MATHEMATICAL MODELING OF ADSORPTION/DESORPTION SYSTEMS FOR CHEMICAL HEAT PUMPS

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

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IN PARTIAL FULFILLMENT OF REQUIREMETS
FOR
DEGREE OF MASTER OF SCIENCE
IN
CHEMICAL ENGINEERING

JANUARY 2011

Approval of the thesis:

MATHEMATICAL MODELING OF ADSORPTION/DESORPTION SYSTEMS FOR CHEMICAL HEAT PUMPS

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ABSTRACT

MATHEMATICAL MODELING OF ADSORPTION/DESORPTION SYSTEMS FOR CHEMICAL HEAT PUMPS

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January 2011, 91 pages

Despite their limited commercial applications, chemical heat pumps (CHP) have been considered as an important alternative to conventional heating and cooling technologies. In this study, the adsorption-desorption of ethanol over activated carbon was applied on the CHP reactor. The ethanol vapor - activated carbon adsorption rate was determined at 30, 60, 90 and 120℃ experimentally by using Intelligent Gravimetric Analyzer (IGA). The experimental adsorption data were used on the transient modeling of reactor by assuming single component gas phase. Then, spatial and temporal temperature, rate of heat transfer, and total amount of heat transferred for a given period were determined. Finally, the calculated adsorption and temperature profiles were integrated over volume to predict performance of heat pump for different reactor geometries. The results showed that, with proper modeling satisfactory performance values can be attained using these systems.

Keywords: Adsorption, Chemical heat pump, Activated carbon

ÖZ

KİMYASAL ISI POMPALARI İÇİN, ADSORPSİYON/DESORPSİYON SİSTEMLERİNİN MATEMATİKSEL MODELLENMESİ

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Ticari olarak az kullanılmalarına rağmen, kimyasal ısı pompaları, yaygın olarak üretilen ısı pompalarına önemli bir alternatiftir. Bu çalışmada etanolun aktif karbon tarafından adsorplanması, kimyasal ısı pompası raeaktörü üzerinde modellenmiştir. Etanol buharının aktif karbon tarafından adsorplanma hızı 30, 60, 90 ve 120 ℃ sıcaklılar için, IGA (Akıllı Kütlesel Analiz) cihazı kullanılarak bulunmuştur. Deneysel adsorplama verisi, adsorplama yatağının tek bileşenli gaz fazı varsayılarak, zamana bağlı modellenmesinde kullanılmıştır. Daha sonra, belli bir zaman aralığında, konuma ve zamana bağlı olarak, sıcaklık, ısı transfer değerleri ve toplam taşınan ısı bulunmuştur. Sonuçta hesaplanan adsorplama ve sıcaklık dağılımları, hacimle entegre edilerek farklı adsorplama yatağı şekilleri için performans değerleri hesaplamıştır. Elde edilen sonuçlar, bu tip sistemlerin, iyi bir modelleme ile, yeterli düzeyde performans değerlerine ulaşabileceğini göstermiştir.

Anahtar Kelimeler: Adsorsiyon, Kimyasal ısı pompası, Aktif karbon

To my mother.

ACKNOWLEDGEMENTS

The author wishes to express his greatest thanks to his supervisor Assoc. Prof. Yusuf Uludağ and co-supervisor Prof. Gürkan Karakaş for their great guidance during the whole study.

The author wishes to thank Prof. Hayrettin Yücel and Alp Yürüm for their guidance, comments and suggestion about adsorption experiments.

The author wishes to thank METU Central Laboratory for analyzing the activated carbon sample.

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CHAPTER 1

INTRODUCTION

Cooling has always been an important process for either domestic purposes or industrial need of preserving different contents. Although, many methods exist for cooling or refrigeration, the most common method used commercially, in today's world, is compression heat pumping. However, although, the most widely used type is compression heat pumping, it is not the only alternative. Furthermore, as far as the operating principle for heat pumping, is concerned, cooling technologies can implement several different physical phenomena for heat transfer from hot to cold region, depending on the system type. For example, while compression heat pumps use the energy change of material, during phase change due to compression or expansion, adsorption heat pumps operate in a manner completely different from compression heat pumps that, they utilize adsorption or desorption of a vapor by the adsorbent. The vacuum effect due to the adsorption causes some stored liquid to boil at the other side, and the required heat input to the boiling does the cooling effect. On the other hand, some heat pump systems that utilize chemical reaction, have been studied in literature, but such studies are limited. In fact, such systems are much complex and harder to build, compared to adsorption heat pumps. Furthermore, they usually use catalysis, and in some approaches use compressors or similar equipment [4]. Therefore, such systems are not considered within the scope of this study.

Regardless of the approach, preferred for cooling, some energy is required for operating the heat pump, since the heat pump transfers heat from cold to hot region, which is against thermodynamics. As the method or the type of the heat pump differs, so does the type of the input energy. While for a compression heat pump, the operating energy is the mechanical energy supplied to the compressor, for an adsorption heat pump, the input work is in form of heat energy, that is used for desorption of the adsorbed liquid from the adsorbent bed. Therefore no mechanical energy is required. Unfortunately, no matter what type of energy is used, heat pumps require energy to operate, and the energy requirement for cooling is significant. In fact, performance of a heat pump is measured through a coefficient, called coefficient of performance (COP), which is the ratio of the useful heat transfer done by the heat pump to the input energy given to the system. COP ranges between 2 and 3 for compression heat pumps and is less than 1 for many alternative approaches. Therefore, the energy requirement of any heat pump is significantly high, and for adsorption heat pumps, it is much higher. On the other hand, the benefit of adsorption heat pumps does not lie on the COP, but on the freedom to choose different sources of energy. For example, if the system is suitable for desorption at around 120 ℃; sunlight, which is one of the most common sources of renewable and free energy, is a possible alternative as the energy source for the system. Furthermore, such an approach can also consider the energy sources like exhaust gases which are not originally free but practically have no cost since they are normally disposed off.

Adsorption heat pumps, have lower COP than commercial compression type heat pumps and therefore, from the usability and profitability point of view, adsorption pumps should never be compared to compression heat pumps via COP. Instead, they should be considered as a tool for using, non-cost energy sources which are not possible as the energy source of compression heat pumps. However, this does not imply that, since the energy input is chosen to be from a free source, the system is usable and beneficial regardless of any performance criteria. In any system, several factors like initial cost, operational and maintenance costs, and equipment size are also important together with the cost of operating energy. Then, the scheme, resulting from the comparison of all these criteria, is supposed to be as satisfactory as possible in order to have adsorption heat pumps in real practice, and in commercial market. In addition, although COP is not the most important criteria or even not important criteria for adsorption heat pumps, it can affect several of the other criteria. For example, if heat pump is designed to be operated with solar energy, solar collectors with satisfactory collector area are required. As a result, as the COP increases, the required area of the collector decreases. This decreases both the system cost and total area occupied by the system. Therefore, even the COP, itself, is not a dominant criteria for such an adsorption pump, still, it should be kept as high as possible, as the size and initial cost of the equipment are considered. On the other side, economy is not the only factor that determines the use of a heat pump and the operating limitations of the system are also important for the usability of the system. Attempts to increase COP that either increase the minimum temperature achieved with the system, or which make the system require high desorption temperatures, also limit the usability of the system. For example, adsorption chillers, which do not make refrigeration but only cooling, usually have higher COP values compared to adsorption refrigerators [10]. However, since this limits the operating range, such an approach does not come up with a significant improvement for the technology [10]. On the other side, systems that utilize chemisorptions also have higher COP compared to physisorption systems but, with this approach higher desorption temperatures are required which prevents use of free energy sources like sunlight [10]. As a result of all these criteria, the use of adsorption heat pumps require, some way to get an optimum COP, without compromising from the operating range flexibility or possibility to use free heat sources .

Operating range of a heat pump is mostly determined by the edge temperature up to which cooling or heating is to be done. Heat pumps are commonly used for cold reserving, which usually occurs below the freezing temperature of water which means cooling to below 0 °C is commonly required. Also, it should be considered that cooling should be supplied with the available free heat source. Furthermore, as the free heat sources are considered, the most common is sunlight. Since, scientific studies are usually inspired by the daily needs, these two factors are widely investigated, and systems that can operate up to freezing temperatures with the use of sunlight have been studied a lot in the literature. Such systems usually consider activated carbon hydrocarbon pair heat exchangers with plate solar collectors. Also, several other studies have considered the use of other sources, such as waste heat. Unfortunately, such studies are usually limited to building an experimental system and performing capacity measurements with respect to operating conditions. In contrast, performance improvement for adsorption heat pump is usually possible by proper choice of the adsorbing material, together with proper modeling of the system geometry, especially the adsorbent bed. In fact, several studies have been made on the adsorption pair selection and effect of material pair on performance of these heat pumps. Furthermore, limited studies also exist on modeling the system geometry but these are mostly limited to bulk and macroscopic scale studies that use several simplified models which not only involve significant error range but also limit the applicability of the model to different geometries.

As the adsorption heat pump concept is considered as whole, taking into account all the problems and needs explained, modeling with enough precision, which is applicable to wide range of system parameters, is required for developing high COP, flexible and more usable systems. This brings the need for reliable modeling tools that can forecast the behavior of different sizes of systems successfully. Also, such modeling should include necessary physical data of adsorption for the chosen adsorption pair. In fact, such a modeling approach is the main focus of this study.

CHAPTER 2

LITERATURE REVIEW

Chemical heat pumps and relevant cooling has been an important topic for many researchers, throughout years, and therefore it has been widely studied. Although, commercial applications almost always use compression heat pumping methods, scientific studies have considered use of several different heat pump principles. The methods considered for heat pumping were mainly, compression, chemical reaction and adsorption. Chemical heat pumps, in fact, can be considered as types which utilize reversible chemical reaction. Although this type did not take considerable attention, several researches are available. For example, in 1998, Kawasaki et al. studied chemical heat pump that utilizes par-aldehyde depolymerization and found a cooling rate of 10 kW per unit catalyst weight. In this study they utilized a high pressure system that continuously polymerized and polymerized par-aldehyde solution, and performed heat transfer using the heat of reaction. The forward and reverse reaction was controlled by type of catalyst used [4]. In 2004 Wang et al. studied the $CaCl_2$ ammonia heat pump that can be an example for both adsorption and chemical heat pumps [10].

More than chemical reaction heat pumps, adsorption cooling has been a widely investigated topic in the recent years. Researchers in their papers mainly argued that these systems are useful due to low grade heat energy usage, which can make use of no-cost sources like sunlight or exhaust gases possible. It is also mentioned that these types of systems have very low COP's compared to commercial systems, and due to the low COP obtained in these systems, the research done is mainly about the performance and optimization of these systems. Although, among these studies most are about results obtained using different experimental systems; many articles that compare different adsorption material pairs, also exist. Even, articles that are about modeling of these systems are not uncommon.

Recently, many researchers have done experiments about adsorption heat pumps and published the performance results, they have obtained. In many of the studies about adsorption heat pumps, the energy source is sunlight because of its zero cost and no environmental side effect; but studies about systems that use other sources like exhaust gases are also available. In 1999, Li and Sumathy studied solar powered ice maker with activated carbon and methanol pair using simple flat ice collector [5]. They investigated the performance of three different activated carbon brands produced in China and selected CHK-3 activated carbon. With their system that has 0.92 m^2 of solar collector area, they could produce 4-5 kg of ice per day with a COP between 0.1 and 0.2. Furthermore, they plotted the COP versus different operation parameters of the system including the evaporation temperature and reported that with an evaporating temperate of 0 °C better COP was gained than evaporation below 0 °C. They also claimed that, for methanol - activated carbon pair; the optimum desorption temperature was 110 °C for having highest COP and claimed that higher desorption temperatures; although increase the capacity, would decrease the COP. In 2003 Anyavu and Ezekve studied adsorption heat pumps and built an experimental model in Nigeria, utilizing a system with 1.2 m^2 solar collector area and 60 kg activated carbon. The system had plate type solar collector and operated using single adsorption bed. Using the experimental setup, they obtained about 200 kj of cooling per day with a COP around 0.08 to 0.1. They also noted that the solar intensity during the expeirment was around 16 Mj/m^2. In 1998 Dous at al. studied heat pump with two adsorption cycles utilizing NaX zeolite water pair. They focused on both heating and cooling operation with the system, obtaining a COP of 1.38 for heating [1]. In 2001 Wang et al. studied adsorption heat pumps as both freezers and chillers. In both types they used activated carbon - methanol as adsorption pair and used large volume absorber beds with relatively less amount of activated carbon. In their experiments they varied the cycle time in order to find the optimal value. For the freezing operation, they found COP around 0.15 to 0.2, while for chilling the COP was up to 0.4. They also claimed that, theoretically it was possible to get up to 2.6 kg of ice per day per kg of adsorbent in freezing system and up to 300W per kg of adsorbent for chilling system [10].

