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Title: Adsorption refrigeration system using zeolite and methanol

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ADSORPTION REFRIGERATION SYSTEM USING ZEOLITE AND METHANOL

Sylwia Danuta Waszkiewicz

A dissertation submitted to the University of Bristol in accordance with the requirements of the Degree of Doctor of Philosophy in the Faculty of Engineering.
Department of Mechanical Engineering

May 2003
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Abstract

An experimental and numerical study is presented on the design, construction and evaluation of a prototype heat driven adsorption cooling system utilising a zeolite CBV 901 and methanol pair. The primary objective of the research was to investigate the possibility of improving the performance of the system by employing a novel pair and enhance the heat and mass recovery in the system. In principle, such machines would utilise waste heat to provide refrigeration.

Zeolite CBV 901 and methanol were selected as a working pair, because this type of zeolite requires a temperature of only 100°C to be fully regenerated. Considerable heat waste is available at this temperature and in addition, it does not cause methanol to decompose.

A novel heat exchanger was designed consisting of finned pipe and a shell. The surface of the heat exchanger was coated with a 1mm thickness of zeolite paste. This design was selected to increase the effective thermal conductivity and heat transfer inside the adsorbent bed.

The adsorption properties of the zeolite/methanol pair were investigated, in order to predict the adsorption equilibrium at certain temperatures. The adsorption of coated zeolite on the aluminium fin was 3-5% lower than in powdered form, which is directly related to the amount of binder in the zeolite paste. A typical loading of 22 gram of methanol per 100 gram of dry zeolite is possible (at adsorbent temperature of 30°C). The experimental values were fitted by the Dubinin-Astakhov equation, which allows the adsorption equilibrium to be predicted for the complete cycle.

An experimental pilot rig was constructed, based on one generator, which contains a 0.5 metre long tube with 50 circular fins on it, coated on both sides with a total 100-grams of zeolite paste. Both Coefficient of Performance and Specific Cooling Power are functions of the cycle time (in theory and experiments).
The Specific Cooling Power for different cycle durations (900-7200 seconds) varies between 50-80 W/kg. The cooling COP achieved is in the range 0.15-0.31. The numerical model was validated against the temperature, pressure, and concentration data obtained from the experimental rig.

Performance predictions suggest further improvements in the system can be obtained by reducing the cycle time and increasing the maximum generator temperature, reducing the system mass and improving the system control.
Acknowledgements

I would like to acknowledge the help and assistance of my supervisors Dr Hind Saidani-Scott and Dr Mike Tierney throughout this project.

I would like to say thank you to all the workshop technicians for their help in building the experimental rig, especially to Mr Mike Darby for his constant support and great sense of humour.

I would also like to thank all those who have passed through the ‘Fish Room’ and made it an enjoyable place to work.

Finally I thank my Family and Friends for their support over the last 3 years.
Acknowledgements
Authors Declaration

The accompanying dissertation entitled 'Adsorption Refrigeration System Using Zeolite and Methanol' is submitted in support of an application for the degree of Doctor of Philosophy in Engineering at the University of Bristol.

The dissertation is based on independent work by the candidate, except where clearly referenced.

No portion of the work referred to in this dissertation has been submitted in support of an application for another degree or qualification in this, or any other university or other institute of learning.

The views and opinions expressed in this thesis are solely those of the author and not the University of Bristol.

I declare that the above statements are true,
Declaration
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Nomenclature

Roman Letters

A*   Energetic asymmetry
A    Area of body
a_0  Limiting adsorption
A_{fd}  Finned area of pipe
A_{f}  Surface area of fins
A_p  Surface area of pipe
COP  Coefficient of performance
COP_h  Heating COP
COP_c  Cooling COP
C    Condenser in cascade system
C_{p}  Heat capacity
C_{p_c}  Specific heat of adsorbent
C_{p_a}  Specific heat of adsorbed phase
C_{p_o}  Specific heat of oil
D_{o}  Heat exchanger tube diameter
d_i  Shell outside diameter
d_2  Coated plate diameter
d_f  Fin diameter
d_i  Inner diameter
d_o  Outer diameter
d_p  Plate diameter
d_p  Pipe diameter
E    Youngs modulus of glass 6.6x10^-4
f    Fugacity
h    Heat transfer coefficient
H    Heat of adsorption per unit mass of absorbate
H_{p,cond}  Specific enthalpy of methanol vapour leaving condenser
H_{p,econd}  Specific enthalpy of methanol vapour leaving evaporator
h_{gas}  Gas enthalpy at bed temperature
h_{gas,bed}  Gas enthalpy evaluated at bed temperature
h_{gas,ev}  Gas enthalpy evaluated at evaporator
h_{liquid}  Saturated liquid enthalpy at condenser
h_{liquid,con}  Enthalpy of condensed liquid
i    Number of samples
i_c  Maximum perimeter perpendicular to flow
K    Ratio of adsorption to desorption constants
k_a  Adsorption constant
k_{Al}  Conductivity of Aluminium
k_d  Desorption constant
k  Conductivity
L    Latent heat of refrigerant at the system pressure
L    Length of pipe
L_c  Characteristic length
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<tr>
<td>LMTD</td>
<td>Log Mean Temperature Difference</td>
</tr>
<tr>
<td>M</td>
<td>Molecular mass</td>
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<tr>
<td>$m_0$</td>
<td>Mass flow rate</td>
</tr>
<tr>
<td>$m_a$</td>
<td>Mass of adsorbate</td>
</tr>
<tr>
<td>$m_{ad}$</td>
<td>Mass of material adsorbed</td>
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<tr>
<td>$m_c$</td>
<td>Mass of adsorbent</td>
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<tr>
<td>$m_z$</td>
<td>Mass of zeolite per plate</td>
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<tr>
<td>n</td>
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<tr>
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<tr>
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<td>Number of plates</td>
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<td>r</td>
<td>Coefficient of regeneration</td>
</tr>
<tr>
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<td>Reynolds Number</td>
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<td>$r_f$</td>
<td>Fin outer radius</td>
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<td>$r_i$</td>
<td>Inner radius of pipe</td>
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<tr>
<td>$r_o$</td>
<td>Pipe outer radius</td>
</tr>
<tr>
<td>t</td>
<td>Time</td>
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<tr>
<td>T</td>
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<tr>
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<tr>
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<td>Valve between heat exchanger and condenser</td>
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Greek Letters

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<tr>
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<tr>
<td>ρz</td>
<td>Density of zeolite</td>
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<td>σ</td>
<td>Stefan Boltzmann constant $5.67 \times 10^{-8}$ W/m$^2$K$^4$</td>
</tr>
<tr>
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<td>Surface coverage or friction filling of the micropore</td>
</tr>
<tr>
<td>φ</td>
<td>Ratio of fin area to finned area</td>
</tr>
<tr>
<td>Θ</td>
<td>$T - T_m$</td>
</tr>
<tr>
<td>Θ₀</td>
<td>$T_0 - T_m$</td>
</tr>
<tr>
<td>ω</td>
<td>Frequency of ac supply</td>
</tr>
</tbody>
</table>
### Subscripts

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Adsorption</td>
</tr>
<tr>
<td>adsorption</td>
<td>Different stages in the cascade cycle</td>
</tr>
<tr>
<td>b</td>
<td>Different stages in the cycle</td>
</tr>
<tr>
<td>l</td>
<td>Different stages in the cycle</td>
</tr>
<tr>
<td>2</td>
<td>Different stages in the cycle</td>
</tr>
<tr>
<td>3</td>
<td>Different stages in the cycle</td>
</tr>
<tr>
<td>4</td>
<td>Different stages in the cycle</td>
</tr>
<tr>
<td>c</td>
<td>Condenser</td>
</tr>
<tr>
<td>c</td>
<td>Different stages in the cascade cycle</td>
</tr>
<tr>
<td>cond</td>
<td>Condenser</td>
</tr>
<tr>
<td>cooling</td>
<td>Cooling</td>
</tr>
<tr>
<td>d</td>
<td>Different stages in the cascade cycle</td>
</tr>
<tr>
<td>DE</td>
<td>Double effect</td>
</tr>
<tr>
<td>desorption</td>
<td>Desorption</td>
</tr>
<tr>
<td>e</td>
<td>Different stages in the cascade cycle</td>
</tr>
<tr>
<td>ev</td>
<td>Evaporator</td>
</tr>
<tr>
<td>f</td>
<td>Different stages in the cascade cycle</td>
</tr>
<tr>
<td>heating</td>
<td>Heating</td>
</tr>
<tr>
<td>i</td>
<td>Pore sizes, see page 12 chapter 3</td>
</tr>
<tr>
<td>input</td>
<td>Input</td>
</tr>
<tr>
<td>j</td>
<td>Pore sizes, see page 11 chapter 3</td>
</tr>
<tr>
<td>k</td>
<td>Point in the cycle</td>
</tr>
<tr>
<td>k'</td>
<td>Point in the cycle</td>
</tr>
<tr>
<td>lam</td>
<td>Laminar</td>
</tr>
<tr>
<td>output</td>
<td>Output</td>
</tr>
<tr>
<td>turb</td>
<td>Turbulent</td>
</tr>
<tr>
<td>z, zeo</td>
<td>Zeolite</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

1.1 Introduction

The objective of this thesis is to investigate the possibility of improving the performance of the adsorption refrigeration system when a new kind of zeolite is employed to work with methanol as a refrigerant. The aim is to derive a predictive method for the plant performance using only data obtained from laboratory-scale experiments, associated with properties of adsorbent/refrigerant pair.

This chapter describes the refrigeration challenge at the present time, connected with ecological problems concerning the emission of CFCs from refrigerating units as well as the poor performance of adsorption systems. The systems could be an excellent replacement of the existing structures in the near future.

1.2 Refrigeration in Recent Years

In the early years of the 20th century, sorption refrigeration was frequently used. Later, with the development of cheap reliable compressors and electrical motors, the improvement in power station efficiency and the introduction of CFCs in the 1930s, sorption refrigeration became a niche technology [1].
Heat-driven sorption refrigeration cycles have existed in the patent literature since at least 1909, and refrigerators were commercially available in the 1920s. In 1929, Miller described several systems, which utilised silica gel and sulphur dioxide as an adsorbent/adsorbate pair [2]. However, recent years have witnessed increasing interest in this technology for many different reasons. The main arguments in favour are that sorption systems are quiet, durable, cheap to maintain and environmentally friendly. In particular, refrigeration is driven by heat, rather than by mechanical work.

Ecological problems concerning the emission of CFCs from refrigerating units have stimulated several theoretical and experimental studies on adsorption cooling systems. Importantly, refrigeration technology is thus required to evolve due to new environmental regulation. The first regulation concerning the depletion of the ozone layer (Montreal Protocol, 1988) prescribed the phasing out of chlorofluorocarbons (CFCs), and ultimately hydrochlorofluorocarbons (HCFCs).

It was realised in the mid-1970s that CFCs allow ultraviolet radiation into the earth’s atmosphere by destroying the protective ozone layer, while preventing infrared radiation from escaping the earth, and thus contributing to the greenhouse effect. The environmental impact of fluorocarbons traces in the atmosphere has shown that CFC emissions are responsible for about one third of the global greenhouse effect.

The discovery of the ozone-depleting properties of CFC and HCFC refrigerants, and of their global warming potential, led to the Montreal Protocol, which scheduled the end of production of CFCs by the end of 1995, and of HCFCs by 2030. The production of these refrigerants has fallen dramatically in recent years [3].

These trends strongly necessitate new systems for space heating and cooling. Moreover, it is useful to find new systems that can effectively use waste heat or low-grade heat.
Research has recently been focused on development of new refrigerants to replace CFCs and HCFCs. These new working fluids are synthetic compounds, namely hydrofluorocarbons (HFCs). Although their ozone-depletion potential is zero, their global warming potential -related to the greenhouse effect- can be large. An alternative to HFCs is the use of naturally occurring substances (refrigerants) like ammonia, carbon dioxide, methanol, water, and air. Other desirable refrigerant characteristics include being non-toxic, non-corrosive, non-flammable and chemically stable, having a high enthalpy of vaporisation (this minimises the mass flow), and of course, being available at low cost. The successful design of an adsorption refrigeration system could potentially solve the problem of ozone depleting chemicals and provide a cheaper alternative to recent systems in the form of higher overall energy conversion efficiencies. This will in turn lower primary fuel costs through reduced demand. Additionally, current methods of refrigeration are not portable and require a ready source of electricity. Consequently, the adsorption systems are considered interesting but more efforts are needed for their development.

Among the proposed technologies, solid sorption systems are in some ways more promising than classical vapour compression machines. They can efficiently use natural gas or solar energy as primary energy source, and they have no significant moving parts (This makes the machine silent and easy to maintain.) Adsorption cooling units are attractive since they can be operated at relatively low temperatures where liquid absorption systems cannot work. (In other words, the temperature lift is favourable). There are some disadvantages of the gas-solid systems proposed, which are mainly related to the high weight and volume of the solid adsorber, which make the system not compact, expensive, thus not suitable for domestic applications [4-6].

Other limitations originating from the inefficient nature of heat and mass transfer inside the adsorber may lead to significant reductions in the performance of the adsorption system. The two types of resistance to heat transfer that can be observed originate from the lack of good physical contact at the metal-adsorbent interface and from the generally low thermal conductivity values of the adsorbent bed [7]. On the other hand, resistances to mass transfer depend on the magnitude of the diffusion coefficient value
of the adsorbate in the adsorbent as well as thickness of the adsorbent bed. It is difficult to achieve an optimum compromise between the high porosity necessary for fast vapour diffusion and the high density required for good thermal conductivity [8].

Therefore, research has focused on improvement of the heat and mass transfer inside the adsorber bed, in order to increase COP of these systems. Additionally, new adsorbent-adsorbate pairs have been studied to improve energy efficiency. New designs of heat exchangers using additives to get better heat transfer and different bed constructions have been proposed [9], [10].

Along with a consideration for energy efficiency, increasing attention has been given to the use of waste heat and solar energy. Adsorption technologies have been used also extensively for separation and purification of gases for the past few decades but their exploitation for refrigeration is limited [11].

1.3 Types of Sorption Systems

It is possible to produce cold energy storage with minimal pollution and energy losses thanks to sorption systems. The working principle consists of the endothermic evaporation of a working fluid, as in most cooling systems. (See Figure 1.1) This evaporation is brought about by the apparent removal of the vapour phase of the working fluid during a reversible physico-chemical process. Initially, the whole assembly is at low pressure and temperature, the adsorbent contains a large concentration of refrigerant within it and the other vessel contains refrigerant gas (A). The adsorbent vessel (generator) is then heated (B), driving out the refrigerant and raising the system pressure. The desorbed refrigerant condenses as a liquid in a second vessel, rejecting heat (C). Finally the generator is cooled back to ambient temperature, readsoiring the refrigerant and reducing the pressure (D). The reduced pressure above the liquid in the second vessel causes it to boil, absorbing heat and producing the refrigeration effect. This process always includes sorption [12], which can be categorized as vapour absorption by a liquid, vapour adsorption on a microporous solid and chemical reaction between a vapour and a solid.
Figure 1.1: Working principles of sorption system

The concept of solid-gas sorption heat powered cycles covers several technologies [13], [14]. The classification of solid-gas sorption systems is presented on Figure 1.2. The two main technologies are concerned as adsorption and chemical reaction (including chemical compounds like ammonia salts or hydrates as well as metal hydrides). In the case of adsorption, physical adsorption on the surface occurs without modification of the solid structure itself. In the case of chemical reaction, chemical changes occur which induce modification of the solid itself. This difference has two main important consequences for refrigeration and heat pump applications. Adsorption is bivariant and includes no volume modification of the solid, whereas chemical reaction is monovariant and includes volume modification of the solid. Moreover, in the case of metal hydrides, the chemical reaction exhibits hysteresis.
The most studied pairs in the sorption community are presented in Table 1.1 below.

<table>
<thead>
<tr>
<th>Process</th>
<th>Possible working pairs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption</td>
<td>Zeolite/water</td>
</tr>
<tr>
<td></td>
<td>Zeolite/methanol</td>
</tr>
<tr>
<td></td>
<td>Silica gel/water</td>
</tr>
<tr>
<td></td>
<td>Activated carbon/methanol</td>
</tr>
<tr>
<td></td>
<td>Activated carbon/ammonia</td>
</tr>
<tr>
<td>Absorption</td>
<td>Lithium bromide/water</td>
</tr>
<tr>
<td></td>
<td>Ammonia/water</td>
</tr>
<tr>
<td>Chemical reaction</td>
<td>Ammonia-inorganic salts and a large family of alkali salts for</td>
</tr>
<tr>
<td></td>
<td>ammonia salts including BaCl₂, MnCl₂, SrCl₂, etc</td>
</tr>
</tbody>
</table>

Table 1.1: Pairs studied in sorption processes

There are many advantages of adsorption systems in comparison with the conventional compression systems. Adsorption systems are environmentally friendly; they can use heat rather than electricity as the primary energy source. They have no moving components and no solution pumps, which make them silent and easy to maintain. Solid adsorbents are not volatile in comparison with absorbents. Almost any refrigerant can be used in such systems and in principle the adsorbent can be manufactured with the optimal pore size distribution for a particular application.
Chapter 1 Introduction

It is important to analyse precisely the performance of an adsorption cycle, based on an accurate determination of the adsorbent-adsorbate behaviour and an exact understanding of the influence of operating conditions. This includes evaluation of the cycled mass of the refrigerant, the isosteric heat of adsorption or desorption and their dependency on the above mentioned factors.

1.4 Variety of Working Pairs

Working pairs for adsorption systems are substances or chemicals, which without changing their properties (mechanical or chemical) allow consumption or production of heat. The amount of heat consumed or released due to the thermochemical process is utilised for production of heating and cooling. Critoph [15], and Srivastava and Eames [11] present a useful discussion of working pairs.

The major requirements of working pairs properties are their high storage capacity, thermal stability within the working conditions (temperature and pressure range), high thermal conductivity, high external heat transfer coefficient, and high specific power output. They should also be transportable (easy to handle), have a small specific volume, be non-corrosive and non-toxic (environmental friendly), have a low viscosity and surface tension. Lebrun and Neveu [16] suggest the following criteria to be considered in a selection of an appropriate working pair:

- economic criteria (cost of working pair itself or cost of equipment),
- performance criteria (temperature rise, specific power production, mass of working pair),
- cost and performance criteria (specific power per unit mass and unit area of exchange surface or temperature rise by unit mass or unit area of exchange surface).

Neveu and Castaing [17] note that the selection of working pairs needs the understanding of the machine characteristics as a function of the target temperature
required. For instance, the final selection of the ideal working pair requires information of the machines characteristics as a function of refrigeration temperature for all the possible combinations of the considered working pairs.

The suitable adsorbents are porous materials that should adsorb a large amount of refrigerant fluid from the vapour phase and present some additional characteristics: wide concentration change over a small temperature range, reversibility of adsorption process for many cycles, low cost and good thermal conductivity. Adsorbents can be utilized in different forms (pellets or powders) when designing the system. Investigations carried out on adsorption beds using, for example, zeolite pellets showed that the initial adsorption rate is high due to the large surface area of the zeolite bed [18], [19]. However, the poor thermal conductivity of zeolite beds (0.15 W/mK) [20] and the poor contact between the zeolite pellets and the heat exchanger wall results in a steep decline in the adsorption rate. This leads to long cycle time and, consequently, to a low thermal output of the heat pump/refrigeration system. Alternatively, zeolite layers could be linked directly to the heat transfer area, resulting in higher thermal conductivities (0.4 W/mK) than zeolite beds. One disadvantage of these layers is the smaller mass transfer area compared to granules. The low diffusivity of the solid may dominate the adsorption process.

Another important element of any refrigeration system is the refrigerant, since the working pair condition and compatibility with the environment principally depend on it. Generally speaking, the refrigerant requirements are high latent heat per unit volume and good thermal stability.

Briefly, the adsorption characteristics of a working pair are described by its adsorption isotherms. These indicate the quantity of adsorbate trapped per unit mass of sorbent on a y-axis. The corresponding x-axis is the pressure of the adsorbate, and data sets are reported for isothermal conditions. The performance of adsorption refrigeration systems is closely related these isotherms. For example, the zeolite-water pair would be better than the active carbon pairs for large temperature lifts ($\Delta T > 40^\circ$C), but the freezing of water constrains its use for temperatures below $0^\circ$. The zeolite-water pair requires
relatively high regenerating temperatures (≥200 °C), whereas the active carbon pair can be operated at low regenerating temperatures (≥100 °C). Table 1.2 gives the heats of adsorption for selected adsorbent/adsorbate pairs.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorbate</th>
<th>Heat of adsorption (kJ/kg)</th>
<th>Density of the adsorbate (kg/m³)</th>
<th>Application area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated alumina</td>
<td>H₂O</td>
<td>3000</td>
<td>1000</td>
<td>Used mostly for desiccant cooling</td>
</tr>
<tr>
<td>Silica gel</td>
<td>Methyl alcohol</td>
<td>1000-1500</td>
<td>703</td>
<td>Unsuitable above 200 °C</td>
</tr>
<tr>
<td>Zeolite (various grades)</td>
<td>H₂O</td>
<td>3300-4200</td>
<td></td>
<td>Natural zeolites have lower values than synthetic</td>
</tr>
<tr>
<td></td>
<td>NH₃</td>
<td>4000-6000</td>
<td>681</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CO₂</td>
<td>800-1000</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH₃OH</td>
<td>2300-2600</td>
<td>791</td>
<td></td>
</tr>
<tr>
<td>Active carbon</td>
<td>C₂H₄</td>
<td>1000-1200</td>
<td></td>
<td>Reacts at 100 °C</td>
</tr>
<tr>
<td></td>
<td>NH₃</td>
<td>2000-2700</td>
<td></td>
<td>Ammonia and methanol are not compatible with</td>
</tr>
<tr>
<td></td>
<td>H₂O</td>
<td>2300-2600</td>
<td></td>
<td>copper at high T</td>
</tr>
<tr>
<td></td>
<td>CH₃OH</td>
<td>1800-2000</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C₂H₅OH</td>
<td>1200-1400</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1.2: Heat of adsorption of some adsorbent/adsorbate pairs [11]

The varying properties of working pairs lead to different designs and development of processes, covering the large temperature range. Table 1.3 shows the different working pairs used for different temperature ranges. Chemical reaction systems are applicable across the entire temperature range listed.
Chapter 1

Introduction

<table>
<thead>
<tr>
<th>Applications/temperature level</th>
<th>Possible systems</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air conditioning/chilled water (+2 °C to +10 °C)</td>
<td>Adsorption</td>
</tr>
<tr>
<td></td>
<td>Chemical reaction</td>
</tr>
<tr>
<td>Refrigeration (-20 °C to 0 °C)</td>
<td>Chemical reaction</td>
</tr>
<tr>
<td></td>
<td>Adsorption</td>
</tr>
<tr>
<td></td>
<td>Metal hydrides</td>
</tr>
<tr>
<td>Freezing (-40 °C to -30 °C)</td>
<td>Chemical reaction</td>
</tr>
<tr>
<td></td>
<td>Metal hydrides</td>
</tr>
</tbody>
</table>

Table 1.3: Solid-gas systems possible for cold production applications [21]

1.5 Thesis Objectives

This thesis will concentrate mainly on the investigation of an adsorption refrigeration system in which the functions of heat transfer and adsorption are integrated, as proposed by the authors in [7, 8], in order to eliminate the significant reductions in the performance of the adsorption system. This will be connected with designing a novel heat exchanger, in which the surface will be coated with an adsorbent with the purpose of increase in a heat transfer in the system. This inevitably leads to faster adsorption processes, but the aim is to check effect of this procedure on system COP, as well as, validate temperature gradients in extended surfaces. As a result a new adsorption refrigeration test facility has to be built.

The objectives can be further detailed as follows:

1. Investigate possible adsorbent/refrigerant pairs;
2. Design a heat exchanger with a coated surface;
3. Develop small laboratory-scale experiments to measure the behaviour of the adsorbent/refrigerant pair;
4. Develop of a pilot-scale adsorption refrigeration rig to validate the system COP;
5. Develop of a mathematical model for calculating the behaviour of the adsorption system, using known data.
References for Chapter 1


Chapter 2

Literature Review

2.1 Introduction

The primary objective of this review is to provide fundamental understanding of the adsorption refrigeration/heat pump systems currently discussed by researchers, and show the potential for further contributions in this area. Adsorption devices are of significance in meeting needs for cooling requirements such as air-conditioning, ice making and medicine or food storage. They are also noiseless, non-corrosive and environmentally friendly. For these reasons the research activities in this sector are still increasing to solve the crucial points that make these systems capable of competing with vapour compression systems. Different arrangements of the systems are presented, as well as a variety of adsorbent-adsorbate pairs used to indicate the present developments and techniques in this sector.

2.2 History of Adsorption Refrigeration [1]

The history of solid adsorption refrigeration starts from as early as 1823, when Faraday had noted the affinity of silver chloride for ammonia. After that Ferdinand Carre tried various combinations in 1859. Further, there was a concept of using the ability of activated carbon to adsorb certain substances on its surface, so that by 1873, Melsens had made an adsorber for ammonia. In 1912, in the USA, Browne and Nichols had used ammonia on copper sulphate. In Germany, Humboldt, in 1924, and a little later Siemens, made machines that used calcium chloride. In 1929 there were several activated carbon refrigerators in Great Britain. In 1930, Amundsen constructed a household refrigerator in which methyl alcohol was adsorbed on carbon.
Chapter 2

**Literature Review**

The adsorbent properties of silica gel were also exploited and in 1928 in the USA an adsorption machine was built to cool wagons, using silica gel and SO\textsubscript{2}. Around 1930, the stock of wagons in America began to be worn out, and in 1935 a large programme of reconstruction and modernisation was launched.

At this stage mechanical refrigeration was considered. The American patent had been granted in 1880, and a few machines were manufactured in America and Europe before 1914. In 1925 two types of refrigeration were put into service in the United States, one with an ammonia compressor driven from an axle (the North American Car Corporation), and the other using an adsorption machine, SO\textsubscript{2} being adsorbed on silica gel.

In 1929 in Great Britain there was a wagon with a methyl chloride compressor, driven by the axle en route and by an electric motor, linked to the grid (the Lightfoot Stone system). In the following year, Halls equipped a wagon with a methyl chloride compressor driven by a diesel engine. Around 1935 in Great Britain, a wagon was tested which had a system in which ammonia was adsorbed on a solid calcium chloride.

The mechanical systems superseded the thermally driven ones, because they were more efficient. For many years adsorption systems were forgotten. From 1950, new chemical compounds were employed for solid adsorption, namely 'molecular sieves' (zeolites), which were much more effective in adsorption machines than, for example, silica gel. Thereafter, the technology of solid adsorption refrigeration was abandoned until the 1970s, when adsorption systems were studied for cooling and heating applications as well as the systems working on continuous cycles for providing heating or cooling in an environmentally friendly way. For instance, a two-bed adsorption chiller has been successfully commercialised in Japan [2], [3]. By making use of silica gel-water working pair, such chillers have managed to economically harness the potential of low-grade waste heat for useful cooling. (This would otherwise be discharged into the environment.)
Figure 2.1: Schematic of two-bed adsorption chiller commercialised in Japan

During recent years experiments on using solar energy for solid adsorption refrigeration or air-conditioning have been made. These systems seem promising for use in developing countries. Solar refrigeration is an important use of solar energy because the supply of solar energy and the demand for cooling are greatest during the same season. It has the potential to improve the quality of life of people who live in areas where the supply of electricity is far from sufficient. It is to be applied to the storage of agricultural products, food and medicines. The solar powered solid adsorption refrigeration system is one of the most promising technologies because it is environmentally friendly with low cost, simple manufacture and low maintenance requirements. Also solar energy is more and more recognised as a priority in developing countries (UNEP report, 1997) [4]. The research work at the moment is on improving efficiency such a systems to be more competitive with the electrically driven vapour compression systems.
2.3 Adsorption Cycles

The frequently cited adsorption refrigeration cycles are [5]:

(a) The basic cycle, which is an intermittent refrigeration cycle when, operated with one bed. Continuous refrigeration can be achieved with two or more beds to shift the heating-cooling phases. In the basic cycle, there is no opportunity for heat recovery.

(b) The continuous heat recovery cycle, which is usually, operated with two adsorption beds. The adsorber to be cooled will transfer heat to the adsorbed to be heated, the heat transfer between two beds includes sensible heat and heat of adsorption. This heat recovery process is useful in increasing COP. Multi-beds could be adopted to get even more heat recovery and thereby a much higher COP.

(c) The thermal wave cycle [6], in which it is assumed that a high temperature gradient exists along an adsorption bed. For a two-bed system, high temperature thermal fluid flows into the adsorber and exchanges heat with the bed, such that the fluid cools rapidly and the outlet temperature is nearly of ambient. After being cooled by the ambient surroundings, the fluid flows into another adsorption bed, recovers heat so that at the exit of the bed, it will be very close to the temperature of the heat source. This design less heat is added to the system, and less heat released to the environment, thus the heat recovery ratio is high and the COP is significantly increased.

(d) The convective thermal wave cycle [7], the concept is the same as thermal wave cycle, however the thermal fluid is the refrigerant itself. Thus the heat transfer between thermal fluid and adsorption bed is direct contact heat transfer, which is incorporated with mass transfer in the system.

(e) The cascading cycle [8,9], in which the working pairs might be zeolite-water/activated carbon-methanol, zeolite-water/ silica gel-water or zeolite-water/zeolite-water. A heat source (at around 200 °C) drives the high temperature stage adsorption refrigeration cycle (typically 100-200 °C for zeolite-water). The sensible heat drives the low temperature stage and the heat
of adsorption of the high temperature stage. For example, activated carbon-methanol or silica gel-water adsorption refrigeration cycles are operated between 30-100 °C and are suitable for regeneration temperature of 100 °C.

The basic cycle is easy to construct and is very suitable for solar refrigeration and also for waste heat recovery refrigeration. The heat recovery cycle is practical as the system has a reasonable COP and is not excessively complicated. The thermal wave cycle is attractive, however, it is not easy for adsorbents to reach very high thermal conductivity. In addition, the thermal fluid velocity is restricted to meet the demand, which reduces the specific cooling power. Similar analysis of costs and benefits applies to the cascading cycle [9]. For real applications, the heat recovery two-bed system is well accepted, however its COP and SCP need to be increased significantly. Obviously various operating procedures will influence the system performance, in particular the useful operation of mass recovery [10]. (This consists of connecting the two beds, equalising their pressure before heat recovery. This process will enlarge the desorbed refrigerant mass. It will thereby increase the refrigeration effect.)

2.3.1 Basic Cycles

Basic adsorption cycle is the simplest version of the adsorption process, and considerably more complicated systems exist.

An adsorption cycle for refrigeration or heat pumping does not have work input, but only heat input. The basic adsorption cycle contains:

(a) an adsorbent bed,
(b) an evaporator,
(c) a condenser,
(d) a throttling valve.
Chapter 2

The adsorbent bed exchanges heat with a heat source at temperature $T_H$ and a heat sink at temperature $T_C$. But the complete adsorption system has a condenser and an evaporator, thus the system exchanges heat with another heat sink (not necessarily the same temperature as the $T_C$) and a heat source at low temperature ($<T_C$). Hence, the refrigerant vapour transfers heat in the adsorbent bed, condenser and evaporator. The cycle is thus a four-temperature cycle, shown in Figure 2.2. Note that $T_C$ is an intermediate temperature. For the system to be useful, $T_C$ must exceed the evaporator temperature and be less than the condenser temperature.

Figure 2.2: General Adsorption Refrigeration Cycle

Figure 2.3: Working principles of the adsorption cooling system.
The mass ratio of adsorbent to adsorbate at equilibrium is a function of the adsorption pressure and adsorbent temperature, i.e. $x = f(p, T)$. Depending on the analysis in the adsorption process, a set of equations can be defined [11]:

- Isothermal adsorption, $x = f(p)_T$, mainly applied in micro-porous adsorption in industrial equipment.
- Isobaric adsorption, $x = f(T)_p$, is used in the design of operation processes.
- Isosteric process, $p = f(T)_x$, is suitable for the calculation of heat of adsorption and desorption.

The isothermal or isobaric adsorption equation is the basis for design and simulation of an adsorption refrigeration process. A basic adsorption cycle can be represented with the aid of the $p-T-m$ diagram as it is shown in a Figure 2.2.

The cycle consists of four processes:

(a) Heating and Pressurisation

At this stage, the adsorbent contains a large concentration of refrigerant. The adsorbent bed receives heat, thus the temperature increases and the adsorbent temperature increases as well. This heating induces a pressure increase from the evaporator pressure to the condenser pressure.

Figure 2.4: Heating and pressurisation
(b) Heating and Desorption

At this stage, the adsorbent bed continues receiving heat while it is connected to the condenser, thus the condenser pressure prevails within the system. Further increase in the adsorbent temperature induce desorption of the refrigerant vapour (the vapour is driven out from adsorbent bed). This desorbed vapour condenses and heat is rejected to the second heat sink at an intermediate temperature.

![Figure 2.5: Heating and desorption](image)

(c) Cooling and Depressurisation

At this stage, the adsorbent bed is cooled. The adsorbent temperature decreases, which induces a change in pressure from the condensation pressure to the evaporation pressure.

![Figure 2.6: Cooling and depressurisation](image)
(d) Cooling and Adsorption

At this stage, the adsorbent bed is cooled while connected to the evaporator, thus the evaporator pressure prevails within the system. The adsorbent temperature continues decreasing, which induces adsorption of the refrigerant vapour (the vapour is driven in the adsorbent bed). This adsorbed vapour is vaporized in the evaporator. The evaporation heat is supplied by the heat source at low temperature. This stage is similar to the evaporation in traditional compression cycles.

![Figure 2.7: Cooling and adsorption](image)

It is important to indicate that the basic cycle, which includes just one adsorbent bed, is discontinuous since effective cooling is present during only one part of the cycle. However, two or more adsorbent beds can be operated out of phase to provide quasi-continuous cooling.

The efficiency for any refrigeration system is associated with the term of Coefficient of Performance (COP). This is generally defined as follows:

\[
COP = \frac{\text{cooling power}}{\text{input power}}
\]  

\[(2.1)\]
However, it is important to emphasise that the COP to be calculated is for the adsorbent bed within the cycle. The Figure 2.2 shows the basic adsorption cycle. This cycle contains the four stages described earlier. The analysis for a basic cycle showed in the diagram could give an appropriate estimate of COP. The COP to be estimated for different refrigerant-adsorbent pairs is following the method indicated by Critoph [12].

The method considers the estimation for COP in cooling (COPc) and heating (COPh). Taking into account the processes showed in the Figure 2.2, these stages are considered as follows:

(a) **Stage 1-2: Isosteric Heating**

A heat input per unit mass of adsorbent is considered. Isosteric heating takes place where the concentration by weight of adsorbate has a constant value $x_{conc}$. (This is the greatest value of $x$ occurring in the cycle). Normally, any mass transfer between the gaseous and adsorbed phases is neglected. The equation for this stage is given by:

$$ q_{12} = \int_{T_1}^{T_2} \left( c_{pz} + x_{conc} \cdot c_{vm} \right) \cdot dT $$

where:

- $c_{pz}$ - is the specific heat of adsorbent, possibly a function of temperature.
- $x_{conc}$ - is the maximum concentration obtained at point 1 by using the evaporating pressure and bed temperature $T_1$
- $c_{vm}$ - is the specific heat of the adsorbed phase at constant volume
- $T_1$ - is the minimum cycle temperature (K)
- $T_2$ - is the temperature at the start of desorption (K)

The integral is the effective specific heat of the unit mass of adsorbent and its associated adsorbate. In theory, there is no expansion of the adsorbate volume when the heat required to raise the temperature is the change in internal energy, thus the specific heat at constant volume is considered. However, in practice the use of specific heat at constant pressure $c_{pz}$ can be considered as a good approximation. The temperature $T_2$
can be calculated taking into account the constant ratio of $T/T_{\text{sat}}$ along an isostere, hence:

$$\frac{T_1}{T_{\text{ev}}} = \frac{T_2}{T_{\text{cond}}} \tag{2.3}$$

(b) Stage 2-3: Isobaric Heating

The heat input per unit mass of adsorbent is considered. Isobaric heating takes place, and the concentration by weight of adsorbate, $x$, varies. The equation for this stage is given by:

$$q_{23} = \int_{r_1}^{r_2} \left( c_{p_z} + x \cdot c_{p_m} \right) \cdot dT + \int_{x_{\text{sat}}}^{x_{\text{min}}} H(p,T) \cdot dx \tag{2.4}$$

where $x_{\text{min}}$ is the minimum concentration and $H$ is the heat of desorption per unit mass of adsorbate. $H$ at any point on 2-3 or 4-1 can be derived from the slope of the isostere on the Clapeyron diagram:

$$H = R \cdot \left( \frac{\partial \ln(p)}{\partial (1/T)} \right) \tag{2.5}$$

R - The gas constant at the system pressure and temperature

Taking into account the constant ratio $T/T_{\text{sat}}$ along an isostere, thus $H$ can be expressed as a multiple of the latent heat $L$ of the refrigerant at the system pressure:

$$H = L \cdot \frac{T}{T_{\text{sat}}} \tag{2.6}$$

(c) Stage 3-4: Isosteric Cooling

The heat rejected per unit mass of adsorbent in the isosteric process 3-4 is analogous to the heat input in stage 1-2. However, the concentration by weight of adsorbate is now at its minimum value $x_{\text{min}}$, hence:

$$q_{34} = \int_{r_1}^{r_4} \left( c_{p_z} + x_{\text{min}} \cdot c_{p_m} \right) \cdot dT \tag{2.7}$$
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where \( T_4 \) may be calculated:

\[
\frac{T_{4_{\text{eq}}}}{T_{\text{cond}}}_4 = \frac{T_3}{T_{\text{cond}}}
\]

(d) Stage 4-1: Isobaric Cooling

The heat rejected per unit mass of adsorbent in the isobaric process 4-1 is analogous to stage 2-3. However, the concentration by weight of adsorbate \( x \) varies and the latent heat is considered at the temperature of evaporation rather than the temperature of condensation. The equation for this stage is given by:

\[
q_{41} = \left( c_{pc} + x \cdot c_{pm} \right) \cdot dT + \int_{x_{\text{conc}}}^{x_{\text{dil}}} \left( H - [h_{\text{gasbed}} - h_{\text{gasev}}] \right) \cdot dx
\]

where:

\[ h_{\text{gasbed}} \] is the gas enthalpy evaluated at the bed temperature (kJ/kg)

\[ h_{\text{gasev}} \] is the gas enthalpy evaluated at the evaporator (kJ/kg)

The second bracketed term in the second integral takes account of the cooling effect on the bed of the cold gas entering from the evaporator.

