.1), which means more heat is needed to drive desorption and more heat has to be released during adsorption, which might result in a longer cycle time. However, a high evaporating temperature also means a high evaporating pressure that may lead to a small mass transfer resistance according to Eq 4.7. Because of these two contrary impacts, the effects of evaporating temperature to cycle time are worthy of further analysis.

Once the effects of geometric side and evaporating temperature to cycle time are clear, their effects on SCP and COP can be analysed. In this chapter the effects of adsorbent bed dimensions and the evaporating temperature to cycle time, COP and SCP will be examined.

Figure 6.1 Effect of evaporating temperature requirement to running cycle.
6.2 Non-equilibrium Adsorption Effects

Prior to analysing the impacts of diameters and evaporating temperature on ART thermal performance, it is worth noting that non-equilibrium adsorption mechanism plays a fairly significant role in the overall mathematical model. Figure 6.2 and Figure 6.3 show respectively the adsorbent temperature and adsorbate concentration development during the heating-desorption process in one particular case. It is clear that the adsorbent temperature approaches equilibrium in about 1.4 hours while the
adsorbate needs about 4.5 hours to reach concentration equilibrium. When consider the full cycle, the difference will be doubled approximately and will become very significant, i.e. about 2.8:9 (the ratio of time for temperature to reach equilibrium to the time of concentration to do the same). Therefore, in a continuously running adsorption refrigeration system, the cycle time should be determined from the perspective of concentration equilibrium rather than adsorbent temperature equilibrium. Moreover, it is proved that the equilibrium adsorption model is not able to predict dynamic thermal performance for rapid-cycled adsorption refrigeration systems.

### 6.3 Parameter Effects on Cycle Time

Cycle time is an important parameter for operating an adsorption refrigeration system. For an ART, the diameters of the adsorbent bed and concentration variation range are the two significant factors contributing to the cycle time. In order to simplify the analysis, the inner diameter of the adsorbent bed of an ART, i.e. diameter of the mass transfer channel, is deemed constant, \( Ri = 20 \text{ mm} \). In other words, only the outer diameter of the adsorbent bed (i.e. \( Ro \) ) is variable. Four outer diameters, \( Ro = 25, 30, 35, 40 \text{ mm} \), are selected to investigate their effects on cycle time. The length of the adsorbent bed is one meter in this analysis. In addition, the evaporating temperature is also a variable that depends on different application requirement. Three typical evaporating temperatures, -5°C, 5°C and 15°C, are selected for ice-making, food storage and air-conditioning purpose respectively, to study the effects on cycle time.

In the following analysis, “ideal cycle time” (ICT) is defined as the time needed for the entire cycle to achieve 90% ideal refrigeration capacity. Figure 6.4 plots the effects of diameter and evaporating temperature on cycle time. Three points can be concluded from this figure. First, with the increase in the outer diameter (i.e. \( Ro \) ), the ideal cycle time at each evaporating temperature is prolonged. This is simply due to the overall heat transfer resistance worsening when the thickness of the adsorbent bed is increased. Second, for the same thickness, when evaporating temperature is higher, a shorter ICT is needed. This is because the mass transfer is strengthened due
to a high system pressure. This result indicates that the mass transfer state can be a significant factor affecting cycle time. Third, the effect of thickness on the ICT becomes more significant when the adsorption system runs at a lower evaporating temperature, which indicates that mass transfer state is worse than that operating at a higher evaporating temperature.

Figure 6.4 Effects of diameter and evaporating temperature on ICT.

6.4 Parameter Effects on COP

Figure 6.5 Effects of diameter and evaporating temperature on COP.

Similar to the above, twelve cases were calculated to reveal the overall influence of diameter and evaporating temperature on refrigeration COP. In the calculation, a
1mm thickness stainless steel cylindrical jacket was assumed to be the jacket of the adsorbent. In Figure 6.5, it is clear that a higher evaporating temperature can contribute to a higher COP at a given adsorbent thickness since more refrigerant can be achieved because of the wider concentration variation. Regarding the effects of diameter, for a given evaporating temperature, greater diameter results in a higher COP. This is because with the increase in adsorbent thickness, the percentage of heat used to heat up the adsorbent’s metal jacket becomes insignificant.