Since the COP in adsorption heat pumps are usually very low, main attempt on the studies of adsorption heat pumps were about increasing the COP, using different parameters that can be optimized for performance, and one of the most commonly studied parameter was the choice of adsorption pair. In 2004 Wang et al. studied performance of different adsorption pairs to be used in ice makers for fishing boats, in which, they compared three different adsorption pairs, activated carbon - methanol, $CaCl_2$ - ammonia and composite adsorbent - methanol. In order to find the performance of activated carbon methanol system, they built a model system and for the other pairs, they used adsorption data, in order to predict the performance of the adsorption pair, as heat pump. With the $CaCl_2$ - ammonia pair, they got the highest cooling power which was around 20 kW. However, they noted that use of chemical adsorbents required high grade energy which was almost impossible to be collected from resources like sunlight, therefore having high cooling power density and COP required high temperature sources like exhaust gases [10]. In 2007 San and Lin, compared three different adsorption pairs, for use in adsorption heat pump. In their study, they used solid side residence model considering a four bed adsorber heat exchanger, and compared the adsorption pair alternatives; activated carbon - methanol, zeolite - water and 13X molecular sieve - water. They found that activated carbon - methanol had the highest efficiency and specific cooling power among the other two. They also noted that 13X sieve water also had very close results to activated carbon - methanol. They also investigated the heat effects inside the adsorber bed during the process, and ended up with the result that, neglecting the effect of temperature increase in the adsorption bed, would result in the over-estimation of the system performance. They also found that as the flow rate of the adsorbate through the bed increases, the effect of temperature increase on the system performance would be less. However, they noted that increasing the adsorbate flow rate was effective, up to a certain level, for increasing the thermal conductivity, and further increase did not make significant benefit. Furthermore, they claimed that increasing desorption temperature would promote the system performance, thus, increase the COP; but added that, depending on the type of adsorption pair, there was certain desorption temperature that resulted in highest COP and further increase in the desorption temperature would, although increase performance, reduce COP [10]. In 2005 Wang et al. studied adsorption heat pumps and compared different adsorbent adsorbate pair alternatives. They studied activated carbon – methanol, activated carbon - ammonia and activated carbon $CaCl_2$ cement composite adsorbent options. They reported that composite adsorbent had the best performance as the adsorbent and when it was used as physical adsorbent with methanol, it resulted a COP of 0.125 and specific cooling power of 32.6 W/kg adsorbent. On the other side, they also reported that when the consolidated adsorbent was used with ammonia in a chemical adsorption system the COP was 1.8 times larger as 0.35 and specific cooing power was 14 times larger as 492 W/kg [16].

In order to increase the performance of adsorption heat pumps many parameters have to be optimized, and one of these parameters is the strength of heat source. In 2007 Gonzales and Rodrigues studied adsorption heat pump that used a parabolic solar collector instead of plane one. They used solar collector with half angles 45℃ and 90℃. They claimed to archive COP values around 0,078 to 0.096 and their system was able to cool 9 kg of water per unit area of the collector from 23 to 2 ℃. As a result of their study, they suggested that the half angles of the collector should be optimized for better COP [17]. In 2004, Wang et al. in their study about ice maker for fishing bats, proposed exhaust gas from engine as the heat source of the system and this made them able to use chemical sorbents such a $CaCl_2$, thus gain much higher COP and cooling power than physical adsorption systems [10].

In order to optimize the performance of adsorption heat pump, although the choice of adsorption pair is the first and basic decision, the design of the adsorption bed is not less important. However, design of a system requires enough accurate modeling, in order to predict the results that could be obtained from certain geometry. In 2007 Anyanwu and Oquege studied transient analysis and performance prediction of adsorption solar refrigerator. They used a test system with 1.2 m^2 solar collector area and compared their transient model results with experimental data. For the adsorbent bed, they used shell type microscopic energy balance and modeled the temperature profile. Their system was using activated carbon and methanol. They claimed to predict the relevant temperatures within satisfactory error range, that they predicted the yield and COP with 5%

and 9% error ranges. They also plotted temperature histogram for the system during refrigeration and regeneration cycles. They also modeled the temperature variation in the cooling water and surfaces of the system with respect to time [12]. In 1998 Dous at al. in their study with two adsorption cycles utilizing NaX zeolite water pair, modeled the adsorption heat pump in a way that they call white box, that is, they took into account the internal structure with heat and mass transfer limitations. They claimed that significant improvement in COP was possible with accurate design and modeling of the system that can make such systems have comparable COPs to compression pumps [1]. In 2002 Miltkau and Dawout studied the adsorption and heat transfer effects in the adsorption and desorption processes of an adsorption heat pump; mainly focusing on zeolite - water adsorption pair. In the modeling part, they used discrete methods with the help of package programs and used a one dimensional model. In the model, they utilized Knudsen diffusion theory for diffusion coefficient and ideal gas law for gas densities together with general mixture rules for liquid uptake and density of the zeolite. As the result, they plotted the temperature profiles with respect to position and time for the zeolite layers inside the adsorber bed [11].

One of the most important disadvantages and most unwanted behavior of adsorption heat pumps is the unavoidable non-continuous operation that; several researchers have proposed systems that can operate near continuous manner. In 2006, San studied analysis of the performance of a multi-bed adsorption heat pump using solid side residence model. Unlike many other studies, in this research San considered a four bed heat pump and claimed that using the four beds at different stages would result in a near continuous operation. In his work San considered and modeled activated carbon - methanol as the adsorption pair and using mathematical model, forecasted the performance of the system with respect to different data including heat and mass transfer resistances in the system. Depending on the results obtained from the computer program he developed, San claimed that increasing cycle time would result an increase in COP and this increase would be more significant up to about 10 minutes time. He also claimed that as temperature inside the bed during adsorption was lowered, the COP would be better. Furthermore he also added that decreasing the grain size of the carbon had similar effect. In case of the evaporating temperature, he found that decreasing the evaporation temperature would make the COP less. He also unsurprisingly found that better the heat transfer, more the COP would be. Finally, he found that as the regeneration temperature was increased, the COP would increase up to about 100 ℃ and reach a maximum value [15]. In 1998 Dous at al. used two bed systems not only as two different systems operating in opposite stages but they proposed a system that has two stage cycle. This way, they claimed to have not only a more like continuous system but also a system with higher COP such that they got COP of 1.56 rather than 1.38 that could be obtained with single stage heat pump [1].

Although not necessarily only for heat pumps, studies about adsorption processes especially for activated carbon and organic liquids are important in literature and can help designing better adsorption heat pumps. For example, In 2005 Menard and Mazet studied the adsorption behavior of activated carbon for CO_2 mainly focusing on the effect of temperature changes on the capacity of carbon and effect of adsorption process on temperature. Furthermore, in their study they included a plot of the temperature profile inside of CO_2 adsorbing activated carbon bed. They also studied the effect of conducting monolith addition to the activated carbon, both in adsorption capacity and temperature profile. Moreover, they compared the conducting monolith added activated carbon with ordinary granular carbon. They found that, addition of high conductive material would increase the thermal conductivity and overall performance of the bed. In their second study, they focused on the regeneration process dealing with the affect of conductivity on the total duration and efficiency of regeneration [13].

As the studies about adsorption heat pumps are concerned in general, adsorption heat pump is an increasingly studied topic recently, despite the fact that, as the COP is concerned, they are incomparable to commercial compression heat pumps. This is most probably due to the environmental concepts and sustainable energy requirements that have been popular in the recent years. However, many of the studies mentioned, have produced results with low COP and cooling power which denote the difficulty of using these systems commercially. On the other side there exist several studies that aim increasing the performance and with water zeolite systems COP up to 0.4 are observed. Unfortunately, this choice limits the usage to chilling, since with water, temperatures below 0 °C are not possible. Using chemical adsorbents like $CaCl_2$ have better results, but hey have the limitations about heating sources and the adsorbate like ammonia are mostly toxic [16]. Moreover, although the activated carbon - methanol is the most widely studied pair, methanol is also not very safe. Therefore, more safe and low melting point materials like ethanol should be proposed. Furthermore, in order to increase the COP to considerable level, highly precise modeling that takes into account the heat and mass transfer limitations should be done.

CHAPTER 3

THEORETICAL BACKGROUND

3.1 Important Design Concepts

3.1.1 Working Principle

Heat pumps differ in internal structure depending on their type, which is in fact, caused by the different working principle. Completely different from compression heat pumps, adsorption heat pumps utilize adsorption and desorption process in connection with evaporation of the adsorbed liquid from the cooler side, in order to perform heat transfer. In simplest form, an adsorption heat pump consist of an adsorption bed, an evaporator and a condenser, three of which are connected with pipes and evacuated such that only adsorbate liquid and its vapor exist in the system. Schematically, an adsorption heat pump can be seen on **figure 3.1** with the most basic approach.

A single adsorption bed heat pump, which can be seen from **figure 3.1**, operates in a cyclic manner with two steps. In the first of these, adsorption is done, which promotes the heat transfer, mainly the cooling affect. Then, as adsorption is complete, the system passes through the second step, in which no cooling is done and instead regeneration occurs, which prepares the system for the next cycle. If the heat pump is used for refrigeration, which is mostly the real case, the stages can be called refrigeration and regeneration. In refrigeration period, absorber adsorbs the vapor inside the system, thus, causes the pressure inside the system to decrease, so that the liquid inside the evaporator boils due to low pressure. As the evaporating liquid fills the system, boiling is promoted with continuous adsorption of the resulting vapor by the adsorbate material. Then, the endothermic nature of evaporation or boiling occurring in the evaporator, causes the liquid temperature to decrease. On the other side, since adsorption is an exothermic process, the adsorption bed should be continuously cooled during this period. As the adsorption process continues and bed is saturated with adsorbate material or gets close to saturation; that, adsorption process stops or slows, refrigeration step is complete and regeneration begins. During regeneration period, in which, the system is prepared for the next cycle; absorption bed is heated so that it releases its adsorbate content. This time, vapor is not directly passed to the evaporator. Instead, it is cooled in the cooler and liquefied. The liquefied vapor is then stored in the evaporator until the next refrigeration step.

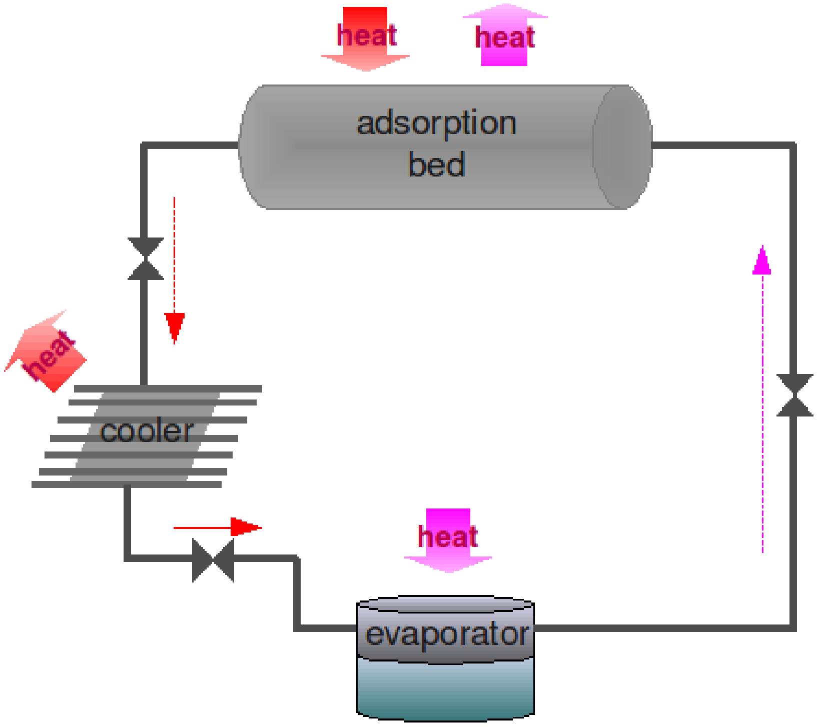

figure 3.1: Operating principle of adsorption heat pump with single adsorption bed. Red arrows represent the fist step (adsorption), magenta arrows represent the second step (regeneration)

Like almost all systems, for heat pumps, a non-continuous, cyclic process is not requested, and, use of two adsorption beds is an effective solution to this phenomenon. In a double adsorption bed heat pump which is shown schematically in **figure 3.2**, in one step of the cycle one of the adsorption beds is an adsorption state, while the other is in regeneration. Then as the step is complete, the roles of the adsorption beds are reversed. As a result, a more continuous cooling is provided compared to single adsorption bed system. Furthermore, in addition to the presence of inactive stage in single adsorption bed system, the adsorption, thus cooling rate, is not constant through one step of adsorption due to the change in the adsorbed concentration that slows the adsorption process. In other words, cooling power is faster at the start of each step and gradually slows down as the adsorption proceeds and the bed gets close to saturation. Such a phenomenon comes up with a variable cooling rate even in the usable adsorption period of the bed. As a result, although double adsorption heat pump does not have idle step, the cooling rate slows through the end of each step, and the cooling power is variable. This can be overcome by using multiple adsorption beds and near continuous heat transfer rates, similar to the applications in compression heat pumps can be attained.