(e) Cooling (Evaporation)

The cooling and the heat rejected to the heat sink in the condenser are evaluated by considering the mass of refrigerant desorbed and then adsorbed per unit mass of adsorbent during every cycle. Thus the net concentration change is \( x_{\text{dil}} - x_{\text{conc}} \). The useful cooling obtained from it is:

\[
q_{\text{ev}} = (x_{\text{conc}} - x_{\text{dil}}) \cdot (h_{\text{gasev}} - h_{\text{liquidcon}})
\]

where:

\[ h_{\text{gasev}} \] is the specific enthalpy of gas leaving the evaporator (kJ/kg),

\[ h_{\text{liquidcon}} \] is the specific enthalpy of the condensed liquid (kJ/kg).
(f) Condensation Heat

The heat rejected by the condenser is the sum of the heat of vaporisation and the sensible heat required by the superheated vapour to be cooled to the condensing temperature. Since the gas is desorbed at a range of temperature between $T_2$ and $T_3$, the heat rejected is evaluated as:

$$q_{con} = -\int_{x_{conc}}^{x_{dil}} h_{gas} \cdot dx + h_{liquid} \left( x_{conc} - x_{dil} \right)$$

(2.11)

where:

$h_{gas}$ - is the gas enthalpy evaluated at the (varying) bed temperature,

$h_{liquid}$ - is the saturated liquid enthalpy in the condenser.

Experimental work has shown that there is only a small error if the hot gas is all assumed to leave the bed at the mean temperature of $T_2$ and $T_3$.

The COP in cooling ($COP_c$) or heating ($COP_H$) for basic refrigeration cycle is defined by:

$$COP_c = \frac{q_{ev}}{q_{12} + q_{23}}$$

(2.12)

and

$$COP_H = \frac{q_{con} + q_{34} + q_{41}}{q_{12} + q_{23}}$$

(2.13)

The two-bed continuous cycle operates with the beds out of phase, to provide continuous cooling power. In thermodynamic terms, it is identical to the basic cycle and has the same COP. Heat can be recovered internally to improve the cycle performance.
2.3.2 Heat and Mass Recovery Cycles

To be economically feasible, adsorption cycles require sufficiently high values of Coefficient of Performance (COP) and Specific Cooling Power (SCP). Therefore, numerous developments on the basic cycle of adsorption refrigeration have been investigated. These include the continuous cycle, the hybrid multi-effect cycle, the forced convection cycle, and the thermal wave cycle. Among these, the intermittent cycle is appropriate for the recovery of solar energy, owing to its simple structure. The continuous cycles (including the continuous heat regenerative cycle and continuous mass recovery cycle) can provide cooling continuously [13], [14].

The heat regeneration process can recover some thermal energy during phase switching between the adsorption and desorption beds. In this process, the temperature difference between two beds is exploited, so that heat can be usefully transferred between them and thermal energy recovered. The heat recovery and heat regeneration processes are two different ways of achieving this operation. In both cases the unit contains two adsorbers, a condenser and an evaporator. In addition the heat transfer fluid has to be circulated between the adsorbers and the heat sources.

Mass recovery is used to convey gaseous refrigerant from the bed with higher pressure to the bed with lower pressure just before phase switching. It is apparent that mass recovery is beneficial to improving the adsorption quantity of a cycle [15].

An adsorption cooling system with two beds using activated carbon and methanol was developed and tested by Wang [16]. The experimental results show that the heat recovery operation between two adsorption beds will increase the COP by about 25% compared with a single adsorber basic cycle system. The optimum cycle time was found to be 40-50 minutes with a heat recovery time of 2 minutes. It was proved that mass recovery is very effective for heat recovery adsorption cooling operation, which may help to obtain a COP increase of more than 10%. It is possible to achieve a COP of
0.5 in a real adsorption air-conditioning system, with a heat source of 100°C at an evaporator temperature of about 5°C.

Guilleminot et al. [17] have been tested a zeolite/water adsorption system suitable for air-conditioning. This consisted of two adsorbers filled with a consolidated composite made of zeolite mixed with a highly conductive matrix. The experimental results of such a heat pump unit operating with heat and mass recovery cycle are presented. The tests were carried for evaporating temperature of 4°C, with a cycle time of 60 minutes. The Coefficient of Performance value obtained is 0.41. For higher evaporation temperatures (T=25-30°C), the mass transfer resistance effect decreases and the COP reaches 0.68.

Pons and Poyelle [18] discussed an advanced adsorption cycle, where vapour is internally recovered between the two adsorbers. Two pairs were evaluated, activated carbon AC35/methanol and zeolite NaX/water, for some typical applications in order to compare the performance. For the zeolite/water pair these applications are heat pumping and air-conditioning, for carbon/methanol ice making. The systems were cooled with water (40°C) or air (50°C) and the COP achieved was for zeolite/water: 0.68 or 0.63, for carbon/methanol: 0.55 or 0.52.

For energy analysis in an adsorption refrigeration cycle, the degree of heat regeneration is represented by the coefficient of regeneration $r$. In general [15]:

$$r = \frac{Q_{\text{reg}} - Q_{\text{reg}}^*}{Q_{\text{reg}}} = \frac{Q_{\text{re}}}{Q_{\text{reg}}}$$  \hspace{1cm} (2.14)

in which $Q_{\text{reg}}$ is the required heat for desorption in the cycle without heat regeneration, $Q_{\text{reg}}^*$ is the required heat with regeneration and $Q_{\text{re}}$ is the exchanged heat during heat regeneration. We can easily find that $r$ indicates the effect of heat regeneration on cooling performance of the cycle as follows.

$$COP^* = \frac{COP}{1 - r}$$  \hspace{1cm} (2.15)
In Equation (4.15), $COP^*$ is the cooling performance of the adsorption refrigeration cycle with heat regeneration (in the absence of regenerator, $r = 0$).

In practice, both mass recovery and heat regeneration are frequently adopted for improving performance.

### 2.3.2.1 Heat Regeneration Cycle

The heat regeneration system is presented in Figure 2.9. There are two beds in this type of cycle, which are operated out of phase. At the end of each half cycle, one adsorbent bed is cold at point 1 and the other is at 3 with high temperature (see Figure 2.8). Heat can be easily recovered between the two adsorbent beds because of this temperature difference. By circulating a thermal fluid between the two adsorbent beds, the energy efficiency can be increased significantly. In an ideal heat recovery process, the two beds will reach the same temperature, one is at point $k$ and the other is $k'$ (see Figure 2.8). Therefore the thermal load for heating can be decreased by $Q_{1-2-k}$. This is the recovered thermal energy, which can reach about 30% or so of the total necessary heat input to the basic cycle [5], [16].

In order to understand the degree of heat regeneration in operation, a parameter, $\varepsilon_t$, called the temperature coefficient of heat regeneration, is introduced as follows:

$$\varepsilon_t = \frac{T_k - T_{k'}}{\Delta T} \quad (2.16)$$

In the above equation, $T_k$ and $T_{k'}$ are the adsorbent bed temperatures after heat regeneration, respectively, and $\Delta T$ is the temperature difference between the two adsorbent beds before heat regeneration.

In general, $\varepsilon_t$ is less than 1 ($T_k < T_{k'}$) in real operation due to the effect of the heat capacity of heat transfer fluid. Even if the heat capacity of the heat transfer fluid were low enough, it would require a prohibitively long time to reach $\varepsilon_t = 1$. 

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Figure 2.8: Diagram of the intermittent and heat regeneration cycle.

Figure 2.9: Schematic system of mass recovery / heat and mass recovery cycle. The dashed line represents thermal fluid flow.
2.3.2.2 Cycle with Mass Recovery

In a two-bed cycle, the two beds are working out of phase. At the end of each half cycle, one bed is hot with high-pressure $P_{\text{cond}}$ and the other is cold with low-pressure $P_{\text{ev}}$ (Points 3 and 1 respectively in Figure 2.10) [5], [16].

Thereafter, the high-pressure adsorber needs to be cooled and depressurised while the low-pressure one needs to be heated. The refrigerant vapour will flow from the high-pressure bed to the low-pressure one in Figure 2.9. Here, the dashed lines represent the thermal fluid flow. The solid lines (and valves) indicate mass recovery and the dashed lines indicate heat recovery.

The pressure in Adsorber 1 decrease due to mass outflow and this will again cause desorption in Adsorber 1. Meanwhile, the pressure in Adsorber 2 increases due to mass inflow and will cause further adsorption. The process is maintained until the two beds reach the same pressure, $P_m$ (see Figure 2.10). Then the connection is broken and each bed continues with heating and cooling process just as in the basic cycle.
This mass recovery process is expected to accelerate the circulation and enhance the cycle cooling power, because the mass flow is direct, so the equilibration of mass is faster than that of heat in the basic cycle.

To simplify the analysis, it is necessary to suppose that all the processes of adsorption refrigeration in Figure 2.10 are in equilibrium, and the heat capacity of the heat transfer fluid can be ignored (heat transfer fluid is used for heating and cooling the adsorbent beds).

In a cycle, the extra quantity of desorbed refrigerant resulting from the mass recovery process should equal that of the extra-adsorbed refrigerant, that is,

\[ \Delta x_{1-1'} = \Delta x_{2-2'} \]  \hspace{1cm} (2.17)

The value of \( \Delta x_{1-1'} \) would reach the maximum if the pressure difference \( P_{3''} - P_{1''} \) becomes zero, but for this to occur, the process of mass recovery would need to be maintained for an infinitely long time.

In order to understand the degree of mass recovery in operation, a parameter, \( e_m \), called the pressure coefficient of mass recovery, is introduced as follows:

\[ e_m = 1 - \frac{P_{3''} - P_{1''}}{\Delta P} \]  \hspace{1cm} (2.18)

In Equation (2.18), \( \Delta P \) is the pressure difference between the two adsorbent beds before mass recovery. When \( e_m = 0 \), there is no mass recovery in the cycle. In later calculations the condition \( e_m \rightarrow 1 \) (or \( P_{3''} \rightarrow P_{1''} \)) will be assumed, although in practice slightly smaller values will occur.
2.3.2.3 Cycles with Heat and Mass Recovery

The process of mass recovery enlarges $\Delta x$, the concentration change of adsorbate in a cycle, as shown in the P-T-x diagram in Figure 2.10.

We can use a heat regeneration process after the mass recovery process because there is a large temperature difference between the two beds. The thermal load can be further decreased so as to improve the cycle performance. In Figure 2.10, this process begins with 1'' and 3'' and ends at k-k', with a common temperature. The system scheme is also shown in Figure 2.9 [15].

In this project the mass recovery process is assumed to be isothermal. The process is divided into two parts operated in two beds as 1-1'' and 3-3''. The process can be simulated utilizing the following model.

1. The vapours desorbed from the high-pressure bed is entirely readsorbed by the low-pressure bed. That is:

$$\Delta x_{1-1'} = \Delta x_{3-3'}$$  \hspace{1cm} (2.19)

2. The final pressure of the two beds is equal to each other,

$$p_{1'} = p_{3'}$$  \hspace{1cm} (2.20)

Initially the final pressure is prescribed. Then the temperature and concentration change of each bed are calculated to modify the supposed pressure, if necessary, to fulfil Equation (2.20), until a satisfactory result is derived.

For the cycle with the heat regeneration the COPc becomes:

$$COP_c' = \frac{q_{ev}}{q_{k-3}}$$  \hspace{1cm} (2.21)

Where:

$$q_{k-3} = \int_{T_k}^{T_s} (c_{pa} + x \cdot c_{pm}) \cdot dT + \int_{x_{di}}^{x_{surf}} H \cdot dx$$  \hspace{1cm} (2.22)
Using a twin bed adsorption refrigeration cycle (for mass recovery only) the COP becomes:

\[
COP_c^{''} = \frac{q_{ev}^{''}}{q_{1-2} + q_{2-3}}
\]  

(2.23)

Where:

\[
q_{1-2} = \int_{T_1}^{T_2} (c_{pe} + x_{conc} \cdot c_{vm}) \cdot dT
\]  

(2.24)

\[
q_{2-3} = \int_{T_2}^{T_1} (c_{pe} + x \cdot c_{pm}) \cdot dT + \int_{x_{at}}^{x_{pm}} H \cdot dx
\]  

(2.25)

And

\[
q_{ev}^{''} = (x_{conc}^{''} - x_{dil}^{''}) \cdot (h_{gas} - h_{liq})
\]  

(2.26)

Using a twin bed adsorption refrigeration cycle (for a mass recovery and heat regeneration) the COP becomes:

\[
COP_c^{'''} = \frac{q_{ev}^{'''}}{q_{4-3}}
\]  

(2.27)

2.3.3 Thermal Wave

Low COP is one of the main problems of adsorption refrigeration. Many different cycles have been studied to improve the COP, with a focus on improving the heat regenerative ratio. One attractive cycle is the thermal wave cycle patented by Shelton [19]. The simulation of the cycle by Shelton showed that the heat regenerative ratio and COP for heat pump are as high as 70% and 1.87, respectively. Many researchers have studied the cycle successfully but the system was not commercialized. The thermal wave cycle utilises a simple heat transfer fluid circulating loop for heating and cooling the two adsorbent beds, in which part of the adsorbent heat can be recovered from the bed being cooled to the bed being heated. Figure 2.11 presents a typical thermal wave
cycle system. Shelton has shown that the temperature of the outlet fluid increases quickly, and the shape of the wave defined rapidly becomes flat. Both of the two features are far from the ideal thermal wave, which is characterised by the steep and large temperature difference between the inlet and the outlet fluid.

The thermal wave is a description of the fluid temperature, which mainly depends on the heat transfer condition.

Heating and cooling of the adsorbent beds is achieved via a heat transfer fluid such as high temperature oil. The oil passes through a heat exchanger in each of the two beds and through two conventional heat exchangers outside the beds. The main function of the bed heat exchangers is to combine a large area of heat transfer surface with a low oil flow rate. One of the external heat exchangers allows the oil to be heated by a gas flame and the other removes heat to supply the heating load (in the case of the heat pump) or to be rejected (in the case of the refrigerator). There is also a reversible oil pump, which can send oil in either direction round the loop.

The cycle consists of two phases. Firstly we suppose the pumping to be anti-clockwise: bed 1 is cold (maximum adsorbent concentration) and bed 2 is hot (minimum adsorbent concentration). When the cycle starts the oil recovers heat from bed 2, has a further
heat addition from the gas heat exchanger and then proceeds to heat bed 1, via the special heat exchanger within it. Bed 1 desorbs refrigerant, which passes to the condenser (giving a useful heat output in the case of a heat pump) and bed 2 adsorbs gas from the evaporator, which provides cooling. In the following phase of the cycle, the pump is reversed and bed 1 is cooled (adsorbing) with bed 2 heated (desorbing) in a similar fashion until the original conditions are reached. Thereafter, the pump can again be reversed.

Up to now, the description could concern simple but limited heat recovery from the beds. However, the system achieves much better performance due to the combination of the special nature of the internal bed heat exchangers and the low oil flow rate. A hot slug of oil entering a cold region of the bed cools rapidly and leaves the bed cold. If the oil has a very low thermal mass flow rate, and there is little conduction within the bed in the direction of the oil flow, then a thermal wave will pass through it. Conversely, high conduction rates normal to the oil flow are necessary in order to achieve a good ratio of adsorbent-to-heat exchanger mass. The wave front propagates through the bed with all of the carbon upstream of the wave hot (low concentration) and that downstream cold (high concentration). The oil emerging from the bed heat exchanger will be cold until the wave reaches the end of the bed, giving a rapid temperature rise when the wave 'breaks through'. At this stage, the pump is reversed for the second half of the cycle and the cooling of the bed sees the wave front pass back down the bed in the other direction.

According to the above discussion, the following conclusions can be drawn: Two factors, the fluid velocity and the equivalent heat transfer coefficient, predominantly influence the characteristic of the thermal wave. To approach an ideal thermal wave, the velocity of the fluid should be low and the equivalent heat transfer coefficient between the fluid and the adsorbent in the bed should be high. However, a low velocity heat transfer fluid would greatly decrease the power density of the system. Moreover, the heat transfer coefficient between the fluid and the adsorbent bed is limited by the characteristic of the porous adsorbent.
Sward, LeVan and Meunier [20] describe a model for a thermal-wave adsorption heat pump cycle. Local equilibrium is assumed, providing the asymptotic best-case performance. The model is utilised to examine the performance of adsorption refrigeration cycle powered by low temperature waste heat sources of 373-393 K. The impact of varying system temperatures, bed cycling frequency, valve position, and different section of the bed are examined. Cycle Coefficients of Performance were greater than 1.2 for the base case of a 393 K heat source, 303 K condenser temperature, and 287 K evaporator temperature, for a cycle utilising a water/NaX zeolite adsorbate/adsorbent pair. From the start to the end of the entire heating process, some portions of the bed experienced loading increases. The location of the inlet/outlet valves in the bed was found to have an impact on the shape of temperature and loading fronts. The introduction of partitions within the bed was found to have only a small impact on the performance of the cycle for the temperatures examined, with sections of the bed undergoing pressurisation in a non-sequential order.

Pons and Poyelle [18] discussed an advanced adsorption cycle, where vapour is internally recovered between the two adsorbers by heat regeneration. Two pairs were evaluated: activated carbon AC35/methanol and zeolite NaX/water. The COPs for these systems using heat recovery process were presented in section 2.3.2. In the case of thermal wave the COPs achieved was for zeolite/water is 0.92 and for carbon/methanol 0.61. It gives an increase in system performance of around 20-30%.

2.3.4 Forced Convection Adsorption Cycles

Critoph [21] described the principle of the forced convection adsorption cycle. It is in some ways similar to the ‘thermal wave’ cycle demonstrated by Shelton [22], described in section 2.3.3.

Rather than heating the bed directly; it is possible to heat the refrigerant gas outside the bed and to circulate it through the bed in order to heat the sorbent [21]. The high surface area of the grains enhances heat transfer, with only low levels of parasitic power needed for pumping.
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The cycle presented here utilises a packed bed of inert material to store heat between the adsorption and desorption phases of the cycle. The highest degree of the regeneration possible leads to good COP. The system consists of two ‘active’ beds, which are packed with activated carbon, and two ‘inert’ beds packed with non-reactive particles such as steel balls. The characteristic size of the carbon and non-reactive particles is in range 1-3 mm. The rest of the system contains ammonia refrigerant in either the liquid or gaseous phase.

Thermodynamic modelling, based on measured heat transfer and porosity data, predicts a cycle COP for a specific carbon of 0.95 when evaporating at 0 °C and condensing at 42 °C. The comparison with the simulation results shows that the COP without an inert bed would be 0.29. The practical COP of 0.56 corresponds to an inert bed effectiveness of 80.3%. The parametric study investigated the following: bed length, flow rate and breakthrough temperature, i.e. the gas exit temperature from the active bed, which is used to trigger the change from desorption to adsorption.

Experimental heat transfer measurements and cycle simulations are presented which show the potential of the concept to provide the basis of a gas-tired air-conditioner in the range 10-100 kW cooling.

In the convective cycle proposed by Critoph [7], the thermally massive heat exchangers in the adsorbent beds are not needed (see Figure 2.12). It recognises that although the bed has poor conductivity, the carbon grains (or other adsorbents) have a very high surface area, which can be used for convective heat transfer. For a carbon-ammonia bed, the ammonia can be heated externally to the bed in a conventional heat exchanger and then pumped through the bed, where it rapidly rejects heat to the carbon. In the process, it will desorb a little more ammonia. The cold ammonia issuing from the other end of the bed completes the loop by returning to the pump and gas heater. The circulation flow rate might be 5 to 10 times the desorption flow rate. This is illustrated in Figure 2.12.
Because the surface area of the grains is so high, the heat transfer per unit mass of bed is higher than that for the conventional heat exchangers. There is also the advantage that there is no heat exchanger thermal mass that is wastefully consuming heat. It is possible to switch the external gas heat exchangers between the adsorbing and desorbing loops so that they are in continuous use rather than being heated and cooled periodically. Thus, their thermal mass has no negative effect.

Additionally, a thermal wave is generated in the bed in a similar fashion to that of the thermal wave system. However, it is more similar to conventional gas regenerators, which also exhibit thermal waves. In order to use the recovered heat, it is necessary to transfer it from the cooling bed loop to the heating bed loop. It was proposed to do this with a further gas-to-gas heat exchanger, and is denoted by the vertical ‘heat’ arrow in Figure 2.12.

Only one phase of the cycle is shown in Figure 2.12, in which bed 1 is heated (desorbing) and bed 2 is cooled (adsorbing). The clockwise flow of refrigerant in the loop for bed 1 takes the gas through the recuperator, where heat is recovered from bed 2, the external heat exchanger, where heat from a gas flame is added, and into the bed. The inlet temperature of gas entering the bed is typically 150-200°C, depending upon
operating conditions and the specific application. The refrigerant gas emerges cold (typically 40-50°C) from the bed until the thermal wave starts to break through.

In the loop for bed 2, the circulation of hot gas is from the bed, through the recuperator, through the external cooler (which provides some of the useful output of a heat pump system), and back into the bed. The gas that emerges from the bed stays hot until the thermal wave starts to break through.

When the two thermal waves start to break through, the opposite phase of the cycle begins. Valves are switched which effectively swap the two beds over so that bed 1 is cooled and bed 2 is heated.

The advantages of this concept are seen as being:

- The cycle is highly regenerative and hence efficient
- There is no complex and expensive heat exchanger within the bed
- There is no added thermal mass due to the use of heat exchangers
- The high heat transfer rate will give rapid cycle times which in turn means that the plant can be smaller in size and cheaper to manufacture.

One disadvantage of the system described is the need for the gas-to-gas heat exchanger required to transfer recovered energy between the fluid loops. It could be both large and expensive and there might be problems when the heat rejected by one bed is not needed at the same time by the other bed. Critoph and Thorpe [23] suggested the use of an inert packed bed regenerator to overcome both problems, as shown in Figure 2.13.
Heat is no longer passed from loop 1 to loop 2 but, instead, the heat recovered from each active bed in desorption is stored in an inert bed and is passed back to the active bed in the next desorption phase. The inert bed could be as simple as a cylinder packed with steel balls and have correspondingly low cost. This is a very efficient regenerator and dispenses with the need for the inter-loop heat exchanger, which could be very costly since the heat transfer is of the same order as the external heat input.

In Figure 2.13, active bed 1 is being heated (desorbing) and active bed 2 is being cooled (adsorbing). Flow in loop 1 is anti-clockwise with cold gas coming out of active bed 1, into inert bed 1 where it is pre-heated, through the heat exchanger where it is supplied with heat from the gas flame, and back into active bed 1 where it transfers heat to the adsorbent. There are thermal waves in both beds, which ensure the optimum use of recycled heat. At the same time as active bed 1 is being heated it desorbs gas which passes through the check valve to the condenser. This produces part of the output of a heat pump or is simply rejected if the machine is a refrigerator. When hot gas starts to break out of active bed 1 the cycle enters the next phase. Whilst active bed 1 is being heated, active bed 2 is being cooled by a clockwise flow of gas. In an analogous process hot gas leaves active bed 2, passes to inert bed 2 where it is cooled (making a thermal wave progress down inert bed 2), passes through the external cooler where it is
further cooled (and giving useful heat output in the case of the heat pump) and re-enters active bed 2 as cold gas. Whilst this process is occurring the active bed simultaneously adsorbs gas from the evaporator producing useful cooling.

When both of these processes (heating of active bed 1 and cooling of active bed 2) are complete, the other stage of the cycle takes place in which active bed 1 is cooled and active bed 2 is heated. This is achieved by switching valves so that the dotted flow paths replace the adjoining paths shown by solid lines.

As the result, Critoph [24] proposes a convective thermal wave with the two 'active' beds filled with activated carbon and the two 'inert' beds packed with non-reactive particles such as steel balls. The high degree of regeneration, which is possible, leads to good Coefficient of Performance.

Thermodynamic modelling, based on measured heat transfer data, predicts a COP of 0.9 when evaporating at 5 °C and condensing at 40 °C, with the generating temperature of 200 °C and a modest system regenerator effectiveness of 0.8. The advantages of the system are:

(a) The four packed beds are in effect low cost, compact heat exchangers with a surface area per unit volume of 1500 m²/m³ or higher.

(b) There are only four conventional heat exchangers, and this is the minimum number allowed by the second low of thermodynamics. In addition to an evaporator and condenser, one is needed to accept high-grade heat in and one to reject the heat of adsorption to the environment.

(c) The cycle is highly regenerative and energy efficient since the packed beds act like large counterflow heat exchangers.
2.3.5 Cascading Cycles

Another means of improving cycle efficiency is to combine two separate cycles such that the adsorption heat rejected by one is sufficient in quantity and temperature to drive the other. This could be done with similar or different adsorbent - adsorbate combinations. Douss [25] experimented with a refrigerator in which a zeolite-water high temperature input cycle drove a carbon-methanol low temperature cycle. Critoph and Turner [26] carried out a theoretical analysis of a cascaded cycle using zeolite-ammonia and carbon-ammonia. These multiple bed cycles all seek to input heat at higher temperatures only and to reject heat at lower temperatures only. Thermodynamic considerations imply that this will lead to higher theoretical COPs. Generally, it has been suggested that theoretical refrigeration coefficient of performance’s as high as 1.8 are possible.

Whilst many configurations have been proposed [27], the multi-effect four-bed cascade cycle will be discussed so as to illustrate the complexity of such cycles. A numerical simulation has been completed to estimate the Coefficient of Performance.

The system configuration of a four-bed cascade adsorption refrigeration cycle [27] is shown in Figure 2.14. There are four adsorbers (A₁, A₂, B₁, B₂), one condenser (C), and one evaporator (E). A₁ and A₂ are part of a high temperature stage, where generation at about 200°C is initiated by heat input. The desorbed water vapour will go through the adsorber B₁ or B₂ in the low temperature stage to release heat for desorption. The adsorption pressures of the two stages are the same because only one evaporator is used in the system.
Figure 2.14. The system configuration of four-bed cascade adsorption refrigeration cycle: T-triple effects arrangement, D- double effect arrangement.

The working principle of the four-bed cascade adsorption refrigeration cycle can be described as follows:
Phase 1:

A₁ serves as a desorber and is heated to a high temperature, while A₂ serves as an adsorber and rejects heat to the desorber B₁. B₂ is also an adsorber, which rejects heat to the heat sink. The desorbed water vapour from A₁ can go through B₁ for further heat recovery, though the cooling process of A₂ normally heats B₁. As shown in Figure 2.15, the step from C to 1 is the adsorption process of adsorber A₂, which is a heat release process. This heat (including sensible heat and heat of adsorption) is not rejected to environment, but to the desorber B₁ to regenerate the low temperature stage, which forms a double effect arrangement (the D arrangement in Figure 2.14). If the desorbed water vapour from desorber A₁ is introduced to desorber B₁ to increase the heat input (the T arrangement in part (a) of Figure 2.14), a triple effect arrangement is formed. Thus, cooling of adsorber A₂ is accomplished by the heat transfer to the desorber B₁, while cooling of adsorber B₂ is accomplished by the heat rejection to the outside environment via a cooler. The cooling effect is induced by adsorption in A₂ and B₂.

![Clapeyron diagram of a four-bed cascading adsorption refrigeration cycle](image)

Figure 2.15. Clapeyron diagram of a four-bed cascading adsorption refrigeration cycle

Phase 2:

Heat recovery progresses in two stages: After adsorption in A₂ and B₂ and the regeneration of adsorbents in A₁ and B₁, appropriate valves are opened to invite to heat recovery. Adsorption starts when the bed pressure is lower than the evaporation
pressure, during the cooling of the beds. This may provide an opportunity to recover some of the adsorption heat, in addition to the sensible heat recovery. The heat recovery processes of the two stages stop at the respective heat recovery temperatures $T_{reg2}=T_{ef}$ and $T_{reg1}=T_{dc}$, shown in Figure 2.15. The heat recovery processes ensure good external heating to generate the high temperature stage will be along line d-3 only instead of a 1-2-d-3. Likewise, external cooling is along f-5 instead of 7-8-f-5.

**Phase 3:**
In phase 3 the phenomena of the first phase are reversed. So after the heat recovery processes of the two stages, $A_1$ is changed into an adsorber and $A_2$ into a desorber in the high temperature stage, while $B_1$ acts as an adsorber and $B_2$ as a desorber.

The above process shows that the desorption process in phase 1 for desorber $B_1$ is furnished by the heat from desorber $A_1$ and adsorber $A_2$ in the high temperature stage. The co-ordination of adsorption and desorption of the two stages is very important to operate the system properly. In addition the desorption pressure in desorber $A_1$ should be higher than desorption pressure of desorber $B_1$ to enable mass transfer. As has been already mentioned, water is the refrigerant in the cascade system; the desorbed vapour can go through the adsorbent bed in desorber $B_1$ to get a triple-effect installation.

Here, a double effect is accomplished with sensible and adsorption heat recovery to regenerate the low temperature stage, in addition to the heat input to the high temperature stage. Consequently a triple effect is accomplished with the heat recovery of the desorbed vapour in the high temperature stage, in addition to the heat used in a double effect arrangement to regenerate the low temperature stage.

In an ideal heat recovery process, the intermediate temperatures $T_7$ and $T_1$ would be equal. Here, $T_7$ is the desorption temperature of the low temperature stage adsorption cycle (5-6-7-8 in Figure 2.15) and $T_1$ is the adsorption temperature of the high temperature stage adsorption cycle (1-2-3-4 in Figure 2.15).
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The maximum energy recovery from the high temperature stage can be arranged by a triple effect system. The sensible heat of the adsorbent bed, the heat of adsorption and the latent heat of refrigerant vapour are fully used to drive the low temperature stage system. The assumption is that the cascading triple effect adsorption cycle is composed of two nearly independent continuous heat recovery adsorption refrigeration cycles. However the two stages are related each other by heat exchange. The low temperature stage (the first stage) and the high temperature stage (the second stage) have COPs of $\text{COP}_1$ and $\text{COP}_2$ respectively, expressed as:

$$\text{COP}_1 = \frac{Q_{\text{ref}1}}{Q_{hg1} - Q_{reg1}}$$

$$\text{COP}_2 = \frac{Q_{\text{ref}2}}{Q_{hg2} - Q_{reg2}}$$

where $Q_{\text{ref}}$: the refrigeration effect, $Q_{\text{reg}}$: the heat regenerated

The two stages contribute refrigeration effects $Q_{\text{ref}1}$ and $Q_{\text{ref}2}$ to furnish the total refrigeration $Q_{\text{ref}}$. Where $Q_{hg}$ is the heat needed for heating generation, which corresponds to the processes 1-2-3 or 5-6-7 of a single stage cycle in Figure 2.15, $Q_{\text{reg}}$ is the heat recovered from the heat recovery process.

The COP of a double effect cascade adsorption cycle can be defined as:

$$\text{COP} = \frac{Q_{\text{ref}}}{Q_{hg2} - Q_{reg2}} = \frac{Q_{\text{ref}1} + Q_{\text{ref}2}}{Q_{hg2} - Q_{reg2}}$$

If Equation (2.24) is applied to Equation (2.30), then it is apparent that:

$$\text{COP} = \text{COP}_2 + \text{COP}_1 \cdot \frac{Q_{hg1} - Q_{reg1}}{Q_{hg2} - Q_{reg2}}$$

According to the first law of thermodynamics:

$$Q_{hg2} + Q_{\text{ref}2} = Q_{1-4-1} + Q_2$$
in which $Q_2$ is the heat released from the desorbed vapour to low temperature stage, $Q_{3-4-1}$ is the sensible heat of cooling process together with the heat of adsorption of the second stage. In an ideal case, the heat released from high temperature stage is used completely to generate the low temperature stage, which gives:

$$Q_{ng1} - Q_{reg1} = (Q_{3-4-1} - Q_{reg2}) + Q_2 \quad (2.33)$$

If (2.32) and (2.33) are combined, then equation (2.31) can be expressed as

$$COP = COP_2 + COP_1 \cdot \frac{Q_{ng2} - Q_{reg2} + Q_{ref2}}{Q_{ng2} - Q_{reg2}} \quad (2.34)$$

Finally, the following equation is obtained:

$$COP = COP_2 + COP_1 \cdot (1 + COP_2) = COP_1 + COP_2 + COP_1 \cdot COP_2 \quad (2.35)$$

The above equation shows clearly the relation between the cascading cycle COP and two independent stage cycle COP$_1$ and COP$_2$. A typical example is that if both stages have COP=0.5, then the COP of the triple effect system is 1.25.

Sometimes cascading cycles contain the mixture of pairs, or even different systems (liquid adsorption or chemical reaction). Moreover, their cooling effect is continuous. Several kinds of advanced cycles have been proposed and tested.

Meunier [28] computed the first and second law efficiencies of cascading cycles using the zeolite/water pair, as a function of the number of cascades.

Zeigler [29] proposed a cascading two-stage sorption system contain a zeolite/water pair in the high temperature stage and a lithium bromide/water pair in the low temperature stage. Moss and Shahidullah [30] proposed a two-stage cycle containing a zeolite/water pair in the high temperature stage and a calcium chloride/methanol pair in the low temperature stage.

Meunier [31] presented four cases of cascading solid adsorbent cycles operating at high regenerating temperatures. One of these cycles is a double effect zeolite/water cycle; the three other cycles consist in a low temperature active carbon/methanol cycle. Production of refrigeration is possible at around $-10^\circ C$ with a COP as high as 0.85.
2.4 Adsorption Pairs

The choice of adsorbent/adsorbate pair used and the design of the adsorbent bed is important. Many researchers examine different working pairs in basic adsorption systems [32], [33]. The most common used are: activated carbon/ammonia, activated carbon/methanol, zeolite/water and silica gel/water. The different adsorption systems using activated carbon, zeolite and silica gel, and their performances are presented in this part of the literature review.

2.4.1 Machines Using Activated Carbon

Many different types of systems have been investigated, using activated carbon as an adsorbent. One of the biggest groups is from the University of Warwick with Dr R. Critoph as the co-ordinator. Various changes were made to improve the heat transfer, Coefficient of Performance, and system cost. Important findings are described below.

Critoph [34] developed a solar refrigerator by using a carbon ammonia cycle in 1994. A bank of 75W incandescent lamps simulated the solar radiation. A number of tests were carried out, at steady and diurnal irradiation with peaks of 100, 750 and 500 W/m$^2$. The largest calculated COP had a value of 0.33 and was obtained at a constant irradiance of 925 W/m$^2$, whilst the lowest value, 0.24, was obtained at a diurnal irradiance of 500 W/m$^2$. The refrigeration machine worked reliably.

As a continuation of the work, Tamainot-Telto and Critoph [35] presented a prototype compound parabolic concentrating (CPC) solar energy collector for sorption refrigeration. It consists of two CPC reflectors, two absorbers and a single glazing cover. The absorber is made of seamless steel tube covered in a selective surface (absorptance 0.95) and contains aluminium fins, activated carbon and ammonia. The
concentration ratio of the collector is about 2.4. It was designed for a solar power input of about 500 W and could provide a cooling power up to 120 W.

Thereafter, Critoph [36] tested ammonia, R32 and butane as refrigerants in new monolithic carbon adsorbents. This included a coconut-shell based carbon known as Speakman 208C, a compressed, monolithic form of the 208C, and a PVDC (polyvinylidene chloride), which can be compressed into shape and carbonised without cracking or deforming.

A test rig was constructed and consisted of a stainless steel vessel for containing the adsorbent. The temperature in the carbon was maintained constant, whilst the vessel pressure was controlled by means of varying the adsorbate inflow. The calculation of the cycle was based in the equation stated by Dubinin and Astakhov [37]. A numeric simulation was developed for some combinations of refrigerants and absorbents in order to find the values of $x_0$, $k$ and $n$, necessary to evaluate the cycle.