6.5 Parameter Effects on SCP

![Graph showing the effect of temperature and diameter on SCP](image)

Figure 6.6 Effects of diameter and evaporating temperature on SCP.

Specific cooling power (SCP) is the refrigeration power produced per kilogram adsorbent per refrigeration cycle, which reflects the efficiency of the refrigeration cycle. From Figure 6.6, it can be seen that the case with the highest evaporating temperature and the smallest outer diameter enjoys the highest SCP. From the definition of SCP, and comparing Figures 6.4 and 6.5, it is not difficult to see that the most significant factor affecting SCP is the evaporating temperature. A higher evaporating temperature can result in a higher COP and also lead to a short ideal cycle time, which both contribute to a higher SCP. Therefore, for a specific application requirement, the evaporating temperature would be fixed; there is not much room to improve SCP.
6.6 Cycle Time Optimisation

![Graph showing effects of cycle time on SCP and COP.](image)

Figure 6.7 Effects of cycle time on SCP and COP.

Besides the thickness of the adsorbent bed and evaporating temperature, the actual operating cycle time (OCT) is another crucial parameter that affects the SCP and COP of an adsorption refrigeration system in practice. In a practical adsorption refrigeration system, COP normally increases with the extension of the OCT since more refrigerant can be desorbed from the adsorbent to generate more refrigeration capacity. However, inappropriately prolonging the OCT would compromise the SCP. Therefore, optimisation of the OCT is important for an adsorption refrigeration system. Figure 6.7 shows the dynamic SCP and COP based on a case study to reveal the room for optimisation to achieve an overall better refrigeration performance. The case study has an outer diameter of 40mm and the required evaporating temperature of 15°C. From Figure 6.7, it can be seen that the SCP reaches its peak value with a very short OCT, about 30 minutes, and then decreases with prolonged OCT. For COP, as stated above, its value increases with cycle time extension. Although the SCP and COP have different and somewhat contrary development trends, it is evident that bout 1.5–2.5 hours is the optimal cycle time needed to achieve optimal SCP and COP.
6.7 Conclusions

In this chapter, the parameter effects on ICT, COP and SCP were studied. The key conclusions can be summarised as follows:

(1) For a given evaporating temperature, greater thickness results in longer ideal cycle time.

(2) For a given adsorbent thickness, high evaporating temperature leads to a short ideal cycle time.

(3) Compared to adsorbent thickness, evaporating temperature has a more significant impact on SCP.

(4) The optimal operating cycle time for achieving overall better performance is much shorter than the ideal cycle time.
CHAPTER 7

ANALYSIS OF POTENTIAL APPLICATION

7.1 Introduction

In the parametric analysis provided in chapter 6, it is found that a higher evaporating temperature and a greater adsorbent bed thickness will result in a higher COP. If the cycle time optimisation was applied, the best cycle time for the highest SCP can be identified for determining the operating parameters. Admittedly, the COP of such a carbon-methanol-based ART working at low evaporating temperature (e.g. -5°C) is very poor and any room to improve COP via optimisation of designing parameters is very limited. Therefore, at this current stage, the ART is recommended for air-conditioning application, in which an acceptable COP can be achieved.

In this chapter, two system integration solutions using individual ARTs, for home application and commercial application respectively, will be proposed. Moreover, an economics analysis, including initial investment, operating and maintenance costs will be analysed for each application case, respectively. Finally, future work on improving application prospect will be suggested.
7.2 System Integration Solution

7.2.1 General Integration Strategy

Since each individual ART can work independently, systematic integration can be easily achieved. The general strategy for system integration is illustrated schematically in Figure 7.1. Considering the non-continuous cooling feature of an ART, each ART’s Module comprises two ARTs Units where each Unit works out of half cycle time to create an overall continuous cooling system. Each ARTs Module can work independently as a normal air-conditioner with appropriate terminal devices. For commercial application typically requiring much greater capacity, ARTs Modules can be integrated into a modular system to achieve greater capacity.