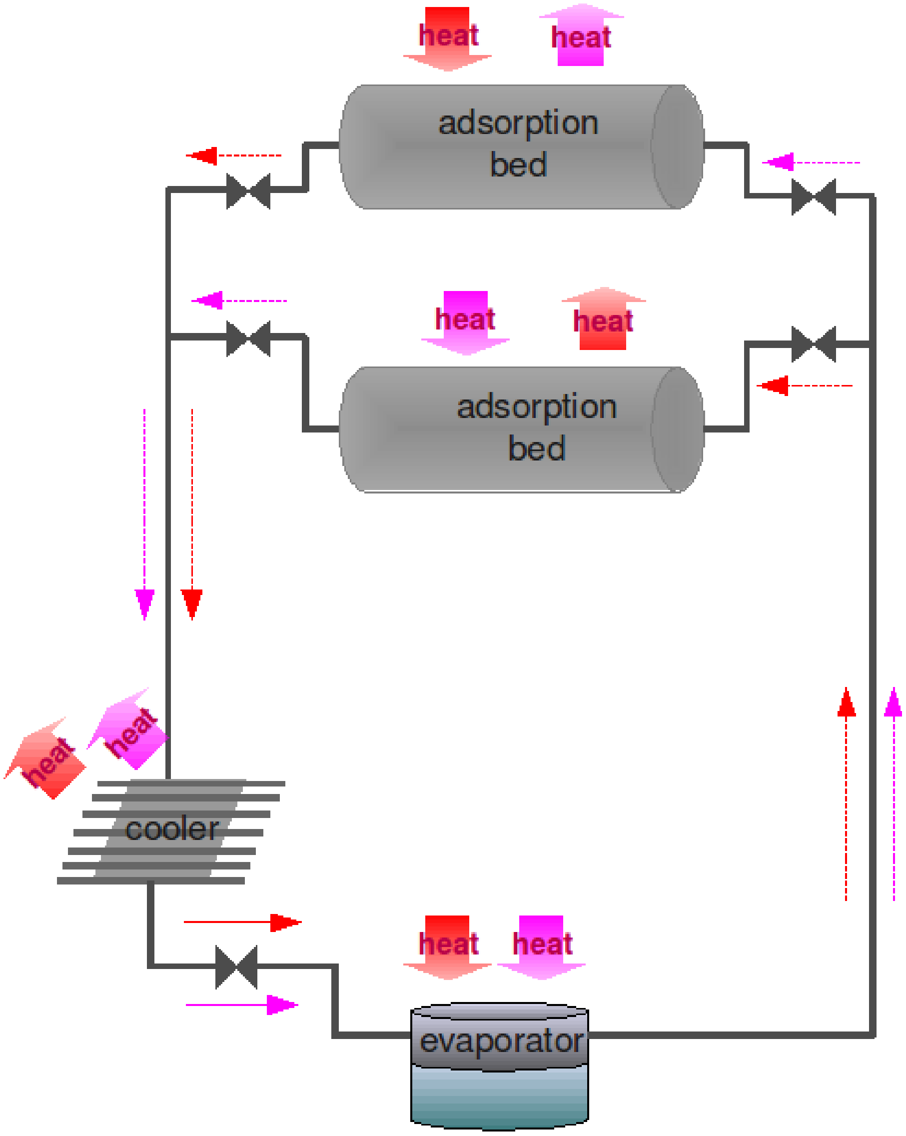

***figure 3.2**: Operating principle of adsorption heat pump with double adsorption bed. Red arrows represent the fist step, magenta arrows represent the second step*

Similar to compression heat pump, an adsorption heat pump also has a target heat source, that should be cooled or heated, a medium through which the heat is disposed off or taken from and also has energy input. In adsorption process, cooling is done through the evaporator and heat is disposed of through the cooler while the process energy is supplied through the heating of the adsorption bed during desorption and this can be thought as analogous to the work input of compression heat pump.

For an adsorption heat pump, in one cycle of the process, cooling effect is equal to the total heat taken by the vaporization of the adsorbate liquid. On the other side, while the heat is disposed, it is lost through the cooler during desorption and also some heat is taken from the system in form of the cooling done on the adsorption bed during adsorption period.

In order to have the best system performance for an adsorption heat pump, the latent heat of the adsorbate, should be as large as possible while its heat of adsorption should be as low as possible. Unfortunately, although, these two properties are the most important factors for efficiency, the heat of adsorption and latent heat are usually similar in orders of magnitude. Therefore, the above two criteria are exclusive and not much improvement is possible by choosing different material pairs that have high latent but low adsorption heat. Therefore, other factors should be considered for better COP.

Beyond the importance of the adsorption or latent heat of the adsorbate materials, several other factors are important for the performance of the adsorption bed. Adsorption or desorption in the adsorption bed is a highly thermal process that, significant amount of heat should be given to or removed from the bed during the adsorption or desorption stages respectively. Therefore, due to the three dimensional nature of the bed, heat should be conducted through the bed during operation, which comes up with the problem of thermal conduction. In case of lack of proper heat transfer inside the adsorbent bed, the temperature inside the bed will be highly non-homogeneous and this comes up with two problems. First, the non-homogeneous temperature profile causes some regions inside to be extremely hot, which can cause damage to the adsorbent and adsorbate material. Second, due to hot zones inside the bed, more heat should be supplied to the bed which increases the observed heat of desorption thus lower the COP. As a result, for better system performance, adsorbents with high thermal conductivity should be preferred. Unfortunately, better conductivity usually requires non porous solid materials, but since adsorption is a surface phenomenon, adsorbate materials should have large surface area and porous materials are preferred as adsorbate. Then, increasing the performance requires the minimization of the heat transfer resistances without compromising from the adsorption capacity and this can be possible either by changing the geometry or the particle size. The finer, the particles are, since the contact between the particles will be better, the heat conductivity will increase but this will decrease the mass permeability of the medium. Unfortunately, permeability of adsorbent is the next important parameter for adsorption bed design. The mass transfer resistance or the permeability of the adsorbent material in fact does not affect the COP value as long as eq 3.1 is considered. Instead, bad mass permeability increases the time required for adsorption or desorption. However, as the time for adsorption or desorption increases, the cooling done per time decreases which in turn decreases the power of the system. In order to overcome this specific power decrease, larger adsorption beds should be used, which in turn causes larger systems and more capital cost.

A successful design of an adsorption heat pump requires a highly effective adsorption bed design, which includes maximizing both heat and mass transfer. For better mass transfer or high permeability, the grains should be kept not too small, which contradicts the heat transfer performance. On the other side, heat transfer can be improved without changing the heat conductivity of the medium, by the help of thermally conductive substances like metal fins. This way the total length of the route of heat through the adsorbate will decrease, which will decrease the temperature resistance and prevent excessive temperature gradient. Then, design of the bed involves deciding on the shape and size of the adsorption bed together with the conductive inputs. However, in order to find the optimum shape and size of the bed, temperature and concentration variations inside the bed during the adsorption or desorption phenomenon should be predicted. Unfortunately, this is not an easy step, rather requires knowing the permeability, diffusivity together with the thermal conductivity of the medium at any temperature. Furthermore, rate of adsorption should also be predicted for any temperature and concentration possible inside the adsorption bed. In addition to the need for physical properties with respect to temperature, pressure and composition, modeling requires simultaneous solution of the mass and heat conservation equations simultaneously, which is not possible through analytic methods but only can be done with numerical methods.

Successful modeling of the system requires knowledge of thermo-physical properties of adsorbent adsorbate pair, together with the adsorption capacities and rates. The heat and mass transfer properties of activated carbon, are available in literature for various liquids and vapors. On the other side, unfortunately, the adsorption data for activated carbon and many adsorbents is mostly in form of isotherms or capacity data, and relations for the rate of adsorption of vapors by activated carbon and other adsorbents, is not widely available. This comes up with problem that, rate of adsorption or desorption of the adsorbate of concern must be available with respect to temperature, vapor concentration and degree of saturation of adsorbent.

3.1.2 Definition Of Efficiency Criteria

As explained in the introduction part, adsorption heat pumps perform cooling effect as the adsorbate boils due to low pressure at the evaporator side and the energy input is the heating supplied to the adsorbent bed during desorption of the adsorbate for regeneration of the system. Therefore, the coefficient of performance COP can be defined as

$$COP = \frac{latent\ heat\ of\ adsorbate}{heat\ of\ desorption} \qquad \textbf{eq 3.1}$$

and this equation defines the first system criteria in terms of adsorption materials. On the other side, several other criteria also exist, one of which is the maximum cooling that can be done or the lowest temperature that can be achieved. Another important criterion is the amount of heat transfer that can be done per unit size of the system, since always it is desired to have the smallest possible system to have the required amount of cooling. As explained above, this performance criterion should be improved by choosing proper materials and successful system design.

The COP itself is not the most important, sometimes even not an important criterion for an adsorption heat pump. Because of the general nature and low COP of adsorption heat pumps, usually free energy sources like, sunlight or waste heat sources are proposed for adsorption heat pumps. Then, other factors like system volume and initial cost are more important. As these factors are concerned, cooling rate per adsorbent amount is an important design criterion. The last but not the least important criterion for adsorption heat pumps is the operating conditions. The melting point of the liquid used as adsorbate, determines the lowest temperature to which the system can do cooling, since having lower temperature values is impossible due to the solidification of the liquid inside the evaporator. For example, water is not a possible alternative for use as adsorbate in refrigerator systems.

3.2 Factors Affecting The Performance Of Adsorption Heat Pumps

As explained in the earlier parts, efficiency is an important factor for adsorption heat pumps to be preferable and commercially available. In fact, main advantage of adsorption heat pumps is not the power efficiency, but the flexibility of energy sources and possibility of using renewable and free energy. However, despite this fact, the power efficiency or COP and the size of the system per cooling amount which determines the initial cost are still important factors. As a result the efficiency is a very important factor to be promoted for adsorption heat pumps, no matter which energy is used

3.2.1 Thermo Physical Properties Of Material Pair

As the criteria explained in the previous section are concerned, one of most important factors for heat exchanger design is the choice of adsorption pair. As COP is concerned, in order to have highest COP, it is important to keep heat of adsorption as low as possible and the latent heat of the adsorbate as high as possible. Latent heat is a function of adsorbate type, operating pressure and cooling temperature while heat of adsorption is a function of adsorbent adsorbate pair, operating pressure and desorption temperature. Therefore, selecting different pairs of adsorbent and especially adsorbate, will have significant effect on the system COP. Unfortunately, adsorption and condensation, or desorption and evaporation, are similar processes as far as the physical change of the molecules is concerned. Then, it is not very likely to find an adsorbent adsorbate pair, such that, the latent heat of the adsorbate is very high but heat of adsorption is relatively very low. Then, the choice of adsorption pair will not be an enough or extremely useful improvement, although it has very significant effect on the COP of the system.

The choice of adsorbent adsorbate pair does not only affect COP of the system but also determines the least temperature that can be achieved with the system. Since the evaporator side can be cooled down to the freezing temperature of the adsorbate, cooling cannot proceed below this temperature. In fact, this is an important criterion that makes water not a possible choice as adsorbate for adsorption type freezers. Furthermore, the choice of material pairs and especially the adsorbent has strict effect on the desorption temperature of the adsorbent bed. The desorption temperature is an important design parameter since, higher the desorption temperature, more limited the possible heat sources are. For example in 2005 Wang et al. Studied $CaCl_2$ ammonia pair and noted that temperatures above 150 °C was necessary which limited the use of their system to high temperature heat sources like exhaust gases [10]. In addition, the choice of adsorbate limits the operating pressure of the system since pressure above the vapor pressure of the adsorbate requires addition of some inert gases into the system. Effects of such an approach will be discussed more in detail in the following part.

3.2.2 Operating Pressure

In an adsorption desorption system, pressure of the vapor is an important factor that strongly affects, the capacity and adsorption desorption rate of the adsorbent. However, in an adsorption heat pump, vapor is supplied to the absorber bed due to the evaporation from the cooler, which makes vapor pressure in the adsorbent bed not a freely chosen parameter. In fact, the partial pressure of the vapor inside the system is limited to the vapor pressure of the adsorbate at the cooling temperature.

Although the partial pressure of adsorbate vapor inside the adsorbent bed is not a freely chosen criterion, the total pressure can be adjusted by admittance of some inert gases into the system. However, such an approach will make the vapor a binary or more complex mixture which will completely change both thermo physical and adsorption properties of the adsorbent adsorbate pair. Therefore, all these affects should be considered for having system pressures higher than the vapor pressure of the adsorbate.

3.2.3 Operating Temperature

For an adsorption heat pump, as the operating temperatures are concerned, mainly two operating temperatures are observed on the system. One of these, is the temperature of the cooler or the minimum temperature to which cooling is done, and the other is the adsorption or regeneration temperature. Among these two, cooling temperature affects the vapor pressure of the adsorbent during cooling period thus the operating pressure of the system. On the other side, regeneration temperature is important, since it determines extend to which, the adsorbent can be regenerated during the regeneration period. This is one of the most important factors for the capacity of the system, since it determines the vapor capacity change of the adsorption bed during the steps of the cycles, which in turn determines the amount of heat transfer done. However, as explained earlier, desorption temperature also cannot be freely chosen since it determines the types of driving energy used by the system, thus can affect the usability of the system.

3.2.4 Adsorption Bed Geometry

As explained in the previous parts, thermo physical properties and operating temperatures inside the adsorption heat pumps have strong affect on the performance, both in terms of COP and capacity. However, the problem arises from the fact that, the beneficial properties about the system are usually exclusive. This comes up with the need for better system designs in terms of geometry that will improve energy efficiency without compromising from system power and operation flexibility. As these criteria are concerned, the most important properties to optimize are the thermal conductivity and mass permeability of the system. Unfortunately, as the material selection is concerned, conductivity and mass permeability are also exclusive. Adsorbents with finer grains usually have higher thermal conductivity but lower mass permeability. Therefore, in order to have adsorbent bed with high thermal conductivity and mass permeability, geometry of the bed should be optimized. This optimal design may include placing fins into the bed, designing the bed in terms of several tubes or several other improvements.