The COP for ammonia was 0.365, three times greater than for R32 and butane. For the adsorbents, monolithic carbon always gave slightly better performance than 208C in COP terms and only required about 75% of the pressure-vessel volume. The PVDC-based carbon had marginally better COP than the carbon monolith at generator temperatures around 200°C.

In a later study, Tamainot-Telto and Critoph [38] constructed a prototype of an adsorbing cooling machine that used an activated carbon-ammonia pair. A finned aluminium steam channel permits heat transfer to a monolithic carbon. The monolith adsorbs or desorbs ammonia. An annular channel bounds the monolithic carbon.

The maximum COP and the specific cooling power over the whole cycle were 0.120 and 60W/kg carbon. One reason for the low COP value was because the generating temperature was low and there was no heat recovery between the heating and the cooling phases.

The numerical model was validated through the comparison between the simulation and experimental results. That model neglected the resistance to mass transfer but took into account the heat transfer in the adsorbent bed and the heat transfer coefficient.
between the adsorbent beds and the fins. The model was about ten times more sensitive to the heat transfer coefficient than to the thermal conductivity of the bed.

Miles and Shelton [39] also tested the activated carbon-ammonia pair. Several prototype systems with a high-efficiency regenerative cycle have been designed, built and tested. Seasonal performance based on this experimental data and computed using the ANSI Standard Z21.40 for performance rating of gas-fired heat pumps is presented.

Wang et al [40] proposed an activated carbon-methanol pair together with spiral plate heat exchangers as a prototype heat regenerative adsorption refrigerator. The adsorption system using 12 kg activated carbon has a cycle time of 40 min. The experimental results show the system can make more than 1-kg ice per kg adsorbent per day.

### 2.4.2 Machines Using Silica Gel

The silica gel pair has been selected for study because its regeneration temperature is lower than that of other adsorbents (below 100°C, and typically about 85°C). It also has a large uptake capacity for water, up to 40% of its dry mass.

Hulse [41] used the adsorption of vapour into silica gel in refrigeration equipment in 1929. The silica gel-sulphur dioxide pair was applied to a propane-fired, air-cooled train refrigeration system for cooling cargo wagons down to −12°C. Chihara, Suzuki, and Sakoda, Suzuki [42] has studied the use of silica gel-water pair in solar cooling. A thermally driven heat pump using a solid-vapour adsorption-desorption cycle was analysed by Shelton et al. [43]. Recently, the use of waste-heat-driven systems has led researches to investigate cycles that can be driven by heat sources with temperatures of less than 100 °C. The silica gel-water pair is well suited to this temperature range.

Chua et al. examined a twin bed adsorption chiller [44]. The system uses silica gel packed around the fins of the heat exchanger tubes, and water. The cycle time and the bed switching time were investigated as a crucial part of system performance.

Matsushita et al. [45] has developed a commercialised silica gel-water chiller that is the object of the present study.
Saha, Boelman and Kashiwagi [46] analysed a chiller consisting of two pairs of heat exchangers, and two fixed adsorbent beds. The system was operated in a pseudo-continuous batch cycle, where the adsorber and desorber repeatedly switched between two modes. When the refrigerant concentrations in the adsorber and desorber approach equilibrium levels, the two units reverse roles and the cycle continues. In other words, the adsorber becomes a desorber and vice versa.

The authors discuss the production rate of chilled water, but in effect, this is closely related the heat load on the evaporator. Therefore, the evaporator heats load and COP increases with the flow rate of cooling water in the condenser, or the heat load in the desorber.

The COP showed a weak sensitivity to operating temperatures. Although the cooling output decreases with smaller regenerating temperature lifts, so does the consumption of driving heat required for sensible heating of the silica gel, metal, and adsorbed refrigerant masses.

Long cycle times (more than 360 seconds) result in COP gains and cooling outputs losses, thus making longer cycle times particularly suited to partial load operation. The maximum cooling output was obtained for cycle times between 180 and 360 seconds, which makes this range ideal for full-loaded operations.

In a second paper Boelman, Saha and Kashiwagi [47] investigated the possibilities of driving the silica gel-water adsorption in commercially available chillers. Their results correlated well against results from the previous work. The highest experimental values of COP, more than 0.4, were obtained with a hot water inlet temperature of 50 °C in combination with cooling water at 20 °C.

The same authors published in a later report [48] the results from their investigation about the influence of thermal capacitance and heat exchanger UA-values (adsorber/desorber, evaporator and condenser) on cooling capacity and COP. The refrigeration cycle and the simulation model were similar to that described below. This study revealed that increasing the mass of the adsorber to 100 kg is beneficial to the
cooling capacity while the power density and the COP decrease moderately. However, the UA-values proposed in the simulation were relatively high in this region. In contrast, for heavy heat exchangers, i.e. \( m_{\text{adsorber}} \) greater than 100 kg, the cooling capacity starts to decrease. This was attributed mainly to the fact that the UA values are too low for these conditions.

Saha and Kashiwagi [49] investigated the possibility of utilising an advanced three-stage cycle, that allows to use heat source at 50°C with a heat sink at 30°C. (That is, the machine use low-grade waste heat.) They found good quantitative and qualitative agreement between the data obtained experimentally and those obtained with the simulation. However, the agreement for the experimental and simulated COP was only qualitative.

Tangkengsirisin et al. [50] proposed the silica gel-water couple for solar-powered adsorption cooling. Metallic solar collectors with fins have been used to increase the thermal conductivity in solar collectors. The addition of activated carbon to the silica gel improves desorption rate and the regeneration temperature of the packed bed.

Oertel and Fischer [51] developed a solar-hybrid cooling system, using solar energy from flat plate collectors and the waste heat of a generating set, operated with producer gas, for the cold storage of agricultural products at temperatures of 2-4 °C in India. A commercially available low temperature (80 °C -90 °C) adsorption cooling system for air-conditioning applications has been modified for operation at cooling temperatures below the freezing point of water. Methanol instead of water is investigated as a refrigerant. Because of the inherent thermodynamic properties of methanol and the lower temperature of operation, the efficiency is reduced. The COP for a commercial adsorption cooling system is about 30%. When operating the system with methanol/silica gel at a chilled water temperature of \( T_0=-2 \) °C, the heating water temperature \( T_h=85 \) °C and the condenser temperature of \( T_c=30 \) °C (COP=0.5).
2.4.3 Machines Using Zeolite

Tchernev and Emerson [52] proposed the development of a gear pump connecting a pair of serpentine, transferring energy between zeolite and a working fluid. Each exchanger had the function of a condenser or evaporator, depending on the direction of the gear pump.

The heat exchanger was designed to generate a sharp temperature front in the zeolite. The features that ensured this were a small Biot number (using a solid geometry length scale) and a low fluid specific heat capacity (relative to that of the zeolite, when augmented by desorption). Thereafter the COP obtained was 1.2.

Schwarz, Keller and Soltes [53] analysed the adsorption of water in a zeolite bed. The rig consisted of a box shaped storage tank with eight thermocouples positioned vertically in the middle of the tank. The sensor measured the temperature of the vapour leaving the zeolite.

As soon the water reached the zeolite, individual water molecules were drawn into the pores, while at the same time, heat was released. The reaction zone rapidly became hotter, so those water molecules not yet adsorbed evaporated on the surface of the zeolite particles.

The surface temperature of zeolite in water could not exceed the saturation temperature of 100°C associated with ambient pressure. If the surface had not been completely wetted, the temperature of the particles increased to 300°C.

During the adsorption phase, the working fluid first filled the micropores, then the macropores, and finally, the void space between the zeolite particles. This order was reversed during regeneration. First, the water that filled the void volume was released.

The regeneration phase can be subdivided into a drying and a storing period. During the drying period, the regeneration energy evaporated the water from the surface, and from macropores inside the zeolite particles. Once the temperature of zeolite exceeded 100°C the storage period started. Any further heat influx released the water adsorbed in the
micropore structure of the zeolite. In this part of the cycle, the zeolite loading decreased with increasing temperature.

With co-workers, Cacciola and Restuccia have built the following systems:

- A shell and finned-tube heat exchanger located in a zeolite bed. Technical and economical development of a system for civil use depends mainly on the solution of heat and mass transfer problems [54].
- A series of adsorbers/desorbers in which thin zeolite layers were bounded to the heat exchanger tubes. Both zeolite-water and carbon-methanol pairs were studied. The former was recommended for air conditioning applications [55].

Their theoretical work supports these experiments, and in some cases identifies the appropriate pairs for given duties. They [56] discuss various applications based on the adsorption/desorption of water vapour in a zeolite. The procedure is based only on thermodynamic calculations using the adsorption data of different types of zeolite. All systems are examined showing the principle of operation, the thermodynamic cycles and the related thermal balances. Zeolite 13Xd is the best to use in a chemical pump, followed by 4A, 3A, and 5A in this order. The Coefficient of Performance is 1.65 and the energetic efficiency is 0.7. This type of zeolite is also the most suitable to be used in the cooling system, where the COP obtained is 0.65 and the refrigeration effect is 0.151 kWh/kg of zeolite. A detailed thermodynamic analysis of simple and regenerative cycles of an adsorption heat pump is also presented [57]. The specific heat of the adsorbate has been studied. The integral functions of the incoming and outgoing energy for the regenerative cycle using two isothermal reactors have been calculated in order to make the model more flexible and accurate. The zeolite-water system is more effective for use in the domestic sector of southern Europe climate than the same system using the activated carbon-ammonia pair.

Hajji and Worek [58] simulated regenerative, closed cycle adsorption cooling or heating systems with a zeolite-oil heat exchanger and water as a refrigerant. Tchernev first described the concept of regenerative heat exchange. The system consists of two containers each having a zeolite-oil heat exchanger located in the centre.
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These containers operate as adsorber and desorber for producing cooling or heating and ton regenerate the desiccant. Two coils are integrated into the wall of each container. If the container operates as a condenser, the heat generated when the adsorbate condenses on the wall is removed by one of the hydronic loops and is discharged in a cooling tower. If the container operates as an evaporator, the adsorbate, flowing on the container wall, evaporates the fluid in a second hydronic loop, which is used to provide cooling. A reversible pump is used to circulate oil at 200°C in a closed loop from a boiler through the zeolite-oil heat exchangers and the oil-air heat exchangers. The oil-air heat exchangers are used to cool the oil to approach the outdoor temperature before entering the container where the adsorption process takes place. For an infinite transport coefficient, the COP for refrigeration is 2.05.

Zhenyan, Yunzhuang and Jiaxin [59] studied a compound zeolite 13X-active carbon adsorbent (CZACA) with water, which enhances the heat transfer in the adsorbent bed by absorbing solar energy directly and decreases the desorption cycle time in a solar cooling system. A special solar cooling tube was used, which had a 41-mm internal diameter and was 1.5 m long. It consisted of adsorbent bed, condenser and evaporator, which formed a complete cooling system. The cycle COP of the system reached its maximum values 0.5 when the desorption temperature was about 20°C higher than the condenser temperature.

Tatlier and Erdem-Senatalar [60] investigated zeolite 4A and 13X-water pairs for a solar adsorption heat pump. Stainless steel wire gauzes, coated with zeolite, are pressed to one surface of the collector to ensure effective heat transfer. The presence of the thermal gradients in a solar collector is observed to decrease the COP values.

Zhang [61] describes an experimental adsorption cooling system driven by the waste heat from a diesel engine. Zeolite 13X-water is used as the working pair and a finned double-tube heat exchanger is used as the adsorber. Experimental results show that this prototype can be successfully used for air-conditioning. The COP of the system is 0.38.
Tchernev [62] proposed a zeolite CBV 901-methanol pair for use in a waste heat driven automotive air-conditioning systems. The low regeneration temperature required with this type of zeolite (100°C) makes it a prime candidate for the cooling system proposed in this thesis.

It can be noticed the COP for adsorption cycles is much lower than Carnot's. Meunier and Neveu [63] analysed cycles in terms of entropy production. In the case of basic cycle for the studied zeolite-water pair, they introduced two equivalent, inter-dependent Carnot cycles. The coupling between regeneration and adsorption temperature and the inverse refrigeration Carnot cycle operating between evaporation and condensation. The difference between the entropic temperatures and the real heat temperatures was an exact measure of the entropy production. The large entropy production due to external thermal coupling was visualised for the two solid-gas systems, at the levels of adsorption and regeneration temperature.

2.5 Heat and Mass Transfer

The possibility of decreasing the cycle times in adsorption refrigeration/heat pump systems drew attention to the limiting factors of the systems. Improving the efficiency of the heat transfer inside the machine and finding the economic compromise between mass and heat transfer at the crucial points is to be considered here [64]. There are mainly two types of resistance to heat transfer in a system containing a solid adsorption bed and heat exchanger tubes. The first one occurs at the metal-adsorbent interface and depends on the physical contact between the materials. The lack of good contact between the metal surface and the adsorbent creates a steep thermal gradient at the interface. The inefficient heat exchange is mainly due to the shape of the adsorbent particles, generally spheres or cylinders, which do not allow a good contact between the adsorbent solid surface and the metal of the heat exchanger. In order to reduce this thermal resistance, a suitable shape of the solid bed with a smooth surface should be sought.

The second resistance is associated with heat transfer inside the adsorbent bed and is inversely proportional to the thermal conductivity of the bed, which is generally low.
As a result of these studies, it may be concluded that the connection between the grains must be as large as possible, binders with high thermal conductivity must be well bound with the adsorbent and consolidated samples must be used [65].

One of the proposals to increase the thermal conductivity of the adsorbent bed involves the formation of a composite material made of metallic foam and zeolite [66]. In order to achieve such a result the zeolite powder is suspended in a silico-aluminate gel and a metallic foam mesh is filled with the paste obtained. The resulting compound is compressed and the composite is withdrawn from the mould after consolidation at 1000 °C for 3 hours. The thermal conductivity of the composite material thus obtained is reported to increase 92-fold with respect to that of a granular bed. However, a crucial point has been overlooked, namely the resistance to mass transfer. The composite material compressed at high temperatures and pressures will be deprived of the high porosity necessary for a good mass transfer since the zeolite will no longer retain its microporous crystalline structure under those conditions. It has been reported that the optimum compromise should be achieved between the high porosity necessary for fast vapour diffusion and the high density required for good thermal conductivity [67]. The resistances to mass transfer which vary in accordance with the extent of the porosity and the thickness of the adsorbent bed might play an equally important role in limiting the performance of the system. Various other designs of adsorption refrigeration/heat pump systems have been proposed, all aiming to improve the heat and mass transfer inside the system.

One of the groups, working in this area is headed by Tatlier from Istanbul Technical University in Turkey. A novel arrangement was proposed to enhance heat and mass transfer in adsorption systems [64]. Zeolite 4A is synthesized as a continuous coatings on thick-walled stainless steel heat exchanger tubes, by way of hydrothermal crystallisation from solutions of sodium aluminosilicates. The amount of zeolite thus synthesized per unit area of a metal support was reported to be equal to 1 mg/cm². This corresponds to a zeolite film thickness of about 5 μm. The thermal conductivity of the composite material obtained this way is much greater than that of the zeolite alone.
From the results obtained, there is almost no temperature or mass gradient in the adsorbent layer and the duration of a single cycle is below 2 minutes.

In a further study the effects of the metal type and the thermal and mass diffusivities of the adsorbent on the performance of an adsorption heat pump were evaluated. (This system used zeolite 4A and water as a working pair [68].) The calculations were performed for two different wall thickness values (0.75 and 2.4 mm) of the heat exchanger tubes and various zeolite layer thicknesses. Copper, nickel and stainless steel heat exchanger tubes were tested for their suitability to be used in the system and the effects of the thermal and mass diffusivities were investigated in the ranges of $0.0004$ to $0.0023$ and $4 \times 10^{-7}$ to $1 \times 10^{-5}$ cm$^2$/s, respectively. As a result, the diffusion coefficient was observed to be the limiting factor for the system. It limited the optimum thickness of the zeolite layer synthesized on the metal tubes. The optimum values for wall thickness of 0.75 and 2.4 mm were found to be around 45 and 90 µm, respectively. The observed effects of the metal type and the thermal diffusivity of the adsorbent were not significant.

A novel method was proposed for the preparation of thicker zeolite coatings required [69]. The coating of the zeolite 4A on a stainless steel tube is prepared on a directly heated substrate, while the reaction in the solution is suppressed by keeping the solution at a lower temperature. The plates were cleaned before coating, and the synthesis was carried out in clear aluminosilicate solutions with a molar ratio of 10 Na$_2$O: 0.2 Al$_2$O$_3$: SiO$_2$: 200 H$_2$O. This composition has been found to be suitable for the preparation of zeolite 4A coatings.

The durations of the adsorption cycles were determined by Tatlier [70] and vary according to the zeolite layer thickness utilized. They were found to be equal to about 2 minutes and 1 hour for the cases employing zeolite thickness layer of 5 and 400 µm respectively.

Restuccia and Cacciola are the second recognized group working on synthesizing zeolites on metal. Their first work was done using the zeolite NaA [71]. Plates of 1cm$^2$, made of aluminium, nickel, stainless steel, titanium, copper and FeCr were investigated with respect to their coatability with this type of zeolite. The metal supports were
cleaned before contact with the zeolite synthesis mixture. Zeolite NaA was synthesized at 80 °C from a clear homogeneous solution with a composition of 5 SiO₂: Al₂O₃: 50 Na₂O: 1000 H₂O. Each synthesis of 3 to 5 hours gives a layer of 3-4 μm. After ten-repeated syntheses a firmly fixed compact layer of 25 μm is obtained. The disadvantage of this method is labour intensive and therefore expensive. Under stirred synthesis condition, thicker zeolite layers, of up to 200 μm each can be formed. The results indicate that the heat transfer properties of the metal supported zeolite system are significantly better than those of the conventional system.

Later, they proposed a new type of adsorbent bed consisting of a zeolite NaA layer chemically bound to metal sheets [72]. The procedure consists of two steps: preparation of zeolite layers starting from NaA zeolite powder with aluminium hydroxide as binder, and then binding of the adsorbent to the aluminium sheets. The binder content in the samples is generally about 20%. The thermal conductivity for a content of binder of 30-40% was measured to be 0.4 W/mK; four times that of a packed bed. The thermal resistance (when the thickness of the adsorbent layer is assumed to be 2 mm) of the new composite was 0.0047 °C/W, one order of magnitude lower than that of a pelletised bed (0.022 °C/W) of the same thickness. The heat transfer coefficient for a coated heat exchanger with a 2mm layer of adsorbent is about 3000 W/m²K, whereas it is 25 W/m²K for pelletised bed. Furthermore, the enhanced heat transfer properties allow an increase, of 4-5 times in the specific power.

A dynamic model was designed to analyse the system. The shorter cycle duration was attributed to the excellent heat transfer conditions provided by the metal bound consolidated powder arrangements. The specific power (per adsorbent unit mass) results in 432 W/kg for coated tubes with 5 mm zeolite 4A layer type bed against 141 W/kg for the pure powder.

Okada et al. investigated a soft solution process for the coating of faujasite type zeolite crystals on glass fibers [74]. Commercial SiO₂-Al₂O₃ glass fibres (SA fibres) and SiO₂ glass fibres (SO fibre) were reacted at 60-150 °C for various times with NaOH solutions containing NaCl mineralizer. The surface of the glass fibers was initially leached by the solution but after a certain time crystals of faujasite type zeolite precipitated on the fibres. Eventually the fibre surface was completely coated because
of an increase in the concentrations of Si and Al in the solution due to dissolution of the fibres, especially SO fibres. The important experimental parameters for the formation of faujasite type zeolite were found to be the mixing ratio of Sa/SO fibres, the reaction time, NaOH concentration and the amount of NaCl added. The lattice constant of the resulting faujasite type zeolite identified was zeolite NaX with a Si/Al ratio of 1.28.

Wojcik et al. [75] presented an adsorption heat pump with a thin synthesised zeolite layers on a heat exchanger. The system works with water as a refrigerant. The adsorber pressure mainly increases because of the rise in vapour mass. Zeolite layers on metal supports have a low amount of zeolite with respect to the void volume, because they are thin (<1 mm). This communication demonstrates that for such system the pressure does not rise by following the isosteric line, but rises with a much smaller slope. Therefore, the synthesis of thick zeolite layers (>1 mm) is more promising in heat pump applications (higher sorption capacity for water). In this respect, zeolite Y might be an option.

Davis et al. has reported a layer thickness as large as 1 mm [76]. The other advantage of zeolite Y is that can be synthesized on copper surfaces; copper heat exchangers have higher thermal conductivity than stainless steel heat exchangers. However, the zeolite/zeolite bond strength is very low because of the small or negligible peel strength. This is a practical disadvantage in handling coated heat exchangers; small shocks during the transportation and installation of the coated heat exchangers may easily result in damages.

Miltkau and Dawoud [77] presented a one-dimensional model describing combined heat and mass transfer during the adsorption/desorption of water vapour into/from a zeolite layer in a small-scale adsorption heat pump. The model is utilized to study the dynamics of both adsorption and desorption process, as well as to examine the influence of both the layer thickness, and the volume of the vapour phase of the adsorber/desorber heat exchanger on their time requirements. The duration of the adsorption process is found to be generally longer than that of the desorption process, depending on the zeolite layer thickness. Reducing the layer thickness by 50% results
in a reduction to 25% in the duration of the adsorption process and to about 33% of the desorption process. In order to get reasonable power densities from an adsorption heat pump using zeolite layers, the layer thickness must not exceed 2.5 mm. Moreover, the volume of the vapour phase of the adsorber/desorber heat exchanger has to be minimized, in order to minimize the unavoidable losses of the COP.

Tamainot-Telto and Critoph [78] investigated the thermophysical properties of monolithic activated carbon with the intention of designing a high performance generator for sorption refrigeration systems and heat pumps using ammonia as a refrigerant. A detailed experimental procedure for the estimation of thermal conductivity, permeability, porosity and specific heat of two types of monolithic carbon as adsorbents is presented. The heat transfer coefficient for the carbon block fabricated from a coarse powder has been measured to be 350 W/m²K. For a fine powder, it is about 800 W/m²K. The permeability of the coarse powder in both the axial and radial direction is significantly higher than that of fine powder. The specific heat of both samples was found to be very close. Typical values obtained with monolithic carbon sample for thermal conductivity is 0.44 W/mK and for carbon specific heat is 1080 J/kg K at 100 °C.

Consequently, the following conclusions can be drawn:

1. It is not useful to put metallic spheres or strips into the bed;
2. Binders and additives (e.g. graphite) with good thermal conductivity, or metallic foam must be well bound with the adsorbent powder;
3. The connection between grain and grain must be as large as possible;
4. Consolidated samples should be used.
2.6 Summary

As it can be seen from this literature review, the main drawbacks of adsorption cycles are their low Coefficient of Performance (COP) and long cycle time. These are mainly caused by the poor heat and mass transfer rate in the adsorption bed. Therefore, research work is mainly focused on how to enhance the cycle performance, for which there are several means. These are:

(a) find better working pairs;
(b) propose new types of adsorption cycles;
(c) intensify the heat and mass transfer in the adsorbent bed;
(d) decrease the cycle time.

In proposing new types of cycles, much has been discussed besides the basic cycle, such as twin-bed continuous cycle, heat recovery cycle, thermal wave cycle, cascade cycle, etc. Among these types of cycles, the basic cycle is suitable for recovering heat from intermittent heat sources, like solar energy; twin-beds cycles may be used to recover low-grade thermal energy, and will provide a pseudo-continuous cooling effect. The heat recovery cycle has a higher thermal efficiency, the thermal wave cycle has the highest theoretical coefficient of performance, but it is difficult to be realized in a prototype system. The cascade cycle can reach a high thermal efficiency, but the complex manufacture and operation of the system will prohibit wider use.

The comparison of the working pair for different types adsorption cycles, their applications and COPs are given in Table 2.1.
<table>
<thead>
<tr>
<th>Adsorbent/adsorbate pair</th>
<th>Application</th>
<th>COP (system type)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC/methanol</td>
<td>Icemaker</td>
<td>0.12-0.135 (solar)</td>
<td>Wang [79]</td>
</tr>
<tr>
<td>AC/methanol</td>
<td>Icemaker</td>
<td>0.12 (solar)</td>
<td>Li [80]</td>
</tr>
<tr>
<td>AC/methanol</td>
<td>Air-conditioning</td>
<td>0.56 (two-bed, heat recovery)</td>
<td>Restuccia, Cacciola [55]</td>
</tr>
<tr>
<td>AC/ammonia</td>
<td>Air-conditioning</td>
<td>0.56 (forced convection)</td>
<td>Critoph [21]</td>
</tr>
<tr>
<td>AC/ammonia</td>
<td>Solar cooling</td>
<td>0.33 (basic system)</td>
<td>Critoph [34]</td>
</tr>
<tr>
<td>AC/ammonia</td>
<td>Solar cooling</td>
<td>0.3 (two-bed, heat recovery)</td>
<td>Vasiliev et al., [81]</td>
</tr>
<tr>
<td>AC/methanol</td>
<td>Air-conditioning</td>
<td>0.5 (two-bed, heat &amp; mass recovery)</td>
<td>Wang [15]</td>
</tr>
<tr>
<td>Zeolite NaX/water</td>
<td>Air-conditioning</td>
<td>1.06 (cascade cycle)</td>
<td>Meunier [31]</td>
</tr>
<tr>
<td>AC35/methanol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zeolite NaX/water</td>
<td>Air-conditioning</td>
<td>0.68 (heat &amp; mass recovery)</td>
<td>Pons, Poyelle [18]</td>
</tr>
<tr>
<td>Zeolite NaX/water</td>
<td>Air-conditioning</td>
<td>1.2 (thermal wave)</td>
<td>Sward, LeVan, Meunier [20]</td>
</tr>
<tr>
<td>Zeolite 4A/water</td>
<td>Air-conditioning</td>
<td>0.43 (two-bed, heat recovery)</td>
<td>Restuccia, Cacciola [55]</td>
</tr>
<tr>
<td>Zeolite 13X/water</td>
<td>Air-conditioning</td>
<td>0.15 (solar)</td>
<td>Tchernev [82]</td>
</tr>
<tr>
<td>Zeolite 13X/water</td>
<td>Cooling system</td>
<td>2.05 (thermal wave)</td>
<td>Hajji, Worek [58]</td>
</tr>
<tr>
<td>Zeolite 13Xd/water</td>
<td>Cooling system</td>
<td>0.65 (basic system)</td>
<td>Restuccia, Cacciola [56]</td>
</tr>
<tr>
<td>Zeolite 13X+active carbon/water</td>
<td>Solar cooling</td>
<td>0.5 (basic system)</td>
<td>Zhenyan [59]</td>
</tr>
<tr>
<td>Zeolite 13X+graphite/water</td>
<td>Heat pump</td>
<td>0.9 (thermal wave)</td>
<td>Pons [83]</td>
</tr>
<tr>
<td>Silica gel/methanol</td>
<td>Cold storage</td>
<td>0.5 (two-bed)</td>
<td>Ortel, Fisher [51]</td>
</tr>
<tr>
<td>Silica gel/water</td>
<td>Cooling system</td>
<td>0.42 (two-bed, heat recovery)</td>
<td>Chua et al. [44]</td>
</tr>
<tr>
<td>Silica gel/water</td>
<td>Cooling system</td>
<td>0.4 (two-bed, heat recovery)</td>
<td>Boelman, Saha [46]</td>
</tr>
</tbody>
</table>

Table 2.1: Performance of different working pairs
A comparison of the working pair for adsorption cycles given in Table 2.1 shows that the zeolite/water pairs give the highest performance (COP up to 1.2). The applications are for ice making, cold storage, refrigeration and air conditioning. Applications in ice making and cold storage have been studied by coupling the solid-adsorption system to solar collectors. However, the maximum COP that could be obtained from the coupled zeolite/water and AC/methanol system is 1.06. The performance of the system depends as well on system design. For example, the highest COP for the basic one-bed system is 0.1-0.3 at specified conditions. However, higher COP can be achieved using thermal wave (1.2) or cascading cycle (1.06).

Heat and mass transfer characteristics of different types of reaction beds are also important consideration influencing the performance of the adsorption system. The literature review shows that two main resistances dominate the transfer of the heat from the thermal fluid to the adsorbent bed:

(a) The first one occurs at the metal-adsorbent interface and depends on the physical contact between the materials

(b) The second resistance is associated with the heat transfer inside the solid adsorbent bed and it is inversely proportional to the effective conductivity.

Arrangements involving adsorbent coatings synthesised on metal surfaces were recently proposed as part of a solution for the first problem. The coatings mostly use zeolite powder. To improve the heat transfer characteristics, limitations due to mass transfer needed to be considered, depending on the type of modification and the properties of the material used (graphite or binder), applying new assemble or mixing techniques, varying combination of material (percent in use), etc. For example, using consolidated zeolite and activated graphite adsorbents as compared with granulated beds could improve the effective thermal conductances of zeolite water system. [83]

As can be seen, many different aspects have to be considered when designing the adsorption system, starting from the adsorption pair, system arrangement and in particular the generator structure. These features are important to obtain the system with high Coefficient of Performance.
Chapter 2

References for Chapter 2


Chapter 2


Chapter 3

Adsorption Theory

3.1 Introduction


\textit{Adsorption: The adhering of atoms or molecules of gases, liquids, or solutes to exposed surfaces (usually of solids).} New Shorter Oxford English Dictionary

The purpose of this chapter is to explain the physical process of ‘adsorption’. The previous literature review covers the historical development of an understanding of adsorption, as well as a variety of expressions used in order to present adsorption process.

3.2 Principles of Adsorption

In 1848, Faraday observed the cooling effect obtained by adsorbing ammonia onto silver chloride. In 1920s, sulphur dioxide and silica gel were used for the air-conditioning of railway carriages in the USA (Leslie, Miller, and Hulse).

The term \textit{adsorption} appears to have been introduced by Kayser to indicate the condensation of gases on free surfaces, as opposed to gaseous \textit{absorption}, where the molecules of gas penetrate into the mass of the absorbing solid. In 1909, Mc Bain proposed the word \textit{sorption} to embrace adsorption on the surface of a material, absorption by penetration into the lattice of the solid and capillary condensation within the pores. Whereas absorption can involve liquid or solid absorbents, adsorption is associated only with solids [1].

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Brunauer [2] defined adsorption as follows: *When the gas or vapour is brought in contact with an evacuated solid the solid takes up a part of it.* The molecules that disappear from the gas phase either enter the inside of the solid or remain on the outside, attached to its surface. The former phenomenon is called absorption, the latter adsorption. Often the two occur simultaneously; the total uptake of the gas is then designated by the term sorption. The solid that takes up the gas or vapour is called the adsorbent, the gas or vapour attached to the surface of the solid is called the adsorbate. Most adsorbents are highly porous bodies with tremendously large internal surfaces. If the gas enters the inside of a solid two things may happen: either the gas merely dissolves in it, forming a solid solution or it reacts with the solid and forms a compound.

As explained by other authors, including Ponec [3], Oscik [4], Ruthven [5] and Suzuki [6], adsorption is a surface phenomenon occurring at the interface of two phases. Cohesive forces, including Van der Waals forces and hydrogen bonding, act between the molecules of all substances. Surface forces or unbalanced forces at the phase boundary cause changes in the concentration of molecules at the solid/fluid interface. The solid and the fluid adsorbed on its surface are referred to as adsorbent and adsorbate respectively. Adsorption due to a physical process is generally referred to as physical adsorption, or physisorption. In chemical process, adsorption is referred to chemical adsorption or chemisorption (involves valency forces). However all types of sorption are exothermic. The heat of adsorption is generally lower in physisorption than in chemisorption.
Chapter 3 Adsorption Theory

The general features, which distinguish physical adsorption from chemisorption, are as follows:

<table>
<thead>
<tr>
<th>PHYSICAL ADSORPTION</th>
<th>CHEMISORPTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lower heat of adsorption (&lt;2 or 3 times latent heat of evaporation).</td>
<td>Higher heat of adsorption (&gt;2 or 3 times latent heat of evaporation).</td>
</tr>
<tr>
<td>Non specific.</td>
<td>Highly specific.</td>
</tr>
<tr>
<td>Monolayer or multilayer. No dissociation of adsorbed species. Only significant at relatively low temperatures.</td>
<td>Monolayer only. May involve dissociation. Possible over a wide range of temperatures.</td>
</tr>
<tr>
<td>Rapid, non-activated, reversible. No electron transfers although polarisation of sorbate may occur.</td>
<td>Activated, may be slow and irreversible. Electron transfers leading to bond formation between sorbate and surface.</td>
</tr>
</tbody>
</table>

Table 3.1: Physical adsorption and chemisorption [5]

Desorption is brought about by either an increase in temperature or a decrease in external partial pressure; some chemisorption processes are irreversible. The general term ‘sorption’ is used when both adsorption and absorption occurs simultaneously. Depending upon adsorbent and adsorbate phases, adsorption system may be classified as solid/gas, liquid/gas, solid/liquid and liquid/liquid.

Another explanation of the term adsorption is the adhesion or retention of molecules of gas or liquid mixture brought into contact with a solid surface resulting from the force field at the surface. The process of adsorption involves separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another [7].

3.3 Adsorption Equation of State

The equations for physical adsorption can be classified into three types: [8]

(a) Adsorption equations based on adsorption speed, which are typically based upon single molecular layer adsorption. This results in the Langmuir equation.
(b) Thermodynamic adsorption equations, which are based on Polanyi adsorption potential theory and the Dubinin mini-pore filling theory
(c) Adsorption equations based on capillary condensation theory, which does not consider the effect of energy distribution around the adsorbent surface, but treats the mini-pores as capillaries. A good example is the Kelvin equation.
As well as the above equations, there are also some empirical equations, of which one example is based upon the assumption that adsorption capacity is a function of temperature and pressure, but the two parameters affect the adsorption independently, thus \( x = f(T, P) = f_1(T) f_2(P) \). The disadvantage of such an equation is that it needs a large quantity of experimental work, and the assumption cannot always express the adsorption characteristics properly.

The available theories to describe the adsorption cycles include the theories of Polanyi, Dubinin-Radushkevich (D-R) and Dubinin-Astakhov (D-A). Many authors have chosen them (with many simplifications) to explain modified basic equations [9].

### 3.3.1 The Langmuir Equation

The simplest and by far the most widely used expression for physical adsorption from ether gas or liquid solutions is the Langmuir equation [10]. This expression is commonly derived through a kinetic approach; in other words, from the assumed rate expressions of both adsorption and desorption and considering adsorption equilibrium as a state of dynamic equilibrium than both the adsorption and desorption rates are the same. The adsorption and desorption rates are assumed to be:

\[
\text{Rate of adsorption} \quad k_a p (1 - \theta) \\
\text{Rate of desorption} \quad k_d \theta
\]

where \( \theta = \frac{x}{x_0} \) and

- \( k_a \) - is the adsorption constant
- \( k_d \) - is the desorption constant
- \( \theta \) - is the surface coverage or frictional filling of the micropores.
- \( x \) - is the adsorbed phase concentration at equilibrium
- \( x_0 \) - is the adsorption capacity of the adsorbent
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\[ p \] - is the partial pressure in the gas phase

At equilibrium:

\[ k_u p(1 - \theta) = k_d \theta \] (3.3)

which, upon rearrangements, becomes

\[ \theta = \frac{x}{x_0} = \frac{Kp}{1 + Kp} \] (3.4)

or

\[ Kp = \frac{\theta}{1 - \theta} \] (3.5)

where

\[ K = \frac{k_u}{k_d} \] (3.6)

At low adsorbate concentrations \((x << x_0)\), Henry’s law is approached and equation (3.4) can be reduced to the Henry type Equation [11].

\[ \theta = Kp \] (3.7)

The Langmuir equation is being limited to single monolayer adsorption and assumes no interaction between nearby molecules on the surface. The energy of adsorption is the same all over the surface; molecules adsorb at fixed sites and do not migrate over the surface.

3.3.2 Freundlich Isotherm

Another type of the equation commonly used is Freundlich isotherm expression: [10]

\[ x = A \cdot p^{1/n} \] (3.8)

The Freundlich equation is the simplest equation for data representation. It does have some defects, namely, it fails to observe Henry’s law behaviour in the limiting situations of \( p \rightarrow 0 \).

The Langmuir expression can be modified in several ways to improve its fit with experiments. One of them is the Langmuir-Freundlich expression, which combine Equations (3.4) and (3.8) and is given as:
The Equation (3.9) contains three parameters: \( x_0 \), \( K \), \( n \) and for certain type of data (adsorption of hydrocarbon on activated carbon) is found to be better in data correlation compare with either Langmuir or Freundlich equations used separate.

### 3.3.3 The BET Equation

Brunauer, Emmett and Teller developed the BET theory [12]. As is in the case of Langmuir isotherm, the theory is based on the concept of an adsorbed molecule, which is not free to move over a surface and which exerts no side forces on adjacent molecules of adsorbate. The BET theory does allow different numbers of adsorbed layers to build up on different parts of the surface. The equation can be represented as:

\[
\theta = \frac{x}{x_0} = \frac{K \left( \frac{p}{p_s} \right)}{1 + \left( K - 1 \right) \left( \frac{p}{p_s} \right) \left[ 1 - \left( \frac{p}{p_s} \right) \right]} \tag{3.10}
\]

where \( p_s \) is the saturation vapour pressure of the adsorbate. Equation (3.10) is used than for multilayer adsorption.