![Figure 7.1 System integration strategy using single ART.](image)

7.2.2 Introduction to Components

(1) Individual ART

Figure 7.2 illustrates a single ART. The generator of the ART is one meter long and the diameter is 3 inches, which may generate a maximum cooling power of 31 W through the cycle time optimisation stated in section 6.6. In order to make the structure more compact for future assembly and integration, the condenser is modified compared to the structure proposed at the beginning of this study. The outer diameter of the finned tube of the condenser is modified so that it is the same size of
the generator’s outer diameter. The valve is designed as an electronic one that controls the status of the adsorption refrigeration cycle.

Figure 7.2 Schematic diagram of a single ART.

(2) ARTs Unit

Figure 7.3 Schematic diagram of an ARTs Unit.
Figure 7.3 demonstrates an ARTs Unit that is integrated with single ARTs. The main dimensions of the unit are marked to show the space requirement for possible application. This unit comprises 24 single ARTs and a shared water jacket, which is able to produce a cooling power of about 750W. This cooling power is calculated based on the total cooling capacity of a cycle and the total cycle time. In other words, in order to achieve continuous cooling ability, physically at least two units are needed.

(3) ARTs Module

![ARTs Module Diagram](image)

Figure 7.4 Schematic diagram of an ARTs Module.

Figures 7.4 and 7.5 illustrate the schematic diagram of an ARTs Module that is integrated with two ARTs Units. Each unit of the module runs out of half cycle, therefore such a module can produce a continuous cooling power of about 1500 W, which is able to provide air-conditioning for a room that is approximately 15 m².
7.2.3 Home Application

If appropriate terminal devices were added to an ARTs module, this module can function as a normal air-conditioner. Figure 7.6 shows a module serving as an air-
conditioner after adding terminal devices. An external water system, i.e. water paths of hot and cooling water connecting to the module are not shown in this figure. Hot water can be derived from a solar or waste heat driven water system. With respects to cooling water, an additional cooling tower is needed to provide continuous cooling water as a heat sink.

7.2.4 Commercial Application

For commercial application that normally requires much greater refrigeration power, multiple modules can be selected to form a modular refrigeration system. According to different air-conditioning approaches, different terminal devices can be added. For example, one shared ice-storage tank can be added to an air-conditioning system employs the ice-storage approach.

7.3 Economics Analysis

The previous chapter has shown that the ARTs module-based refrigeration system is suitable for home and commercial application from the technique view. However, the economic aspect is also an important factor that affects the application of this technology. This chapter will do a preliminary economic assessment of the application.

Firstly, the initial capital investment of one module is assessed. One module consists of 48 ARTs and a shared water jacket and some water tubes. All the materials used in the module are assumed to be purchased and assembled in China where material and labour costs are much cheaper than that in developed countries. Table 7.1 shows the estimated initial capital investment on one ARTs module with a 1.5 KW cooling capacity. It can be seen that the initial capital investment is US$1249 per ARTs module. Compared to the major market air-conditioners, such as Panasonic and Mitsubishi, the price of a 3.0 KW air-conditioner is currently about US$1000. Clearly, if two ARTs modules were employed to form a 3.0KW modular system, the initial capital investment will be US$2498, which is about 2.5 times to that of traditional air-conditioners.
Table 7.1 The estimated cost of the initial capital investment of one ARTs module

<table>
<thead>
<tr>
<th>Parts</th>
<th>Quantity</th>
<th>Unit</th>
<th>Cost (RMB)</th>
<th>Total Cost (RMB)</th>
<th>Equal to (US $)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brass condenser</td>
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<td></td>
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<tr>
<td>Brass evaporator</td>
<td>48</td>
<td>piece</td>
<td>1920</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stainless steel generator</td>
<td>48</td>
<td>piece</td>
<td>1440</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Activated carbon</td>
<td>97.2</td>
<td>kg</td>
<td>778</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>14.5</td>
<td>kg</td>
<td>53</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Circulation pipe</td>
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<td>piece</td>
<td>480</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control valve</td>
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<td>piece</td>
<td>960</td>
<td></td>
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<td></td>
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<tr>
<td>External water adaptors</td>
<td>4</td>
<td>piece</td>
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<td></td>
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<tr>
<td>Labour cost</td>
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<td>hour</td>
<td>160</td>
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</table>

Besides initial capital investment, operating and maintenance costs are the other two main expenditures. Different home and commercial usage are assumed for comparing operating costs using the ARTs modular system and traditional air-conditioning system, which is summarised in Table 7.2.