3.2.5 Physical Properties Of Adsorbent

Thermo-physical properties of adsorbate material are important factors for heat pump design and performance. Especially the transfer resistances for heat and mass are important for the adsorption rate and capacity. Since the adsorbate has to travel through the adsorbent medium during adsorption and desorption, mass permeability of the medium is an important factor. Also, since during sorption processes significant amount of energy is taken or released; materials with high thermal conductivity are more preferable. Furthermore, during the operating cycle of an adsorption heat pump, the bed is heated and cooled periodically, in order to perform alternating adsorption and desorption steps. During heating or cooling, some part of the heat is used for sensible heating of the bed. Therefore, in order to have high COP, adsorbate materials with low specific heat are more beneficial.

CHAPTER 4

EXPERIMENTS DONE ON ACTIVATED CARBON

Within this study for adsorption heat pumps, one of the most important data is the capacity of activated carbon together with rate of adsorption. Therefore, in order to find the adsorption properties of different types of activated carbons with different hydrocarbons, constant pressure variable temperature and constant temperature variable pressure experiments were done during which, total weight of the activated carbon was measured with respect to time. During the experiments, a commercial activated carbon produced in china was used. It was in cylindrical pellet form, with an average particle diameter of 2 mm and length 2-4 mm. Furthermore, the activated carbon sample used in the experiments was also analyzed at Middle East Technical University, Central Lab, for surface characteristics and void fraction. The results are given in appendix A.

4.1 Methodology For Adsorption Capacity And Kinetics

As explained previously, the modeling of the system required physical properties of the activated carbon hydrocarbon pair. Moreover, getting these properties from experimental results required adsorption experiments under certain preset constant conditions, during which adsorption rate or total adsorption capacity was to be recorded. These experiments were mainly of two types which were capacity measurements and adsorption kinetics experiments. During these experiments, adsorption amount with respect to time was recorded. In capacity measurement experiments, total adsorbed amount was to be measured under certain temperature and pressure conditions while in kinetic experiments the adsorbed amount was to be measured with respect to time, again under constant conditions of temperature and pressure.

4.2 IGA System

During the experiments carried out for the study, a system called IGA (Intelligent Gravimetric Analyzer), manufactured by Hidden Company UK., was used. IGA mainly aims to measure the weight of an adsorbent, which adsorbs vapor under preset constant conditions. IGA consists of an adsorption bed called reactor, a liquid reservoir and some control valves. Also, multiple gas inlets and vacuum pumps are connected to the system for balancing the pressure to desired level or doing gas sorption experiments. Since the IGA system has to keep not only pressure but also temperature constant, furnaces or water baths also can be mounted to the reactor in order to have the desired temperature or sequences of temperatures. A diagram of IGA system located in METU Chemical Engineering Department, which was taken from the documents of the device, can be seen in figure 4.1.

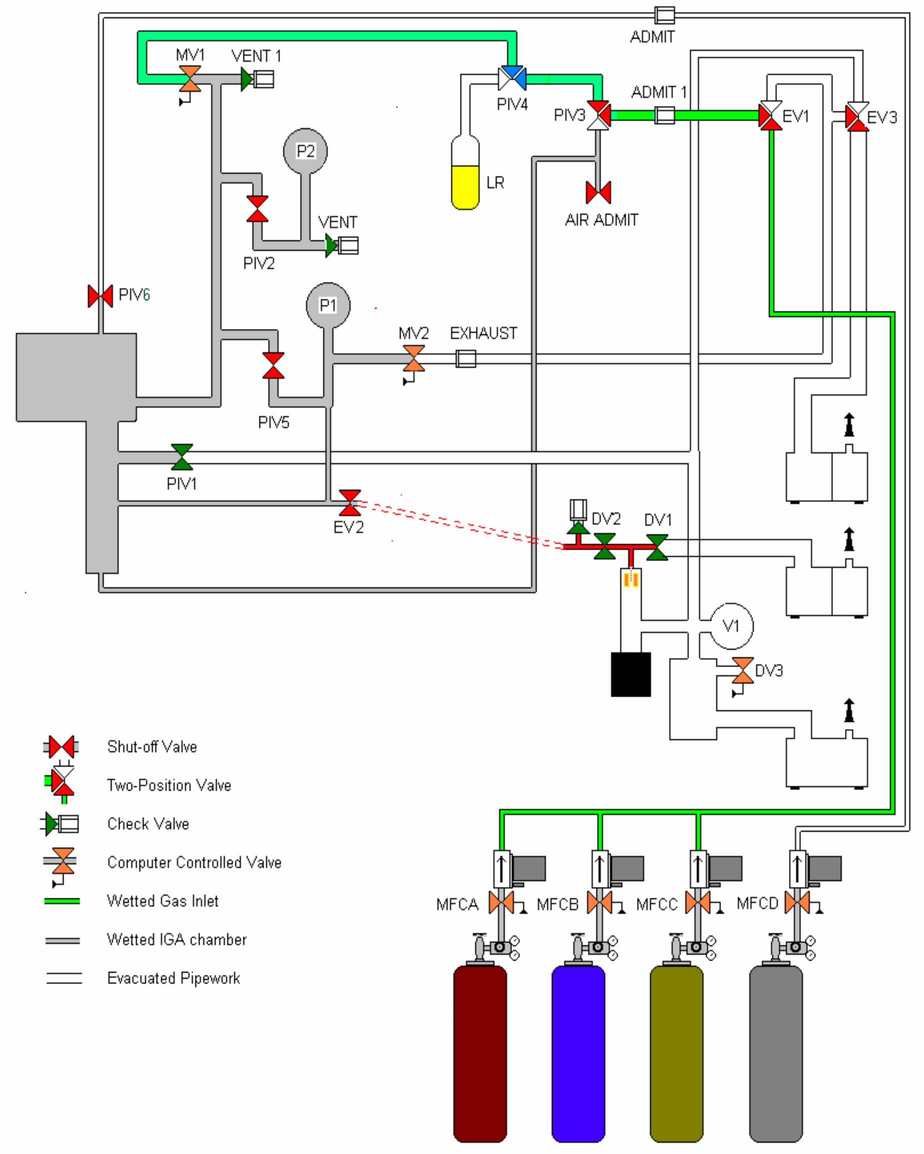

***figure 4.1** : Schematic drawing of IGA*

During an experiment with IGA, the sample is loaded to the sample container that is made of quartz and then it is hung to the system's scale that holds the sample container in the reactor. Then, the reactor is closed and sealed that, the inside of the reactor is completely isolated from environment, in terms of mass transfer. As a result, only mass transfer to the system is through the inlet valves that let vapor or gas to the reactor, and exit through the vacuum pump that evacuates the vapor phase inside the reactor. After the sample is loaded, since precise measurement is desired, the sample has to be cleaned to satisfactory degree, which is called regeneration. Regeneration of the sample is done by holding the adsorbate sample inside the reactor and increasing the temperature of the system under vacuum conditions. This removes the impurities like adsorbed moisture present inside the adsorbent molecular structure before it is placed into the reactor. At vacuum and high temperature conditions, the sample is left for enough time so that these impurities are released from the adsorbent. After regeneration, the experiment is started.

As the capabilities of IGA are considered in general, the system can be used in order to perform constant temperature variable pressure experiments such as isotherm plots or variable temperature experiments, in which either sorption kinetics or capacities are determined. However, the main type of experiment used for this study was kinetics determination, under constant temperature and pressure.

4.3 Adsorbate Comparison

During design of an adsorption heat pump, thermo-physical properties of the adsorbate are important, which makes adsorbate selection a critical issue. In adsorbate selection, comparison was done on different hydrocarbon types, which were acetone, n-pentane and ethanol. However, since the performance of an adsorption heat pump is the combined function of both adsorption capacity of the adsorbent for the vapor, and the latent heat, in comparison of the hydrocarbons, neither the capacity nor the kinetics alone can give enough foresight for the performance of the system. As a result, comparison was done using the product of capacity and latent heat.

In adsorption heat pump design, the adsorption kinetics is the last but not the least important criterion, as factors like system size and cooling power per adsorbent mass are considered. The faster the adsorption or desorption occurs, the smaller the cycle time and as a result, in a certain period with the same amount of adsorbate material, more heat transfer occurs. Therefore the materials with higher adsorption or desorption rates are more preferred.

During the capacity experiments, fist the sample is loaded to the reactor of the IGA and it is regenerated. Then for adsorption experiments, the sample is left for equilibrium at around 120 ℃, that, it is similar to the conditions at the end of a desorption cycle of an adsorption bed. Then, the system temperature is set to 40 ℃ and an adsorption phenomenon is recorded as weigh of the sample with respect to time. On the other hand, desorption experiments are done in the opposite manner that the system is first left for equilibrium at 120 ℃, which is close to the situation at the end of a regeneration step of a heat pump. Then, temperature is set to 40 ℃ and weight is recorded.

4.4 Experiments On Operating Pressure

As explained earlier, for an adsorption heat pump, pressure is not a completely independent parameter and the partial pressure of vapor is equal to the vapor pressure of the adsorbate liquid. On the other side, the effect of increasing pressure using inert has some advantages like decreasing the need for system wall strength and avoiding leakages into the system. However, deciding on the pressure of operation should consider effect of vapor dilution on the adsorption performance. Since adsorption is a surface phenomenon between the surface of adsorbent and adsorbate vapor, theoretically the capacity is not supposed to differ considerably with the presence of the inert gas. During pressure experiments the methodology used for adsorbate comparison experiments is followed using the same adsorbate, ethanol with different pressure environments. The results are given in part 6.1.2.

4.5 Experiments For Kinetic Data

Modeling done on activate carbon manly included the parameters, adsorption rate and physical characteristics of activated carbon. Although, the thermo physical properties of adsorbents like activated carbon and adsorbates like hydrocarbons were available in literature, they were either in form of experimental data or predictor models. Also adsorption rate have not been widely studied. Even, mostly the study done on activated carbon adsorption is presented in form of isotherm data and unfortunately, it is not possible to calculate the instantaneous adsorption rate values from isotherm plot. In fact, finding the adsorption rate constants requires kinetic data of adsorption process, based on time. Therefore, constant pressure and temperature, adsorption vs. time experiments were done. In these experiments, IGA was used and the process was carried out under constant pressure and temperature for different temperature values. During these experiments, the system was first evacuated and left for complete equilibrium at high temperature with vacuum conditions. Then, after the system reached stability the pressure of the IGA was set to the target pressure and weight was recoded with respect to time. The results are given in 6.1.3.

CHAPTER 5

MODELING OF THE SYSTEM

As mentioned in the previous parts, in order to make adsorption heat pumps more efficient, proper modeling is required. Since the capacity limitations occur mostly because of adsorption process rather than the evaporation, proper modeling must include the adsorption rate, which is affected by the temperature and pressure conditions inside the adsorbent bed, together with the degree of saturation. As a result, modeling requires the rate of adsorption or desorption at any physical condition that is possible inside the adsorption bed. Then, this rate should be used for determining the amount of adsorbate adsorbed on the bed at any given time. However, this will also require some known initial condition and boundary conditions. Also, since at any instance, the needed information is the total amount of adsorbate, it is clear that the modeling should include some governing differential equations to be solved in time domain. Since the system has a complex nature including not only mass but also heat and temperature limitations, the solution model has to include more than one governing differential equation, that should take into account all the physical system effects. In this modeling, two governing equations are used which are mass and heat conservation equations.

5.1 The Proposed System Type

Modeling of the system requires deciding on system type. As far as the literature about CHP's is considered as whole, many studies exist with different absorbent adsorbate pairs. Then, the fist step of designing an efficient system, is to decide on the most suitable adsorption pair and decision should include not only the performance of the system, but also the operating conditions and the available energy sources. The common possible alternatives for adsorbent are activated carbon, chemical adsorbents like $CaCl_2$, and zeolites; while common possible adsorbates are methanol, ethanol, water, ammonia and some other hydrocarbons. However, the chemical adsorbates like $CaCl_2$ can be used with adsorbates like ammonia but desorption of such systems occurs at high temperature close to 170 °C [10]. Therefore such a system is not suitable for solar heat pumps and usability is relatively limited. On the other side, although water is a possible cheap and non toxic adsorbate material with relatively high latent heat, it is not possible for freezing systems since at 0 °C the adsorbate itself will freeze. Then the most suitable choices for adsorption pair include activated carbon or zeolite as adsorbent with hydrocarbon or alcohol as adsorbate since such an alternative is suitable to use with low grade energy sources and perform freezing.

As far as factors other than system temperatures and operating conditions are considered, the costs of the materials and environmental affects like toxicity should also be considered. Previous study about adsorption heat pumps show that, both activated carbon and zeolites give acceptable results as adsorbents. However, activated carbon is a much easier to produce material than zeolites, therefore activated carbon is selected as the adsorbent for this study. On the adsorbate side, although have been widely studied in literature, methanol and ammonia are toxic alternatives so they are not preferred. Then possible alternatives are acetone, ethanol and n-pentane.