The advantage of the BET is that can be fitted to different shapes of adsorption isotherm. In 1938, the classification of isotherms was proposed which consisted of five shapes shown in Figure 3.1. It is not possible to predict the shape of the isotherm for a given system, but it has been observed that some shapes are often associated with particular adsorbent or adsorbate properties.
The isotherms for microporous adsorbents, in which the pore size is not very much grater than the molecular diameter of the sorbate molecule, are normally of Type I. Charcoal, with pores just a few molecules in diameter, usually gives Type I isotherm. A non-porous solid is likely to give Type II. If the cohesive forces between adsorbate molecules are greater than the adhesive forces between the adsorbate and adsorbent, a Type V isotherm is likely to be obtained for a porous adsorbent and a Type III for a non-porous one. An isotherm of Type IV suggest the formation of two surface layers either on a plane surface or on the wall of a pore very much wider than the molecular diameter of the sorbate. The isotherms of Types II and III are generally observed only in adsorbents in which there is a wide range of pore sizes. In such systems there is a continuous progression with increasing loading from monolayer to multilayer adsorption and than to capillary condensation. The increase in capacity in high pressures is due to capillary condensation occurring in pores of increasing diameter as the pressure is raised. In the multilayer region, the adsorbed molecules will behave more like a liquid film. The amount of capillary condensation that occurs will depend on the pore sizes and their distribution as well as on the concentration in the gas phase.
3.3.4 Polanyi Potential Theory

Adsorption potential theory is based upon the potential energy distribution around the adsorbent surface, which is a theoretical model to describe multi-molecular layer adsorption. In this theory, the adsorbed layers are contained in an adsorption space above the adsorbent surface, which can be seen in Figure 3.2. The space is composed of equipotential contours, the separation of the contours corresponding to a certain adsorbed volume. Polanyi [13] suggested that the potential of a point in adsorption space is a measure of the work done by surface forces in bringing one mole of adsorbate to that point from infinity. (Or a point at such a distance from the surface that those forces exert no attraction) His model pays attention to the changes of Gibbs function at the surface brought about by adsorption. However, the physical model was not described in detail. Later, Dubinin [14] further developed this model; thus this theory is now also called as Dubinin-Polanyi adsorption potential theory.

![Figure 3.2: The concept of adsorption space used by Polanyi.](image)

Polanyi assumed that the adsorption potential energy $\varepsilon$ is independent of temperature over a wide temperature range, that is:

$$\left( \frac{\partial \varepsilon}{\partial T} \right)_{\nu,s} = 0$$

(3.11)
where \( V^s \) is adsorption volume, the potential function \( \varepsilon = f(V^s) \) is suitable for all temperature ranges for a known gas, and is thus called the characteristic adsorption function.

This assumption was verified for non-polar absorption and for a polar system with low coverage (Zhang, 1988). Based upon the Polanyi assumption [13], potential \( \varepsilon \) can be presented around the surface of the adsorbent. Adsorbed gas exists in a compressed state by the attractive forces acting from the surface (where \( \varepsilon = \varepsilon_{\text{max}} \)) to a certain distance (where \( \varepsilon = 0 \)) into the surrounding space. In this case, the adsorbate exists in a compressed state and its density is not constant, being a maximum at the solid surface and a minimum at \( \varepsilon = 0 \). Polanyi proposed that the adsorption potential \( \varepsilon \) might be represented by the equation for isothermal work of compression:

\[
\varepsilon = R \cdot T \cdot \ln \frac{P_2(T)}{P_1(T_{\text{sat}})}
\]

(3.12)

where:

- \( P_2 \) is the pressure of the compressed adsorbate on an equipotential surface, which equals the saturation pressure at \( T \),
- \( P_1 \) is the vapour-adsorbate equilibrium pressure corresponding to \( T_{\text{sat}} \), the fluid temperature at the evaporator or condenser,
- \( T \) is the adsorbent bed temperature.

So, \( \varepsilon \) is a function \( P_1 \) and \( T \) for a certain adsorbate, for which \( R \) is constant because \( P_2 \) is a quantity dependent on \( T \).

The equilibrium adsorption capacities is \( x = M_a / M_c = \rho V^s / M_c \), where \( \rho \) is a density of the liquid adsorbate at the adsorbent temperature, \( M_a \) and \( M_c \) are the mass of adsorbate and adsorbent respectively. Thus the adsorption potential energy \( \varepsilon \) can be expressed as \( \varepsilon = f_1(V^s) = f_2(x) \) or we can write \( x = f(\varepsilon) \).

Equation (3.12) is valid for all vapours and gases, so ideally the curve could be plot \( x \) versus \( \varepsilon \) and be valid for any material. In reality, the correction for the different interactions between adsorbent-adsorbate pairs has to be included.
3.3.5 The Dubinin-Radushkevich Equation

Dubinin and Radushkevich [14] have found that the adsorption potential in Equation (3.11) can be expressed as a Gaussian distribution function (the D-R equation):

\[ x = x_0 \cdot \exp \left( - k \cdot \left( \frac{e}{\beta} \right)^2 \right) \]  

(3.13)

where \( x_0 \) is explained as limiting adsorption capacity, \( k \) is a constant determined by the surface of the adsorbent, and \( \beta \) is the affinity coefficient which is determined by the adsorbent-adsorbate pair.

3.3.6 The Dubinin-Astakhov Equation

The theory [15] is based on the concept of the temperature invariance of a characteristic curve. This expresses the distribution of the degree of filling, \( \theta \), of the volume of the adsorption space versus \( A \), the differential molar work of adsorption. The observation of temperature invariance follows experimental observations, originally noted by Polanyi, but with a different interpretation. Determining the differential molar work of adsorption as a decrease in Gibbs' free energy (\( A = -\Delta G \)):

\[ A = RT \ln \left( \frac{p_s}{p} \right) = 2.303RT \log \left( \frac{p_s}{p} \right) \]  

(3.14)

where \( p_s \) is the pressure of the saturated vapour of the substance under study (standard reference state) at the temperature \( T \) or fugacity, and \( p \) is the equilibrium pressure. The characteristic curve equation of the theory may be represented as follows:

\[ \theta = \exp \left[ -kA^2 \right] = \exp \left[ -\left( \frac{A}{E} \right)^2 \right] \]  

(3.15)

An equivalent form of equation above is:

\[ \theta = \frac{x}{x_0} \]  

(3.16)
where \( x \) is the adsorption at temperature \( T \) and equilibrium pressure \( p \), and \( x_0 \) is the limiting adsorption value corresponding to the filling of the whole volume of the adsorption space \( W_0 \), or of the micropore volume. In addition, \( k \) or \( E \) are parameters of the distribution function \( (E = 1/\sqrt{k}) \). The limiting adsorption \( x_0 \), depends on the temperature as a result of the thermal expansion of the substance adsorbed. The temperature changes of \( W_0 \) are neglected. Let \( \rho^* \) be the density of the substance adsorbed at a limiting micropore filling, then:

\[
x_0 = W_0 \rho^* \tag{3.17}
\]

The term \( \rho^* \) is calculated to a good approximation according to M. M. Dubinin and K. M. Nikolaev [15] from a set of the physical constants of the substance. (These are the densities of the bulk liquid at the boiling point, and the constant \( b \) in the van der Waals equation, calculated from the critical temperature and pressure).

Later Dubinin and Astakhov suggested a quasi-Gaussian distribution equation based upon the theory of mini-pores filing, which is suitable for a distributes of adsorption mini-pores sizes:

\[
x = x_0 \cdot \exp\left(-\left(\frac{\varepsilon}{E}\right)^n\right) \tag{3.18}
\]

This is called the D-A equation, in which there are three constants. Dubinin suggested that \( n \) can be an integer between 2 and 6, \( E \) is the characteristic adsorption work determined by the energy properties of the adsorption system. It was later verified that \( n \) can be a non-integer, which extends the applications of Equation (3.18). This equation is simple but is only suitable for adsorbents with uniform surfaces and weak polar adsorbates.
According to the theory of Dubinin-Radushkevich [14], the volume $V$ occupied by the adsorbate is related to the total pore volume $V_0$ and to $\varepsilon$ by the following relation:

$$V = V_0 \cdot \exp \left[ - \left( \frac{B}{\beta^2} \right) \cdot \varepsilon^2 \right]$$  \hspace{1cm} (3.19)

where:

- $\beta$-is the affinity coefficient, taken as a ratio of the adsorbate molar volume at the temperature $T$ to that of a reference gas (normally benzene) at the same temperature,
- $B$-is a function of the adsorbent microstructure.

$$V = V_0 \cdot \exp \left[ - \left( \frac{B}{\beta^2} \right) \left( R \cdot T \cdot \ln \frac{P_2}{P_1} \right)^2 \right].$$  \hspace{1cm} (3.20)

In addition, the correlation between temperature and pressure for saturated adsorbate can be represented for example by the Clausius-Clapeyron Equation [16]:

$$\ln P = A - \frac{C}{T}$$  \hspace{1cm} (3.21)

where: $A, C$-depend on the adsorbate.

Substituting all this into D-R Equation (3.18) and introducing the density $\rho(T)$, the mass adsorbed $M(T, T_{sat})$ becomes:

$$M(T, T_{sat}) = M_0(T_{sat}) \cdot \rho(T_{sat}) \cdot \exp \left[ - \left( \frac{B}{\beta^2} \right) \left( R \cdot C \cdot \frac{T}{T_{sat}} - R \cdot C \right)^2 \right]$$  \hspace{1cm} (3.22)

where:

- $M_0(T_{sat}) = V_0(T_{sat}) \cdot \rho(T_{sat})$ because $\rho(T)$ is constant as $\rho(T_{sat})$ around the surface of the adsorbent when $T=T_{sat}$.

To allow a better fit to some adsorbent characteristics, an extension of the equation is introduced as in the following equation, which employs a variable index $n$ instead of 2:

$$M(T, T_{sat}) = M_0(T_{sat}) \cdot \rho(T_{sat}) \cdot \exp \left[ - \left( \frac{B}{\beta^2} \right) \left( R \cdot C \cdot \frac{T}{T_{sat}} - R \cdot C \right)^n \right]$$  \hspace{1cm} (3.23)
Introducing the mass ratio $x$ of adsorbed mass to the mass of adsorbent in this equation, and writing it in a simple form, Equation (3.23) becomes:

$$x(T, T_{sat}) = x_0(T_{sat}) \cdot \exp \left[ -k \cdot \left( \frac{T}{T_{sat}} - 1 \right)^n \right]$$

(3.24)

where $k$ represents value of $(B/\beta^2)(RC)^n$, which determined by the characteristics of both adsorbent and adsorbate and which is independent of temperature.

In the context of the theory presented above, Teng, Wang and Wu [9] simulated a basic adsorption cycle. Their study showed that $x_0$, $k$ and $n$ are important parameters for the performance of the adsorption cycle. From their results, it can be observed that there was one combination of $k$ and $n$ for a maximum COP and another different combination for a maximum refrigeration capacity. However, for the design of an adsorption system, there should exist an optimal combination of $k$ and $n$ for COP and refrigeration capacity. These authors presented a description of the influence of other parameters as $T_{amb}$, $T_{cond}$ and generator mass in the COP and refrigeration capacity. Unfortunately this study was only theoretical and their results were not checked experimentally.

### 3.3.7 Improved Adsorption Equation

There are several non-idealises in the reality that influence the accuracy of the above theories, and merit further corrections.

(a) **Modification of the assumption of an ideal gas.**

Wang and Wang [8] proposed improvements to the adsorption equations. They considered the real behaviour of vapour of the main refrigerants. Ammonia, water and methanol vapours are not ideal gases, as a result the Equation (3.2) was modified by including the fugacity instead of the pressure. Then:

$$\varepsilon_r = R \cdot T \cdot \ln \frac{f_1}{f_2}$$

(3.25)
Chapter 3 Adsorption Theory

$f_2$ and $f_1$ are the fugacities that replace pressures $P_2$ and $P_1$ respectively. The authors considered the polarity of the refrigerant by introducing the Martin-Hou state equation of polar gases. The last improvement to the equations was by considering a Gaussian normal distribution of the adsorption minipores, the result was:

\[
x = x_0 \cdot \exp \left( -R \cdot T \cdot \ln \left( \frac{f_1}{f_2} \right) \right)^{\frac{E_x}{T}} \quad (3.26)
\]

(b) Consideration of the polarity of adsorbents

The common refrigerant adsorbates in adsorption refrigeration are methanol, water, and ammonia. They are all strongly polar gases. Regarding the state equation of polar gases, the Martin-Hou equation (or more simply, the M-H equation) is commonly used. The constants in the M-H equation can be determined easily, and can be applied over a wide range of condition. It has been shown that the relative error of the M-H equation is less than 1\% if it is used for non-hydrocarbon gases, and it is more suited for the polar molecules such as water, methanol and ammonia. The M-H equation can be expressed as:

\[
p = \sum_{i=1}^{5} \frac{f_i(T)}{(V - b)^i} = \frac{RT}{V - b} + \frac{A_2 + B_2 T + C_2 \exp(-KT / T_c)}{(V - b)^2} + \frac{A_3 + B_3 T + C_3 \exp(-KT / T_c)}{(V - b)^3}
\]
\[
+ \frac{A_4}{(V - b)^4} + \frac{A_5 + B_5 T + C_5 \exp(-KT / T_c)}{(V - b)^5} \quad (3.27)
\]

in which $K=5.475$, and there are eleven constants shown in table below.
Table 3.2: Constants of M-H equation for various refrigerants

<table>
<thead>
<tr>
<th>M-H constants</th>
<th>Methanol</th>
<th>Water</th>
<th>Ammonia</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_2 \times 10^7$</td>
<td>-1.181884</td>
<td>-0.7347924</td>
<td>-0.51407794</td>
</tr>
<tr>
<td>$A_3 \times 10^9$</td>
<td>0.9823941</td>
<td>0.3367519</td>
<td>0.25238453</td>
</tr>
<tr>
<td>$A_4 \times 10^{10}$</td>
<td>-4.911565</td>
<td>-0.6221217</td>
<td>-0.71432305</td>
</tr>
<tr>
<td>$A_5 \times 10^{11}$</td>
<td>-10.96979</td>
<td>-0.9647009</td>
<td>-0.64793943</td>
</tr>
<tr>
<td>$B_2 \times 10^4$</td>
<td>0.9605366</td>
<td>0.5867358</td>
<td>0.47427270</td>
</tr>
<tr>
<td>$B_3 \times 10^8$</td>
<td>-5.55264</td>
<td>-2.162056</td>
<td>-1.1981187</td>
</tr>
<tr>
<td>$B_4 \times 10^8$</td>
<td>41.58169</td>
<td>2.432953</td>
<td>1.1981187</td>
</tr>
<tr>
<td>$b \times 10^2$</td>
<td>0.1265582</td>
<td>0.06601304</td>
<td>0.10464551</td>
</tr>
<tr>
<td>$C_2 \times 10^8$</td>
<td>-4.55933</td>
<td>-2.37388</td>
<td>-1.1226807</td>
</tr>
<tr>
<td>$C_3 \times 10^{10}$</td>
<td>5.609259</td>
<td>1.365615</td>
<td>0.79905689</td>
</tr>
<tr>
<td>$C_5 \times 10^{13}$</td>
<td>-8.947510</td>
<td>-0.4708418</td>
<td>-0.40828723</td>
</tr>
<tr>
<td>$k$</td>
<td>5.475</td>
<td>5.475</td>
<td>5.0</td>
</tr>
</tbody>
</table>

(c) Considerations of non-uniform distribution of adsorption mini-pores.

The modified D-R Equation (3.13) with fugacity is:

$$x = x_0 \exp\left( -k \left( \frac{\varepsilon}{\beta} \right)^2 \right) = x_0 \exp\left( -B_j \left( \frac{T^2}{\beta^2} \ln^2 \left( \frac{f_0}{f} \right) \right) \right)$$ (3.28)

Considering that most of the commonly used materials, such as activated carbon, and zeolite, have a heterogeneous collection of mini-pores, adsorption should be expressed in the form of a sum of contributions from different pore sizes,

$$x = \sum_j x_{0j} \exp\left( -k_j \left( \frac{\varepsilon_j}{\beta} \right)^2 \right) = \sum_j x_{0j} \exp\left( -B_j \left( \frac{T^2}{\beta^2} \ln^2 \left( \frac{f_0}{f} \right) \right) \right)$$ (3.29)

where $B_j = k_j R^2$, $x_{0j}$ and $B_j$ correspond to a given size of mini-pores. For the sake of mathematical convenience, the continuous distribution $f(B)$ for the adsorption concentration $x_{0j}$, and $x_{0j} = f(B_j) \delta B_j$ can be used. The sum is then replaced by the integral
Chapter 3 Adsorption Theory

\[ \int_{0}^{\infty} f(B) dB = 1 \quad (3.30) \]

For a given size of mini-pore characterised by \( B_j \), the adsorption equation can be treated as \( x_j = x(T, p, B_j) \). For an adsorption surface, the total adsorption capacity can be integrated with the characteristic adsorption of mini-pores multiplied by its distribution to get:

\[ x = \int_{0}^{\infty} x(T, p, B) f(B) dB \quad (3.31) \]

Two groups of adsorption pores with different distributions (uniform and non-uniform) can be discussed.

(a) Uniform distribution of pore sizes (examples are activated carbon fibre, carbon zeolite, etc.)

The pore sizes are limited to a small range \([B_1, B_2]\), thus the pore distribution function can be assumed as a constant, \( f(B) = \text{const} \ (B_1 < B < B_2 \text{ and } \Delta B = B_2 - B_1 \to 0) \). Thus, we get a distribution function as:

\[ f(B) = \frac{1}{B_2 - B_1} \quad (3.32) \]

which yields Equation (3.29) as:

\[ x = \int_{B_1}^{B_2} \frac{1}{B_2 - B_1} x(T, p, B) dB \quad (3.33) \]

In the limit that the range of pore sizes is sufficiently narrow \( \Delta B \to 0 \), and thus \( x(T, p, B) = \text{const} = x_{B_1} , (B_1 \leq B \leq B_2) \) in this range. The simple form obtained is:

\[ x = x_i = x_{i0} \exp \left[ - \left( \frac{RT \ln(f_0 / f)}{E_i} \right)^{n_i} \right] \quad (3.34) \]
(b) Non-uniform distributions of pore sizes in adsorbent surface (examples are activated carbon, zeolite, etc.)

The non-uniform pore adsorption can be treated as collection of pores of various sizes. The random distribution of pore sizes can usually be supposed as a Gaussian normal distribution with a half-width of $\Delta$ (Stoeckli, 1977),

$$f(B) = \frac{1}{\Delta \sqrt{2\pi}} \exp\left[-\frac{(B - B_0)^2}{2\Delta^2}\right]$$  \hspace{1cm} (3.35)

where $B_0$ is a constant. In Equation (3.35) the characteristic pore size $B$ is corresponding to the adsorption capacity $x(T, p, B) = x_{B_0} \exp\left(-k(\varepsilon / \beta)^2\right)$, thereby

$$x = \int_0^\infty f(B) x_{B_0} \exp(-By) dB$$  \hspace{1cm} (3.36)

The variable $y = (T / \beta)^2 \ln^2(f_o / f)$ already contains the adsorptive-dependent shifting factor $\beta$ (affinity factor), and therefore simplifies the overall graphical representation. The total adsorption concentration of the pores in the solid is given by the normalised condition:

$$x_0 = \int_0^\infty x_{B_0} f(B) dB$$  \hspace{1cm} (3.37)

From a mathematical point of view, the general expression Equation (3.36) is an integral of a Laplace type with the D-R Equation as main core equation. This yields a Gaussian-based equation for the filling of the pores (Stoeckli, 1977):

$$x = x_0 \exp(-B_0y) \exp(y^2 \Delta^2 / 2) [1 - \text{erf}(z)] / 2$$  \hspace{1cm} (3.38)

This is a modified equation, where $z = (y - B_0 / \Delta^2) \Delta / 2$, and $\text{erf}(z)$ is the error function. This equation contains three parameters: $x_0, B_0$ and $\Delta$, which can be determined by adsorption experiments.
3.4 Summary

Different equilibrium equations are used, depending on adsorption pair. In Table 3.3, the equations mostly used by researches to fit the experimental data are presented.

### Table 3.3: Adsorption equilibrium equations summary

<table>
<thead>
<tr>
<th>Adsorbent/adsorbate pair</th>
<th>Equilibrium equation</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC/butane</td>
<td>Modified Dubinin-Astakhov (D-A) equation</td>
<td>Critoph [17]</td>
</tr>
<tr>
<td>AC/R22</td>
<td>$x = x_0 \exp \left[ -k \left( \frac{T}{T_{sat}} - 1 \right)^{n} \right]$</td>
<td></td>
</tr>
<tr>
<td>AC/ammonia</td>
<td>Modified D-A equation</td>
<td>Qu et al. [18]</td>
</tr>
<tr>
<td>Zeolite 13X, 4A, 5A/water</td>
<td>Dubinin-Astakhov equation</td>
<td>Tatlier et al. [19]</td>
</tr>
<tr>
<td>Zeolite NaX/water</td>
<td>Dubinin-Radushkevich (D-R) equation</td>
<td>Ben Amar, Sun, Meunier [20]</td>
</tr>
<tr>
<td>AC/ammonia</td>
<td>$x = x_0 \exp \left[ -k \left( -\frac{A}{E} \right)^{n} \right]$</td>
<td></td>
</tr>
<tr>
<td>Zeolite NaX/ammonia</td>
<td>D-R equation</td>
<td>Sun, Pons [21]</td>
</tr>
<tr>
<td>Zeolite 4A, 13X/water</td>
<td>$\ln(p) = a(w) + b(w)/T$</td>
<td>Restuccia, Cacciola [22] Zang [23]</td>
</tr>
<tr>
<td>AC/ammonia</td>
<td>Hajji [24]</td>
<td></td>
</tr>
<tr>
<td>AC/methanol</td>
<td>D-A equation</td>
<td>Wang [8]</td>
</tr>
<tr>
<td>Zeolite/water</td>
<td>Freundlich equation</td>
<td>Saha, Boelman [25]</td>
</tr>
<tr>
<td>Silica gel/water</td>
<td>Langmuir equation</td>
<td>Ng et al. [26]</td>
</tr>
</tbody>
</table>

The Dubinin-Astakhov and Dubinin-Radushkevich are the equations mainly used now. However, data for some adsorbent/adsorbate pairs need to be fitted using Freundlich or Langmuir equations, which in some cases are giving better match.
References for Chapter 3


Chapter 3

Adsorption Theory


Chapter 4

COP Predictions for Different Pairs

4.1 Introduction

The objective of this chapter is to predict the Coefficient of Performance and best possible working pair for given adsorption refrigeration system, using the models presented in Chapter 2. Calculations apply to the basic cycle, cycle with heat and mass recovery and cascading cycles using the manufacture’s data for zeolite CBV 901 and methanol, zeolite 13X/water and activated carbon/ammonia pairs.

4.2 Adsorption Cycles Calculations

The available data for each refrigeration cycle had been taken from existing literature (for basic adsorption refrigeration cycles) and from charts in the cases of heat regeneration and mass recovery.

- For the water and zeolite 13X pair [1]
- For the methanol and zeolite CVB901 [2]
- Finally, for ammonia and 208C carbon [3]

The following tables indicate all available values used for the calculation for each refrigeration-adsorbent pair, in order to calculate the COPc. The evaporation and condensation temperatures are similar in the case of zeolite pairs, whereas ammonia cycle works on lower environment temperatures.
### TABLE 4.1: H₂O and Zeolite 13 X

<table>
<thead>
<tr>
<th>Variable</th>
<th>Units</th>
<th>Basic cycle</th>
<th>Heat regeneration</th>
<th>Mass recovery</th>
<th>Heat - Mass recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>T₁=Τ₁’’</td>
<td>K</td>
<td>310.8</td>
<td>-</td>
<td>310.8</td>
<td>310.8</td>
</tr>
<tr>
<td>T₂</td>
<td>K</td>
<td>344.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>T=Τ₃’’</td>
<td>K</td>
<td>477.4</td>
<td>477.4</td>
<td>477.4</td>
<td>477.4</td>
</tr>
<tr>
<td>Tₑv</td>
<td>K</td>
<td>282</td>
<td>282</td>
<td>282</td>
<td>282</td>
</tr>
<tr>
<td>Tₑcond</td>
<td>K</td>
<td>310.8</td>
<td>310.8</td>
<td>310.8</td>
<td>310.8</td>
</tr>
<tr>
<td>Xₐ₁</td>
<td>%</td>
<td>8</td>
<td>8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Xₑconc</td>
<td>%</td>
<td>23</td>
<td>23</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>T₂’’</td>
<td>K</td>
<td>-</td>
<td>-</td>
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<td>321.9</td>
</tr>
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<td>Tₖ=Tₖ’’</td>
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<td>-</td>
<td>394.1</td>
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<td>394.1</td>
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<tr>
<td>Xₐ₁’’</td>
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<td>-</td>
<td>-</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Xₑconc’’</td>
<td>%</td>
<td>-</td>
<td>-</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>M</td>
<td>kg/kmol</td>
<td></td>
<td></td>
<td>18.02</td>
<td></td>
</tr>
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### TABLE 4.2: CH₃OH and Zeolite CVB 901

<table>
<thead>
<tr>
<th>Variable</th>
<th>Units</th>
<th>Basic cycle</th>
<th>Heat regeneration</th>
<th>Mass recovery</th>
<th>Heat - Mass recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>T₁=Τ₁’’</td>
<td>K</td>
<td>308</td>
<td>-</td>
<td>308</td>
<td>308</td>
</tr>
<tr>
<td>T₂</td>
<td>K</td>
<td>337</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>T=Τ₃’’</td>
<td>K</td>
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<td>373</td>
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<td>K</td>
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<td>280</td>
<td>280</td>
<td>280</td>
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<tr>
<td>Tₑcond</td>
<td>K</td>
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<td>308</td>
<td>308</td>
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<tr>
<td>Xₐ₁</td>
<td>%</td>
<td>2.5</td>
<td>2.5</td>
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<td>-</td>
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<tr>
<td>Xₑconc</td>
<td>%</td>
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<td>-</td>
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<tr>
<td>T₂’’</td>
<td>K</td>
<td>-</td>
<td>-</td>
<td>331</td>
<td>331</td>
</tr>
<tr>
<td>Tₖ=Tₖ’’</td>
<td>K</td>
<td>-</td>
<td>340.5</td>
<td>-</td>
<td>340.5</td>
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<tr>
<td>Xₐ₁’’</td>
<td>%</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Xₑconc’’</td>
<td>%</td>
<td>-</td>
<td>-</td>
<td>18</td>
<td>18</td>
</tr>
<tr>
<td>M</td>
<td>kg/kmol</td>
<td></td>
<td></td>
<td>32.024</td>
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TABLE 4.3: NH₃ – 208C carbon

<table>
<thead>
<tr>
<th>Variable</th>
<th>Units</th>
<th>Basic cycle</th>
<th>Heat regeneration</th>
<th>Mass recovery</th>
<th>Heat - Mass recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>T₁=T₁”</td>
<td>K</td>
<td>303</td>
<td>-</td>
<td>303</td>
<td>303</td>
</tr>
<tr>
<td>T₂</td>
<td>K</td>
<td>350</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>T=T₃”</td>
<td>K</td>
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<td>473</td>
<td>473</td>
<td>473</td>
</tr>
<tr>
<td>Tₑv</td>
<td>K</td>
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<td>263</td>
<td>263</td>
<td>263</td>
</tr>
<tr>
<td>Tₑcond</td>
<td>K</td>
<td>303</td>
<td>303</td>
<td>303</td>
<td>303</td>
</tr>
<tr>
<td>Xₐ₈</td>
<td>%</td>
<td>5.35</td>
<td>5.35</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Xₑ₈</td>
<td>%</td>
<td>19.35</td>
<td>19.35</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Tₑ₂”</td>
<td>K</td>
<td>-</td>
<td>-</td>
<td>333</td>
<td>333</td>
</tr>
<tr>
<td>Tₑₘ=Tₑₘ’</td>
<td>K</td>
<td>-</td>
<td>388</td>
<td>-</td>
<td>388</td>
</tr>
<tr>
<td>Xₐ₄”</td>
<td>%</td>
<td>-</td>
<td>-</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Xₑ₄”</td>
<td>%</td>
<td>-</td>
<td>-</td>
<td>22.7</td>
<td>22.7</td>
</tr>
<tr>
<td>M</td>
<td>kg/kmol</td>
<td>17.04</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The \( C_p \) values expressed in \( \frac{kJ}{kgK} \) were calculated as follows:

\[
\frac{C_p}{R_u} = a + bT + cT^2 + dT^3 + eT^4
\]

(4.1)

<table>
<thead>
<tr>
<th>Refrigerant</th>
<th>Range [K]</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>e</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>300-1000</td>
<td>4.09</td>
<td>-1.108⁻³</td>
<td>4.152⁻⁶</td>
<td>-2.964⁻⁹</td>
<td>0.807⁻¹²</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>257-364</td>
<td>21.152</td>
<td>0.07092</td>
<td>2.59⁻⁵</td>
<td>-2.85⁻⁸</td>
<td>-</td>
</tr>
<tr>
<td>NH₃</td>
<td>300-1000</td>
<td>3.591</td>
<td>0.494⁻³</td>
<td>8.345⁻⁶</td>
<td>-8.383⁻⁹</td>
<td>2.730⁻¹²</td>
</tr>
</tbody>
</table>

Table 4.4: Variables for each refrigerant. [4]

\( R_u \) Universal Constant Gas, 8.314 \( \frac{kJ}{kmolK} \)

\( C_p \) was obtained from experimental data for all adsorbents.
Applying the method described and using the available data for each cycle, the summaries of heats are given in the following tables.

### Table 4.5: H$_2$O and Zeolite 13 X

<table>
<thead>
<tr>
<th>kJ/kg</th>
<th>Basic cycle</th>
<th>Heat regeneration</th>
<th>Mass recovery</th>
<th>Heat – Mass recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_{12}$</td>
<td>63.259</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$q_{23}$</td>
<td>660.644</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$q_{ev}$</td>
<td>353.81</td>
<td>353.81</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$q_1''2''$</td>
<td>-</td>
<td>-</td>
<td>21.493</td>
<td>-</td>
</tr>
<tr>
<td>$q_2''3''$</td>
<td>-</td>
<td>-</td>
<td>790.308</td>
<td>-</td>
</tr>
<tr>
<td>$q_k3$</td>
<td>-</td>
<td>537.179</td>
<td>-</td>
<td>537.179</td>
</tr>
<tr>
<td>$q_{ev}''$</td>
<td>-</td>
<td>-</td>
<td>448.16</td>
<td>448.16</td>
</tr>
</tbody>
</table>

### Table 4.6: CH$_3$OH and Zeolite CVB 901

<table>
<thead>
<tr>
<th>kJ/kg</th>
<th>Basic cycle</th>
<th>Heat regeneration</th>
<th>Mass recovery</th>
<th>Heat – Mass recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_{12}$</td>
<td>81.059</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$q_{23}$</td>
<td>271.663</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$q_{ev}$</td>
<td>212.56</td>
<td>212.56</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$q_1''2''$</td>
<td>-</td>
<td>-</td>
<td>68.130</td>
<td>-</td>
</tr>
<tr>
<td>$q_2''3''$</td>
<td>-</td>
<td>-</td>
<td>352.916</td>
<td>-</td>
</tr>
<tr>
<td>$q_k3$</td>
<td>-</td>
<td>262.756</td>
<td>-</td>
<td>262.756</td>
</tr>
<tr>
<td>$q_{ev}''$</td>
<td>-</td>
<td>-</td>
<td>271.77</td>
<td>271.77</td>
</tr>
</tbody>
</table>
Chapter COP Predictions for Different Pairs

### Table 4.7: NH$_3$ and 208C carbon

<table>
<thead>
<tr>
<th>$kJ/kg$</th>
<th>Basic cycle</th>
<th>Heat regeneration</th>
<th>Mass recovery</th>
<th>Heat – Mass recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_{12}$</td>
<td>30.168</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$q_{23}$</td>
<td>304.736</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$q_{ev}$</td>
<td>155.38</td>
<td>155.38</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$q_{1''2''}$</td>
<td>-</td>
<td>-</td>
<td>21.365</td>
<td>-</td>
</tr>
<tr>
<td>$q_{2''3''}$</td>
<td>-</td>
<td>-</td>
<td>431.657</td>
<td>-</td>
</tr>
<tr>
<td>$q_{k3}$</td>
<td>-</td>
<td>284.423</td>
<td>-</td>
<td>284.423</td>
</tr>
<tr>
<td>$q_{ev''}$</td>
<td>-</td>
<td>-</td>
<td>229.74</td>
<td>229.74</td>
</tr>
</tbody>
</table>

The COP’s estimated for each refrigerant-adsorbent pair with regard to the equations given in Chapter 2, (2.12), (2.21), (2.23) and (2.27), are as follows:

<table>
<thead>
<tr>
<th>Refrigerant</th>
<th>Basic cycle (COPc)</th>
<th>Heat regeneration (COPc')</th>
<th>Mass recovery (COPc'')</th>
<th>Heat – Mass recovery (COPc''')</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O – Zeolite 13 X</td>
<td>0.489</td>
<td>0.617</td>
<td>0.552</td>
<td>0.8516</td>
</tr>
<tr>
<td>CH$_3$OH – Zeolite CVB 901</td>
<td>0.64</td>
<td>0.809</td>
<td>0.685</td>
<td>1.034</td>
</tr>
<tr>
<td>NH$_3$ – 208C carbon</td>
<td>0.464</td>
<td>0.546</td>
<td>0.507</td>
<td>0.8077</td>
</tr>
</tbody>
</table>

Table 4.8: COP comparison for different cycles

As can be seen in the table 4.8, zeolite CBV 901 and methanol give the best results for a working pair in the adsorption refrigeration systems. The results above have been evaluated assuming that the adsorption refrigeration cycle follows isosteric and isobaric processes. There is no significant heat capacity in the machine structure and there is equilibrium at all the times.
The use of heat regeneration in the system is more effective than mass recovery. If the heat regeneration and mass recovery methods are considered as separate processes, their benefits, when applied to a basic cycle, e.g. for methanol, are:

(a) COP benefit (mass recovery) = 0.685 - 0.64 = 0.045
(b) COP benefit (heat regeneration) = 0.809 - 0.64 = 0.169
(c) COP benefit (heat and mass recovery) = 1.034 - 0.64 = 0.394

The sum of (a) and (b) will give the COP gain of 0.214, which is the heat regeneration and mass recovery processes considered in isolation, versus 0.394, if the processes are employed together.

Some more COP predictions were made considering single bed adsorption refrigeration cycle using zeolite and methanol. These results are shown on the graphs below.

The calculations were done using a Visual Basic program within the Excel spreadsheet. All methanol and zeolite properties needed for COP evaluation were considered in the program. All the data is presented in Appendix A. Figure 4.1 shows the COP predictions as a function of the minimum and maximum cycle temperatures (T₁ and T₃). The evaporation and condensation temperatures used for calculations are 10 and 35 °C respectively. The highest COP = 0.647 can be achieved in a cycle, where T₁ = 40 °C and T₃ = 105 °C. For minimum cycle temperature higher than 40 °C the COP values are decreasing.
A further set of calculations was done for constant values of \( T_1 \) and \( T_3 \), which were taken from a graph above for the highest COP value (\( T_1=40 \, ^\circ C, \ T_3=105 \, ^\circ C \)). This time the COP was checked for different evaporation and condensation temperatures. The results are shown in Figure 4.2. The COP values are increasing with higher evaporation temperature and decreasing with higher condensation temperature.

Figure 4.1: COP predictions for \( T_{ev}=10 \, ^\circ C \) and \( T_{cond}=35 \, ^\circ C \) as a function of \( T_1 \) and \( T_3 \)

Figure 4.2: COP predictions for \( T_1=40 \, ^\circ C \) and \( T_3=105 \, ^\circ C \) for different \( T_{ev} \) and \( T_{cond} \)
Another important factor in COP calculations for adsorption refrigeration cycle is the mass of heat exchanger per unit mass of zeolite in it. The modelling was completed for a regular cycle where $T_{ev}=10\,^\circ C$, $T_{cond}=35\,^\circ C$, $T_1=35\,^\circ C$ and $T_3=100\,^\circ C$. Increasing mass of the heat exchanger decrease the COP values.

The COP of cascading cycle with two independent cycles, for example zeolite 13X/water and zeolite CBV 901/methanol, can be predicted. It can be done using the Equation (2.35), when the COP of the first cycle is 0.489 and the second one 0.64. For this specific cycle, the cascading effect will give the COP of 1.4.
4.3 Summary

This chapter, which investigated novel adsorption systems, using different adsorbent/adsorbate pairs including zeolite CBV 901 and methanol, has shown very promising results. The simulations done using real data gave a first insight into the system performance and how different working adsorbent/refrigerant pairs may influence it.

As can be seen from the analysis, there is a great potential to improve on the design and operation of adsorption systems. Heat regeneration can be helpful as well as mass recovery in improving the system COP. In a continuous cycle of adsorption refrigeration, both mass recovery and heat regeneration is beneficial to the cycle performance. However, the increase of COP is mainly a result of heat regeneration, although mass recovery contributes to the cooling capacity, with little effect on COP.