Table 7.2 Assumed usage information for home and commercial users

<table>
<thead>
<tr>
<th>User</th>
<th>Daily Time (Hours)</th>
<th>Days annually(D)</th>
<th>Electricity fee (US $/KW)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>90</td>
<td>0.25</td>
</tr>
<tr>
<td>Commercial</td>
<td>8</td>
<td>260</td>
<td>0.15</td>
</tr>
</tbody>
</table>
Concerning maintenance costs, honestly, enough studies are still lacking on the long term performance of the adsorption refrigeration system. Maintenance fee for the existing adsorption refrigeration system is not yet available. In this preliminarily economic analysis, the maintenance fee for both the ARTs modular system and traditional air-conditioning system is neglected.

In order to compare the total cost versus using time to understand the economics of the ARTs modular system, it is assumed that a space needs a 3 KW cooling power for home and commercial use, respectively. The hot fluid input into the ARTs system is assumed to be free since the hot fluid is derived from a waste heat source.

Figure 7.7 plots the total cost versus use time using two ARTs modules and using traditional air-conditioners. It can be seen that although the initial capital investment for the ARTs modular system is much higher than that of the traditional products, the total cost of using the ARTs system will be lowest when the use time exceeds nearly 10 years. The advantage of the ARTs system for commercial purposes is therefore quite clear.

Figure 7.7 Total cost versus use time employing the ARTs system and traditional air-conditioning system, respectively.
7.4 Conclusion and Recommendation

The above application analysis makes it possible to conclude that the ARTs module-based air-conditioning system can compete with current air-conditioning systems, in terms of technical and economic features.

However, one disadvantage of this ARTs system is that it needs much larger space (larger plant) for the system to operate. This is caused by the limited sorption ability of the adsorbent. Artificially increasing the sorption ability can greatly reduce the volume of the ARTs system. Studies of chemical sorption have made certain progress, which may produce a new adsorbent with greater sorption ability; then the volume of such ARTs system can be reduced by replacing the new working pair.

Moreover, the long-term performance of such an ARTs system is a crucial issue that has not been extensively looked at. The issue of potential decomposition of methanol has been pointed out by Hu (1998), which is a critical issue for long-term performance.

In conclusion, the ARTs module-based system has great potential. In the meanwhile it is recommended that more work be done in order to develop a new working pair with super sorption ability that is efficient and reliable in the long-term performance.
CHAPTER 8

CONCLUSIONS

This thesis involved a systematic study of the ART in terms of examining the adsorptive properties, 1-D dynamic mathematical model, parametric analysis and application potential. Contributions and conclusions can be summarised as follows:

(1) Adsorptive property study

An adsorptive property testing was conducted. The sensitivities to the calculations of system performance from each parameter in different adsorption equations (i.e., Langmuir equation, Freundlich equation, and Dubinin-Astakov equation) were studied.

(a) D-A equation works best for presenting the adsorptive properties of the tested activated carbon/methanol working pairs. In contrast, the Langmuir equation is not suitable because it has the least agreement with experimental data. Moreover, any parameter errors in Langmuir format would cause a huge variation in system performance calculations, especially errors concerning the parameter $Q_a$.

(b) Freundlich and D-A isotherm formats are recommended for presenting adsorptive properties of carbon-methanol working pairs.
(2) *Modelling of the refrigeration cycle*

A 1-D dynamic model was developed and took into consideration of the interfacial convection within adsorbent particles and a transient pressure process. The following conclusions are drawn from the numerical and experimental study.

(a) The simulation results agree well with the experimental data in terms of the adsorbent temperature development, system pressure variation, and the amount of dynamic desorption/adsorption. The model can be used for both the intermittent and continuous operated systems since non-equilibrium adsorption, heat transfer resistances and mass transfer resistances are considered comprehensively.

(b) The temperature of gaseous fluid (methanol vapor) can be predicted due to the two-temperature treatment employed in the model. The two-temperature treatment can help provide better thermal performance prediction for those systems run with frequent mass recovery process in which the temperature of adsorbate fluid may have a considerable impact on the adsorbent bed.