5.2 The Proposed Adsorption Bed

In order model the heat pump, fist, the part of the system to be considered should be set. In an adsorption heat pump, flow of the fluid between evaporator and condenser, is driven by the adsorption/desorption processes taking place in the reactor between these two components. Therefore the reactor is the hearth of the CHP and investigation of the system entails a detailed understanding of the reactor both at macroscopic and microscopic levels. Due to the ease of production and strength of walls, in chemical applications cylindrical systems are widely preferred. In this study a cylindrical reactor shown in figure 5.1 is considered. Ratio between the inner and outer radii of the bed is 0.5. Simulations are done on three different beds having r_0 of 10 cm, 5 cm and 2.5 cm. Annular space of the reactor is filled by active carbon. During adsorption stage, vapor from the evaporator flows through the inner core and then moves to the packed section through the permeable wall. On the other hand, during desorption cycle, flow of vapor is reversed as vapor transfers from the packing to the inner core and then flows to the condenser. Cooling or heating of the reactor is provided by a fluid flowing in the reactor jacket.

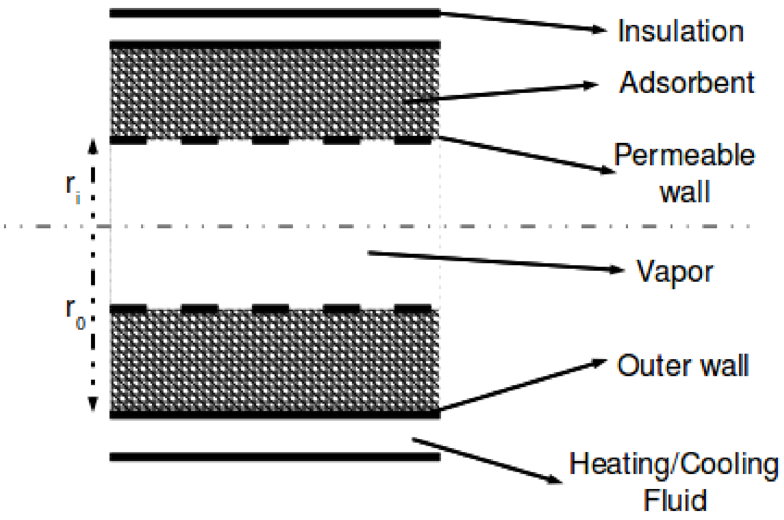

figure 5.1 : *Adsorption bed geometry*

In order to model heat and mass transfer in the packing, the general governing equations are employed along with appropriate boundary and initial conditions. The governing differential equations are first simplified based on number of assumptions. Some of those assumptions are listed below:

- Length of the reactor is sufficiently larger than its diameter so that transfer of material and energy occur in radial direction only.

- Heat transfer resistance of the reactor walls is negligible.

- Heat transfer rates from the outer wall of the reactor jacket and through the inner packing surface are negligible.

- Pressure in the reactor is uniform and it is determined by the vapor pressure of the hydrocarbon either at evaporator or condenser temperature. All pressure drops associated with the flow of the hydrocarbon vapor through conduits and packing are also negligible.

Implication of the fourth assumption is that single component vapor concentration, C_{bulk}, and density, ρ_{bulk}, in the void space are only dependent on the temperature through ideal gas relation. This requires instantaneous transfer of vapor species to the packing in response to temperature change and to vapor adsorption/desorption. A constraint for this crucial assumption can be obtained by an order of magnitude analysis on hydrodynamics basis. Assuming that flow of the vapor through the packed bed is represented by the Kozeny-Carman equation, the uniform pressure assumption is justified provided that

$$O\left[\frac{R_{ads}\, l^2 \mu \left(1-\varepsilon\right)^2}{C_{bulk}\, d_p^2\, \varepsilon^3}\right] << \frac{1}{150} \qquad \textbf{eq 5.1}$$

Here R_{ads}, l, μ, ε, and d_P represent net adsorption rate per unit bed volume, a characteristic length, e.g. inner radius of the reactor, vapor viscosity, void fraction of the bed and diameter of a spherical carbon particle, respectively. In obtaining this constraint, macroscopic relation between the superficial vapor velocity and adsorption rate is also utilized.

As Kozeny-Carman equation is concerned, the right side of the equation is dimensional with the unit of pressure. Therefore, it is necessary to decide on the level of acceptable error with units. As the heat pump with ethanol as adsorbent is concerned, the pressure inside the system is supposed to be around 100 mbar which is 10000 Pa. Then 100 Pa of pressure difference inside the adsorption bed is highly acceptable and can be treated as homogeneous vapor concentration. In other words, when the right hand side is calculated with unit Pa, value less than 100/150 is satisfactory for validating constant pressure assumption. From the numerical simulations, the maximum rate of adsorption inside the bed is around 2.5 mol/m^{3}s. The, particle size of the activated carbon is about 2 mm and characteristic length, the inner radius, is about 25 mm. On the other hand, although the viscosity varies with temperature, for hydrocarbon vapors it is around 0.01 cP. As a result, the ratio given in eq 5.1 becomes approximately 0.01 which much is les than 100/150. Thus, the constant pressure assumption is validated.

The validation of constant pressure assumption, eliminates mass transfer limitations for bulk phase. Then, the rate of change of adsorbed concentration inside the bed, is the only significant parameter for mass balance. The adsorption rate, R$_{\text{ads}}$ relates to the amount of adsorbed material through

$$R_{ads} = \frac{\partial C_{ads}}{\partial t}(1-\varepsilon) \qquad \textbf{eq 5.2}$$

where C$_{\text{ads}}$ is the moles of adsorbed species per unit bed volume. eq 2.3 is instrumental in obtaining the amount of adsorbed material both in microscopic and macroscopic scales by incorporating the adsorption kinetics. In order to find adsorption rate, a form of linear driving force equation, which is given below, is employed [14].

$$\mathrm{R_{ads}} = \frac{\partial \mathrm{w}}{\partial \mathrm{t}} \mathrm{k_s} \alpha_\mathrm{v} (\mathrm{W} - \mathrm{w}) \qquad \textbf{eq 5.3}$$

In this equation w is the adsorbed amount and W is the capacity, in terms of weight ratio while $k_s \alpha_v$ has a constant value, that depends on temperature. These quantities are experimentally determined. T is the point-wise temperature and it is determined, using the thermal energy equation given below.

$$k_e \left[\frac{\partial}{\partial r} r \frac{\partial T}{\partial r} \right] + R_{ads} \Delta H_{ads} = \left[Cp_c \rho_c (1-\varepsilon) + Cp_{bulk} \rho_{bulk} \varepsilon \right] \frac{\partial T}{\partial t} \qquad \textbf{eq 5.4}$$

where the terms in the brackets on he right hand side of eq 5.4 represent the average heat capacity of the bed. The source term includes heat of adsorption, ΔH_{ads}, along with the reaction rate. Its exothermic or endothermic nature is, therefore, captured by the net direction of the reaction being either adsorption or desorption. Effective thermal conductivity, k_e, for the multiphase and complex geometry system of this study is very critical. It should include all appreciable modes of heat transfer through the packed bed. For this purpose, methodology outlined by Smith [1] is followed. This methodology mainly assumes thermal conductivity has separate contributions from bulk and solid phases. Bulk phase contribution consists of fluid conductivity, turbulent diffusion convection and radiation. However for the system of ethanol vapor, since the vapor is a very dilute phase and has low velocity from the bulk contributions, only radiation term is significant. Then the effective thermal conductivity can be given as

$$k_e = \varepsilon_b \left[k_c + \frac{d_p c_p G}{Pe_r \varepsilon_b} + 4 \frac{\sigma}{2-\sigma} d_p \frac{T^3}{100^4} \right] + (1-\varepsilon_b) \left[\frac{h\, k_s d_p}{2\, k_s + h\, d_p} \right] \qquad \textbf{eq 5.5}$$

Where ε_b, k_c, c_p, G, σ, d_p and k_s are the void fraction, fluid conductivity, specific heat of fluid, fluid mass velocity, emmisivity of solid particles, particle diameter and solid conductivity respectively. The first group, with coefficient ε_b, represents the bulk phase contrubution and the second one, with coefficient $(1-\varepsilon_b)$, accounts for the conduction due to the solid phase. The bulk phase contribution also consists of three elements which are, fluid conductivity, heat trasfer due to turbulent flow and heat trasfer by radiation, respectively. However, since the system modeled in this study operates under very low concentaration and flow rate inside the bed is also low, the vapor conductivity and turbulent diffusion contribution can be negleceted. Then eq 5.4 becomes,

$$k_e = \varepsilon\left[4\frac{\sigma}{2-\sigma}\, d_p\, \frac{T^3}{100^4}\right] + (1-\varepsilon)\left[\frac{h\, k_s d_p}{2\, k_s + h\, d_p}\right] \qquad \textbf{eq 5.6}$$

where k_e only depends on radiative and solid conductivity terms. The coefficients were found from Smith's book[1] Furthermore, the term ΔH in the energy balance, is an important parameter to be determined. The method applied by Tan and Hamid in a study about activated carbon, can be used. With that approach, adsorption enthalpy can be expressed as,

$$\ln(K_d) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R} \qquad \textbf{eq 5.7}$$

where term K_d is the distribution function [19].

It is convenient to express effective C_P in terms of density of the adsorbent and concentration of the adsorbate. In an adsorbent adsorbate system, considering an infinitely small control element with volume V, the mass of the adsorbent can be expressed as

$$m_{adsorbent} = \rho_{adsorbent}\, V_{adsorbent} \qquad \textbf{eq 5.8}$$

or

$$\mathrm{m}_{\mathrm{adsorbent}} = \rho_{\mathrm{adsorbent}} \ \mathrm{V}(1-\varepsilon)$$

eq 5.9

Where m is mass, ρ is the density, $V_{adsorbent}$ is the volume occupied by the adsorbent inside the control element, ε is the void fraction. On the other side mass of adsorbate will be

$$\mathrm{m}_{\mathrm{adsorbate}} = \mathrm{C}_{\mathrm{adsorbate}} \ \rho_{\mathrm{adsorbate}} \ \mathrm{V}_{\mathrm{void}}$$

eq 5.10

or

$$\mathrm{m}_{\mathrm{adsorbate}} = \mathrm{C}_{\mathrm{adsorbate}} \ \rho_{\mathrm{adsorbate}} \ \mathrm{V} \ \varepsilon$$

eq 5.11

where V_{void} is the void volume inside the control element. Combining all the equations gives,

$$C_{Peffective} = C_{Padsorbent} \ \rho_{adsorbent} \ (1-\varepsilon) + C_{Padsorbate} \ \rho_{adsorbate} \ \varepsilon$$

eq 5.12

In order to solve the coupled adsorption and energy equations two initial and two boundary conditions are needed. For the initial condition of the concentration, carbon surfaces can be considered free of adsorbate at the beginning of the process. Furthermore the bed content can be assumed at room temperature at time zero. As the process continues final state of the last cycle is considered as the initial condition of the following cycle. As far as the boundary conditions are concerned, under the light of the listed assumptions and simplifications the followings can be employed:

$$\frac{\partial T}{\partial r} = 0 \qquad \text{at } r=ri \qquad \textbf{eq 5.13}$$

$$-k_e \frac{\partial T}{\partial r} = h_f\left(T - T_f\right) \qquad \text{at } r=r_o \qquad \textbf{eq 5.14}$$

where h_f is the heat transfer coefficient between outer reactor wall and fluid in the jacket with a constant bulk temperature of T_f.

5.3 Numerical Solution Of The Proposed System

The governing differential equations given in previous part required, simultaneous solution of two equations that are related thorough the adsorption rate. In order to solve the problem, the system was discretized spatially and temporarily. In fact, the assumption of infinite length makes the problem 1 dimensional in only r direction, that two vectors were enough to represent the system in discrete manner for an instant. As the discrete system, two matrices were used, one for adsorbed concentration and the other for temperature. The columns of these matrices represent the radial dimension while the rows represent the time instances. Therefore, use of 2 dimensional matrices in order to store the concentration or temperature was useful in order to keep the temperature and concentration profile for the complete simulation time axis. In order to solve this system, fist, initial conditions were filled into the proper elements of the matrices. Then, central difference was used in order to find the differential terms in the conservation equations. Then, boundary conditions were applied to the edge nodes. On the other hand, in time iteration explicit forward difference method was used. The algorithm for the calculation was as shown in figure 5.2.