The mass recovery process will significantly enhance the cooling capacity of the system. Whether the mass recovery process will promote the cycle COP or not, will depend on the operating conditions. The cycle with mass recovery and heat recovery for zeolite and methanol has the highest COP of 0.64 among the calculated cycles. The concept of the cascading cycle shows potential as well, because if we consider a typical example with two separate stages, where both have COP of 0.5, then the cascading effect will give the COP of 1.25.

It is very important to choose an appropriate set of temperatures for each cycle, like evaporation and condensation temperature, which is connected with refrigerant properties and minimum and maximum adsorbent temperature. Their influence on the system performance can be essential.
References for Chapter 4


Chapter 5

Assessment of Physical Properties of Zeolite CBV901 and Methanol

5.1 Introduction

One of the most important elements of any refrigeration and heat pump system is refrigerant, since the working pair conditions and compatibility with the environment principally depend on it. Generally speaking, the refrigerant requirements are high latent heat per unit volume and good thermal stability. Briefly, the adsorption characteristics of adsorbents are determined from the adsorption isotherms. These indicate the amount of a substance adsorbed.

The literature shows that it is important to analyse precisely the performance of an adsorption cycle based on an accurate determination of adsorbent-adsorbate (refrigerant) behaviour. There have been many refrigerant-adsorbent pairs suggested for solid-sorption cooling and heating. Choosing the most appropriate adsorbent-adsorbate pair is connected with efficiency of the adsorption system [1]. A suitable adsorbent should:

- have a large adsorption capacity for the selected adsorbate,
- be easily regenerated regarding the pressure and temperature ranges of operation.

Whereas, an adsorbate should:

- have a high latent heat of vaporisation,
- a suitable boiling point.

The lower the temperature at which adsorption occurs relative to the boiling point of the adsorbate, the higher will be the amount adsorbed.
Chapter 5  Assessment of Physical Properties of Zeolite CBV901 and Methanol

The major advantage that solid sorbents have over liquid systems is the large range of suitable materials available and the ability to engineer them for a particular application. The number of liquid adsorbent-refrigerant pairs that give reasonable performance is very limited and governed by unalterable chemistry and physics. When using physical adsorption, almost any refrigerant may be used and, in principle, an adsorbent can be manufactured with the optimal pore size distribution for the particular application. Because of their open porous structure, solid sorbents are capable of adsorbing large quantities of a variety of refrigerant gases, ranging from water, ammonia, and carbon dioxide to various hydrocarbons at room temperature. In recent times, the pairs used include ammonia-activated carbon, methanol-activated carbon, methanol-silica gel, water-silica gel and water-zeolite [2].

Since adsorption is essentially a surface phenomenon, a practical adsorbent must have a high specific surface area, which means small diameter pores. It is necessary to review accepted knowledge about the nature of adsorbents and adsorbates alike. The adsorbent can be in several forms – pelletised, monolithic or adhered, and these are important when designing the adsorption system with regard to mass transfer. Conventional adsorbents such as active carbons, zeolites and silica gels have relatively wide pore size distributions; as a result they can adsorb large quantities of many gases within their micropores. The size of the micropores is another important property for characterising the adsorptivity of adsorbents. Materials, such as zeolite and active carbon can be specifically produced with a precise pore size distribution appropriate to a particular separation.

An important classification is; [3]

- **Hydrophilic** or polar adsorbents have affinity with polar substances such as water or alcohol. Zeolites, silica gels and silica-alumina are examples of these adsorbents.
- **Hydrophobic** or non-polar adsorbents have more affinity with oil or hydrocarbons than water. Carbonaceous and polymer adsorbents are adsorbents with these characteristics.
In addition, the quantity of refrigerant adsorbed depends on the temperature of the adsorbent and the system pressure.

If the process requires a refrigerant at high pressure, ammonia is the best choice. Ammonia has no ozone depletion potential and is considered as a greenhouse gas. However, it is toxic and incompatible with copper and brass.

Water has the advantages of being non-toxic, environmentally friendly and "free". Unfortunately, it is not strongly adsorbed by carbons, but adsorption cycles with water as refrigerant are based on water-zeolite or water-silica gel pairs.

Zeolites can absorb methanol [4]. Methanol is environmentally friendly, but decomposes at temperatures around 150°C, so cannot be used for very high temperature cycles.

This chapter focuses on measurements of the properties of zeolite CBV 901 and methanol, which have been chosen as the working pair in an adsorption refrigeration system. The pair isotherms are the inputs in the prediction of COP. Some of the potential extraneous factors have been measured such as air ingress and methanol evaporation, which might influence the adsorption time.

### 5.2 Pair Description

There are several limitations to the use of conventional granular forms of adsorbent. Firstly, heat transfer through packed beds is slow, limiting the refrigeration effect. Secondly, most conventional adsorbents require a regeneration temperature in the range of 200°C to 250°C, restricting the coefficient of performance. Issues related to the choice of adsorbate include flammability, toxicity, stability and gas dynamics.

It has been proposed that monoliths, prepared by binding powder to a substrate, would result in effective heat and mass transfer [5], [6]. However, it has been difficult to prepare sufficiently resilient layers with thickness in excess of 2mm.

The specific volume of the adsorbate also limits performance, either because of choking or frictional resistance. Generally, water is not useful for high heat loads.
Alternatively, ammonia is toxic and corrodes copper and brass fittings. Most alcohols are environmentally friendly, but are dehydrated and catalytically decomposed during desorption at 150 °C to 200 °C.

Zeolite CBV 901 and methanol are selected as a pair presented by Tchernev [7], because this new type of zeolite needs to be heated only to 100 °C to be fully regenerated. This temperature does not cause methanol to decompose (see Figure 5.1).

![Figure 5.1: Isosteres of zeolite CBV 901 and methanol [7]](image)

### 5.3 Methanol Properties

The properties of methanol are needed in later study, to explain the measured properties of zeolite/methanol as well as to calculate the system COP from the data obtained from tests.

#### 5.3.1 Available Data

Methanol (or methyl alcohol, or wood alcohol) is the simplest of a long series of organic compounds termed alcohols. Methanol is a colourless and tasteless liquid, with a faint odour. It is completely miscible with water and organic solvents, and is very hygroscopic. Its chemical and physical properties (extracted from manufacturer data sheet [8]) are shown in Table 5.1.
# Chemical Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>CH₃OH</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>32.042 g/mol</td>
</tr>
<tr>
<td>CAS number</td>
<td>67-56-1</td>
</tr>
<tr>
<td>Water solubility</td>
<td>Miscible, 100g/100g water at 25 °C</td>
</tr>
<tr>
<td>Freezing point</td>
<td>-97.7 °C</td>
</tr>
<tr>
<td>Boiling point</td>
<td>64.6 °C (at atmospheric pressure)</td>
</tr>
<tr>
<td>Standard Heat of formation</td>
<td>-201.3 MJ/kmol</td>
</tr>
<tr>
<td>Gibbs Free Energy</td>
<td>-162.62 MJ/kmol</td>
</tr>
</tbody>
</table>

# Critical Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Critical temperature</td>
<td>512.6 K</td>
</tr>
<tr>
<td>Critical pressure</td>
<td>81 bar abs</td>
</tr>
<tr>
<td>Critical volume</td>
<td>0.118 m³/kmol</td>
</tr>
</tbody>
</table>

# Liquid Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>791 kg/m³ at 20 °C</td>
</tr>
<tr>
<td>Heat of vaporization</td>
<td>1102 kJ/kg</td>
</tr>
<tr>
<td>Viscosity: a = 555.3</td>
<td>b = 260.6</td>
</tr>
</tbody>
</table>

\[
\log(\text{viscosity}) = a \left[ \frac{1}{T} \right] - b \text{ mNs/m}^2
\]

# Vapour Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat capacity: a = 21.152</td>
<td>b = 0.07092</td>
</tr>
<tr>
<td>c = -0.0000259</td>
<td>d = -2.85E-08</td>
</tr>
</tbody>
</table>

\[Cp = a + bT + cT^2 + dT^3\text{ kJ/kmolK}\]

| Vapor pressure: a = 18.5875 | b = 3626.55            |
| c = -34.29                  |                        |

\[\ln(P) = a - \frac{b}{(T + c)}\text{ torr}\]

Table 5.1: Properties of methanol

## 5.3.2 Measurement Methods

The saturation vapour pressure of methanol is well known, as reported above. However, its measurement can be used as part of a calibration check when liquid and vapour are in thermodynamic equilibrium. The method, which is used to produce results later in Chapter 5, is to introduce a known quantity of liquid methanol into an evacuated vessel.
Methanol properties can be measured by the introduction of a known amount of liquid methanol into an evacuated vessel. Thereafter it has two purposes:

a. The vessel can be filled with air to measure its influence on methanol evaporation and zeolite adsorption.

b. The low-pressure methanol vapour can be adsorbed onto zeolite, and the resulting pressure change can be used to infer equilibrium data (more detail is provided in section 5.5 Adsorption isotherms).

The vacuum vessel was a modified thick walled, 1 litre, glass jar originally manufactured by Kilner and readily available. Figure 5.2 shows the schematic diagram of the set up, which Prasertmanukitch used at Bristol University, for a similar set of tests using activated carbon/toluene pair [9].

![Schematic diagram of the vacuum chamber](image)

The original flexible, polymer laminated steel cap was replaced with a 10mm thick, machined stainless steel with 3 tapped ports. One port was connected to a calibrated K-Type thermocouple with sufficient length to reach the zeolite bed (for later use). The second port was connected to an Edwards’s Speed Drive needle valve, which allowed...
accurate control over the inlet/outlet of the vessel. An Edwards model E2M5 vacuum pump provided vacuum, capable of pulling down to the order of $10^{-2}$ mbar.

The final port was connected to a Baraton gauge head (0-1000 torr range with ±0.05 torr resolution) controlled and monitored by a Chell gauge controller. Chell Instruments Ltd initially calibrated this system [10] on April 1986 (Ref: MK 1458). To check this calibration, the gauge was calibrated again for air using a factory calibrated Pirani PR10-K vacuum gauge connected to a Piranil controller. (This was a two-point calibration at vacuum and atmospheric pressure to adjust and zero the output). In addition, the gauge was also checked for its sensitivity to methanol vapour pressures, as well as to different temperatures.

Figure 5.3 shows the actual pressure reading of the gauge compared against calculated values (for methanol) assuming either the ideal gas law or saturation pressure (Equation 5.1). These values represent upper boundaries on pressure. (The real transition from ideal gas to saturation is more gradual, and necessitates the calculation of a compressibility factor).

$$P = \min\left(\frac{nRT}{V}, P_{\text{sat}}(T)\right)$$  \hspace{1cm} (5.1)

Where the volume is, $V = 993\text{ml}$. The volume of the fully assembled chamber was found by comparing the dry mass with the mass when the filled with water. The Mettler Teledo PR2003 electronic scale (Calibrated by SCC on 16/09/97) used had a resolution of ±0.001g. Allowing for the possibility of trapped air bubbles, the estimated volume of the chamber was believed to be within ±1ml or 0.1% accuracy.

Initially, the chamber was vacuumed down to < 0.05 torr with an Edwards E2M2.5 high vacuum pump. Then a known amount of liquid methanol was added to the chamber with a 100μl syringe (accuracy ±1μl) until saturation was achieved (the saturation pressure of methanol at 30°C is 162.8 torr). The pressure reading from the vacuum gauge gave a second indication of the methanol concentration in the chamber.
The saturation pressure of methanol at 30°C is 162.86 torr; beyond this saturation point, as evident in the calibration, the pressure should be independent of the quantity of methanol added. Before saturation, the calculated pressure agrees with the pressure reading to within ±4%. The inaccuracy would most probably be attributed to the accuracy of the Hamilton-Bonaduz 100µL syringe used (±1µL optical accuracy) and the possibility of trapped air bubbles. Taking into account all the possible errors, the accuracy of the system was believed to be within ±5%. At this temperature the saturation does not reach actually the pressure of 162.86 torr, but as it can be seen in Figure 5.3, the vapour apparently approaches equilibrium at 135 torr. The explanation of this process might be condensation in top of the experimental rig, where the connection to the pressure gauge is located. The temperature of this part is not controlled by the water bath.

The chamber was also subjected to leak tests by vacuuming the chamber down and leaving it for at least 6 hours. The results showed that the chamber gained less than 0.05 torr over a 6-hour period as long as adequate vacuum grease (DOW corning high vacuum grease) was applied to the o-ring.
5.4 Physical Attributes of Zeolites

The paragraph describes the basic structure of zeolites and its benefits, the use of Malvern 2600 series to check the particle size of powdered zeolite and coating experiments done to achieve better heat and mass transfer in the adsorption bed.

5.4.1 Microscopic Structure

The zeolite frame is very strong and extremely non-linear, thereby providing this family of materials with unique adsorption properties that permit extremely high efficiencies for adsorption cycles.

Zeolites form a family of materials with a open, cage-like crystal structure. The atoms, oxygen, silicon, aluminium, and one of the alkaline metals or earth’s, are arranged in such a manner that they form cavities interconnected by channels or tunnels on the atomic scale [11]. Because of this open, porous structure, zeolites are capable of adsorbing large quantities of various refrigerant gases, ranging from water vapour, ammonia, methanol and carbon dioxide to various fluoro-, chloro-, and hydrocarbons at room temperature. The basic building blocks of zeolites are tetrahedras consisting of four oxygen anions and one centrally positioned silicon or aluminium cation.

Figure 5.4: Structural framework of type A zeolite and FAU zeolites.
The aluminium and silicon atoms are positioned at the junction, while the oxygen atoms form bridges between the tetrahedras (type A zeolite). Owing to the strong electrical charge in the lattice framework, zeolites adsorb all polar and non-polar molecules that will fit into their specific framework. Synthetic zeolites are manufactured in a hydrothermal process. Mixing NaOH, Al₂O₃, SiO₂ and water produces a gel. Heating this gel to temperatures between 50°C and 300°C results in a microcrystalline zeolite with a diameter between 1 and 100 μm. Depending on the nature of the added metal cations, the key properties of the zeolite, such as pore size, shape and capacity are tuneable.

The adsorption energy is caused mainly by the interaction of the polar moments of the refrigerant molecules with the strong internal crystal field of the non-linear cage structure. Zeolites exhibit saturation behaviour in their pressure dependence. At ambient temperature zeolites can adsorb large quantities of refrigerant vapour even at low partial pressure. When the zeolite is heated it desorbs most of the refrigerant vapour even at high condenser temperatures and pressures.

Zeolites benefits are: they can dry more completely than another adsorbent, remain effective at relatively high process temperatures, dry mixed streams without altering stream composition, purify and dry in one step, provide high product recovery and separations and lower investment and operating cost.

5.4.2 Zeolite Powder

The zeolite powder is essential to produce the zeolite coating on the adsorbent bed surface to improve the heat and mass transfer in the system.

Different varieties of zeolites were available from suppliers. The important physical properties (for adsorption purposes) were; size, density and the average surface area per unit mass (BET). The manufacturer provides these data, but in addition a Malvern 2600 Series [12] diffraction based particle sizer was used to analyse the particle size for zeolite CBV 901 and 13 X samples.
The Malvern was fitted with a 63mm lens capable of analysing samples within the range of 1.2 – 110 μm. Calibration of the Malvern was initially checked using a 10μm, calibrated, glass sample. The dispersion medium used was water. After satisfactory results, a small sample of zeolite was added to the water filled dispersion chamber until the software indicated that enough carbon was present. A magnetic stirrer in the chamber ensured that carbon powder was well dispersed in the water.

One of the many results generated with the Malvern analyser, which was a volume average, is shown in Figure 5.5. The result shown is zeolite CBV 901, with a nominal diameter of 15μm. The sample was analysed twice to increase accuracy. All the results are tabulated in Table 5.2.

![Particle size analyser](image)

**Figure 5.5: Malvern analyser results for zeolite CBV 901**
Table 5.2: Properties of zeolites used

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Type</th>
<th>Nominal Size</th>
<th>BET (m²/g)</th>
<th>Density (kg/m³)</th>
<th>Size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite CBV 901</td>
<td>15 μm</td>
<td>780</td>
<td>590</td>
<td>15.51</td>
<td></td>
</tr>
<tr>
<td>Zeolite CBV 901</td>
<td>15 μm</td>
<td>780</td>
<td>590</td>
<td>15.94</td>
<td></td>
</tr>
<tr>
<td>Zeolite 13 X</td>
<td>13 μm</td>
<td>500</td>
<td>641</td>
<td>12.96</td>
<td></td>
</tr>
<tr>
<td>Zeolite 13 X</td>
<td>13 μm</td>
<td>500</td>
<td>641</td>
<td>12.85</td>
<td></td>
</tr>
</tbody>
</table>

* Malvern machine at Harwell

Figure 5.6 shows the magnified picture of zeolite CBV 901 under a SONY capture camera attached to an optical microscope. The large clumps (some as large as 40μm) suggested that agglomeration of the powder took place when did drying occur and was the probable cause of the larger than expected particle size, which could influence its adsorption characteristics.

Agglomeration could be the cause of an apparently larger than specified particle size. Coulson & Richardson [13] suggested that this particular problem becomes more significant when the particles are smaller than 10μm. Agglomeration can arise from interaction between particles as a result of the following: mechanical interlocking, surface attraction, electrostatic attraction or effect of moisture.
5.4.3 Coated Plates

In the literature, two practical methods to improve the heat transfer inside the adsorber bed are presented. The first method uses a solid adsorbent composite with high thermal conductivity and a suitable shape to adapt to the heat exchanger geometry. The second one creates a thin adsorbent layer.

Restuccia & Cacciola [6], [14] and Tatlier & Erdem-Senatalar [15] have suggested a solid adsorbent thin layer connected with the heat exchanger wall by physical or chemical methods. In this way, the thermal resistance between the heat exchanger wall and the adsorber bed would be negligible.

Tatlier and Erdem-Senatalar have coated aluminium surfaces with zeolite by a direct synthesis from a reaction mixture. They used a complex construction to synthesise Zeolite 4A on a metal sheet, by heating it from one side, while the other side is being coated from the colder alumino-silicate solution.

In contrast to this, Restuccia and Cacciola have worked with a ready zeolite powder and aluminium hydroxide as binder. The binder should create the bond to the metal (aluminium sheets) and increase the equivalent thermal conductivity of the adsorbent (zeolite CBV 901). With this coating, zeolite layers with a thickness of 2mm can be produced. To create a stable composite material, for temperatures above 250 °C, it was necessary to use 10-40% of binder. By creating a chemical bond layer, the heat transfer inside the adsorber bed could be significantly improved. With respect to a similar palletised bed with equal adsorbent mass, the bed volume could be reduced by 30-35 %. Nowadays, most of the adsorption cycles operate with zeolite grains, which are embedded or filled in the space between fins. However, one of the disadvantages is that the thermal conductance is very bad. To improve the heat transfer between the heat exchanger and the adsorbent, the thermal conductance must be better. This can be achieved by coating the heat exchanger with the adsorbent.
Assessment of Physical Properties of Zeolite CBV901 and Methanol

Zeolite CBV 901 as an adsorbent with methanol as a refrigerant was selected as a working pair after literature review. Following a discussion with Dr Peter Timms, in the Department of Chemistry at Bristol University, starch and wallpaper paste binders were investigated. These kinds of binders are practical at low cycle temperatures (below 100°C). (Indeed, starch is now employed commercially as a binder in ceramic filters, heated at 400°C). The first step was the preparation of the zeolite layers by mixing the zeolite powder (for the coating tests zeolite 13X and CBV901 were used) with the binder (starch and wallpaper paste-WPP). After adding different quantities of water and stirring the solution, the slurry was applied to the aluminium sheets and dried for 24 hours at ambient conditions. The experiments were also done with different treated metal surfaces.

The difficulties were with choosing a proper binder, which after mixing with zeolite will not block the pore system. The experiments were also done with different treated metal surfaces. The aluminium surface was treated chemically. First the surface was degreased with acetone, and then the specimen was placed in an etching solution of chromic sulphuric acid, in a beaker placed in a water bath at 60 °C for 20-30 minutes. The second method of treating the surface was to use Emery cloth 100 grit. The pictures below present plates with a variety of treatments, as presented in Table 5.3.

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>Surface preparation</th>
<th>Binder</th>
<th>Layer thickness</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Emery cloth</td>
<td>Starch 10%</td>
<td>1mm</td>
<td>Figure 5.7, Good connection</td>
</tr>
<tr>
<td></td>
<td></td>
<td>WPP 10%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Emery cloth</td>
<td>Starch 10%</td>
<td>3mm</td>
<td>Figure 5.8, Surface cracked</td>
</tr>
<tr>
<td></td>
<td></td>
<td>WPP 10%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Emery cloth</td>
<td>Starch 10%</td>
<td>1mm</td>
<td>Figure 5.9, Samples dried in 200 °C, destruction of binder (starch)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>WPP 10%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Emery cloth</td>
<td>Starch 10%</td>
<td>1mm</td>
<td>Figure 5.10, Samples dried in 120 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>WPP 10%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Chemically</td>
<td>Starch 10%</td>
<td>1mm</td>
<td>Figure 5.11, Good connection and surface structure</td>
</tr>
<tr>
<td></td>
<td></td>
<td>WPP 10%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Chemically</td>
<td>Starch 5%</td>
<td>1mm</td>
<td>Figure 5.12, Good connection and surface structure</td>
</tr>
<tr>
<td></td>
<td></td>
<td>WPP 5%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.3: Coated plated preparation experiments
If the zeolite layer was too thick (>2mm), it cracked and the adsorption properties decreased (Figure 5.8).

The layer surface depends on the binder and the mass of water used: With wallpaper paste, the surface has in general a higher roughness than the samples bound with starch. By using more water, the slurries had a higher viscosity and it was possible to create more even layers.

After drying in ambient conditions, some of the samples were heated in an oven at 200 °C. The results are shown in Figure 5.9. The sample with a starch as binder was destroyed. The other sample did not lose its binding property. By heating samples to 120 °C, the result was better, but the zeolite-starch layer still showed signs of deterioration (Figure 5.10).
For the next set of experiments the aluminium plates were treated in dichromate sulphuric acid, which chemically activated the aluminium sheets. A better connection between the plate and the adsorbent was achieved (Figures: 5.11 and 5.12).
As a crude test of the adsorption ability of the zeolite, the samples were dried for 3 hours at 100 °C in an oven to ensure that moisture was adsorbed from the ambient. After putting the samples on an electronic scale connected to the computer, it was possible to measure the weight at defined intervals and thus infer the moisture adsorbed from the ambient. The samples were saturated after 2 hours. In general, the ratio moisture content to the mass of zeolite was between 17.8 and 19 %.
5.5 **Assessment of Adsorption Isotherms**

The apparatus described in section 5.3 can be employed to assess isotherm data. In these series of tests, each zeolite sample (contained in a stainless steel basket) was exposed to pure methanol vapour (that is not diluted in an inert gas or air). Temperatures ranged from 25 to 75 °C and methanol quantities were from 0.05 to 0.5 mL (this is governed by the resolution of the micro syringes). The simplified schematic flow diagram of the rig is shown in Figure 5.13 (for full details please refer to Figure 5.2). This was suitable for methanol pressures in the range 1-250 torr.

![Flow diagram of pure component test rig](image)

*Figure 5.13: Flow diagram of pure component test rig (also see Figure 5.2)*
Figure 5.14: Vacuum system in a water bath

The zeolite basket was suspended inside the sealed glass chamber, which was submerged under a temperature controlled water bath. Temperature was controlled with a Grant Instrument® 20l JBJ series water bath, with a Grant Instrument® type K0 temperature controller and mixer (±1°C stability).

Throughout the test, the pressure was logged (every 2 seconds) with a Hewlett Packard HP 3456A digital voltmeter, which has a resolution of ±5µV. As investigated in section 5.3, the whole system accuracy was calculated to be within ±5%. The bulk of this inaccuracy was attributed to the Hamilton-Bonaduz 100µl syringe used, which has ±1µl optical accuracy (equivalent to ±225 ppm).

5.5.1 Experimental Procedures

For each run, a maximum of 0.5g of dried zeolite was weighed using a Sartorius 2024MP micro balance (±0.01mg resolution, last calibrated by European Instruments in August 1994). It was placed into the stainless steel basket with a dried glass-fibre filter, which was used to pre-line the coarse mesh basket.
After suspending the basket inside the glass chamber, the whole system was connected to an Edwards E2M2.5 high vacuum pump for evacuation. The vacuum level attained from this pump is typically < 0.01 torr.

Before any methanol was added, the chamber was submerged under the water bath until the internal temperature (measured with an internal thermocouple as shown in Figure 5.13) reached the required value (Approximately 15-20 minutes was required).

A controlled quantity of liquid methanol was added through an N-Series Speed Drive needle valve connected to 100μl Hamilton-Bonaduz Scheweiz glass syringes. These had an optical resolution of ±1μl respectively.

Each point on the isotherm was derived as follows: a known volume of methanol was added to the system, whereupon the indicated pressure initially increased – indicating evaporation. This was followed by a decrease in pressure – indicating adsorption. Typical trends are shown in Figure 5.15.

![Diagram](image)

Figure 5.15: Typical trends of pure component tests.
The mass of material adsorbed can be found as follows:

\[ m_{ad} = i \cdot \delta m - \frac{P_s V}{RT} - m_L \]  

(5.2)

Where, \( i \cdot \delta m \) represents the total mass added to the system (by the injection of \( i \) samples, each of mass \( \delta m \)). The mass in gaseous phase follows from the perfect gas law, where \( P_s \) is the steady state pressure. The final term describes other losses, and is assumed to be equal to zero.

The saturated zeolite was again weighed at the end of each run. However, substantial mass loss (mostly due to desorption) was evident. Figure 5.16 show a logged mass of saturated zeolite left on a microbalance. It could be observed that rapid desorption takes places within the first few minutes of the sample being exposed to ambient condition, thus mass analysis was inconclusive.

![Desorption in air at room temperature](image)

Figure 5.16: Observed mass loss of saturated zeolite in ambient condition
5.5.2 Miscellaneous Tests

The first set of tests indicates the system characteristics for different structures of zeolite as a sample, and assists in identifying sensible conditions for a second set of tests. The following were varied:

a. Zeolite arrangement (powder, coated)
b. Adsorbate type
c. Temperature

Figure 5.17 shows the plot of calculated equilibrium adsorption capacity $x$ (also known as loading) against pressure for powder samples at 30, 40 and 60°C.

In all cases, there was a clear general trend that $x$ increases with increasing pressure $P$ as anticipated. On the other hand, higher temperature will resulted in lower $x$.

![Isotherms of powdered zeolite CBV 901-methanol](image)

Figure 5.17: Isotherms of powder zeolite CBV 901 and methanol
Another set of experiments was prepared for a coated plate sample, the preparation of which was described in section 5.4.2.

![Isotherms of coated zeolite CBV 901 and methanol](image)

Figure 5.18: Isotherms of coated zeolite CBV 901 on metal plates and methanol

The loading is slightly lower than that for the powdered zeolite. The calculations did not take the binder mass in the paste under consideration.

The comparison of the maximum adsorption for different temperatures is presented in a Table below.

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Powder zeolite adsorption [%]</th>
<th>Coated zeolite adsorption [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>25</td>
<td>22</td>
</tr>
<tr>
<td>40</td>
<td>18</td>
<td>16</td>
</tr>
<tr>
<td>60</td>
<td>14</td>
<td>11</td>
</tr>
</tbody>
</table>

Table 5.4: Zeolite adsorption for different temperatures

The decrease in maximum adsorption for coated zeolite might be connected with the use of the binder in the mixture, which can influence the zeolite properties. However,
Chapter 5  Assessment of Physical Properties of Zeolite CBV901 and Methanol

The difference is not more than 2 to 3% between the powdered and coated forms, so it is acceptable to use it in design of the generator.

Each curve had 3 characteristic parts:

a. An initial steady increase in \( x(P) \) for lower \( P \).

b. An asymptote as equilibrium saturation was reached.

c. An increase in \( x(P) \) when \( P \in [100,150] \) torr.

The third part of the curve was not a typical BET type adsorption behaviour for zeolite. There were two possible causes; one was the unexpected adsorption and the other was condensation elsewhere in the system.

a. Adsorption by O-Rings

A rubber O-ring was used to seal the glass chamber to the stainless steel lid. It is conceivable that methanol might have been adsorbed within the rubber as methanol pressures increased towards the saturation value.

b. Condensation

The vacuum gauge has a \( \varnothing 10 \) mm by ~50mm stem located between the submerged chamber and the electrical housing. This was a cooler region in which vapour could condense. The resulting temperature profile was minimised by insulating the stem with expanded polystyrene. Even then, the maximum temperature difference recorded was 20°C when the chamber was at 70°C (the highest test temperature).
5.5.3 Effects of the Temperature

This series of tests investigated the effects of temperature on the adsorption capacity of zeolites, \(x\). By controlling the temperature in the water bath, the temperature range used was between 30°C and 70°C. Samples of dried coated zeolite CBV 901 on aluminium plates were used mainly for these tests. This is because they were easier to handle avoiding any possible mass losses, as well as for the reasons given in section 2.5. The results are plotted on Figure 5.23.

As the temperature was raised from 30°C to 70°C it become obvious that equilibrium adsorption capacity decreased, as found in section 5.5.2.

![Isotherms of zeolite and methanol](image)

Figure 5.19: Effects of temperature on adsorption capacity of zeolite

The maximum equilibrium adsorption capacity, \(x\), was reduced from ~22% to ~5% as the temperature rose from 30°C to 70°C.
5.5.4 Repeatability

A second set of experiments was repeated to confirm the loadings for different temperatures. The results are presented in Figure 5.20.

![Isotherms of zeolite CBV901 and methanol](image)

Figure 5.20: Isotherms of zeolite CBV901 and methanol

There were small variances in the maximum adsorption for pairs of experiments at the same temperature, which coincided with earlier comment regarding extraneous adsorption or condensation. This variance might be probably associated with small masses of methanol added to the system. Here the accuracy of the micro syringe would have played a more important role on repeatability. Furthermore, small air pockets trapped along the methanol inlet line could have influenced the apparent mass taken up by the zeolite.
5.5.5 Adsorption Isosteres

Adsorption isotherms for zeolite and methanol presented in section 5.5.4 are the first step in deriving adsorption isosteres. From Figure 5.20, (p, T) pairs corresponding to loadings from the set \( x \in \{2, 20\}\% \) were fitted to piecewise linear equations. Results of this procedure are presented in figure below.

Figure 5.21: Isosteres form isotherms for zeolite and methanol

This information can be compared with isosteres obtainable for the same pair by Tchernev (Figure 5.1 in section 5.2). The assessment of the two sets of isosteres for zeolite CBV 901 and methanol is presented in Figure 5.22.
Figure 5.22: Isosteres comparison for zeolite and methanol

The measured isotherms for zeolite and methanol are not too distant from the Tchernev isosteres, which were obtained experimentally as well. The full set of both sets of isosteres is presented in Figure 5.23. The thick, black lines represent Tchernev’s isosteres. The lines supplemented with symbols are isosteres from Figure 5.21.

Figure 5.23: Isosteres comparison (full set)
5.6 Adsorption Properties of Zeolite and Water

The purpose of this section is to verify the adsorption behaviour of zeolite CBV 901 and water, which might be considered as an alternative refrigerant. A further objective is to test if any extraneous moisture will interfere with methanol adsorption.

5.6.1 Test Results

In this part another adsorbate, which in this case is water, was tested on zeolite CBV 901 coatings. The experimental rig used, was presented in section 5.5. The influence on adsorption properties of different temperatures (30, 40 and 50 °C) was verified. The results are presented in Figure 5.24.

![Isotherms of zeolite CBV 901 and water](image)

Figure 5.24: Isotherms of zeolite CBV 901 and water
A different type of adsorption isotherms appears, when water is applied as an adsorbate. The response of the system is unexpected, and the anomalous, high apparent values of x can be attributed to condensation of moisture inside the vessel. The saturation vapour pressure for water is presented on the graph, and in the table below.

<table>
<thead>
<tr>
<th>Temperature (^{\circ}C)</th>
<th>Water saturation pressure [Torr]</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>31.81</td>
</tr>
<tr>
<td>40</td>
<td>55.32</td>
</tr>
<tr>
<td>50</td>
<td>92.42</td>
</tr>
</tbody>
</table>

Table 5.5: Saturation pressure of water

An additional aspect of the adsorption of water on coated zeolite is that the samples decompose after the tests, which means that a high water presence degrades the binder. This process can be observed in the Figure 5.25, which shows one of the samples after three tests.

Figure 5.25: Coated zeolite sample decomposition after presence of water
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This fact can be explained by reaction between the binder and water, which reduces the adhesion of the zeolite paste to the aluminium plate. It means that this kind of sample preparation is unsuitable, when water is present as the principle adsorbate.

5.7 Comments on the Influence of Air Ingress

In any practical refrigeration system under partial vacuum, there will be a potential for air ingress. This could slow the adsorption process, by providing an inert barrier to diffusion in the inter-particle spaces.

The purpose of this section is to investigate the influence of air presence in the system.

5.7.1 Air Influence on Methanol Evaporation

The reason for doing this is that the process time $t$ could mask any attempt to evaluate adsorption time. The first part of experiments was carried out only for methanol. The experimental rig presented in section 5.5, was used. The chamber was vacuumed to a pressure below 1 torr and than placed in water bath with controlled temperature of 30°C. After the system had stabilised, exactly 2 ml of methanol was added with a micro syringe. Three sets of experiments were prepared: firstly with no air in the system, secondly with an initial air pressure of 50 torr air and finally with 100 torr. The pressure was logged every 2 seconds. The results are plotted in Figure 5.26.
Methanol evaporation at 30°C (0.2mL methanol)

It can be observed from the shapes of the lines that the air slows slightly the methanol evaporation, but this process is not essentially a limiting factor in future system performance. The time needed for methanol evaporation in different environment is presented in Table 5.6.

<table>
<thead>
<tr>
<th>Air in system [torr]</th>
<th>Time for methanol evaporation [sec]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>60</td>
</tr>
<tr>
<td>50</td>
<td>120</td>
</tr>
<tr>
<td>100</td>
<td>240</td>
</tr>
</tbody>
</table>

Table 5.6: Air influence on methanol evaporation

5.7.2 Influence of Air on Adsorption

The influence of air on zeolite adsorption was the second part of experimental work in this section. The procedure was the same as for methanol evaporation, except that a dried, zeolite sample had been placed in the chamber (an aluminium plate coated with zeolite paste).
Air influence on adsorption properties of zeolite CBV 901 and methanol

![Graph showing air influence on adsorption properties of zeolite CBV 901 and methanol](image)

Figure 5.27: Zeolite-methanol adsorption at $30^\circ$C

<table>
<thead>
<tr>
<th>Air in system [torr]</th>
<th>Time for methanol adsorption [sec]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>&lt;10</td>
</tr>
<tr>
<td>50</td>
<td>20</td>
</tr>
<tr>
<td>100</td>
<td>40</td>
</tr>
</tbody>
</table>

Table 5.7: Air influence on methanol adsorption

The comparison between the time for methanol evaporation and adsorption is presented in Table 5.8.

<table>
<thead>
<tr>
<th>Air in system [torr]</th>
<th>Time for methanol evaporation [sec]</th>
<th>Time for methanol adsorption [sec]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>60</td>
<td>&lt;10</td>
</tr>
<tr>
<td>50</td>
<td>120</td>
<td>20</td>
</tr>
<tr>
<td>100</td>
<td>240</td>
<td>40</td>
</tr>
</tbody>
</table>

Table 5.8: Air influence on methanol evaporation and adsorption
In this condition, the adsorption properties of zeolite are decreasing with rising amount of air in the system, which delays the adsorption process. The mechanism is the mass transfer of methanol through the inert air. As can be seen from comparison made in Table 5.8, the evaporation of methanol takes much longer in all the cases than adsorption. This indicates that the cycle times will be governed more by methanol evaporation. This kind of behaviour will increase the cycle time and decrease the whole system performance.

5.8 Thermo-Gravimetric Analysis (TGA)

Measurements of adsorption capacity in previous tests (section 5.5 to 5.7) have been based on concentration changes or pressure changes in the gaseous phase. In all previous cases, it has to be assumed that any recorded depletion of methanol vapour equals adsorption into the zeolite. This would leave some margin for error (methanol had an affinity for certain material surfaces).

In thermo-gravimetric analysis (TGA), the mass of the zeolite sample is monitored directly. A typical [15] resolution of a TGA is ±0.01mg with a temperature range of up to 1,000°C. The aim of this work is to cross check previous results.

5.8.1 Experimental Set up

Traditionally, a TGA is used to monitor the mass decay of materials on heating. However, with some modifications, it could be used to monitor weight gain from adsorption. Figure 5.46 shows a schematic diagram of the modified Stanton Redcroft TG760 TGA machine [15], [16] last calibrated by Thorn Scientific Services [17] on 18 July 2000 (ref. TGA10017). The original glass “casing” which sealed the whole system was connected such that a nitrogen-methanol gas mixture could be introduced. This enables the chamber to be filled with a constant flow of contaminant. Excess gas was vented out at the bottom of the electric furnace.
5.8.2 Experimental Procedure

The zeolite was initially dried at a temperature of 100°C for > 24 hours. It should be pointed out that drying was done in laboratories at the University of Bristol, and samples were sealed before transport to the TGA device at Harwell Laboratory, 160 km distant.