(c) The concept and mathematical definition of the transient pressure process are introduced into the model. The transient boundary condition effectively describes the shift in the adsorption process’s dominant driving forces, which can improve the accuracy of other existing models.

(3) *Parametric analysis*

The main points of the parametric analysis can be summarised as follows:

(a) For a given evaporating temperature, greater thickness results in longer cycle time.

(b) For a given adsorbent thickness, high evaporating temperature leads to a short cycle time.

(c) Compared to adsorbent thickness, evaporating temperature has a more significant impact on SCP.
(d) The optimal cycle time for achieving overall better performance is much shorter than the time needed for reaching a higher COP.

(4) Potential of application

The following recommendations made based on a preliminary analysis of the ART system’s potential application:

(a) ARTs-based refrigeration system is competitive in terms of operating cost, especially for commercial applications.

(b) ARTs system needs a much larger space (larger plant), which is a disadvantage for this kind of system. Artificially increasing the sorption ability of the adsorbent may reduce the volume of the ARTs system substantially.

(c) Uncertain reliability in the long-term performance of such an ARTs system is an important issue that may affect its large scale application.
APPENDICES

APPENDIX A

Thesis Assessment Details

A.1 Examination Documents

Please see the end of the Appendix.

A.2 Examiners Reports

Please see the end of the Appendix.
APPENDIX B

Publications Arising From This Work


(3) **Zhao YL**, Hu E, Blazewicz A. Thermodynamic modelling of the activated carbon-methanol adsorption refrigeration tube with considerations of Interfacial convection and transient pressure process. (*Renewable Energy*, *Under review.*)

(4) **Zhao YL**, Hu E, Blazewicz A. Comparison and sensitivity analysis of different isotherm formats with activated carbon and methanol adsorptive properties testing data. (*Heat and Mass Transfer*, *Under review.*)
APPENDIX C

Experimental Data

This section comprises the experimental data regarding the adsorptive properties’ testing and the mathematical model validation.

C.1 Experimental Data of Adsorptive Properties Testing

C.1.1 Experimental data of activated carbon sample 207C

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<th>$P$ (Pa)</th>
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### C.2 Experimental Data of Model Validation

#### C.2.1 Experimental data of pressure variation in process 1-2-3

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Dear Yongling Zhao,

THIS IS TO CERTIFY that on the 5th day of January, 2011, you submitted three copies of your thesis entitled 'Study of Activated Carbon/Methanol Adsorption Refrigeration Tube and System Integration' for the degree of Master of Engineering Science by Research. We wish you a successful examination outcome.

You must now apply to graduate. Please see overleaf.

[Signature]

ANNE WITT
Director, Adelaide Graduate Centre
11 March 2011

Mr Yongling Zhao
9B Meadow Avenue
CAMPBELLTOWN SA 5074

Dear Mr Zhao

Outcome of Thesis Examination

I am writing to advise you of the outcome of your thesis examination. I am pleased to inform you that, subject to the following conditions, you will qualify, academically, for the award of the degree of Master of Engineering Science:

- complete the specified amendments to the thesis to the satisfaction of your supervisors and Head of School/Discipline or delegated Postgraduate Coordinator;

- deliver one hard-bound and one electronic copies of the suitably amended thesis to the Adelaide Graduate Centre together with the enclosed completed Proforma confirming that the required amendments have been made. You are permitted a maximum of three months from the date of this letter to undertake the required amendments and to lodge the copies and Proforma with the Graduate Centre. If, in exceptional circumstances, you require additional time to complete the revisions, you may apply to the Dean of Graduate Studies for permission. The application, setting out in detail the reasons for your request, must be endorsed by your Principal supervisor and the Head of School or the Postgraduate Coordinator.

- meet the relevant closing date to lodge amended theses in order to qualify, academically, for the award of the degree. Should the relevant closing date fall due BEFORE the “three-months date”, you must also meet the relevant closing date to lodge amended theses. If the day falls on a weekend or public holiday, the deadline will be the first working day following the weekend or public holiday.

Information about the closing dates to lodge amended theses, conferral dates and graduation presentation ceremony dates is provided in the enclosed sheet.