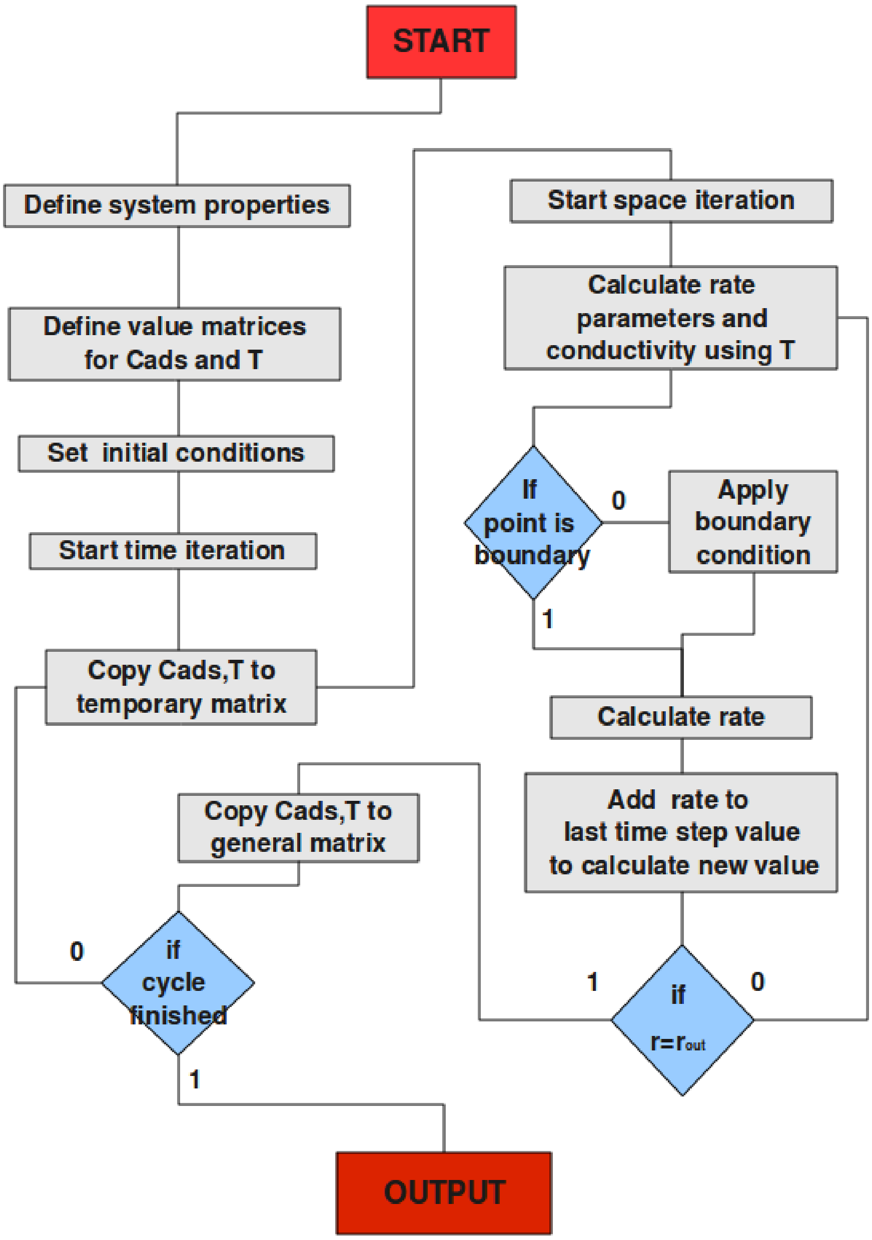

figure 5.2 : Solution algorithm

CHAPTER 6

RESULTS AND DISCUSSION

6.1 Evaluation Of Experimental Data

6.1.1 Choice Of Adsorbate

As explained previously, choice of adsorbate is an important, part of designing suitable and high performance systems. During the studies one of the first decisions to make is to distinguish between different adsorbate materials. Also, due to the objective of the study, the adsorbent material was preset as activated carbon. Within the context of this research, three different adsorbate materials acetone, n-pentane and ethanol were studied. As explained earlier, since an adsorption heat pump utilizes the latent heat of the adsorbed material between adsorption and desorption stages, the performance of the system is determined by the difference between the adsorption capacities of the adsorbent materials at adsorption and desorption temperatures, multiplied by the latent heat of the liquid. As a result, in order to decide on which adsorbate to use, the parameter to measure was the difference between adsorption capacities.

As adsorbate comparison the methodology explained in 4.3 was applied for three adsorbate candidates, acetone, n-pentane and ethanol. **Table 6.1** shows the results with three adsorbates for adsorption and desorption. Comparison experiment for n-pentane and acetone were carried out at 500 mbar while pressure for ethanol experiment was 100 mbar. The results indicated that, acetone and ethanol gave higher capacity as the performance criteria were considered. However n-pentane although was strongly adsorbed, it was released much less than the other two hydrocarbons during desorption period. Therefore it was not suitable to be used in heat pumps as compared to acetone or ethanol. Furthermore, ethanol was slightly better in performance and was selected for adsorbate modeling.

Table 6.1 : *Adsorbed amount values (weight/weight) for ethanol n-pentane and acetone during adsorption (Ads),at 40 °C, and desorption (Des), at 120 °C.*

Time (min)	**Acetone**		**N-pentane**		**Ethanol**	
	Ads.	**Des.**	**Ads.**	**Des.**	**Ads.**	**Des.**
30	0.21	0.16	0.33	0.26	0.11	0.15
60	0.31	0.11	0.42	0.23	0.26	0.07
90	0.37	0.10	0.44	0.23	0.36	0.06
120	0.40	0.09	0.44	0.22	0.42	0.06

6.1.2 Choice Of Operating Pressure

As explained in the experimental section part, operating pressure is also an important parameter in design of the system. In order to determine the affect of operating pressure on the system performance, activated carbon ethanol experiments were carried out at two different pressures as 100 mbar and 900 mbar. For 100 mbar experiments since the vapor pressure of ethanol at the experiment temperatures was higher than the equilibrium pressure, 100 mbar, pure vapor was used. On the other side for 900 mbar experiments the total pressure was provided by addition of inert gas, N_2, to the system.

Table 6.2 : *Adsorbed amount (weight/weight) values for ethanol with high and low pressure system adsorption, for adsorption (Ads),at 40 ℃, and desorption (Des), at 120 ℃.*

Time (min)	**High Pressure**		**Low Pressure**	
	Ads.	**Des.**	**Ads.**	**Des.**
30	0.07	0.10	0.11	0.15
60	0.12	0.06	0.26	0.07
90	0.16	0.05	0.36	0.06
120	0.20	0.04	0.42	0.06

Results showed that addition of inert to the system in 900 mbar experiments considerably decreased system performance in terms of both rate and capacity. From **Table 6.2**, which shows the adsorption values for both pressure conditions, it can be seen that, low pressure system adsorbs or desorbs about twice of the dilute high pressure system. As a result low pressure was used in the modeling.

6.1.3 Evaluation Of Kinetic Results

As explained previously, IGA experiments were carried out in order to build a tool for adsorption rates for different physical conditions. On purpose, experiments were carried out at different physical conditions. However, it was not suitable to use the data directly in modeling, due to two reasons. First, if the raw data was used for modeling, then the applicability of the simulating tool would be limited to the experiments done. Second, the numerical and mathematical structure of the modeling makes it more preferable to have a mathematical function that can give the adsorption rate using physical parameters as arguments. Therefore, eq 6.1, an integrated form of eq 5.3, was used [14],

$$\ln(W - w) = k_s \alpha_v T + C$$

eq 6.1

where t is time and C is integration constant. The resulting parameters were as in **Table 6.3**.

Table 6.3 : *$k_s\alpha_v$ values wrt. time*

Temperature	**$k_s\alpha_v$**	**C**
30 °C	0.0517	-1.0671
60 °C	0.0947	-1.9022
90 °C	0.1354	-3.3708
120 °C	0.139	-4.8265

Since the found parameters only rely on theoretical approaches, verifying the validity of the model is required. For validation, the kinetic curves themselves were used. The experimental kinetic curves and theoretically plotted ones for 30, 60, 90, and 120 °C are shown in **figure 6.1** and the theoretical results are satisfactorily close to experimental data.

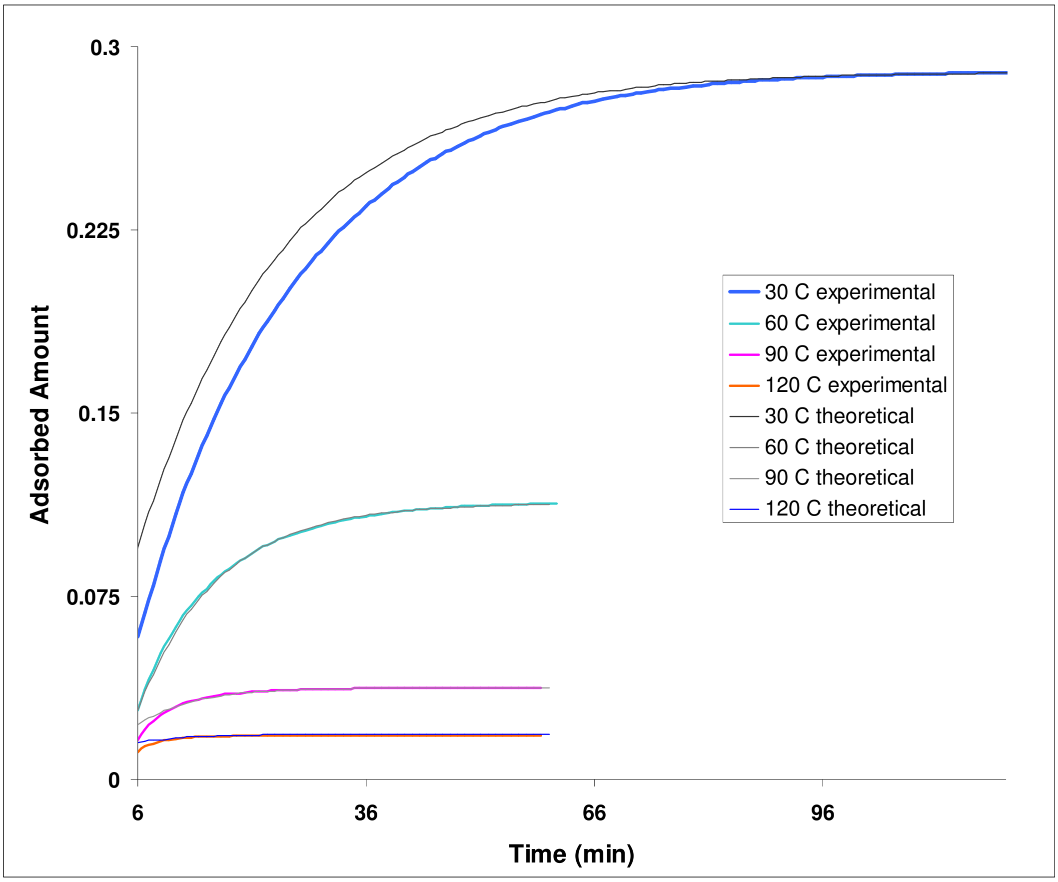

figure 6.1 : *Comparison of theoretical and experimental adsorbed amount (weight ratio) vs. time plots*

Calculation of instantaneous adsorption rate using eq 5.3 requires value of capacity, W. Although value W is available for the four experiment temperatures, it is need for the complete rage of possible temperatures in adsorbent bed. Therefore Dubinin-Radushkevich equation given as

$$W = W_0 \exp\left\{-D\left[\ln\left(\frac{P_s}{P}\right)^n\right]\right\} \qquad \text{eq 6.2}$$

was used where P_s is the saturation pressure of vapor [14]. The P_s term in eq 6.2 was calculated using Antoine equation which is

$$\log_{10}(P) = A - \left(\frac{B}{T+C}\right) \qquad \text{eq 6.3}$$

and constants A,B and C was taken from nist.gov web page [20]. When the equilibrium capacities at four different temperature were fitted on eq 6.2 the constants were found as below.

W_0 :0.3955

D : 0.0006049

n :1.156

In order to calculate rate from eq 5.3, $k_s\alpha_s$ value should be determined. In fact $k_s\alpha_v$ depends on temperature and can be determined from eq 6.4 [14]

$$k_s\alpha_v = \frac{F_0 D_s}{R_p^2} \qquad \textbf{eq 6.4}$$

Also D_s can be given as in eq 6.5 [14].

$$D_S = D_{S0} \exp\left(\frac{-Ea}{RT}\right)$$ **eq 6.5**

Rearranging eq 6.4 and eq 6.5 gives

$$k_s \alpha_v = \frac{F_0 D_{S0}}{R_p^2} \exp\left(\frac{-Ea}{RT}\right)$$ **eq 6.6**

Fitting eq 6.6 to available experimental data gives $F_0 D_{S0}/R_P^2$ and Ea as 5.013 and 11276 j/mole respectively. The found E_a corresponds to 245 kj/kg is reasonable when compared to results of Saha et al. [14].

The kinetic results were also useful for determination of adsorption enthalpy with the method explained in eq 5.7. Using the end points of the four different kinetic curves at different temperatures, capacities at these temperatures were determined. Then the distribution coefficients, calculated from these capacities, were used in accordance with eq 5.7 and adsorption isostheric enthalpy was found as 28099 j/mol. The result, is around 610 kj/kg and about three times of the Ea calculated from Dubinin-Radushkevich. This is in accordance with the study of Saha et al. [14] where they claim to have Ea value, about 30% of experimentally found enthalpy.

6.2 Temperature And Concentration Profiles During Adsorption And Desorption

As explained previously the performance or power of the system is determined by total adsorbed or desorbed amount of vapor. Total amount is obtained by integration of concentration profile inside the bed with respect to space. On the other side, the concentration inside the bed is determined mostly by the temperature profile inside the bed.