A sample was then placed in a platinum crucible (~Ø5mm x 3mm), suspended on one side of the microbalance. Once loaded, the electric furnace could be raised to completely surround the crucible.

The experiment started at a higher temperature (~150°C), lower temperatures could be achieved rapidly with the water-cooling jacket. It must be noted that during this initial heating, only nitrogen was allowed to flow through the chamber. Once a steady zeolite mass was achieved and noted, methanol was introduced by connecting the nitrogen
flow with methanol vessel. On saturation, the zeolite was reweighed and temperature was reduced such that another isotherm could be found. The change in mass and temperature was recorded on a chart recorder.

The test conditions were as follows:

- Mass of zeolite sample = 10 mg
- Zeolite type = CBV 901
- Zeolite size = 15μm
- Reported air-flow temp. $T_a \in \{24, 26, 32, 38\}$ °C
- Reported furnace temp. $T_f \in \{25, 50, 100, 150\}$ °C

The two reported temperatures correspond to a thermocouple located near the bed and one in the furnace (the exact location and calibration is not known). However, there is an obvious discrepancy between the two. The assumed thermocouples positions are shown in the heat flow diagram, Figure 5.29.

![Heat flow diagram](image)

**Figure 5.29:** Heat flow diagram in the modified TGA
Assessment of Physical Properties of Zeolite CBV901 and Methanol

Heat transfer calculations were done by Prasertmanukitch [9], which shows that the expected temperature sample is between the air-flow and furnace temperatures. The heat balance on the crucible could be approximated by the following Equation (5.3):

\[
\left( \frac{\sigma \varepsilon_0}{h} \right) (T_a^4 - T_f^4) = (T_c^4 - T_e^4) 
\]

(5.3)

The values of \( T_c \) had been computed for \( h = 9 \text{ W/m}^2\text{K} \) (corresponding to laminar flow with \( Nu = 3.66 \)), the Stefan-Boltzmann constant, \( \sigma = 5.67 \times 10^{-8} \text{ W/m}^2\text{K}^4 \) and surface emissivity, \( \varepsilon_0 \in [0.1, 0.2] \). The estimates (which indicated an uncertainty of 15°C) are tabulated below (Table 5.9).

<table>
<thead>
<tr>
<th>( T_a )</th>
<th>( T_f )</th>
<th>( T_c (\varepsilon_0 = 0.1) )</th>
<th>( T_c (\varepsilon_0 = 0.2) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>25</td>
<td>24</td>
<td>24</td>
</tr>
<tr>
<td>26</td>
<td>50</td>
<td>28</td>
<td>29</td>
</tr>
<tr>
<td>32</td>
<td>100</td>
<td>38</td>
<td>44</td>
</tr>
<tr>
<td>38</td>
<td>150</td>
<td>51</td>
<td>62</td>
</tr>
</tbody>
</table>

Table 5.9: Estimated crucible temperature, \( T_c \).

5.8.3 Results

Time restrictions forced analysis of only two runs of zeolite CBV 901. The results were repeatable to within ±2% as tabulated in Table 5.4. Thus, only one of the results using zeolite CBV 901 is shown in Figure 5.30.
Chapter 5  Assessment of Physical Properties of Zeolite CBV901 and Methanol

Equilibrium adsorption capacity, x (%)

<table>
<thead>
<tr>
<th>Furnace setting (°C)</th>
<th>Zeolite CBV 901</th>
<th>Zeolite CBV 901</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Run 1</td>
<td>Run 2</td>
</tr>
<tr>
<td>25</td>
<td>29</td>
<td>30</td>
</tr>
<tr>
<td>50</td>
<td>20</td>
<td>22</td>
</tr>
<tr>
<td>100</td>
<td>13</td>
<td>12</td>
</tr>
<tr>
<td>150</td>
<td>2.5</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 5.10: TGA results

It must be noted that the equilibrium adsorption capacities, x (circles) were based on the equilibrium mass after initial heating with nitrogen and not the mass of zeolite added initially. This is important since some moisture adsorption (~7%) may well have occurred on transportation. The shaded region represents the instant when methanol was introduced.

These tests again confirmed the general trends that adsorption capacity decreases with increasing temperature.
5.9 Dubinin-Astakhov Equation Fitting

The aim of this section is to fit the experimental data obtained in section 5.5 to the Dubinin-Astakhov equation, which was presented in chapter 3. This procedure produces the constants $x_0$, $k$ and $n$. After that, the concentration of the methanol vapour in the zeolite can be predicted by using the D-A equation, which will be only a function of adsorbent and saturation temperatures. The D-A equation will be used in the final chapter to predict the concentration of the methanol vapour in the adsorbent bed, when adsorption and desorption processes occur.

5.9.1 Experimental Data Fit

The experimental data, presented in Figure 5.32 were processed.

A MATLAB program was used to fit the data; this was developed by Dr Roger Thorpe from University of Warwick and applied after consultation. The program inputs are the data for adsorbent temperature, saturation temperature, concentration of the adsorbate and a weighting factor, which is used to give greater importance to data values with

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Figure 5.32: Experimental isosteres for zeolite and methanol
Chapter 5  
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Extracted results of all 2 tests (from Table 5.10) are plotted in Figure 5.31 as well as the results from the adsorption tests carried out for powder and coated zeolite in previous sections. It could be seen that there was an apparently linear trend between temperature and adsorption capacity at this particular concentration. This general trend was in broad agreement with previous test in sections 5.5 - 5.7.

However, the adsorption capacity decreased from 29% down to 3% when flow temperature increased from 23°C to 38°C. The change was substantially more significant than previously found in sections 5.5-5.7 where a similar decrease in $x$ was only found when temperature increased from 30°C to 100°C. This justifies the assertion made earlier that the true crucible temperature is far higher than the reported air temperature.

![Concentration of methanol](image)

Figure 5.31: Concentration of methanol (TGA analysis and experimental results comparison)
high concentration. The programme plots the data and its associated curve of best fit, and lists values for $x_0$, $k$ and $n$ in D-A equation. The result for this set of data is presented in Figure 5.33.

![Graph showing data points and a fitted curve](image)

**Figure 5.33: MATLAB fitting curve for experimental data**

The values found are:
- $x_0=0.2180$
- $k=28.4788$
- $n=1.7$

Hence:

$$x = 0.2180 \cdot \exp \left[ -28.4788 \cdot \left( \frac{T}{T_{sat}} - 1 \right)^{1.7} \right]$$  \hspace{1cm} (5.4)

The typical error for using Equation 5.4 is ± 3 to 5%.
5.10 Summary

This Chapter gives the assessment of physical properties of zeolite CBV 901 and methanol, which were chosen as a working pair, because of the low temperature of regeneration for this type of zeolite (100°C).

The findings can be summarised as follows:

(a) The powdered form of zeolite can be used to prepare the zeolite paste with a binder (5% of wallpaper paste in a mixture), with which the adsorbent bed can be coated. The metal surface has to be prepared (treated chemically) before coating. A layer thickness of 1 mm can be obtained.

(b) Vacuum tests have been developed in order to predict the adsorption isotherms for powdered zeolite as well as for coated plates. Subsequently the obtained results indicated a set of \( x \) that was found for the powdered zeolite is higher than for coated forms.

(c) Thermal Gravimetric Analysis gave highly repeatable results. However, despite the widespread use of this technique, there remain some uncertainty about the sample temperature.

(d) The presence of air in the system influences the methanol evaporation and adsorption. The evaporation of methanol requires more time than adsorption. The evaporation process will govern the cycle time.

(e) The constants were found for the D-A equation using the isosteres obtained from experimental isotherms. This facilitates predictions of the concentration of methanol vapour in an adsorption bed during the adsorption and desorption process.
Chapter 5  
Assessment of Physical Properties of Zeolite CBV901 and Methanol

References for Chapter 5


[10] Chell Instruments Ltd, North Walsham, Norfolk, Tel. 01692 402 488


[12] Courtesy of Dr Keith Morris, AEA Technology, Harwell, Didcot Oxfordshire, OX11 0QJ

Chapter 5  
Assessment of Physical Properties of Zeolite CBV901 and Methanol


[16] Instrument Specialists Inc., TGA 1000: 2402 Spring Ridge Drive, Suite B Spring Grove, IL 60081, USA

[17] TGA: Courtesy of Dr. Morris K., AEA Technology, Harwell, Didcot Oxfordshire, OX11 OQJ

[18] Thorn Scientific Services Ltd, 34 Taylor Road, Ashtead, Surrey KT21 2HY
Chapter 6

Design of an Adsorption Generator

6.1 Introduction

The adsorber is the most critical component of adsorption refrigeration systems. It is necessary to ensure satisfactory rates of heat transfer in all parts of this unit. This will give adequate cycle times and COP.

Note that Chapters 4 and 5 have dealt with the choice of a working pair and the properties of the CBV 901 and methanol pair in particular. This choice is an important factor in heat exchanger design.

6.2 Review of Other Working Designs

Some of the heat exchangers commonly used for adsorption cycles are:

- Plate-fin heat exchangers (Figure 6.1), [1]
- Flat-pipe heat exchangers (Figure 6.2), [2]
- Spiral-plate heat exchangers (Figure 6.3), [3]
- Shell and tube (with fins) heat exchangers (Figure 6.4), [4].
Figure 6.1: Typical assembly and cross-flow arrangement of plate-fin heat exchangers.
a) Plate fin exchanger assembly, b) Cross-flow arrangement

Figure 6.2: Flat-pipe heat exchangers. 1. Thermal fluid flow channel, 2. Adsorbent embedded

Figure 6.4: Shell and tube heat exchanger as an adsorber. 1. Thermal fluid in, 2. Thermal fluid out, 3. Connection to condenser, 4. Fins, 5. Coil tube, 6. Connection to evaporator

The advantages of a plate-fin heat exchanger are the small temperature difference (between inlet and outlet) and high thermal effectiveness. The large heat transfer area per unit volume and the low weight per unit transfer are further advantages.
In the flat-pipe heat exchangers, the thermal fluid may bring good thermal contact between adsorbent and the metallic wall, so the heat transfer is good. The main disadvantages are the temperature difference along the bed and the specific manufacture techniques needed.

The spiral-plate heat exchanger promises good heat transfer properties, compact size, low cost and wide availability. Finned shell and tube heat exchangers are simple in structure and cheap, but the thermal resistance between adsorbent and fins is high.

The initial characteristics to be considered when designing the heat exchanger are:

- Zeolite layer, the thickness of which influences the adsorption process time
- Geometry
- Working fluid for heating/cooling
- Materials
- Operating Conditions of the adsorbent bed

### 6.2.1 Zeolite Layer

Experimental studies [5], [6] have shown that the adsorbent can be synthesized on the surfaces of heat exchanger as continuous coatings using binders with high thermal conductivity. Also, it is indicated that the thermal conductivity of the resulting composite is greater than that of a granular bed. Thus, it seems that using thin films for zeolite can be advantageous.

Tatlier et al. [7] indicate that for a given metal thickness of the heat exchanger, there is an optimum zeolite layer thickness, $\delta_z$. The ratio of the metal/zeolite thickness influences significantly the COP of the adsorption refrigeration system. For thicker layers of zeolite, adsorption takes much longer than desorption, although almost no difference is observed for thin layers. On the basis of Tatlier's analysis, it is assumed that the optimum thickness of the zeolite layer is in the range of 1mm to 1.5mm.
6.2.2 Geometry

The main obstacle to achieving a good U-value would be a bad contact between the adsorbent and the heat exchanger wall. To avoid this problem, the zeolite layer is bonded chemically to the heat exchanger surface.

The heat exchanger must not only be compatible with the zeolite layer coating, but also it must be simple in structure and cheap. The shell and tube type heat exchanger has these characteristics.

The tube side could have fins in order to increase the heat transfer area. Whilst this provides a more compact design through increased effective area, it also increases the inherent thermal resistances between adsorbent and fins and between the tube and fins.

6.2.3 Working Fluid for Heating and Cooling

Wang et al. [8] and others suggest the use of oil as thermal fluid to control the heat capacity ratio, which strongly influences the COP. This fluid is preferred given its good thermal stability, thermal conductivity and specific heat capacity.

6.2.4 Materials

Tatlier [7] shows that the tube thermal conductivity is important factor in the determination of the U-values.

Materials such as Aluminum (Al) and Copper (Cu) are economic and also very good conductors (the thermal conductivity for copper is 385W/mK, and for aluminium 205W/mK). In some cases copper is not compatible with methanol, because of the corrosion possibility [9]. Therefore, aluminum is considered as a material of construction for a heat exchanger.
6.2.5 Operation Conditions of the Adsorbent Bed

The selection done through Chapter 5 for the most suitable adsorbent-adsorbate pair provides the operating conditions required to design the heat exchanger. These as follows:

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Expected temperatures and pressures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum zeolite temperature for adsorption</td>
<td>$T_1=35 , ^\circ C$</td>
</tr>
<tr>
<td>Maximum zeolite temperature for desorption</td>
<td>$T_3=100 , ^\circ C$</td>
</tr>
<tr>
<td>Methanol evaporation</td>
<td>$T_{ev}=7.5 , ^\circ C$</td>
</tr>
<tr>
<td>Methanol condensation</td>
<td>$T_{cond}=35 , ^\circ C$</td>
</tr>
<tr>
<td>Adsorbent bed pressure during evaporation</td>
<td>$P_{ev}=50 , \text{torr}$</td>
</tr>
<tr>
<td>Adsorbent bed pressure during condensation</td>
<td>$P_{cond}=200 , \text{torr}$</td>
</tr>
</tbody>
</table>

Table 6.1: Adsorption cycle conditions

6.3 Design of an Experimental Generator

Adequate rates of heat transfer ensure faster cycles, and ultimately more compact equipment. Unfortunately, zeolites are poor thermal conductors, and a finned heat exchanger is necessary. The adhesive adsorbent will have to be packed on and between the fins. Coating the fins with an adsorbent paste could be a suitable way of performing this task. The surface area of the fins is a factor that should be taken into serious consideration when designing a heat exchanger for this purpose. A larger fin surface area would not only lead to better conduction, but probably a better adsorption due to an increased mass of adsorbent.
The simplest construction (for the university laboratory) was a finned shell and tube type exchanger (See Figure 6.5). The heat exchanger consists of a single tube with circular plates fitted on it. All plates are coated with zeolite paste. First, the fluid that will circulate through the tube of the heat exchanger needs to be heated and cooled rapidly. The working fluid should have a high boiling point, and adequate thermal conductivity and heat capacity, plus a sufficiently low viscosity to promote turbulent flow. The selected working fluid was Shell’s Transcal N mineral oil.

Aluminium is the most suitable material of construction, because it does not react with methanol, on the shell-side of the heat exchanger.

The transient thermal performance of a shell and tube heat exchanger with coated fins (Figure 6.5) was calculated as a function of the tube diameter, the diameter of the fins and thickness of the layer. [10]
6.3.1 Choice of Coating Arrangements

Initially, the zeolite volume per plate (coated on both sides) was calculated from:

\[ V_z = 2 \cdot \frac{\pi}{4} \cdot (d_f^2 - d_0^2) \cdot \delta_z \]  
(6.1)

Where:  
- \( d_f \) is the fin diameter,  
- \( d_0 \) is the pipe outside diameter,  
- \( \delta_z \) is the zeolite layer thickness.

The zeolite mass per plate is:

\[ m_z = \rho_z \cdot V_z \]  
(6.2)

After that the number of fins situated on a tube was obtained from:

\[ n_f = \frac{m_{z,\text{needed}}}{m_z} \]  
(6.3)

The primary objective was to place 100g of zeolite on the heat exchanger surface for a given shell. It was found that 50 fins of outside diameter 76mm were needed. They were placed on a nominal \( \frac{1}{2}'' \) (12.7mm) outside diameter tube. Fifty plates were coated with a 1mm thick layer of zeolite or less in some cases, which gave the total mass of zeolite 100 g [11].
6.3.2 Heat Transfer Coefficient at the Oil-Tube Interface

The heat transfer coefficients were calculated assuming:

(a) physical properties apply to the mean oil temperature
(b) the pipe wall is highly conductive
(c) steady, turbulent flow
(d) temperature is constant across the pipe diameter.

Hence, if the speed of the oil is 0.5 m/s, the heat transfer coefficient can be calculated using the Dittus Boelter equation for Nusselt number [11]:

\[ Nu = 0.023 \cdot Re^{0.8} \cdot Pr^{n} \] (6.4)

where \( n = 0.4 \) for heating and 0.3 for cooling.

The Reynolds and Prandtl numbers were calculated from the following Equations:

\[ Re = \frac{u \cdot \rho \cdot d_0}{\mu} \] (6.5)

\[ Pr = \frac{c_p \cdot \mu}{k} \] (6.6)

The heat transfer coefficient was found from the Nusselt number:

\[ Nu = \frac{h \cdot d_0}{k_{\text{eff}}} \] (6.7)

Now, by substituting Equations (6.5), (6.6), and (6.7) in Equation (6.4), the heat transfer coefficient of oil was calculated for heating and cooling at different temperatures. The necessary data were input into an Excel spreadsheet and the variations of the heat transfer coefficient with pipe diameter and oil temperature were generated. These predictions were calculated for an oil velocity of 0.5 m/s. They are represented graphically in Figures 6.6 and 6.7 given below.
Figure 6.6: Variation of the heat transfer coefficient with pipe diameter and oil temperature for adsorption

Figure 6.7: Variation of the heat transfer coefficient with pipe diameter and oil temperature for regeneration

The expected heat transfer coefficient was high for higher oil temperature and decreased with pipe diameter (Figures 6.6, 6.7). In addition, the heat transfer coefficient for the regeneration process (Figure 6.7) is higher than the one for adsorption (Figure 6.6). Some comparisons can be made after calculating h in various environments. (See Figures 6.8 and 6.9.)
Both shapes of curves from Figures 6.8 and 6.9 are similar. It can be observed that the heat transfer coefficient decreases with lower velocities values, and it is higher for adsorption (at the same working fluid velocity).

The heat transfer coefficients for the heat exchanger were calculated, using the dimensions and data presented above.
In the final design, the following values were thought appropriate:

- inner diameter of tube 10mm,
- oil velocity 0.5 m/s,
- heat transfer coefficient (at 20°C) is 132 W/m²K,
- heat transfer coefficient (at 120°C) is 560 W/m²K.

### 6.3.3 Temperature Distribution

This section is associated with the prediction of the temperature distribution in the heat exchanger fin during the heating cycle. This was modelled in Matlab and the program is presented in Appendix B.

![Figure 6.10: Finite difference grid for the wall-fin-zeolite system](image)
In the model, the net energy into element in time step $dt$ was presented as:

$$
\begin{align*}
&\{UA_{\text{left}}(i,j)(T_{i-1,j} - T_{i,j}) + UA_{\text{right}}(i,j)(T_{i+1,j} - T_{i,j}) \\
&+ UA_{\text{top}}(i,j)(T_{i,j+1} - T_{i,j}) + UA_{\text{bot}}(i,j)(T_{i,j-1} - T_{i,j})\}dt = \\
&\text{mass}_{i,j} \cdot C_{p,i,j} \cdot [T_{\text{NEW},i,j} - T_{i,j}]
\end{align*}
$$

(6.8)

One array included the heating fluid, tube wall, the fin elements and the zeolite elements. At the beginning, the various $UA$ values were calculated and stored as separate arrays so that the $T_{\text{NEW}}$ array could be worked out in different time steps from the $T_{\text{OLD}}$ values. The areas $A$ were calculated as cylindrical at different radiuses. The $U$ values were taken from conduction everywhere except at the fluid-wall area and between fin-zeolite. For example to calculate $U$ between the fin and zeolite nodes:

$$
\frac{1}{U} = \frac{t_f/2}{k_{Al}} + \frac{t_z/2}{k_z}
$$

(6.9)

where:
- $t_f$ is the fin cell thickness
- $t_z$ is the zeolite cell thickness
- $k_{Al}$ is the aluminium fin conductivity
- $k_z$ is the zeolite conductivity

The thermal conductivity of the zeolite part was taken as 0.43W/mK from reference [7].

At the adiabatic boundaries the appropriate $U$ values were set to zero. This was done for the surroundings; because no heat could be removed to the outside and on the wall-zeolite boundary, to make sure that the heat transferred to the zeolite come only from the fin.

To keep the case simple, the mean specific heat for the zeolite over the heating and cooling that included the sorption heat was calculated from:

$$
C_{p,\text{mean}} \approx \frac{Q_{T_1-T_3}}{T_3 - T_1}
$$

(6.10)

$$
Q_{T_1-T_3} = C_{p,z} (T_3 - T_1) + x_{\text{mean}} \cdot C_{p,m} \cdot (T_3 - T_1) + (x_{T_3} - x_{T_1}) \cdot H
$$

(6.11)
The following aspects were taken into account to predict the temperature distribution in the system as well as the zeolite tip temperature as a function of time:

(a) the influence of heat transfer coefficient (oil-wall)
(b) the influence of zeolite layer thickness
(c) the influence of fin radius
(d) the influence of fin thickness.

All the results are tabulated in Appendix B and selected data are shown graphically below. Figure 6.11 shows how the different heat transfer coefficients influence zeolite heating in the base heat exchanger geometry. (The heating fluid was at 120°C.)

With a heat transfer coefficient of 560 W/m²K (see section 6.3.2) the zeolite should approach the fluid temperature in 300s of heating time.

Figure 6.11: Zeolite tip temperature as a function of time and heat transfer coefficient between oil and tube wall.

Figure 6.12 shows, how the zeolite layer thickness would change the time for heating the zeolite coating to required temperature. For layers between 0.5 to 2.5 mm thick the difference in the temperature is only 1K. Layers thicker than 2.5mm will substantially increase the cycle time.
Figure 6.12: Zeolite tip temperature as a function of time and zeolite layer thickness.

Figure 6.13 show that the fin length is important, because longer fins increase the heating time. On the other hand fin thickness has little impact on a cycle time (Figure 6.14).

Figure 6.13: Zeolite tip temperature as a function of time and fin length
The temperature difference within the zeolite layer itself during heating appears to be less than 1 K.
6.4 Conclusions

The specifications of the test facility are as follows:

<table>
<thead>
<tr>
<th>Number of tubes</th>
<th>1</th>
<th>Zeolite layer</th>
<th>1 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of fins</td>
<td>50</td>
<td>Mass of zeolite</td>
<td>100 g</td>
</tr>
<tr>
<td>Tube length</td>
<td>0.5 m</td>
<td>Thermal fluid</td>
<td>Oil Transcal N</td>
</tr>
<tr>
<td>Pipe diameter</td>
<td>Inner=10 mm</td>
<td>Oil velocity</td>
<td>0.5 m/s</td>
</tr>
<tr>
<td></td>
<td>Outer=12.7 mm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Material</td>
<td>Cover: Al</td>
<td>T_{input of oil}</td>
<td>Heating: 120 °C</td>
</tr>
<tr>
<td></td>
<td>Pipe, fins: Al</td>
<td></td>
<td>Cooling: 20 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6.2: General specifications

(All the drawings of the parts of the heat exchanger are presented in Appendix C.)

The calculations apply to the methanol-zeolite CVB901 pair (see Chapters 4 and 5), which showed the highest COP value. The selection of aluminium as the tube wall reduced the influence of thermal resistances by conduction. (Additionally, aluminium does not react with methanol.) The adsorbent (zeolite) provided the more significant thermal resistance due to both its low thermal conductivity and the lack of good contact between the adsorbent and the heat exchanger wall. If the zeolite layer is synthesized on heat exchanger surface using a chemical binder [7], the inherent thermal resistance is reduced. In the heat exchanger design, we considered a synthesised zeolite layer equal to 1 mm.

A finned tube heat exchanger was selected. It can be easily coated with zeolite, is simple to construct and is relatively cheap Transcal N oil was selected at the thermal fluid, because it has good heat capacity ratio and an acceptable thermal stability.
At the thermal fluid-tube wall interface the convective heat transfer coefficient was sensitive to oil velocity, oil temperature and tube diameter. During adsorption, the maximum temperature of 100°C is to be reached by the zeolite. From the simulations a satisfactory heat transfer coefficient is obtained if the thermal fluid passes through the tube, with a pipe inner diameter equal to 10, at 0.5 m/s and 120 °C.

Finally, simulated results were obtained for the temperature distribution in heat exchanger with a variation in zeolite and fin thickness as well as the fin length. These showed the system capable of dealing with heating. However a compact, cheap and reliable heat exchanger is required, the shorter geometry had been chosen, which includes a 0.5m long tube with 50 fins.
References for Chapter 6


Chapter 7

Experimental Apparatus

7.1 Introduction

This chapter describes the design and construction of a laboratory scale pilot plant, plus necessary experimental methods and procedures.

The plant is intended to facilitate the investigation of the cooling effect achieved using zeolite CBV 901 and methanol as a working pair in the system. The coefficient of performance of the plant was extremely small, and the plant should be considered as a test facility rather than a demonstration refrigerator. The plant is sufficiently flexible to permit certain physical effects to be studied in isolation, rather than as a part of a refrigeration cycle. One constraint on the experimental work was the small budget (~£500 per year).

7.2 Experimental Rig Design and Construction

7.2.1 General Arrangement

A schematic of the experimental rig is presented in Figure 7.1. The test rig consists of five main parts, which are:

a) The methanol evaporator;
b) The adsorption generator;
c) The methanol condenser with receiver;
d) The hot and cold oil tanks, which are connected with heating/cooling system for generator;
Chapter 7

Experimental Apparatus

e) The cold water reservoir.

In essence, the generator extracts vapour from the evaporator, causing cooling. The remaining equipment is used to recover methanol from the generator and return it, in liquid form, to the evaporator. The system is designed for a cooling load, in the evaporator, of up to 200W. A detailed description follows.

Figure 7.1: Experimental rig schematic layout
Valve V1 connects the evaporator to the generator. The generator itself is connected to the condenser (valve V2). To enable heat transfer and thus regeneration of the bed, the generator is connected to an oil circulation loop by two three-way (V5, V6) valves, which are operated manually. Instead of having a single cycle, the heating and cooling systems are separated from each other (the generator has to be heated and cooled periodically). When the generator is heated the methanol vapour pressure increases, such that methanol is rejected via V2 to the condenser. The condenser is fitted with a receiver, to measure the volume of condensate in a given time interval. The condensate passes via a capillary tube and valve V3 to the evaporator. The capillary tube acts as an expansion valve, which reduces the methanol pressure. A separate system provides cooling water to both the condenser and the (colder) oil tank.

### 7.2.2 Methanol Evaporator

The methanol evaporator is build as a 1 litre capacity cylinder, sealed with a flanged lid. The seal is made with 6 x M6 bolts and a nitrile o-ring. The required amount of methanol is added to the evaporator with a 100mL syringe, which is connected to the top plate using stainless steel tubing and a 6.34mm needle valve, supplied by Swagelok [1]. Other connections to the evaporator are (See Figure 7.2):

- A stainless steel capillary tube; where condensed liquid methanol returns to the evaporator from the condenser
- Valve V1, linking the evaporator with the generator (Edwards [2] Speedivalve NW16 fittings;)
- Connection to a Edwards high vacuum pump (model E2M5); the best vacuum obtained is 1 torr
- A pressure gauge ($P_{ev}$) (ASG NW16 1000mbar active strain gauge, produced by Edwards, accuracy of ±0.2% full scale). This is connected to an AGC Active gauge controller, which can drive up to 3 active gauges automatically recognising the types of active gauge connected
Chapter 7  Experimental Apparatus

- A K-type probe thermocouple; placed inside evaporator to monitor the liquid methanol temperature ($T_I$)

Figure 7.2: Methanol evaporator
The engineering drawings for the evaporator and associated parts of the system are presented in Appendix C.

7.2.3 Generator

The generator design utilises a shell and finned tube. The design procedure was presented in Chapter 6, which gives the final construction parameters. The schematic of generator can be seen in Figure 7.3. All parts are made of aluminium. The inside tube of 12.7 mm diameter has 50 circular fins of 76 mm diameter and 2 mm thickness placed on it, with a 10 mm separation obtained by spacing rings made of Nylon 66. The second function of the nylon rings is to insulate the non-finned surface of the pipe from heat losses.

The diameter of the shell is 101.6mm. (The drawings with all dimensions are presented in Appendix C.) It has an inlet and an outlet for methanol vapour, as well as for heating/cooling fluid.
Consequently, the generator has two sides:

- Methanol; methanol vapour from the evaporator moves to the outer surface of the fins (which are heated or cooled periodically)
- Oil; the heating/cooling loop for oil passes through inside of the tube, and allows heat transfer between the metal and fluid

Additional parts of the generator are:

- The pressure gauge ($P_{\text{gen}}$); This is an ASG NW16 with a reported accuracy of ±0.2% full scale, connected to AGC Active gauge controller
Figure 7.4: Generator top with active strain gauge and oil outlet for heating/cooling loops

- K-type probe thermocouples; placed inside generator to monitor the methanol vapour temperature in different places inside ($T_2, T_3, T_4$), plus one at the end of the fin ($T_5$) to monitor the heat exchanger temperature while heated or cooled with oil

One of the most important aspects of the generator is the set of fins. Their preparation was presented in Chapter 5. The fins are circular, surface treated chemically and coated with zeolite paste (See Figure 7.5).

Figure 7.5: Single fin coated with zeolite paste
Fifty fins of this type were placed on the 0.635m section of pipe and secured at each end of the pipe with an aluminium-retaining ring, which can be seen on Figure 7.6. This design facilitated changes to the number of plates on the pipe and their spacing.

Figure 7.6: Inside part of the generator; 12.7mm pipe with fins coated with zeolite paste

Figure 7.7 presents a photographic record of the generator during its construction. Thereafter, the generator was insulated with a 2cm thickness of glass fibre, plus an aluminium foil radiation shield.

Figure 7.7: The generator
The top and bottom (A and B) connect the generator with the heating/cooling utilities. The side connections are to the evaporator (C) and condenser (D), as described previously.

### 7.2.4 Condenser

![Figure 7.8: Methanol condenser scheme and real view](image-url)
Chapter 7

Experimental Apparatus

The condenser presented in Figure 7.8 consists of:

- A glass vessel of 75 mm diameter, supplied by QVF [3], with all necessary flanges and fittings
- Top and bottom plates designed and manufactured specially for the condenser at the University of Bristol workshop (see drawings in Appendix B)
- A stainless steel coil connected to the top plate with NPT fittings supplied by Swagelok
- The liquid methanol receiver designed and manufactured with all connections (see appendix 1); this is a glass tube (diameter=40 mm, length=180 mm, thickness=5mm) fitted with NW40 connections at each end

The thickness of the glass was checked using the equation 7.1:

$$ P_{\text{cond}} = 2.2 \cdot E \left( \frac{\delta}{d} \right)^3 $$

where $E$ is the Young’s module = 6.6x10^4 MPa, $d$ is the diameter of the tube and $\delta$ is the thickness of the tube.

$$ \delta \geq d \cdot \left( \frac{P_{\text{cond}}}{2.2E} \right) $$

From equation (7.2) the thickness of the glass $\delta \geq 0.5$mm (the glass tube thickness is 5mm), so there is a factor of 10 for safety.

- A K-type probe thermocouple ($T_{\delta}$) was placed inside condenser
- A Budenberg capsule vacuum pressure gauge (0+-1 bar range)

The Condenser is connected to the evaporator and generator using Edwards vacuum fittings with nitrile o-rings and clamps sealed with vacuum grease. The pipe work between the evaporator, bed and condenser is made from stainless steel. The valves V1, V2 and V3 are Speedivalves- these are manual operation isolation valves (SP16K) with a nominal bore size of 16 mm produced by Edwards, fitted with NW16 connectors. The valve body is made from aluminium and the complete valve is leak tight to better than $10^{-6}$ mbar. The completed methanol loop is presented in Figure 7.9 below.
Figure 7.9: The evaporator, generator and condenser connected together to perform in methanol cycle
7.2.5 Heating and Cooling Loop for Generator

The heating/cooling system for the generator includes two separate tanks, each of 104 litres volume, made of copper sheet and insulated with foam, produced by *The Copper Cylinder Company, Birmingham, UK*. They are connected together and with the generator by copper piping, either 15 or 22 mm diameter, and with two 3-way quarter turn SS 12.7mm BSP ball valves (V5, V6) manually operated and supplied by *RS Components* [4]. The ball valves allow the system to be switched between heating and cooling. The pump supplied by *Jabsco* [5] (model 53080-2003) is situated in the cycle to circulate the fluid. The schematic of the system is presented in Figure 7.10.

![Figure 7.10: Schematic layout of cooling and heating loop for generator](image)

The fluid in hot tank is heated to the required temperature with a stainless steel immersion heater of 2 kW power and regulated by a *Eurotherm* [6] thyristor and temperature unit (range 0 to 400 °C). The cold tank is cooled by the separate water system. The first part of the procedure is to heat the generator with the fluid from the hot tank from 35 °C to around 100 °C. After that, the switch over between the tanks is made using valves V5 and V6. The cold tank is reduces the generator temperature back
to ~35 °C. Thereafter the temperature in the cold tank will have risen slightly; the water loop is used to mitigate this effect.

Figure 7.11: The hot/cold tanks connections

7.2.6 Water Loop

The water loop is presented as a part of complete experimental rig in Figure 7.1. It consists of:

- The water reservoir, 100 litres capacity
- The laboratory refrigeration unit, produced by Townson & Mercer Ltd, which allows us to decrease the temperature of the water supply,
- The domestic central heating circulator water pump (model UPS 15-50) produced by Grundfos [7], flow 4.5 m³/h, head 6 m, length 130 mm
- Copper piping, 15 and 22mm diameter, with a set of manually operated brass gate water system valves supplied by RS components, to switch the flow between condenser and cold tank if necessary.
- A K-type thermocouple is placed in the container to monitor the water temperature ($T_w$).
7.3 System Instrumentation

After construction of the experimental rig, a set of thermocouples, pressure gauges, and data loggers was added to the system to facilitate data acquisition.

7.3.1 Thermocouples

A set of K-type thermocouples was attached to the to monitor the system temperature. All the thermocouples were fitted with quick wire connectors; the line plugs and sockets were supplied from RS Components. The temperature accuracy of the thermocouples was ±0.5 °C. Two types of thermocouples were used:

- Probe thermocouples, which were specially fitted in the system parts using nitrile o-rings and designed nuts in order to decrease the system leakage (placed inside evaporator, generator and condenser)
- Surface attached thermocouples; placed on outside surface of generator (to monitor the shell temperature), the oil inlet and outlet to generator, on the hot tank surface and inside water bath

7.3.2 Pressure Gauges

Two types of pressure gauges were used in the system:

- An Active Strain Gauge, ASG NW16 1000mbar, produced by Edwards, accuracy of ±0.2% full scale, corrosion resistant, made of SS 316; to monitor pressure changes in evaporator and generator
- A Budenberg capsule vacuum pressure gauge (0–1 bar range), to check the pressure range in the condenser
7.3.3 Data Control

Two data loggers were employed to acquire the data from thermocouples and vacuum gauges:

- **ADU**- Autonomous Data Acquisition Unit, MM 700 Series, produced by *ELE International*, where all the thermocouples were attached. The control process and data logging was performed utilising the dedicated ADU software running on standard 486/win 3.11 PC. All the experimental data was logged at 10 seconds intervals (sampling frequency of 1 Hz per channel) and written to floppy disk for processing and analysis at a later stage.

- **AGC**- Active Gauge Controller, produced by *Edwards*, which can drive up to 3 active gauges automatically recognising the types of active gauge connected (evaporator and generator gauges). This allows the unit to scale the output accordingly to display the correct pressure range. Reconfiguring the controller simply by means of unplugging one head and plugging in another. The RS232 serial communication option gives full remote control of the AGC by a host computer. An ASCII character string protocol allows all functions to be controlled and data to be captured for storage and processing. The AGC can continuously show the reading from any of attached heads. The experimental data was logged at 10 seconds intervals.
7.4 Leakage Tests

7.4.1 Leak Tests

The purpose of this part was to detect the leakage into the system. The system was connected to a mass spectrometer. Parts of the system were covered with foil and helium (supplied by BOC gases) passed on the outside of the main rig connections. The mass spectrometer was employed in order to detect any helium passing through the rig seals [8].

Whenever helium is detected; audio and visual signals are given on an arbitrary scale from 0 to 10. The spectrometer took ~15 minutes to return to its ambient reading following the detection of helium. Any indication of helium resulting in rig connections being broken, resealed, and rechecked.

7.4.2 Vacuum Tests

After testing the experimental rig seals with helium samples, a set of vacuum tests was completed. In each test the complete system was vacuumed to between 1 and 5 torr pressure. Thereupon, the system was separated from the pump and pressure gains were recorded with the AGC.

The reason for this part was to predict the air ingress into the system, and its likely influence on overall performance. The evaporator and generator were chosen for these tests after using helium sampling, because even after resealing small amounts of helium were detected by mass spectrometer (2±3 in the scale). It was decided not to test the condenser, because of holding by it the vacuum for a very long time (3 months) with pressure gains of < 5 torr.
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The first vacuum tests were carried only for the generator. The results are presented in Figure 7.12. It can be observed from the figure that resealing the generator parts decreased the pressure gain slightly to 1 torr/hr. The general leakage from the generator is 1.5 torr in one hour, which is satisfactory for further experiments.