Comprehensive information about graduation, including closing dates, is available on the Graduations website at:


You must regularly view “Access Adelaide” to check your current graduation details.
When your attendance at the graduation presentation ceremony is confirmed on “Access Adelaide”, you may wish to advise your supervisor(s) of the time and date in the event that he/she/they/may also wish to attend.

- discharge any outstanding obligations to the University prior to the closing date of your nominated graduation ceremony.

Please note that until you have fulfilled the conditions stipulated above, you have not officially qualified for the degree.

For your information, I enclose copies of the examiners’ reports. In order to expedite your qualification please discuss the required thesis amendments with your supervisors and Head of School/Discipline as soon as possible. Two soft bound copies of your thesis entitled “Study of Activated Carbon/Methanol Adsorption Refrigeration Tube and System Integration” are available for collection from the Adelaide Graduate Centre. I shall advise you when the other copy is available for collection. On collection, please ensure that you provide photographic identification in the form of, for example, a University card, driver’s licence or passport. Should you choose to authorise someone else to collect the copies on your behalf, that person will need to provide evidence of your authorisation (e.g. a signed letter from you) together with an acceptable form of photographic identification.

Congratulations on your achievements to date.

Yours sincerely

[Signature]

for ANNE WITT
Director, Adelaide Graduate Centre

Encs: Examiners’ reports
Thesis Lodgement for ADTP Confirmation of Amendments to Thesis “Graduation” information sheet

cc: Head, A/Professor Bassam Dally, School of Mechanical Engineering
Postgraduate Co-ordinator, Dr Lei Chen, School of Mechanical Engineering
Supervisor(s): (examiners’ reports enclosed) Dr Eric Hu, Dr Antoni Blazewicz
Convenor, Faculty of Engineering, Computing and Mathematical Sciences
HDC International Student Liaison Officer
Examiner's Report on Master Thesis of Yongling Zhao

The study reported by master thesis of Yongling Zhao is organized well on adsorption refrigeration tube (ART) theoretically and experimentally. The research approach by modeling, validation of the model, parameter analysis, and proposal of practical solution using integrated groups of ART for home or domestic application is very careful and significant from the viewpoint of developing a new technology as well as educating an engineer. Especially, the physical and mathematical modeling and the model validation are very interesting to understand the mechanism of phenomena in ART as well as develop ART systematically. Since literature review of the related field is carried out very well, the originality of this study is clear. From these reasons, I allege confidently that the paper summarizing some parts of this thesis can be published by International Journal on thermal engineering or energy conversion field. After further work to downsize and promote the long-term operation of the ARTs system, I expect that the ARTs Module would be applied actually.

However, there might be some errors of spelling in this master thesis, e.g.,

P.i, L.17 2.3.2 Heat Recovery Cycle
P.i, L.18 2.3.3 Mass Recovery Cycle
P.i, L.19 2.3.4 Cascading Cycle
P.i, L.20 2.3.5 Other Advanced Cycles
P.ii, L.19 3.4.2 Format Impact on \( Q_r \)
P.ii, L.20 3.4.3 Format Impact on COP
P.ii, L.21 3.4.4 Sensitivities of the Parameters
P.2, L.27 takes into account of convective heat transfer
P.91, L.3 taking into consideration of the local thermal
P.104, L.5 the total cooling capacity of a cycle
P.111, L.1 took into consideration of the interfacial

Examined by Akira Nishimura, Assistant Professor of Mie University
14 January 2011
Examiner's comment on Zhao' thesis, entitled, “STUDY OF ACTIVATED CARBON/METHANOL ADSORPTION REFRIGERATION TUBE AND SYSTEM INTEGRATION”.

The thesis describes the theoretical and experimental investigation of an adsorption refrigeration method, in particular the unique design of a compact Adsorption Refrigeration Tube (ART) that can be integrated to operate as a cooling or heating machine. Given the short span of the candidature, it is commendable that the student has accomplished quite substantial work, both on the theoretical modeling and experiments. Given the quality of systematic research, I recommend the award to Master degree. I am of the opinion that the student should be encouraged to continue on the same direction and I believe valuable research work could be derived in less than two years.

Sincerely,

Kim Choon NG

Professor, ME Dept., NUS
And Visiting Professor, KAUST, SA.