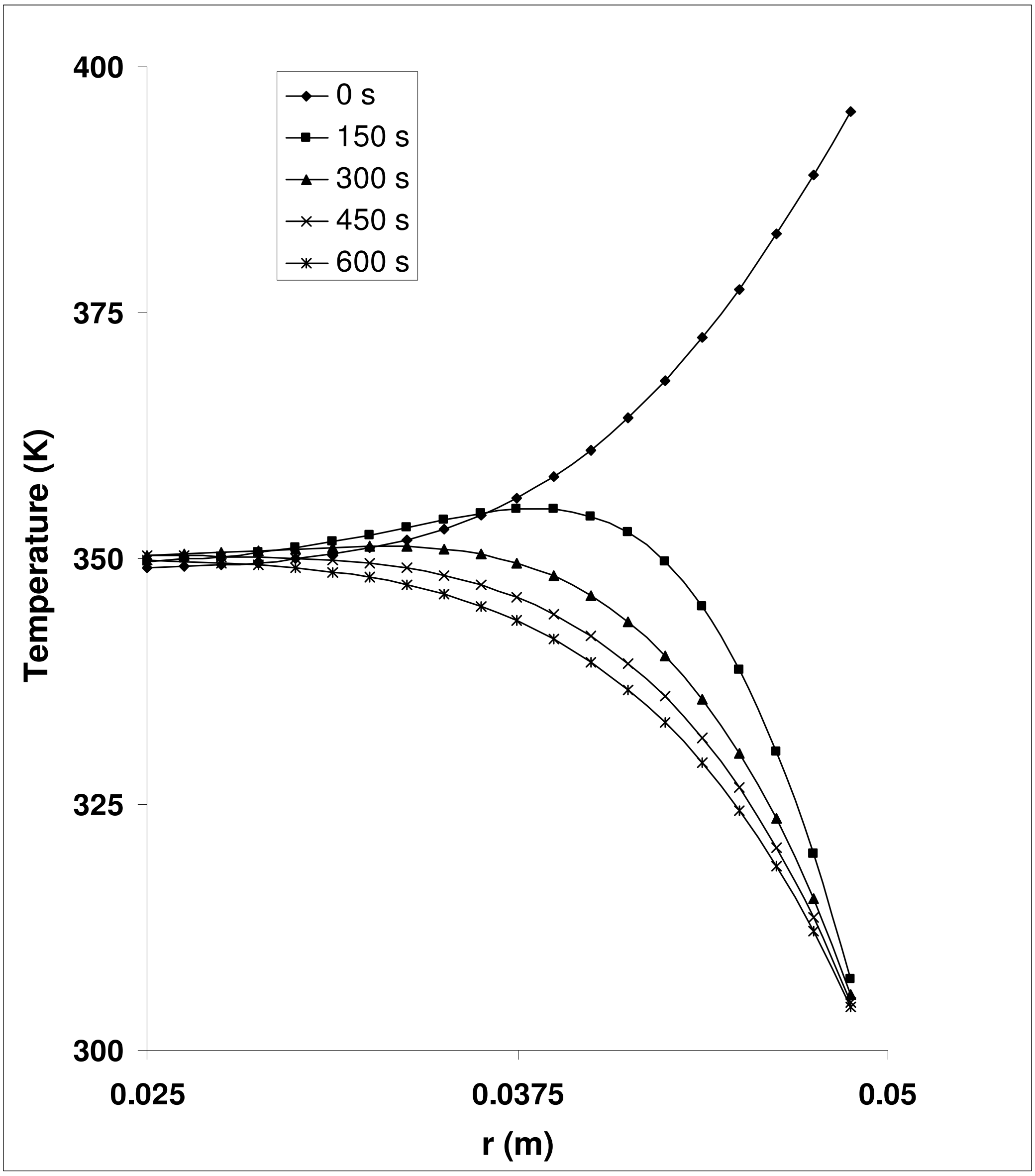

***figure 6.2** : Temperature profile with respect to time for 600s adsorption stage for r=0.05*

figure 6.2 and **figure 6.4** show the temperature and adsorbed amount profiles inside the adsorption bed, respectively. Temperature plot shows that, as the outer temperature is changed to the cooling temperature, the outer part of the bed initially cools rapidly and almost reaches the temperature of the cooling fluid. However, the middle parts of the bed respond much slowly to the cooling. Within the same period, the temperature in the middle region gradually and slightly decreases. The concentration and temperature profiles go hand in hand as adsorbed material concentration is strongly dependent on the temperature. Due to high heat transfer resistance in the packing, cooling effect is confined to the regions close to the outer surface. Therefore, the highest adsorbate concentration is observed in the coolest section of the bed. It should also be noted that, after successive adsorption and desorption cycles, heat of adsorption and desorption coupled with external heating or cooling leads to almost uniform profiles near the inner boundary of the bed. These profiles are insensitive to the external cooling and heating due to the thermal resistance of the bed. Moreover, almost constant concentration with respect to time indicates that no significant reaction is taking place in this region. That in turn results in negligible adsorption/desorption heat generation.

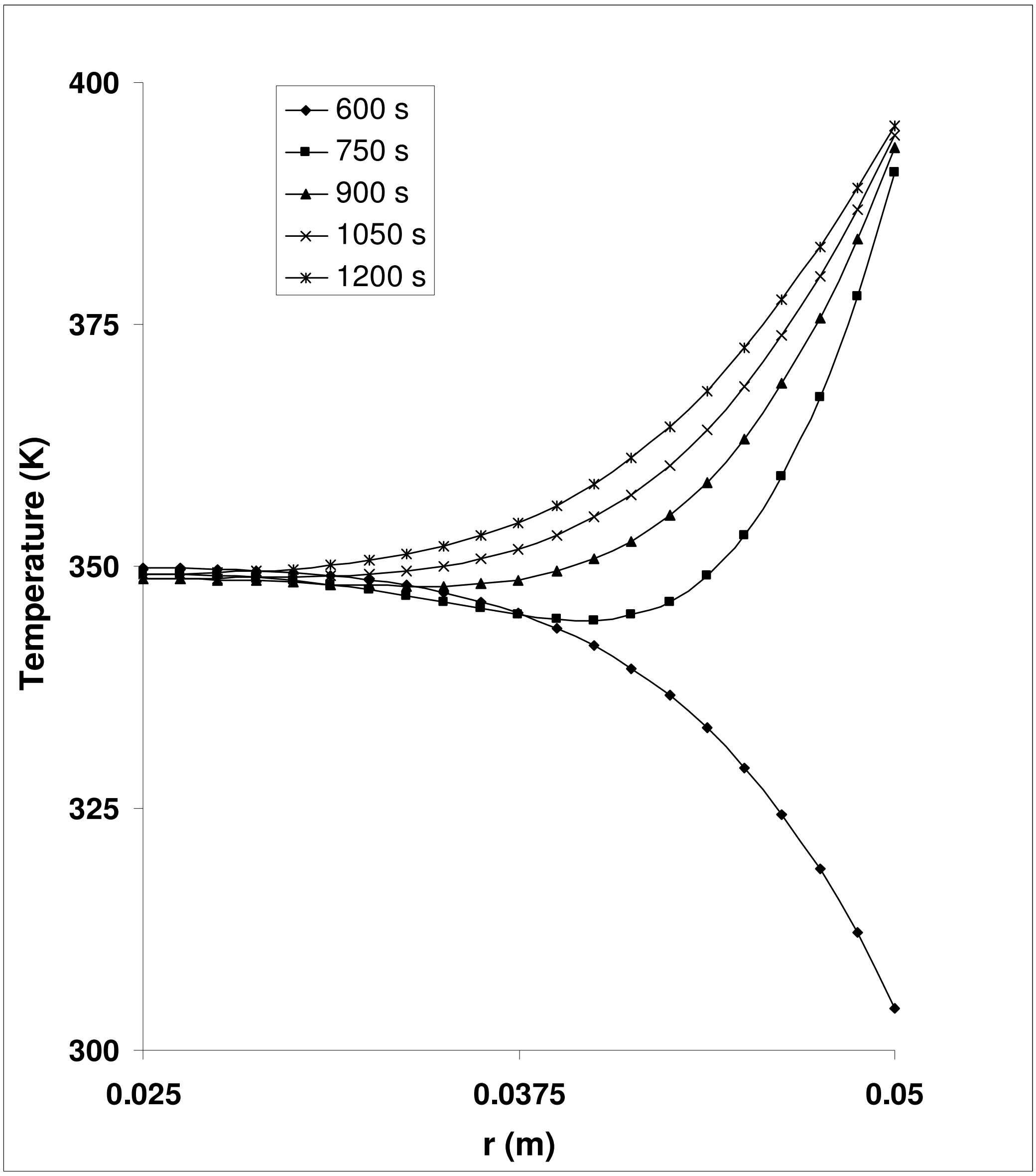

figure 6.3 : *Temperature profile with respect to time for 600s regeneration stage for r=0.05m*

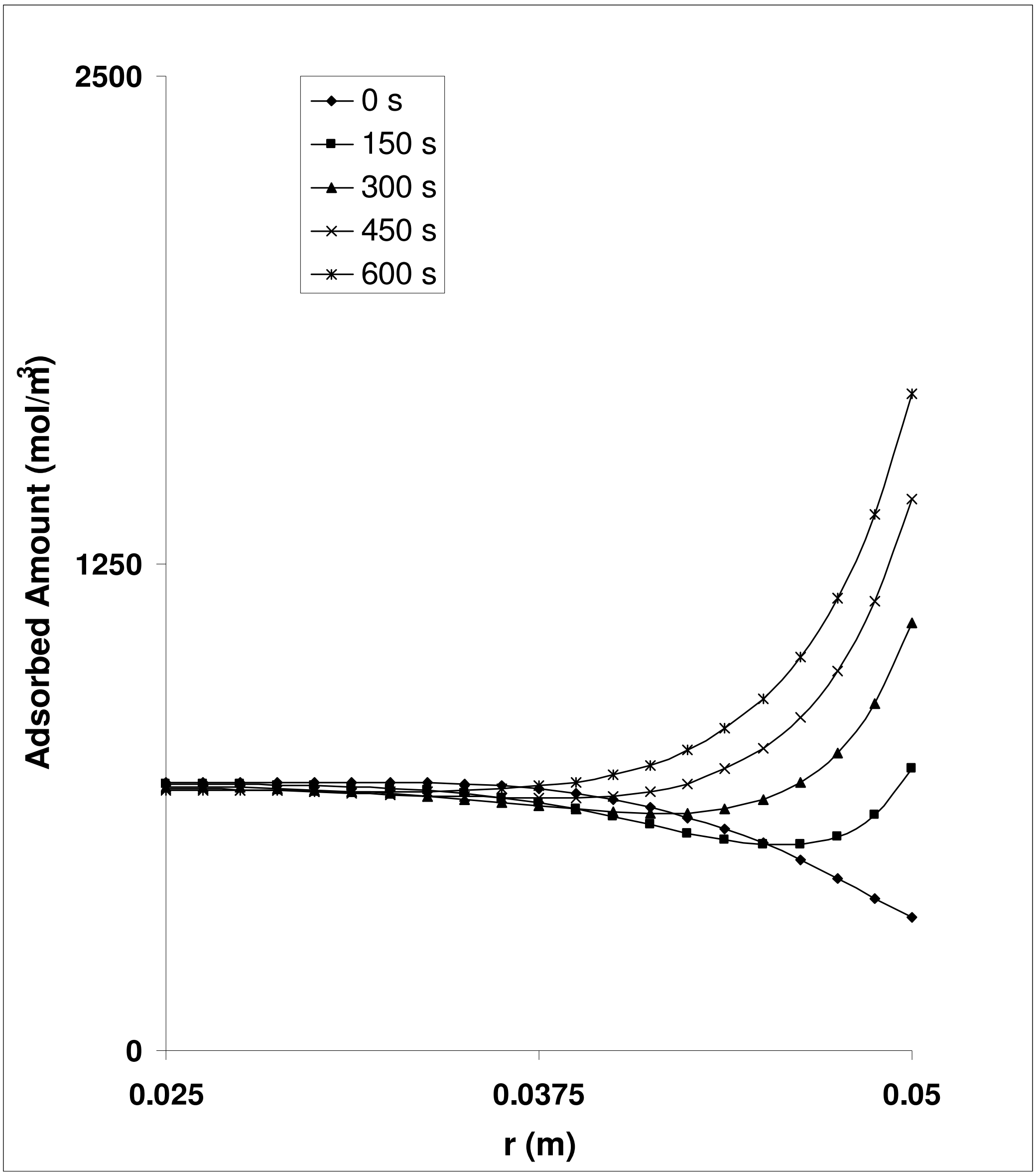

figure 6.4 : *Adsorbed amount profile with respect to time for 600s adsorption stage for r=0.05*

The concentration profile inside the bed increases with decreasing temperature but has a different pattern than temperature that, it increases gradually through the end of the adsorption step. The gradual behavior of concentration, different than temperature is an important result that shows the time dependence of the system. This validates the time dependent model in this study. In other words, the concentration inside the bed is not determined by the temperature, but the adsorption rate is determined by the temperature and adsorbed concentration is determined by both the temperature and time elapsed for adsorption. Therefore, the studies that do not include time dependent modeling might have significant error.