![Leakage tests in generator](image)

Figure 7.12: Leakage tests in generator

The same set of tests was carried out for the evaporator. Firstly, it was vacuumed down to 1 torr and then disconnected from the other parts of the system. Pressure gain was recorded as a function of time. The effect of this test is presented in Figure 7.13 below.
The pressure loss of 5 torr per one hour from evaporator can be noticed in Figure 7.13. Subsequently, all the connections were resealed with greater amount of vacuum grease and fresh PTFE tape. Next, the evaporator was checked again with the result of 2 torr pressure loss in one hour. This will not influence particularly the system performance, so no additional tests were carried out.

Above results are satisfactory, when related to measurements of air influence on evaporation and adsorption in Chapter 5. Almost no change in methanol evaporation or zeolite adsorption rate was detected for 50 torr air pressure inside the vacuum chamber. Because of that, the pressure loss of 5 torr per hour is acceptable.
7.5 Operating Procedures

7.5.1 Introduction

The experimental rig system has to be prepared before commencing experimental runs. It is necessary to arrange the heating and cooling systems as well as set up the main parts of the rig: the evaporator, generator and condenser. The experimental data was obtained and logged on the computer throughout each experiment.

7.5.2 System Initialisation

The system initial preparation consists of following steps:

(a) The heating/cooling loop is set up; the immersion heater in the hot tank is switched on in order to reach the temperature necessary to regenerate the generator in desorption phase.

(b) The cold water tank is cooled to 15°C with the laboratory refrigeration unit. Vacuum is applied to the rig to pressures of <50torr (generator) and <200 torr (condenser).

(c) The evaporator loop is charged, with a calculated volume of methanol. For example if 260 g of zeolite is employed in the system with a maximum adsorption of 20 %, the minimum amount of methanol in the system is 52 g or 70 mL. The evaporator is then charged with about 50% more than this; typically with 100 mL of methanol.

(d) The system valves are set to correct positions.

(e) The data logging systems are initialised.


### 7.5.3 Data Logging

The data from the experimental rig was acquired and logged by two computers implementing the instrumentation and equipment discussed in section 7.3 of this chapter. During each experiment run the following parameters were logged:

a) The cycle time [seconds]

b) Temperatures [°C]

- \( T_{I} \) - temperature in evaporator
- \( T_{2} \) - temperature in generator (bottom part)
- \( T_{3} \) - temperature in generator (middle part)
- \( T_{4} \) - temperature in generator (top part)
- \( T_{5} \) - temperature on the fin in generator (far end of the fin)
- \( T_{6} \) - temperature in condenser
- \( T_{7} \) - temperature of the heating/cooling fluid flowing to generator (IN)
- \( T_{8} \) - temperature of the heating/cooling fluid flowing from generator (OUT)
- \( T_{9} \) - temperature of the fluid in the hot tank
- \( T_{10} \) - temperature of the water in the reservoir
- \( T_{11} \) - temperature on the generator surface outside (bottom)
- \( T_{12} \) - temperature on the generator surface outside (right plate)
- \( T_{13} \) - temperature on the generator surface outside (left plate)
- \( T_{14} \) - temperature on the generator surface outside (top)

2) Pressure [torr]

- \( P_{ev} \) - pressure in the evaporator
- \( P_{gen} \) - pressure in the generator
The methanol concentration in the generator during adsorption was calculated using the Dubinin-Astakhov equation presented in Chapter 5. The results were presented as (g of methanol/g zeolite) as a function of cycle time.

### 7.5.4 Cycle Time

The system cycle times were defined during the experiments. It was related to the heating and cooling time in generator. The cycle varies from 30 minutes to 2 hours. The first experiment runs were done for total cycle time of approximately 1 hour. Than the time was reduced down to 30 minutes by changing the heating fluid from water to oil, which allows moving to higher temperatures, as well as reduces the total cycle time, which is highly influenced by the heating process.

### 7.6 Summary

This chapter discusses the rig design and assembly of the test facility. The main parts of the rig are the evaporator, generator and condenser, and it is supported by heating/cooling loops. The thermocouples and pressure gauges were situated in the system in order to monitor temperature and pressure changes during the cycles.

The set of vacuum test was completed on the rig, in order to predict the air infiltration into the system, and its likely influence on overall performance. All system was checked and poor connections resealed. The general leakage from the generator is 1.5 torr in one hour and from evaporator and generator 5 torr, which is satisfactory for further experiments.

The system is designed for a cooling load, in the evaporator, of up to 200W. The amount of zeolite placed in the generator can be between 100-500 grams. The operation temperatures of the system are 20-120 °C.
References for Chapter 7


[2] Edwards, Severn Science Ltd., 5 Short Way, Thornbury Industrial Estate, Thornbury, South Gloucester, UK, Telephone: +44 (0) 1454 414723, Fax: +44 (0) 1454 281680


8.1 Introduction

This chapter will present the experimental data associated with the facility described in Chapter 7. Several sets of data were logged and analysed for various external heating temperatures and cycle times. The experimental runs are presented in Table 8.1.

<table>
<thead>
<tr>
<th>Run</th>
<th>Cycle time [min]</th>
<th>Cycle Min/Max temperatures [°C]</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>40-75</td>
<td>Short cycle, low T, water as a heating fluid</td>
</tr>
<tr>
<td>2</td>
<td>120</td>
<td>30-80</td>
<td>Long cycle, high T, water as a heating fluid</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>20-80</td>
<td>Short cycle, low T, oil as a heating fluid</td>
</tr>
<tr>
<td>4</td>
<td>120</td>
<td>25-95</td>
<td>Long cycle, high T, oil as a heating fluid</td>
</tr>
</tbody>
</table>

Table 8.1: Runs carried out on pilot rig

The results for the cycles can be predicted in the same way as the idealised cycle ABCD, which was used for the COP validation procedure for a single-bed system, presented in Figure 8.1.
There are many non-idealities, which will cause real cycles to deviate from the shapes presented above. These include the thermal inertia of the casing, which is made of aluminium and directly connected to the pipe passing the heating fluid. Thus, the heating is not instantaneous. Also, the temperature distribution in the fins during the heating/cooling processes depends on the pipe-fin connection. Moreover, there is a large quantity of gas phase vapour per unit of zeolite mass, so the processes AB and CD might not be isosteric. The evaporation and adsorption times depend on the permeability of the zeolite coating, and can be affected by air presence in the system. The control systems might lead to further deviations, because the valves are operated manually.
8.2 Generator Heating and Cooling Cycles

The experimental rig is presented in Figure 8.2. The explanation of the system and the experimental procedure was presented in Chapter 7.

Figure 8.2: Experimental rig scheme
8.2.1 Generator Temperature Cycles

The variations of the temperatures with time were recorded, for the thermocouples from $T_1$ to $T_{14}$ (see section 7.5.3); thermocouple locations are presented in Figure 8.2. The experiments 1 and 2 were carried out with water as a heating/cooling fluid.

The set of temperatures will be presented for Run 1. The complete set of temperatures can be seen in Figure 8.3 plus isolated temperature subsets in Figures 8.4-8.8.

![Figure 8.3: Complete temperature cycle (Run 1)]
Figure 8.4: Temperature at the fin tip ($T_3$) and in the gas space ($T_2$, $T_3$, $T_4$), (Run 1)

Figure 8.5: Temperatures on the generator shell (Run 1)
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Figure 8.6: Heating/cooling temperatures in (T7)/out (T8) generator (Run 1)

Figure 8.7: Temperature in hot tank (T9) and cold water reservoir (T10), (Run 1)
The temperature of the hot tank represented by thermocouple $T_9$ reaches 96 °C. This allows the generator to achieve a temperature of 76 °C on the far end of the fin (thermocouple $T_3$). In the cooling cycle, the lowest temperature is approximately 25 °C.

The variations of the generator temperatures with time for different cycle times are presented in Figure 8.9. For a long cycle time (Run 2), about 2 hours for one heating/cooling cycle, the maximum temperature of the generator is 80 °C and goes down to 20 °C in the cooling cycle. For short cycle of 30 minutes (Run 1), the temperature level is between 25 to 75 °C. As it can be seen, increasing the cycle time will not produce higher temperature in the generator than 80 °C.
The set of the temperatures for heating and cooling process is presented in Figure 8.10 (Run 1). The temperature of water in hot tank is 96 °C, in the cold tank 15 °C. During the cycle, the tanks are switched on/off depending on whether the system is in the adsorption or the desorption stage. The temperature of the heating/cooling fluid passing the generator varies from 2-5 °C from temperature of water in the tanks. There is not a large heat loss on the way to the generator.

Figure 8.10: Heating/cooling cycle for generator
Surprisingly, the temperature of the fins inside the generator cannot get higher than 76-78 °C. There is a large heat loss inside the generator, which is connected with construction of this component.

The generator temperatures recorded during Run 2 show that hot fluid passing through the heat exchanger is heating other parts to quite high temperatures, especially the shell. (Figure 8.11, thermocouples $T_{11}$-$T_{14}$)

The reason for this is that there is good heat conductivity through the top and bottom plates of the heat exchanger, which are directly placed on the heating/cooling pipe and give a direct connection to the generator shell.

![Figure 8.11: Generator full temperature set (Run 2)](image)

After two of sets of experiments with water as a heating/cooling fluid, the next step was to apply the Transcal N oil to the system (Run 3 and 4). The results for this type of cycle can be seen in Figure 8.12 as a set of temperatures for the system during Run 3. The temperature of the hot oil reaches 135°C. This gives the highest generator temperature of 96°C. The 100°C required for zeolite CBV 901 full regeneration can be achieved with oil as a heating fluid.
The only disadvantage is the large heat loss associated with heating the casing, as was observed with earlier experiments. Different design could improve it, for example using a glass shell for generator. Depending on the heat source, it might be preferable to heat the generator externally.

With regard to the shell side, glass will be able to reduce possible effects of heat transfer due to conduction to the cover from the flange junctions in the heat exchanger. The metallic cover surface could also produce radiation effects. In this way, this effect could be reduced and the heat transfer in the adsorbent bed will not be affected.

### 8.2.2 Generator Pressure Cycles

The variation of generator saturation pressure with time is presented in Figure 8.13. The minimum and maximum saturation pressures are approximately 90 and 210 torr, as indicated by *The Edwards* software. The first part of the experiments was carried out with two active strain pressure gauges placed in the bottom and top parts of the generator, with readings indicating the difference of 2 torr (the top pressure was around 2 torr higher than the lower part of generator). The pressure in the evaporator was only monitored with a *Budenberg* capsule vacuum pressure gauge (0±1 bar range), so
precise readings were not possible, which explains the shape of the bottom part of the graph in Figure 8.13.

![Figure 8.13: Saturation pressure of methanol in generator during Run 1](image)

The valve V1 between generator and evaporator was opened manually, when the pressure in the generator was close to the evaporator pressure. The diagram shows that evaporation pressure was not controlled accurately with the simple vacuum gauge (see the circle in Figure 8.13). This caused an undesirable delay in the generator with the evaporator, which means that the generator pressure was much lower than the pressure level in evaporator.

Because of problems with reading the correct evaporator pressure, and the small difference in pressure inside the generator, one of the active strain gauges from generator was moved and placed in the evaporator. The next set of experiments (Run 2) was carried out with more precisely measured pressures in the evaporator and generator. The results are presented in Figure 8.14.
Figure 8.14: Controlled pressure readings in the evaporator and generator (Run 2)

Figure 8.14 shows that monitoring the pressures in the evaporator and the generator allows less fluctuation in pressure when connecting the two elements together.

Figure 8.15: Pressure in the evaporator and generator for experiments with oil as a heating/cooling fluid (Run 3)
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The pressure changes in the evaporator and generator for the system working with oil as a heating/cooling fluid are presented in Figure 8.15. The only difference between water and oil as a heating fluid is that higher temperature and pressure levels in the experimental rig are obtained for oil. The minimum and maximum saturation pressures were approximately 110 and 300 torr.

8.2.3 Generator Concentration Cycles

The generator concentrations were calculated by applying the Dubinin-Astakhov equation, obtained for experimental data in section 5.9.1 (Equation 5.4). The Dubinin-Astakhov equation is used to predict the methanol vapour concentration within the generator during adsorption/desorption processes. The D-A equation is recalled below:

\[
x = 0.2180 \cdot \exp \left[ -28.4788 \cdot \left( \frac{T}{T_{\text{sat}}} - 1 \right)^{1.7} \right]
\]  (8.1)

The true temperature \( T \) of the generator is needed to calculate \( x \), but there is of course a temperature gradient along the fin. As a first approximation, the temperature on the tip of the fin will be used for the calculations and for plotting the cycles. This is the estimated temperature of the generator bed.

The saturation temperature, \( T_{\text{sat}} \) in [K], is calculated from the measured methanol saturation pressures [torr] by applying the equation from Table 5.1 in section 5.3:

\[
T_{\text{sat}} = \frac{3626.55}{18.5875 - \ln(P_{\text{sat}})} + 34.29
\]  (8.2)

The computed methanol concentration in the zeolite plates varies with time, and it is presented in Figure 8.16 for Run 2.
The minimum and maximum concentration of methanol in generator with water as a heating fluid are approximately 0.10 kg methanol/kg zeolite and 0.20 kg methanol/kg zeolite respectively giving the maximum concentration change over each complete thermodynamic cycle of approximately 0.10 kg methanol/kg zeolite (i.e. a concentration swing of 10%). Note that there is a large temperature difference between the generator (at 76°C), and the heating liquid reservoir (at 94°C). Had the generator achieved the full loading liquid temperature, than the concentration change would have been as high as 15%. This can be compared with the following; after the condensation process, 8 mL of liquid methanol was collected, which (given 100 grams of zeolite in the generator) corresponds to 8% concentration swing.

Figure 8.16: Methanol concentration in generator (Run 2)
Figure 8.17 gives the concentration of methanol in the generator for the cycles run with oil as a heating fluid, which allows a higher regeneration temperature. This time the minimum and maximum concentration of methanol in the generator are approximately 0.08 kg methanol/kg zeolite and 0.18 kg methanol/kg zeolite respectively, giving the maximum concentration change over each complete thermodynamic cycle of approximately 0.10 kg methanol/kg zeolite (concentration swing of 10%). The maximum temperature in generator during heating process is 96°C. It can be argued that increasing the regeneration temperature and changing the operating conditions for the desorption process will give a higher concentration swing.
8.2.4 Temperature – Pressure Cycles

Temperature – pressure diagrams based on the generator internal temperature and saturation pressure are presented in Figure 8.18. The heating/cooling fluid was water.

![Temperature-pressure diagram]

This diagrams determined from experimental data can be compared to the ideal adsorption cycle presented in Figure 8.1. The ideal cycle consists of two isosteric and two isobaric processes, which are plotted in Figure 8.18. The first run represents the cycle lowest temperature of 40°C, whereas, the next two runs were done for 30°C. The evaporation pressure is around 90 torr and condensation pressure 220 torr.

The set of different cycles for Run 3 and 4 is available in Figure 8.19.
As mentioned before in this section, the similarity can be observed and for each run the isobars and isosteres can be sketched, which can represent the ideal adsorption cycle. These cycles can be drawn on isosteres obtained for zeolite CBV 901 and methanol in chapter 5. Figure 8.20 presents all the runs from Figure 8.18 and 8.19, together with isosteres.
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The Figure 8.20 shows that almost all the experimental cycles are in the area of the isosteres, which are from 2 to 20% concentration of methanol in zeolite. The only difference is for Run 3, where the cycle goes outside the 20% isostere. This run was done for a very low temperature $T_I = 20^\circ C$ at the start of adsorption process. The maximum concentration of methanol for this cycle could be around 22-24%, which was not within the measured conditions (Chapter 5) represented by the isosteres. The lowest temperature considered for this set of experiments was $30^\circ C$. The high adsorption (25%) of zeolite can be achieved. The stage TGA tests on powdered zeolite samples show that for $25^\circ C$, the maximum equilibrium adsorption capacity can be as high as 29%.

Another explanation for this behaviour might be connected with actual generator temperature. The temperature at the far end of the fin was taken to plot the Temperature – Pressure cycles for each run.

Considering, for example, the middle temperature of the fin during the process will move the T-P cycles to the right on Figure 8.20, because the temperature for each point taken will increase to maximum $10^\circ C$.

A Matlab program was used (presented in Chapter 6) to calculate the experimental temperature distribution in the fin during the heating process. The heating water temperature of $94^\circ C$ and the far end fin temperature were taken from the experimental data. The heat transfer coefficient is $50 \text{ W/m}^2\text{K}$ with reference to numerical data from section 6.3.3. The results are presented in Table 8.2 below.
<table>
<thead>
<tr>
<th>Heating Time [min]</th>
<th>0.00635 Pipe connection</th>
<th>0.01308</th>
<th>0.01981</th>
<th>0.02654</th>
<th>0.03327</th>
<th>0.04 Fin tip</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position on the fin [m]</td>
<td>2</td>
<td>94</td>
<td>57.1</td>
<td>41</td>
<td>32.6</td>
<td>28.5</td>
</tr>
<tr>
<td>4</td>
<td>94</td>
<td>67.4</td>
<td>55.3</td>
<td>48.9</td>
<td>45.7</td>
<td>44.7</td>
</tr>
<tr>
<td>6</td>
<td>94</td>
<td>71.7</td>
<td>61.4</td>
<td>55.9</td>
<td>53.1</td>
<td>52.3</td>
</tr>
<tr>
<td>8</td>
<td>94</td>
<td>74.3</td>
<td>65</td>
<td>60</td>
<td>57.5</td>
<td>56.7</td>
</tr>
<tr>
<td>10</td>
<td>94</td>
<td>75.9</td>
<td>67.5</td>
<td>62.9</td>
<td>60.6</td>
<td>59.8</td>
</tr>
<tr>
<td>15</td>
<td>94</td>
<td>78.6</td>
<td>71.3</td>
<td>67.3</td>
<td>65.3</td>
<td>64.8</td>
</tr>
<tr>
<td>20</td>
<td>94</td>
<td>80.2</td>
<td>73.7</td>
<td>70</td>
<td>68.2</td>
<td>67.7</td>
</tr>
<tr>
<td>25</td>
<td>94</td>
<td>81.3</td>
<td>75.3</td>
<td>71.9</td>
<td>70.3</td>
<td>69.7</td>
</tr>
<tr>
<td>30</td>
<td>94</td>
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<td>83.3</td>
<td>78.2</td>
<td>75.4</td>
<td>73.9</td>
<td>73.5</td>
</tr>
<tr>
<td>45</td>
<td>94</td>
<td>83.8</td>
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<td>74.7</td>
<td>74.3</td>
</tr>
<tr>
<td>50</td>
<td>94</td>
<td>84.2</td>
<td>79.4</td>
<td>76.8</td>
<td>75.4</td>
<td>75</td>
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<td>84.5</td>
<td>79.9</td>
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<td>60</td>
<td>94</td>
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<td>80.3</td>
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<td>76.5</td>
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</tr>
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<td>94</td>
<td>85.1</td>
<td>80.7</td>
<td>78.3</td>
<td>77.1</td>
<td>76.7</td>
</tr>
</tbody>
</table>

Table 8.2: Temperature distribution in the fins during heating process

The Figure 8.21 represents the results from the Table 8.2. As can be seen that there is a typical 10°C difference in the temperature distribution through the fin during the heating process.
As it can be seen from Figure 8.21, the middle temperature of the fin is almost similar to the tip fin temperature (there is the difference of 4°C between at the end of the heating process). This is a bit overestimated, because the temperature at the root of the fin was unknown. So, the tip fin temperature will be taken to plot the T-P cycles.

8.3 Heating Power

The calculations for heating power, cooling power and COP are based on calculations done for activated carbon/ammonia system by Davies [1]. The COP of a single bed system will be estimated for Run 3.

The heating power might be expressed as:

$$P_{heating} = \frac{Q_{heating}}{t_{cycle}}$$  \hspace{1cm} (8.3)

where:

- $P_{heating}$ is the heating power [W]
- $Q_{heating}$ is the heat input to the generator [J]

$$Q_{heating,zeo} = \int_{T_{zo}}^{T_{zo}} M_{zo} \left[ c_{p,zeo}(T) + x \cdot c_{p,m} - h_{ads} \left( \frac{\partial x}{\partial T} \right) p_{sat} \right] dT$$  \hspace{1cm} (8.4)
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\( Q_{\text{heating,all}} = \int_{t_{\text{start}}}^{t_{\text{end}}} M_{\text{zeo}} \left( c_{p,\text{zeo}}(T) + xc_{p,m} - h_{\text{ads}} \left( \frac{\partial x}{\partial T} \right) \right) + M_{\text{Al}} c_{p,\text{Al}} \, dT \) (8.5)

\( t_{\text{cycle}} \) is the cycle time [s]

Therefore, the heating power for the zeolite only is:

\[ P_{\text{heating, zeo}} = \frac{35.8 \cdot 10^3}{1800} = 20 \, W \]

The heating power for the zeolite and aluminium is:

\[ P_{\text{heating, all}} = \frac{60.8 \cdot 10^3}{1800} = 34 \, W \]

These are the complete values for the heating power taken over the complete cycle duration.

8.4 Cooling Power

The cooling power might be expressed as:

\[ P_{\text{cooling}} = \frac{\Delta x_{\text{cooling}} \cdot M_{\text{zeo}} \cdot (h_{g,\text{evap}} - h_{f,\text{cond}})}{t_{\text{cycle}}} \] (8.6)

where:

- \( P_{\text{cooling}} \) is the cooling power [W]
- \( \Delta x_{\text{cooling}} \) is the change in concentration during the cooling half-cycle [kg methanol/ kg zeolite]
- \( M_{\text{zeo}} \) is the mass of the zeolite in the generator [kg]
- \( h_{g,\text{evap}} \) is the specific enthalpy of methanol vapour leaving the evaporator [J/kg]
- \( h_{f,\text{cond}} \) is the specific enthalpy of methanol liquid leaving the condenser [J/kg]

\[ P_{\text{cooling}} = \frac{(0.18 - 0.08) \cdot 0.1 \cdot (2318 - 1197) \cdot 10^3}{1800} = 6.22 \, W \]
The specific cooling power per unit mass of zeolite is:

\[ P_{sp,cooling,zeo} = \frac{P_{cooling}}{M_{zeo}} = \frac{6.22 \ \text{W}}{0.1 \ \text{kg}} = 62.2 \ \text{W/kg} \]

The specific cooling power per unit mass of zeolite and aluminium is:

\[ P_{sp,cooling,all} = \frac{P_{cooling}}{M_{zeo} + M_{Al}} = \frac{6.22 \ \text{W}}{0.1 + 0.5} = 10.4 \ \text{W/kg} \]

During the cooling process methanol boils in the evaporator and is re-adsorbed into the zeolite paste in the generator. The average mass flow rate of methanol returning to the generator during the cooling process is given by:

\[ m = \frac{\Delta x_{cooling} \cdot M_{zeo}}{\Delta t_{cooling}} \quad (8.7) \]

where:

- \( m \) is the average methanol mass flow rate [g/s]
- \( \Delta t_{cooling} \) is the cooling half-cycle duration [s]

Therefore, the methanol mass flow rate is:

\[ m = \frac{(0.18 - 0.08) \cdot 100}{900} = 0.011 \ \text{g/s} \]

### 8.5 Coefficient of Performance

The true COP is very low, because most heat is lost to the environment. In particular, the casing acts as a “thermal flywheel”, and is ultimately responsible for heat transmission between hot and cold utilities, without any useful work. The following is an idealised form, based on observations in-situ.

The Coefficient of Performance (COP) is a measure of the experimental rig efficiency. The cooling COP for the zeolite only is:

\[ COP_{zeo} = \frac{P_{cooling}}{P_{heating,zeo}} = \frac{6.22}{20} = 0.32 \]

The cooling COP for the zeolite with aluminium is:
The COP obtained from experimental data is lower than expected from the COP validation calculations (0.64 for basic cycle–Chapter 4). The lower COP can be connected with system non-idealities. The explanation of some problems can be achieved by comparing the measured data versus a numerical model.

### 8.6 Numerical Modelling

A numerical model was written in Matlab, to compare the measured values with the numerical for temperature distribution in the generator, pressure change in the system during adsorption/desorption processes and the heat load during the cycle. All aspects of the model are presented in Appendix D.

The calculations for a single bed model were done for a set of initial values, which are presented in Table 8.4.

<table>
<thead>
<tr>
<th>$T_{ev}$</th>
<th>$8^\circ$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{cond}$</td>
<td>$30^\circ$C</td>
</tr>
<tr>
<td>$T_1$</td>
<td>$20^\circ$C</td>
</tr>
<tr>
<td>$T_3$</td>
<td>$95^\circ$C</td>
</tr>
</tbody>
</table>
The results are available in Figures 8.22-8.28 below:

Figure 8.22 represents the temperature distribution in the generator parts during one cycle. The temperature of the pipe during heating is 95 °C during cooling 22 °C. The shell temperature increases as the adsorbent bed is heated; the same process was observed during experiments. This confirms a high heat loss in the system, which will increase the cycle time. More importantly, the shell stores the heat during the heating phase, thus making an addition demand on the hot utility. This stored heat is then transferred during the cooling phase, such that additional cold utility is needed.

The second aspect of this model was to find the temperature distribution in the fin. During the experiments, the temperatures on the pipe and at the end of the fin were recorded. (Finite difference calculations were done to obtain the temperature distribution during the heating process.) The results show that the difference between the middle and tip temperatures is 4 °C which is an overestimate, because the real temperature of the fin root is unknown. (The tip temperature is taken for plotting the P-
The same results can be seen from the numerical model. The temperature difference between the tip and middle fin is presented in Figure 8.23. The highest value is predicted to be 0.35°C.

Figure 8.23: Temperature difference between fin tip and middle

Figure 8.24 shows the prescribed evaporator and condenser pressures in the system during the cycles, which are 50 and 160 torr. (The experimental pressures were slightly higher.) The change of the pressure in the adsorption bed during the experimental procedures follows the shape obtained in the model. In the scenario considered here, over and under pressures were permitted, associated with manual valve operation. (This problem was discussed in the experimental part of this chapter.)
Figure 8.24: Pressure distribution in the system

Figure 8.25 indicates the rate of methanol vapour desorption during the cycle. The highest rate of desorption occurs at the beginning of the heating process, and adsorption is fastest at the start of cooling. The same behaviour where observed during the properties tests on the zeolite/methanol pair.

The concentration of the methanol vapour in zeolite (loading) was modelled numerically. The results are presented in Figure 8.26. The maximum loading of 20% and minimum of 3% can be observed, which is not excessively dissimilar to the experimental data.
Chapter 8

Experimental Results and Performance Analysis

Figure 8.25: Desorption rate of methanol

Figure 8.26: Concentration change during the cycle
The next two graphs show the heat loads in the system and the heat loss component throughout the cycle. The largest heat transfers occur at the beginning of the heating and cooling processes, which is expected. Figure 8.27 represents the heat loads in the system. A significant amount of heat is dispersed to the casing; this is almost half of the heat input. The heat balance error is presented in Figure 8.28 and the maximum error of $4.5 \times 10^{-4}$ W appears at the first stage of adsorption/desorption processes, which can be connected with the heating/cooling procedure. Such small discrepancies can be associated with numerical rounding errors.

![Figure 8.27: Heat loads in the system](image-url)
Figure 8.28: Heat balance error

As a result of the numerical model, a COP of 0.51 is predicted. The numerical value is comparable with the first COP validation, which was 0.64 (see Chapter 4). The experimental values are much lower, than predicted ones, which is connected with system operation: the system should be operated automatically. There is also a large heat loss to the environment, which influences the cycle time.
8.7 Summary

Several sets of experimental data were obtained from the experimental rig, for various generating temperatures and cycle times. Results including Coefficient of Performance are presented in Table 8.2. It can be seen that the mass of the heat exchanger will noticeably influence the system performance.

The COP obtained from experimental data is lower than expected from the COP validation calculations (0.64 or 0.57 for the basic cycle). A shorter cycle time will improve the system performance. A very important issue is the mass ratio in the generator. The large transfer areas per unit volume will give a better performance of the system, which in turn makes demands on manufacturing methods. Thereupon, predictive codes can be used to tackle more complicated heat exchanger arrangements.

The numerical model gives further insight into the processes, which occur in the system. The temperature and pressure distribution is presented and the experimental graphs follow the shape of the numerical once. The values vary, but this might be connected with system control. A large heat loss to the casing is predicted, which can be observed during the experimental run. The shell temperature increases to high values especially during the heating process. The heat loss fraction appears to be between 30-36%.

References for Chapter 8

Chapter 9

Final Discussion and Conclusions

9.1 Discussion

The objective of this thesis was to investigate the possibility of improving the performance of an adsorption refrigeration system when new a kind of zeolite is employed to work with methanol as a refrigerant. The aim was to derive a predictive method for the plant performance using only the data obtained from laboratory-scale experiments associated with the properties of the adsorbent/refrigerant pair.

This thesis concentrated mainly on an investigation of an adsorption refrigeration system in which the functions of heat transfer and adsorption are integrated, in order to eliminate the impact of thermal gradients on the performance of the system. This necessitated the design of a novel heat exchanger; here the surface area was coated with zeolite. This inevitably leads to faster adsorption process, but the aim is to check the effect of this procedure on system COP, as well as to validate temperature gradients in extended surfaces.

It was necessary to select the refrigerant pair carefully, since it influences the COP of adsorption refrigeration systems. The methanol-zeolite CVB901 pair showed the highest COP value. This pair was also chosen to work in the adsorption system, because of its low temperature of regeneration (100 °C). It was observed that the thermal resistances due to convective and conductive heat transfer strongly limits the heat transfer. Hence, their values were increased as much as possible by choosing an
appropriate pipe diameter and liquid flow rate. In this way, their influence is significantly reduced.

As a first step, an assessment of the physical properties of zeolite CBV 901 and methanol was done. A powdered form of zeolite was used to prepare a zeolite paste with a binder (5% of wallpaper paste in a mixture), with which the adsorbent bed was coated. The metal surface was prepared (treated chemically) before coating. A layer thickness of 1mm can be obtained. Tests have been developed in order to measure the adsorption isotherms for powdered zeolite as well as for coated plates. The set of loadings \(x\) subsequently found for the powdered zeolite were marginally higher than for the coated forms.

The data were fitted to the Dubinin-Astakhov equation, using the isosteres interpolated from experimental isotherms. This information was later used to predict the concentration of methanol vapour in the adsorption bed during the adsorption and desorption processes.

The presence of air in the system influences both evaporation and adsorption processes. The evaporation of methanol is much slower than adsorption. Under these conditions it is felt that the cycle time will be limited principally by evaporation.

A shell and finned tube heat exchanger was selected. It can be easily coated with zeolite, is simple to construct and is relatively cheap. Transcal N oil was selected as the thermal fluid, because it has a good heat capacity ratio and an acceptable thermal stability. Selecting aluminium as the tube wall material reduced thermal gradients within the fins. It is a good thermal conductor and does not react chemically with methanol. The adsorbent (zeolite) provides a more significant thermal resistance due to both its low thermal conductivity and the potential lack of good contact with the heat exchanger wall. However, if the zeolite layer is synthesised on a surface using a chemical binder, the inherent thermal resistance is reduced. Thus, in the heat exchanger design, a synthesised zeolite layer with a thickness of 1 mm was used.
Finally, the results obtained for the heat transfer with a variation in the number of fins showed this system capable of dealing with the required thermal duty. Since a compact, cheap and reliable heat exchanger was required, a short geometry was chosen, which includes a 0.5m long tube with 50 fins.

The pilot experimental rig was designed and assembled. The main parts of the rig consist of the evaporator, generator and condenser, and the rig is supplemented with heating/cooling loops. The system was designed for a cooling load, in the evaporator, of up to 200W. The amount of zeolite placed in the generator can be between 100-500 grams. The operation temperatures of the system are 20-120 °C.

Thermocouples and pressure gauges were situated in the system in order to monitor temperature and pressure changes during the cycles. A set of vacuum tests was completed on the rig, in order to predict the air infiltration into the system, and its likely influence on overall performance. The system was checked and any poor connections resealed. The general leakage from the generator was 1.5 torr in one hour and from the evaporator and generator 5 torr, which is satisfactory for further experiments.

Several sets of experimental data were obtained from the experimental rig for various generating temperatures and cycle times. The experimental rig performance results including Coefficient of Performance for both, the zeolite only and zeolite-aluminium, vary between 0.15-0.31 depending on the cycle time. The mass of the heat exchanger strongly influences the system performance.

The COP obtained from experimental data is lower than expected from the COP validation calculations (in the range 0.51-0.64 for a basic cycle). The difference is connected with a large heat loss in the experimental rig during the cycle run. A shorter cycle time will improve the system performance. One very important issue is the mass ratio in the generator. The large transfer areas per unit volume will give better system performance, but will make demands on manufacturing methods. Thus, predictive codes can be used to tackle arrangements that are more complicated.
The numerical model offers an insight into the processes, which occur in the system. The temperature and pressure distribution is presented, and the experimental graphs follow the shape of the numerical ones. The values vary, but this might be connected with system control. A large heat loss to the environment is predicted and can be observed during the experimental run. The shell temperature increases to high values during the heating process.

**9.2 Conclusions**

The main objectives of the current research were to design, build and evaluate a heat driven adsorption refrigeration system, using zeolite CBV 901 and methanol as a working pair, with improved heat and mass transfer properties in the generator.

Several previously reported adsorption systems use granular forms of adsorbent materials, which require a large space in the rig and increase the overall cost of the system. The second problem connected with the use of a granular form is poor heat and mass transfer within the bed and a long regeneration time, thereby extending the total cycle time.

In the present research the areas of study are:

1. Application of a new zeolite, CBV 901, that requires a low temperature for regeneration, such that the chemical decomposition of methanol is prevented. Low temperature waste heat might be used to operate the system.
2. The use of zeolite paste for coating the generator surface in order to enhance the heat transfer area between the heating/cooling fluid and zeolite, improve the zeolite regeneration process, and decrease the cycle time.
3. Utilisation of a finned tube adsorption generator, working as a part of a heat driven cooling system.
An experimental rig has been constructed employing a single finned tube generator. The system was operated under different cycle times, which varied from 900 to 7200 seconds and produced a maximum specific cooling power of 80 W/kg. The cooling Coefficient of Performance was between 0.15-0.32.

A numerical model has been developed for use in predicting the temperature distribution, pressure, concentration and heat loads of the experimental rig. Numerical predictions confirm some aspects of experimental rig results. The calculated COP of the system is 0.51, which is much higher than the one obtained experimentally. This confirms the high heat losses in the system.

The objectives of the thesis have been achieved, although further research is required in order to be able to build the appropriate refrigeration system and make it suitable for direct application.

9.3 Recommendations

The suggestions for the future work include:

(1) A further investigation into zeolite paste, binder properties, zeolite layer thickness, and crystal size. The objective would be to increase the amount of adsorbent in the system and decrease the adsorption time;

(2) An analysis of generator design, including the mass and surface area of zeolite coatings. Better insulation is required to decrease the heat loss from the system;

(3) System automatisation to improve the system operation;

(4) Investigating the effects of differently designed heating/cooling system for the generator, in order to improve the cycle time;

(5) Investigating the influence of the system modification (two bed, with heat and mass recovery, cascade) on the Coefficient of Performance.
Energy balance on a packed bed

A control surface is put around the bed, plus input / output gas.

Assumptions:
(a) System mass of adsorbate is constant throughout cycle
Appendix A  COP Validation Model

At any point in time the internal energy can be presented as:

\[ E = U_L + U_H + m_z C_z T + m_a u_a(T) + m_g u_g + m_{HX} u_{HX} T \]

Here \( U_L, U_H \) are the internal energies of the upper and lower gas envelopes, \( m_z \) is the zeolite mass, \( m_a \) is the mass of material adsorbed, \( u_a \) is the specific internal energy of the gas phase, \( m_g \) is the mass of the gas phase inside the container, \( m_{HX} \) is the heat exchanger mass.

\[ dQ + dW = dE = dU_L + dU_H + (m_z C_z + m_{HX} C_{HX}) dT + d(m_g u_g) + d(m_a u_a(T)) \]

Now \( dW = -d(p_L V_L + p_H V_H) \)

\[ dQ = dH_L + dH_H + (m_z C_z + m_{HX} C_{HX}) dT + d(m_g u_g(T)) + d(m_a u_a(T)) \]

Now \( H_L = m_L h_L \) and for constant \( p_L, T_L, h_L \) is constant

\[ dQ = h_L dm_L + h_H dm_H + \sum m_i C_i dT + d(m_g u_g(T)) + d(m_a u_a(T)) \]

Where \( i \in \{ \text{zeolite, heat exchanger} \} \)

Assumptions:

1. Normalise by stating \( m_z = 1 \)
2. At any point on the cycle, either \( dm_L = 0 \) or \( dm_H = 0 \) or both
3. Mass is conserved, so \( m_{L_{\text{max}}} = m_{H_{\text{max}}} \)
Represent the cycle as follows:

The minimum mass of gas in the vessel is determined by the available volume, $V$, assume $X_{\text{min}}$ occurs at C and the mass of gas $m_{g,\text{min}} = \frac{V}{v(T_c, P_L)}$ where $v$ is the specific volume.

The maximum mass is likewise $m_{g,\text{max}} = \frac{V}{v(T_a, P_H)}$.

So $m_{l,\text{max}} = m_{H,\text{max}} = m_z \left( X_{\text{max}} - X_{\text{min}} + V \left( \frac{1}{v(T_c, P_H)} - \frac{1}{v(T_a, P_L)} \right) \right)$ and this is the mass compressed per cycle $m_{\text{cyc}}$.

Then $m_{\text{cyc}} = m_z \left( X_{\text{max}} - X_{\text{min}} + V \left( \frac{1}{v(T_c, P_H)} + \frac{1}{v(T_a, P_L)} \right) \right)$.
Appendix A

COP Validation Model

Thereafter:

\[ Q_{abc} = (m_{cyc})h_H + (T_c - T_a) \sum m_i C_i + V \left( \frac{u_g(T_c, p_H)}{v(T_c, p_H)} - \frac{u_g(T_a, p_L)}{v(T_a, p_L)} \right) + m_z (X_{\min} u_a(T_c) - X_{\max} u_a(T_a)) \]

\[ Q_{cda} = (-m_{cyc})h_L + (T_a - T_c) \sum m_i C_i + V \left( \frac{u_g(T_a, p_L)}{v(T_a, p_L)} - \frac{u_g(T_c, p_H)}{v(T_c, p_H)} \right) + m_z (X_{\max} u_a(T_a) - X_{\min} u_a(T_c)) \]

Check \( Q_{abc} + Q_{cda} = m_{cyc} (h_H - h_L) = H_H - H_L \)

In the limit \( V \to 0 \)

\[ Q_{abc} = (T_c - T_a) \sum m_i C_i + m_z (X_{\min} (h_H - u_a(T_a)) - X_{\max} (h_L - u_a(T_c))) \]

Now \( u_a(T_a) = h_a(T_a) - p L \nu_a \)

where \( p L \nu_a = 0 \) (ignoring the effects of \( p \) on \( u \))

\[ h_H = h(T_H, p_H) \approx h(T_a, p_H) + c_{pg} (T_H - T_a) \]

so \( h_H - u_a(T_a) \approx h_{ag}(T_a, p_H) + c_{pg} (T_H - T_a) \)

and \( h_L - u_a(T_a) \approx h_{ag}(T_c, p_L) + c_{pg} (T_L - T_c) \)

[u_a is not reported widely. Assume a value that gives a sensible result for h_{ag}]

where \( h_{ag}(T, p) \) is the enthalpy of adsorption at stated \( T, p \)
Appendix A

COP Validation Model

Calculations procedure:

1. Specify \( T_L \Rightarrow P_L \Rightarrow h_H \) (set \( m_e=1 \))
2. Specify \( T_H \Rightarrow P_H \Rightarrow h_i \)
3. Specify \( T_a \Rightarrow X_{\text{max}} \)
4. Specify \( T_c \Rightarrow X_{\text{min}} \)
5. Specify \( V \Rightarrow m_{\text{cyc}} \)
6. Specify \( \sum m_i C_i \)
7. Get \( Q_{abc}, Q_{cda} \)
8. Get \( h_f(p_H) \)
9. \( Q_{\text{cond}} = m_{\text{cyc}} (h_H - h_f(p_H)) \)

The Coefficient of Performance:

\[
COP = \frac{Q_{abc}}{m_{\text{cyc}}(h_H - h_f(p_H))}
\]
Appendix B

Heat Exchanger Matlab Model

The Matlab Program:

```matlab
%Heat transfer from the heating/cooling fluid to the single fin

clear

%Input data
L=5;  %number of zeolite layers
F=2;  %number of fin layers
C=10; %number of zeolite columns(through the fin)
W=2;  %number of tube wall columns
D=0.004;  %tube OD (m)0.0127
Lf=0.040; %fin length (m)
tw=0.0012;  %tube wall thickness (m)
tz=0.001;  %zeolite thickness (m)
tf=0.010;  %aluminium fin thickness (m)
l=tf+tz;  %unit length (m)
ts=0.001; %outside cells (m)
h=500;  %heat transfer coefficient
CpZ= 1351;  % Cp of pure zeolite (J/kgK) normally =836(1572)
rhoZ=590;  %zeolite density(kg/m^3)
kZ=0.4;  %zeolite conductivity
CpM=1100;  % Cp of methanol (J/kgK)
xO=0.2180;  % data for D-A equation (xO, k, n)
k=28.4788;
n=1.7;
CpAl=880;  %Aluminum Cp (J/kgK)
rhoAl=2700;  %Aluminum density (kg/m^3)
Cpoil=2260;  %oil Cp (J/kgK)(T=100C)-or Cpoil=1970 at 20C
rhooil=820;  %oil density (kg/m^3) (T=100C)- or rhooil=871 at 20C
kfoil=0.127;  %oil conductivity (W/mK) at 100C
kAl=200;  %Aluminum conductivity (W/mK)
rhosurr=800;  %density of surrounding
delt=5e-4;  %time step (s)
Cpsurr=200;
unitwidth=0.001;
thickness=1;

%PRELIMINARY CALCULATIONS
N=L+F+2;  %number of rows (zeolite thickness + 1/2fin thickness)
M=C+W+2;  %number of columns(zeolite+1 for tube wall)
```
Appendix B Heat Exchanger Matlab Model

%SET UP ARRAYS
R=zeros (M+l,1); %vector of cell in radius from middle of pipe to end of fin
Z=zeros (1,N+1); %vector of cell in length of half fin+zeolite

%TEMPERATURES
Te= 290 * ones(M,N); % Initial condition
Te(1,1:N) = 393; % Boundary condition - indicates temperature of heating fluid.

%RADIUS VECTORS
R(2)=(D/2)-tw;
R(3:4)=[(D/2)-tw+tw/W:D/2]; %tube inside dia
R(5:M)=[D/2+Lf/C:D/2+Lf]; %tube wall
R(M+l)=D/2+Lf+ts; %end radius

%HEIGHT VECTORS
Z(2)=ts;
Z(3)=ts+tf/2; %next 1/2
Z(4)=Z(3)+tf/2; %1/2 aluminum height.
Z(5:N)=[(ts+tf+tz/L:tz/L:ts+tf+tz)]; %zeolite thickness
Z(N+l)=ts+tz+tf+ts;

%Define Matrices for cells
A=zeros(M,N); %areas matrix (m^2)
mass=zeros(M,N); %mass matrix
UN=zeros (M,N); %U values matrix (North)
US=zeros (M,N); %U values matrix (South)
UW=zeros (M,N); %U values matrix (West)
UE=zeros (M,N); %U values matrix (East)
CP=zeros (M,N); %Cp values matrix
RM=zeros(M+l,N+l); %radius matrix
ZM=zeros(M+l,N+l); %height matrix
RHO=zeros(M,N); %rho values matrix

%DENSITY
RHO(1,1:N)=rhol;
RHO(2:3,2:N-1)=rhoAl;
RHO(4:M-1,2:N-1)=rhoZ;
RHO(2:M-1,1)=rhosurr;
RHO(2:M-1,N)=rhosurr;
RHO(M-1,1)=rhosurr;

%U values
UN(2:M-1,N-1)=0;
UN(2:3,2:N-2)=1/((Z(3)-Z(2))/kAl);
UN(4:M-1,4:N-2)=1/((Z(5)-Z(4))/kZ);
UN(4:M-1,2)=1/((Z(3)-Z(2))/kAl);
UN(4:M-1,3)=1/((Z(4)-Z(3))/(2*kAl))+((Z(5)-Z(4))/(2*kZ));

US(2:M-1,2)=0;
US(2:3,3:N-1)=1/((Z(3)-Z(2))/kAl);
\[
US(4:M-1, 5:N-1) = 1/((Z(5) - Z(4))/kZ);
US(4:M-1, 3) = 1/((Z(3) - Z(2))/kAl);
US(4:M-1, 4) = 1/((Z(4) - Z(3))/2kAl) + (Z(5) - Z(4))/(2kZ));
\]

\[
UE(M-1, 2:N-1) = 0;
UE(3, 4:N-1) = 0;
UE(4:M-2, 4:N-1) = 1/((R(5) - R(4))/kZ);
UE(2:M-2, 2:3) = 1/((R(4) - R(2))/2kAl);
UE(2, 4:N-1) = 1/((R(3) - R(2))/kAl);
\]

\[
UW(4:M-1, 4:N-1) = 0;
UW(2, 2:N-1) = 1/((1/h) + ((R(3) - R(1))/2kAl));
UW(3, 2:N-1) = 1/((R(4) - R(2))/2kAl);
UW(4:M-1, 2:3) = 1/((R(4) - R(2))/2kAl);
UW(5:M-1, 4:N-1) = 1/((R(5) - R(4))/kZ);
\]

\% RADIUS Matrix
\[
RM(2) = (D/2) - tw; % tube inside dia
RM(3:4) = [(D/2) - tw + tw/W:D/2]; % tube wall
RM(5:M) = [D/2 + Lf/C:Lf/C:D/2 + Lf]; % end radius
RM(M+1) = 0;
\]

\% for s = 2:N+1
RM(:, s) = RM(:, 1);
end
\% for i = 1:M
\% for j = 1:N
RMM(i, j) = RM(i+1, j) - RM(i, j);
end
end
\% for i = 1:M
\% for j = 1:N
RMP(i, j) = RM(i, j+1) + RM(i, j);
end
end

\% HEIGHT Matrix
\[
ZM(2) = ts; % outside
ZM(3) = ts + tf/2; % 1/2 alumimum height.
ZM(4) = ZM(3) + tf/2; % next 1/2
ZM(5:N) = [ts + tf + tz/L:tz/L:ts + tf + tz]; % zeolite thickness
ZM(N+1) = ts + tz + tf + ts;
\]

\% for s = 1:M+1
ZM(s, :) = Z(1, :);
end
\% for i = 1:M
\% for j = 1:N
ZMM(i, j) = ZM(i, j+1) - ZM(i, j);
Appendix B

Heat Exchanger Matlab Model

end
end

% Area

for i=1:M
  for j=1:N
    Area(i,j) = ZMM(i,j) * RMM(i,j);
  end
end

% Mass

for i=1:M
  for j=1:N
    mass(i,j) = RHO(i,j) * RMM(i,j) * ZMM(i,j) * unitwidth;
  end
end

% CP values

CP(2:3, 2:N-1) = CpAl; % aluminum Cp
CP(4:M-1, 2:N-1) = CpZ; % zeolite Cp
CP(1, 2:N-1) = Cpoil; % oil Cp
CP(1:M, 1) = Cpsurr; % outside Cp
CP(1:M, N) = Cpsurr;
CP(M, 2:N-1) = Cpsurr;

% Area N and S

for i=1:M
  for j=1:N
    AreaN(i,j) = RMM(i,j) * unitwidth;
  end
end

for i=1:M
  for j=1:N
    AreaS(i,j) = RMM(i,j) * unitwidth;
  end
end

% Area W and E

for i=1:M
  for j=1:N
    AreaW(i,j) = ZMM(i,j) * unitwidth;
  end
end

for i=1:M
  for j=1:N
    AreaE(i,j) = ZMM(i,j) * unitwidth;
  end
end
% Main Calculation Loop
Tnext = Te; % initialise values at next time step.
for Time = 1:600000 % 300s
    for i = 2:M-1
        for j = 2:N-1
            QN = UN(i,j) * AreaN(i,j) * (Te(i,j+1) - Te(i,j));
            QS = US(i,j) * AreaS(i,j) * (Te(i,j-1) - Te(i,j));
            QE = UE(i,j) * AreaE(i,j) * (Te(i+1,j) - Te(i,j));
            QW = UW(i,j) * AreaW(i,j) * (Te(i-1,j) - Te(i,j));

            Tnext(i,j) = Te(i,j) + ((QN + QS + QW + QE) * delt) / (mass(i,j) * CP(i,j)); % Value at next time step.
            Qtotal(i,j) = QN + QS + QW + QE * delt;
        end % end j
    end % end i
    Te = Tnext; % Update estimate of temperature.
    if Time == 10000
        Q10total(:, :, thickness) = Qtotal;
        Te10(:, :, thickness) = Te;
    end
    if Time == 20000
        Q20total(:, :, thickness) = Qtotal;
        Te20(:, :, thickness) = Te;
    end
    if Time == 60000
        Q30total(:, :, thickness) = Qtotal;
        Te30(:, :, thickness) = Te;
    end
    if Time == 120000
        Q60total(:, :, thickness) = Qtotal;
        Te60(:, :, thickness) = Te;
    end
    if Time == 240000
        Q120total(:, :, thickness) = Qtotal;
        Te120(:, :, thickness) = Te;
    end
    if Time == 360000
        Q180total(:, :, thickness) = Qtotal;
        Te180(:, :, thickness) = Te;
    end
    if Time == 600000
        Q300total(:, :, thickness) = Qtotal;
        Te300(:, :, thickness) = Te;
    end
end % end time
The data arrays for base case and heat transfer coefficient of 500W/m²K. The fin layer thickness is 1mm, the fin length of 40mm, the fin thickness of 2mm. The first line in array, represented by numbers in green is the heating fluid temperature, then two lines of black- this is tube wall temperature. The numbers in blue- it is the fin temperature distribution and finally the red part is the zeolite temperature.

(1) time=5s

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### Appendix B  Heat Exchanger Matlab Model

#### (3) time=30s

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#### (5) time=120s

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Appendix B  Heat Exchanger Matlab Model

(6) time=180s

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381.8727 381.8726 381.8401 381.7887 381.7500 381.7242 381.7113
381.8543 381.8540 381.8215 381.7700 381.7313 381.7055 381.6925
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381.8243 381.8240 381.7914 381.7397 381.7009 381.6750 381.6621
381.8127 381.8124 381.7798 381.7281 381.6892 381.6633 381.6503
381.8035 381.8032 381.7705 381.7187 381.6799 381.6539 381.6409
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381.7919 381.7916 381.7589 381.7071 381.6682 381.6422 381.6292
381.7896 381.7893 381.7566 381.7048 381.6658 381.6398 381.6268

(7) time=300s

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390.4573 390.4572 390.4498 390.4381 390.4292 390.4233 390.4204
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390.4478 390.4478 390.4403 390.4285 390.4197 390.4137 390.4108
390.4468 390.4467 390.4393 390.4275 390.4186 390.4127 390.4097
390.4462 390.4462 390.4387 390.4269 390.4181 390.4121 390.4092
Appendix C

Experimental Rig Drawings

Drawing no. 1: General assembly of generator
Drawing no. 2: Finned pipe
Drawing no. 3: Generator ending plate I
Drawing no. 4: Generator ending plate II
Drawing no. 5: Generator ending plate III
Drawing no. 6: Flat slip-on flange for generator
Drawing no. 7: Cover tube I
Drawing no. 8: Cover tube II
Drawing no. 9: Plate
Drawing no. 10: Spacing ring
Drawing no. 11: Pipe connections to valves
Drawing no. 12: Condenser-glass pipe connection
Drawing no. 13: Glass pipe
Drawing no. 14: Glass pipe-valve connection
Drawing no. 15: Condenser top
Drawing no. 16: Condenser bottom
Drawing no. 17: Evaporator assembly
Drawing no. 18: Evaporator cylinder
Drawing no. 19: Evaporator top
*filling on aluminium pipe 1/2" dia
as a spacing ring between plates*
<table>
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<th>PROJECTION:</th>
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<td></td>
<td><strong>Al</strong></td>
<td></td>
<td><strong>S. Wyszyniec</strong></td>
<td>21/05/2007</td>
<td></td>
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<td><strong>16</strong></td>
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Appendix D

Matlab Numerical Model for Adsorption System

The equations used in model:

1. Temperature distribution in the fin:
   \[ k \left( \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) \right) = \rho \cdot c_p \cdot \frac{\partial T}{\partial t} + 2 \cdot \frac{h}{\delta_{\text{fin}}} (T - T_{\text{gas}}) + 2 \cdot j \cdot \frac{h_{\text{adv}}}{\delta_{\text{fin}}} \]
   \[ j \] is the mass flux

   Boundary conditions:
   
   (a) \( r = R_i \), \( T = T_{\text{pipe}} \)
   
   (b) \( r = R_o \), \( \frac{\partial T}{\partial r} = 0 \)

2. Mean fin temperature:
   \[ \overline{T_{\text{fin}}} = \frac{\int_T_{\text{fin}} \cdot dA}{A} = \frac{\int_{R_i}^{R_o} T_{\text{fin}}(r) \cdot dr}{R_o^2 - R_i^2} \]

3. Heat flow from the pipe to the shell:
   \[ Q_{\text{pipe-shell}} = 2 \cdot 2\pi \cdot h \cdot \left( \frac{T_{\text{pipe}} - T_{\text{shell}}}{\ln(R_o / R_i)} \right) \cdot \delta_{\text{shell}} \]

4. Heat flow from gas to the shell:
   \[ Q_{\text{gas-shell}} = h_{\text{shell}} \cdot A_{\text{shell}} \left( T_{\text{gas}} - T_{\text{shell}} \right) \]
(5) Shell temperature change in time:
\[
\frac{\delta T_{shell}}{\delta t} = \frac{\Sigma Q}{m_{shell} \cdot c_p}
\]

(6) Mass flux \( j \)
\[
 j = \sigma \cdot c \cdot (x - x^*(p,T))
\]

\( \sigma = \frac{m_{zeo}}{A_{fns}} \) - is the density of zeolite [kg/m\(^2\)]

\( x^* = f(p,T) \) - is the concentration equilibrium value taken from D-A equation
\[
\frac{\delta x}{\delta t} = c \cdot (x - x^*)
\]

\( c \) - is the constant, rate coefficient (\( c = 0.01 \) 1/s – this is a guess)

(7) The heat balance:

**Mode 1: Heating**
\[
m \cdot c_v \left( T_{fin} - T \right) + hA \left( T_{fin} - T \right) + h_{shell} \cdot A_{shell} \left( T_{shell} - T \right) = 0
\]

**Mode 2: Desorption**
\[
m \cdot c_v \left( T_{fin} - T \right) = m \cdot c_v \left( T_{gas} - T \right)
\]

**Mode 3: Cooling**
\[
m \cdot c_v \left( T_{fin} - T \right) + hA \left( T_{fin} - T \right) + h_{shell} \cdot A_{shell} \left( T_{shell} - T \right) = 0
\]

**Mode 4: Adsorption**
\[
m \cdot c_v \left( T_{ev} - T \right) = m \cdot c_v \left( T_{fin} - T \right)
\]

(8) Heat error = heat input – heat losses from the fin (heat transfer + adsorption + heat accumulation):
\[
e = -\pi Dk \left( \frac{\partial T}{\partial r} \right)_{R_i} - 2\pi \left( R_0^2 - R_i^2 \right) h \left( T_{fin} - T_{gas} \right) - 2\pi \left( R_0^2 - R_i^2 \right) \cdot j \cdot h_{ads}
\]
\[
- \delta_{fin} \cdot \pi \left( R_0^2 - R_i^2 \right) \cdot \rho \cdot c_p \frac{\partial T_{fin}}{\partial t}
\]
MATLAB code:

```matlab
% just5iters
% this script attempts 5 iterations of the system

clear
initialConditions

time = 0;
heatIn = 0;
finChars; % This gets finMatrix, which permits evaluation of gradients
% in the fin. finMatrix might well change with times.

for i = 1:(keyTime(4)/10)
    for j = 1:10
        setPressure; % sets pressure.
        setWorkingFluidTemperature; % sets temperature in the pipe.

        jFlux = getMassFlux (xLoad, Pgas, Told, 1); % Mass fluxes.
        xLoad = getMassFlux (xLoad, Pgas, Told, 2); % New loadings.
        netDesorption = meanFluxes (jFlux, xc) * finArea; % Mass transfer out
        of fins.

        setMass; % Set mass in vessel.
        Tfin = meanFluxes (Told, xc); % Mean fin temperature.
        Tshell = changeShellTemperature(Tgas, Tshell, Tpipe); %
        getNewGasTemperature; % Change Tgas.

        Told = changeFinTemps (finMatrix, jFlux, Tgas, time, Told, Tpipe, w);
        TfinNew = meanFluxes (Told, xc); % Mean fin temperature after time
        step.

        heatAcc = cp * (w * finArea/2) * rho * (TfinNew - Tfin)/ dTime;
        time = time + dTime;
        if (setMode(keyTime, time)) == 1
            heatIn = heatIn + nFin * 3.14152 * w * pipeDia * getHeatFLux
                      (finOuterRadius, kcond, Told, w, xc);
        end

        if (setMode(keyTime, time)) == 2
            heatIn = heatIn + nFin * 3.14152 * w * pipeDia * getHeatFLux
                      (finOuterRadius, kcond, Told, w, xc);
        end
    end
end

np = length (xc);
% Sort info for plotting
XVAL(i,1)= time;
TEMPER (i,1) = Tfin;
TEMPER (i,2) = Tshell;
TEMPER (i,3) = Told(np,1);
TEMPER (i,4) = Tpipe;
TEMPER (i,5) = Tgas;
EFFIC (i,1) = (Tfin - Tgas)/(Tpipe-Tgas); % Fin effectiveness
factor.
EFFIC (i,2) = DAEquation (Pgas, Told(np,1))/meanFluxes(xLoad,xc);

LOAD(i,1) = massZeolite * meanFluxes (xLoad,xc); % Mass of methanol
adsorbed.
```
Appendix D

Matlab Numerical Model

DESORBRATE(i,1) = finArea * meanFluxes(jFlux,xc);

% Rate of desorption - kg/s.

% The following line can be used for test purposes, to give approximately the same result as is found with o.c.
HLOAD(i,1) = nFin * w * pipeDia * kcond * (Told(1,1)-Told(2,1))/((0.2427-0.1671)*finOuterDia); % Heat Load.

HLOAD (i,2) = DESORBRATE(i,1) * hads;
HLOAD (i,3) = finArea * htc * (TfinNew - Tgas);
HLOAD (i,4) = heatAcc;
HLOAD (i,5) = 2*2*3.14152*shellThickness*kcond*(Tpipe-Tshell)/log(760/127); % Heat loss.

Herror (i,1) = (HLOAD(i,1)- HLOAD(i,2)-HLOAD(i,3)-HLOAD(i,4))/(HLOAD(i,1));
if (HLOAD(i,1) < 1.e-4) % to prevent singularities, overwrite v. small heat loads.
    Herror(i,1)=0;
end

PRESSURE(i,1) = Pgas;
PRESSURE (i,2) = saturationPressure(Tevap);
PRESSURE (i,3) = saturationPressure(Tcond);

end
plot (XVAL, TEMPER);
plot (XVAL, PRESSURE);
plot (XVAL, LOAD);

function Tnew = changeFinTemps (aMatrix, jFlux, Tgas, time, Told, tPipe, w)

setSystemCharacteristics; % Set up system variables.
np = length (jFlux); % Number of collocation points
for iCount = 2:np-1
    rhsVector (iCount,1) = ...
    rhsVector (iCount,1) = (-rho*cp*Told(iCount,1)/dTime) -(jFlux(iCount,1) * hads / w) -
    rhsVector (iCount,1) = (-rho*cp*Told(iCount,1)/dTime) - ( 2 * htc / w) *Tgas;
end
rhsVector (1, 1) = tPipe ;
rhsVector (np,1) = 0;

Tnew = inv(aMatrix) * rhsVector; % could speed this up by inverting matrix outside loop.

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function ts = changeShellTemperature (Tgas, Tshell, Tpipe)
setSystemCharacteristics
    heatFlowFromPipe = 2*2.3.14152*shellThickness*kcond*(Tpipe-Tshell)/log(760/127);
% remember that the pipe touches the shell in two places.
    heatFlowFromGas = shellArea * shellhtc * (Tgas - Tshell);
total = heatFlowFromPipe + heatFlowFromGas;
ts = Tshell + (total/(shellMass * shellcp))*dTime;

function x = DAequation (p,T)
Tsat = saturationTemperature (p);
% Note that it is possible to get condensation on the fin! This is because of the temperature gradient, which means the pressure in the vessel(induced by the temperature of the fin root) is > Psat a the (cooler) fin tip.
if (T<Tsat)
    x = 0.2180;
else
    x = 0.2180 * exp (-28.4788 *((T/Tsat)-1)^1.7);
end

% script file to deal with conduction in a fin.
% the following equation is solved
% k.grad^2(T) + (2.h/w) (T - Tgas) + (J/w).h_ads = rho.cp.dT/dt
% boundary conditions T is specified at r = 12.7/2 mm
% dT/dr = 0 at other end of fin.
% set up a matrix so that
% A.T = T.old + V

np = length (xc); % number of collocation points.
finMatrix = kcond*(finOuterRadius^2)*gradit2(xc,1);
myGrad = (finOuterRadius-1) * gradit(xc,1);
for iCount = 2:np-1
    finMatrix(iCount,iCount) = finMatrix(iCount,iCount) + (2*htc/w) - (rho*cp/dTime);
    finMatrix(iCount,iCount) = finMatrix(iCount,iCount) - (rho*cp/dTime) - (2*htc/w);
end
for iCount = 1:np
    finMatrix (1,iCount) = 0;
    finMatrix (np,iCount) = myGrad(np,iCount)/ finOuterRadius;
end
finMatrix(1,1)=1;
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function hf = getHeatFlux (finOuterRadius, kcon,T,w, xc)
% Vector of gradients.
myg = (1/finOuterRadius) * gradit(xc,1) * T;
hf = -kcon * myg(1,1);

function jm = getMassFlux (xx, pGas, tt, flag)
% This function gets a set of mass fluxes, from each fin.
% The fluxes are expressed at kg.m-2.s-1
% setting flag = 1 returns the mass fluxes
% setting flag = 2 returns a new value of the loadings.

setSystemCharacteristics

np = length (xc); % number of collocation points.
for i = 1:np
xstar = daEquation ( pGas, tt(i,1)); % Loading at saturation.
xss(1,i)= xstar;
if (flag == 1)
part(i,1) = sigmaZeolite * rateCoeff * (xx(i,1) - xstar);
end
if (flag == 2)
part(i,1) = xx(i,1) - dTime * rateCoeff * (xx(i,1) - xstar);
end
end
jm = part;

% getNewGasTemperature.
% This part carries out a crude energy balance on the gas volume.
% The time dependent terms are ignored, and we assume that when the
unit is open to the evaporator the mass adsorbed = the mass flow in
(actually, there are small differences owing to temperature induced
density changes)
% mflow * cv * (Tx - T) + hfin*Afin*(Tfin - T) +hshell*Ashell*
(Tshell-T)= 0
% mflow = mDesorb if the zeolite is being regenerated and the
generator is sealed. Tx = Tfin (mode 1).
% mflow = mDesorb if the generator is open to the condenser (mode 2).
% Tx =Tfin
% mflow = 0 if the generator is sealed and cooled.
% mflow = -mDesorb if the generator is open to the evaporator (mode
4).Tx = Tevap.

myMode = setMode(keyTime,time);
if (myMode == 1) % Regeneration - vessel sealed.
    Tx = Tfin;
    mFlow = netDesorption;
elseif (myMode ==2) % To condenser.

Appendix D  Mexlab Numerical Model

```
Tx = Tfin;
mFlow = netDesorption;
elseif (myMode == 3) % Cooling - vessel sealed.
mFlow = 0;
elseif (myMode == 4) % Adsorption.
  mFlow = - netDesorption;
  Tx = Tfin;
end

coefficientOfT = mFlow*cvMethanol + finArea*htc + shellArea*shellhtc;
constantTerm = mFlow*cvMethanol*Tx + finArea*htc*Tfin + shellArea*shellhtc*Tshell;
Tgas = constantTerm / coefficientOfT;

function gvm = getVapourMass (Pgas, Tgas)
setSystemCharacteristics
  gvm = Pgas * shellVolume / (Rgas * Tgas);

function g = gradit (xc, alpha)
% returns a matrix that can be used to find gradients.
% set alpha =1 for radial systems.
% set alpha = 0
np = length (xc); % # collocation points.
alpha = 0;
for i = 1:np
  for j = 1:np
    Q(j,i) = xc(j,1)^(i-1);
    C(j,i) = Q(j,i)*(i-1)/xc(j,1)^(l+alpha);
    D(j,i) = (i-1)*(i+alpha-2)*Q(j,i)/xc(j,1)^2;
  end
end
  g = C * inv (Q);

function g = gradit2 (xc, alpha)
% returns a matrix that can be used to find gradients.
% set alpha =1 for radial systems.
np = length (xc); % length of vector.
for i = 1:np
  for j = 1:np
    Q(j,i) = xc(j,1)^(i-1);
    C(j,i) = Q(j,i)*(i-1)/xc(j,1)^(l+alpha);
    D(j,i) = (i-1)*(i+alpha-2)*Q(j,i)/xc(j,1)^2;
  end
end
  g = D * inv (Q);

% File sets initial conditions.
% System specification.
% A set of collocation points referring specifically to the pipe and outer fin diameters for this system. Use these and alpha = 1 in calls to routines to get gradient terms.

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```
setSystemCharacteristics; % Defines vars set system.
% Temperatures.
Tshell = Tpipe; % estimate of shell temperature.
Tgas = Tpipe; % gas temperature in K.
% Pressures
Pgas = saturationPressure (Tevap); % Starts cycle at evaporator pressure.
% Mass of vapour in system.
vapourMass = getVapourMass (Pgas, Tgas);
% Initial temperature in generator.
np = length (xc); % Number of collocation points.
for j = 1:np
    Told(j,1) = Tpipe; % initial fin temperature.
xLoad (j,1) = DAEquation (Pgas, Tpipe); % loading of zeolite - w/w.
jFlux (j,1) = 0.00; % mass flux to fin.
end

function v = meanFluxes (jm, xc)
% This function integrates mass and heat fluxes at the collocation points, to give the average flux into the system from a fin.
j = ceff*Q, where xc stores powers of x.

delta = 127 / 760; % Ratio of inner to outer diameters.
%
np = length (xc); % number of collocation points.
for i = 1:np
    for j = 1:np
        Q(j,i) = xc(j,1)^((i-1);
    end
end
COF = inv(Q) * jm; % gives the coefficients for polynomial, jm = c1 + c2x + ...
top = 0; % top part of result.
bottom = 0.5 * ( 1 - delta^2); % bottom part of result.
for j = 1:np
    top = top + COF(j,1) * ( 1 - delta ^ (j+1))/(j+1);
end
v = top/ bottom;

function p = saturationPressure (T)
% This function returns the saturation pressure of methanol in Pa, where T is temperature in Kelvin.
p = (exp(18.5875-3626.55/(T-34.29))) * 1e5/760;
function T = saturationTemperature (p)
% Gives the temperature (in Kelvin) for a given saturation pressure
% (in Pa)
% p = (exp(18.5875-3626.55/(T-34.29))) * 1e5/760
T = 34.29 + 3626.55/(- log (760 *p/1e5) + 18.5875); % nb - log is to base e.

% setMass
% This script sets up the mass of vapour in the system.
myMode = setMode(keyTime, time);
if (myMode == 4)
    vapourMass = getVapourMass (Pgas, Tgas);
elseif (myMode == 2)
    vapourMass = getVapourMass (Pgas, Tgas);
elseif (myMode == 1)
    vapourMass = vapourMass + netDesorption * dTime;
elseif (myMode ==3)
    vapourMass = vapourMass + netDesorption * dTime;
end

function m = setMode (keyTime, time)
% Determines the mode of operation.
% 1 adsorption - open to evaporator.
% 2 presurisation and heating - sealed.
% 3 desorption - open to condenser.
% 4 depressurisation and cooling - sealed.
if (time < keyTime(l)) myMode = 1;
elseif (time < keyTime(2)) myMode = 2;
elseif (time < keyTime(3)) myMode = 3;
elseif (time < keyTime(4)) myMode = 4;
else
    disp ('error in setMode at time = ')
    time
    myMode = 4;
end
m = myMode;

% setPressure
% This script sets up the system pressure.
myMode = setMode(keyTime, time);
if (myMode == 4)
    Pgas = saturationPressure (Tevap);
elseif (myMode == 2)
    Pgas = saturationPressure (Tcond);
elseif (myMode == 1)
    Pgas = vapourMass * Rgas*Tgas/ shellVolume;
elseif (myMode ==3)
    Pgas = vapourMass * Rgas*Tgas/ shellVolume;
end
% System characteristics applies to 4 internal points \( xc = [0.167105 \; 0.242651 \; 0.752412 \; 0.948876 \; 1.0] \);
\( xc = [0.167105 \; 0.201715 \; 0.328978 \; 0.510503 \; 0.704019 \; 0.869906 \; 0.974234 \; 1] \);
\( n_{\text{ColPoints}} = 8 \); % number of points in \( xc \) (internal + external).
\( xc = [0.167105 \; 0.242651 \; 0.479761 \; 0.152412 \; 0.948876 \; 1.0] \);
\( n_{\text{ColPoints}} = 6 \);

\( T_{\text{evap}} = 273 + 8 \); % evaporator temperature.
\( T_{\text{cond}} = 273 + 30 \); % condensor temperature.

\( T_{\text{hot}} = 273 + 95 \); % hot utility temperature.
\( T_{\text{cold}} = 273 + 22 \); % cold utility temperature.

\( \text{massZeolite} = 0.100 \); % mass of zeolite, in kg.
\( \text{finArea} = (100 \times 3.14152 \times 0.25 \times (0.076^2 - 0.0127^2)) \); % area of finning.
\( \sigma_{\text{Zeolite}} = \text{massZeolite}/\text{finArea} \);
\( \text{finLength} = (760 - 127)/2000 \); % fin length.
\( \text{finOuterRadius} = 76/2000 \); % fin outer dia - needed for normalisation.
\( \text{pipeDia} = 0.0127 \);
\( w = 0.002 \); % fin thickness (aluminium part).
\( n_{\text{Fin}} = 50 \); % number of fins.

\( \text{shellArea} = (2 \times (3.14152 \times 0.1^2)/4) + (3.14152 \times 0.1 \times 0.6) \); % area for heat transfer
\( \text{shellcp} = 200; \)
\( \text{shellhtc} = 3; \)
\( \text{shellThickness} = 0.01 \); % check this.
\( \text{shellMass} = \text{shellArea} \times \text{shellThickness} \times 2000 \); % check this.
\( \text{shellVolume} = 3.14 \times (0.1^2 / 4) \times 0.6; \)

\( \text{htc} = 3; \)
\( \text{rateCoeff} = 0.01 \); % rate coefficient for adsorption/ desorption.
\( \text{hads} = 1000000 \); % heat of adsorption in J.kg-1. Needs adjustment.
\( \text{kcond} = 200; \); % thermal conductivity of aluminium.
\( \text{cp} = 880 ; \); % heat capacity
\( \text{rho} = 2700; \); % density of aluminium should be enhanced to account for zeolite layer.

\( \text{cvMethanol} = 0.7 \); % guess at the specific heat capacity of methanol.
\( \text{Rgas} = 259.8 \); % specific gas constant for methanol in J.kg-1.K-1

% Gas Volume in generator
\( \text{gasVol} = 0.6 \times 3.14152 \times (0.1^2)/4; \)

\( \text{dTime} = 1; \); % time increment.

% times for heating, desorption, cooling, adsorption.
\( \text{keyTime(1)} = 40; \)
\( \text{keyTime(2)} = 500; \)
\( \text{keyTime(3)} = 540; \)
\( \text{keyTime(4)} = 1000; \)
Appendix D  
Matlab Numerical Model

% setWorkingFluidTemperature  
% This script sets up the system pressure.  
myMode = setMode(keyTime, time);  
if (myMode == 1)  
    Tpipe = Thot;  
elseif (myMode == 2)  
    Tpipe = Thot;  
elseif (myMode == 3)  
    Tpipe = Tcold;  
elseif (myMode ==4)  
    Tpipe = Tcold;  
end

function tt = tPipe (time)  
% function finds the pipe temperature versus time.  
tt = 283;  
% tester.m  
% this m-file tests the orthogonal collocation matrixes  
acoeff = 1;  
bcoeff = -3  
rad = 5 * xc;  
np = length (xc);  
for i = 1:np  
    predVal (i,1)= acoeff-bcoeff*log(rad(i,1));  
    predGrad (i,1)= -bcoeff/rad(i,1);  
end  

disp ('now try 1/r(d/dr(r.dT/dr)) = const; has solution T = 0.25*const*r^2')  
disp ('this checks compatibility between the dT/dr and del T terms')  
const = 10  
for i = 1: np  
    predVal (i,1) = 0.25 * const * rad(i,1)^2;  
    losses (i,1) = const;  
end  

disp ('now try 1/r(d/dr(r.dT/dr)) = const; has solution T = 0.25*const*r^2')  
disp ('this checks compatibility between the dT/dr and del T terms')  
const = 10  
for i = 1: np  
    predVal (i,1) = 0.25 * const * rad(i,1)^2;  
    losses (i,1) = const;  
end  

gradit2(xc,1)*predVal/ (rad(np,1))^2  
gradit(xc,1)*predVal/ (rad(np,1))  
flux = gradit(xc,1)*predVal/ rad(np,1);  
2 * flux(1,1)*rad(1,1)*3.14159 = 2 * flux (np,1) *rad(np,1) *3.14159  
(0.5*const*rad(1,1))*3.14159*2*rad(1,1)-  
(0.5*const*rad(np,1))*3.14159*2*rad(np,1)  
meanFluxes (losses, xc) * 3.14159 * (rad(np,1)^2 - rad(1,1)^2)  
const * 3.14159 * (rad(np,1)^2 - rad(1,1)^2)