At desorption step processes occur just the opposite manner. Analogues to adsorption step, as the temperature is increased to heating temperature, fist the outer parts quickly respond than the middle parts while temperature of inner parts almost are almost constant. However, there exists a slight difference of patterns in **figure 6.4** and **figure 6.5** that in desorption step, rate of change of concentration decreases during the cycle. This is due to difference in the driving force of the process. In adsorption step, the process is promoted by the vapor pressure while in desorption the process is promoted by the temperature and adsorbed concentration. Then in adsorption step since the vapor pressure is constant, adsorption occurs almost with the same rate while in desorption, rate decreases with time due to the decrease in adsorbed concentration.

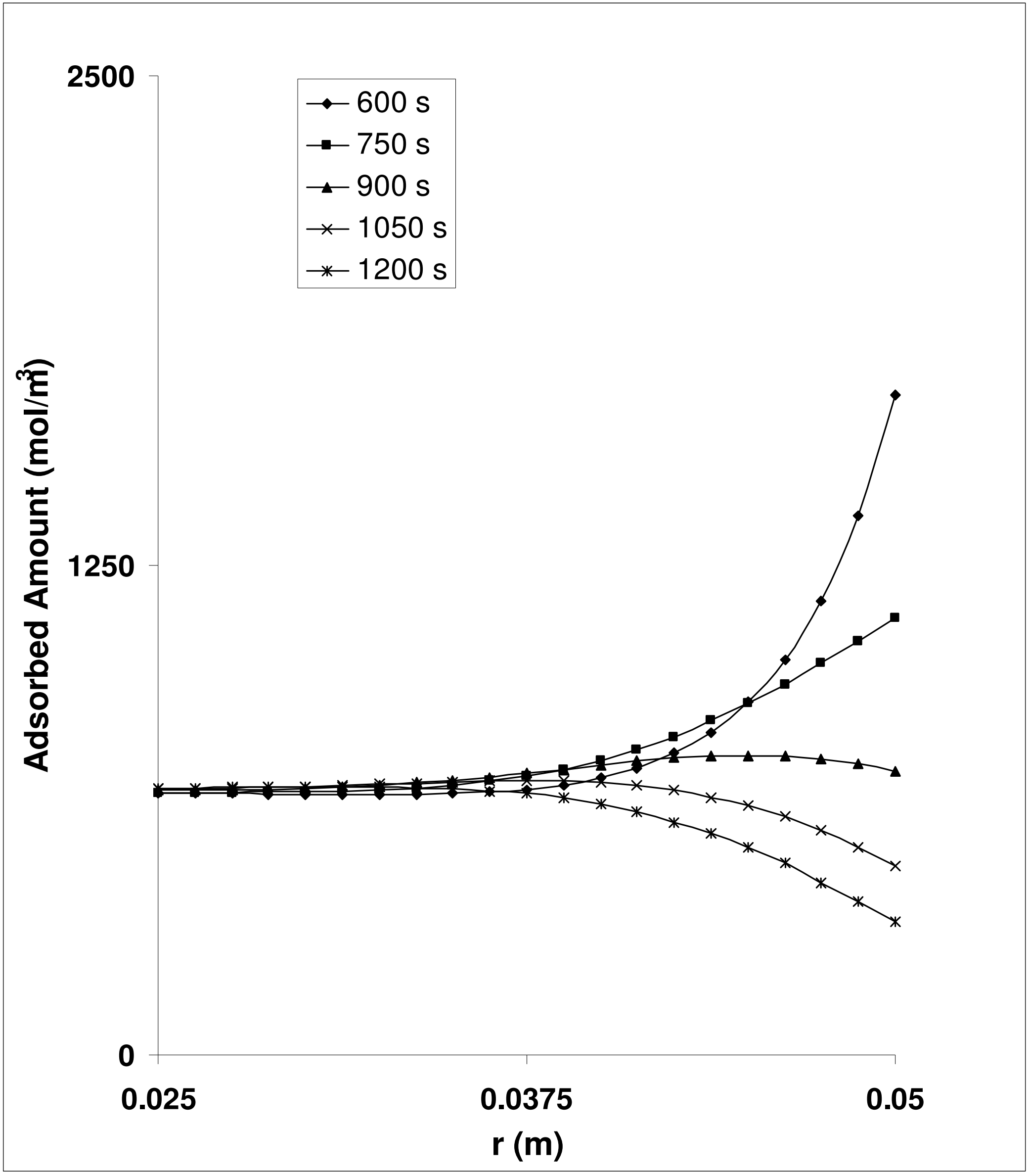

figure 6.5 : *Concentration profile with respect to time for 600s regeneration stage for r=0.05 m*

As the plots for temperature and concentration for r=0.05 m are concerned one of the most important results is that, within the inner half of the bed the temperature changes very slightly during adsorption and regeneration steps that, about half of the adsorbent is never used. In order to overcome this phenomenon the radius should be decreased, which is also simulated in this study and shown in the next four plots.

Within these graphs it seen that as the radius decreases, temperature at inner the side of the adsorbent also changes as the outer temperature is reversed.

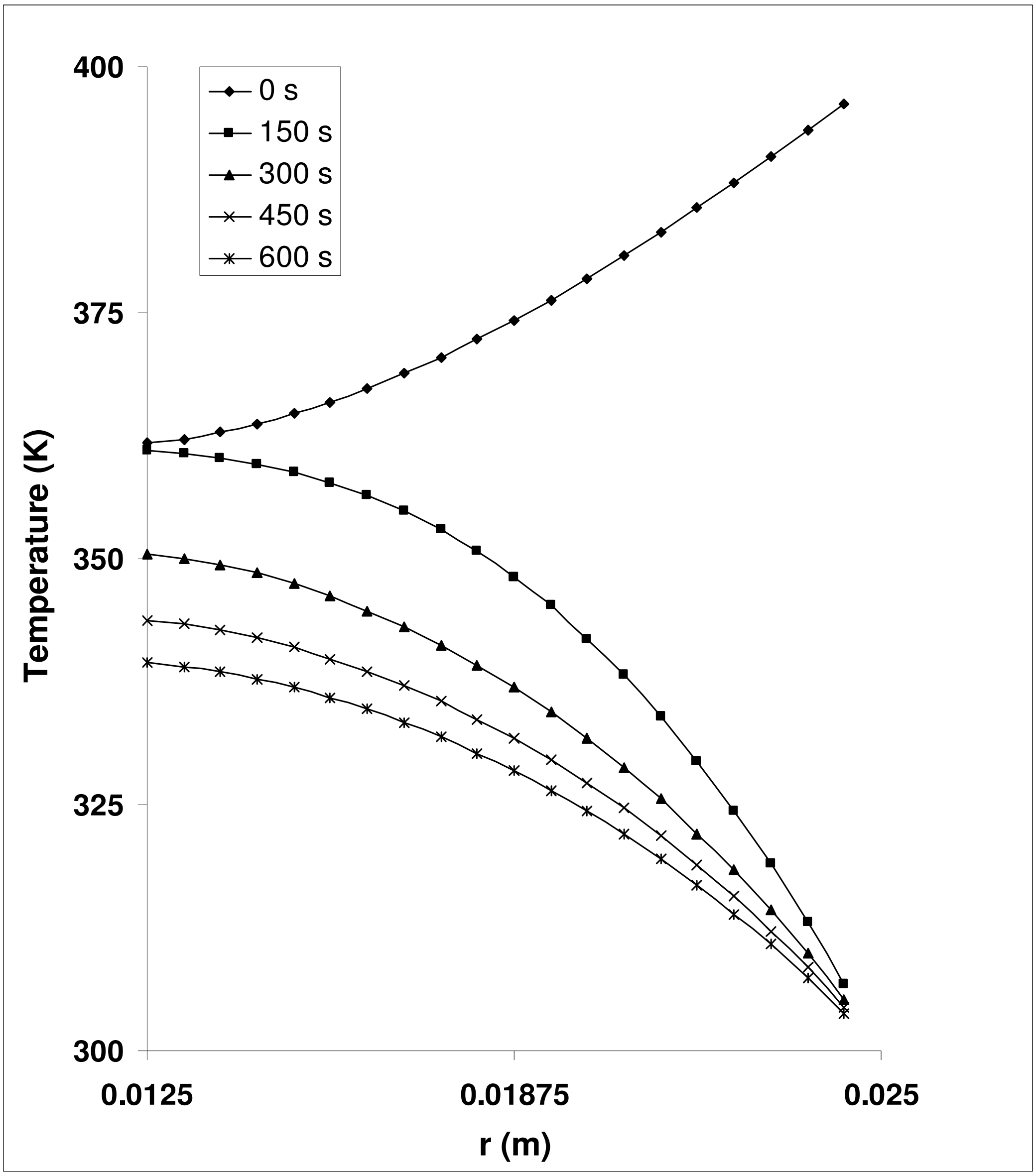

figure 6.6 : *Temperature profile with respect to time for 600 s adsorption stage for r=0.025m*

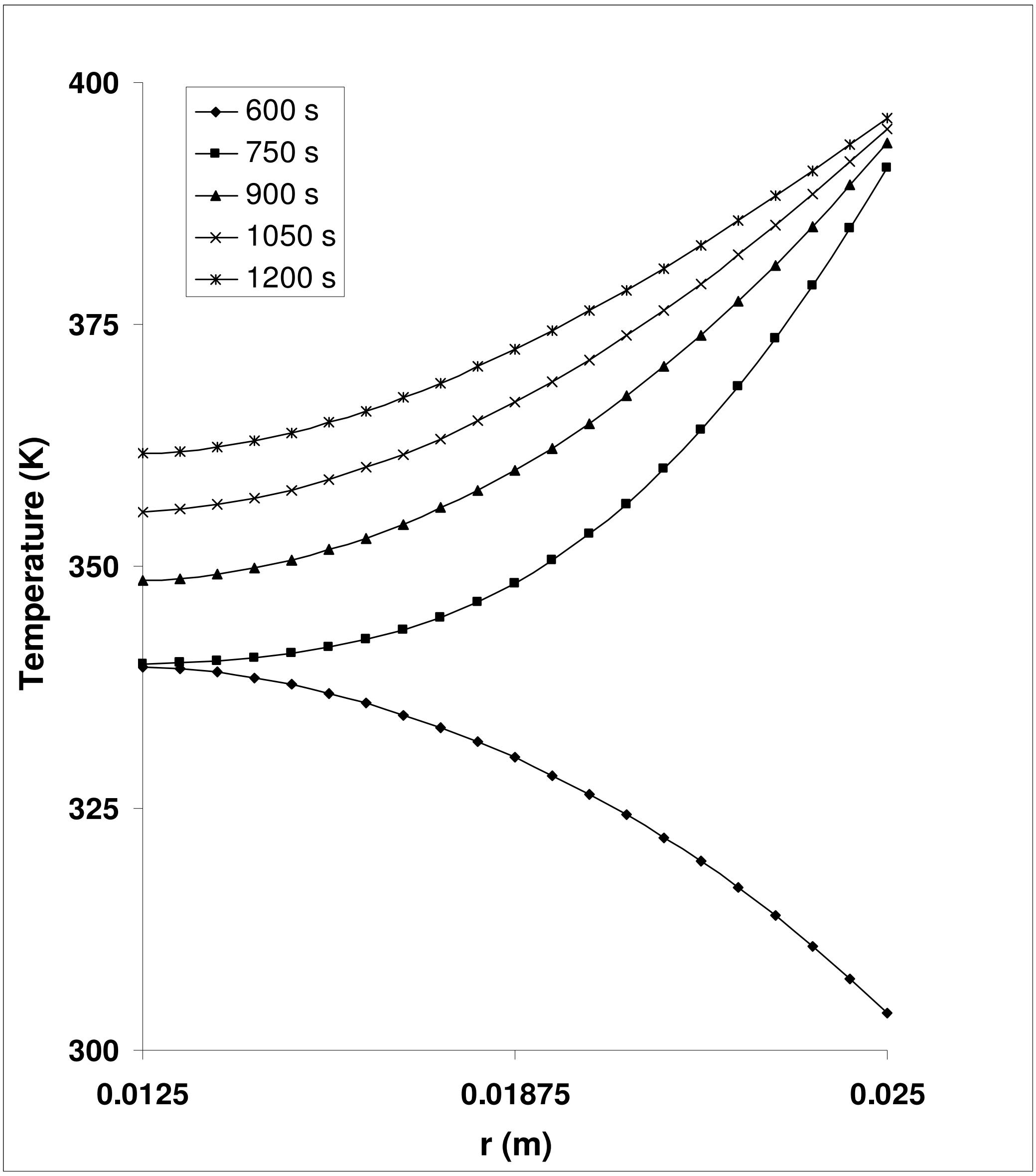

figure 6.7 : *Temperature profile with respect to time for 600 s adsorption stage for r=0.025m*

Since the change in concentration is mostly due to temperature change, the more homogeneous temperature causes more homogeneous concentration profile. From the figure 6.8 and figure 6.9 it is seen that as the radius is decreased, since the idle parts at the inner parts are mostly eliminated, the capacity of the adsorbent is used more efficiently.

As the temperature profiles inside the bed of r=0.05m are considered, when the temperature at the outer side is reversed from hot to cold or vice versa, the inner parts initially change in opposite manner which may seem to be unexpected profile pattern. However, the reason for such a pattern is the slow response of the middle and inner parts of the bed, to temperature change at outer edge. When the temperature at the outer wall is reversed, initially the middle region is not affected because of heat resistance. Then and the inner parts exchange heat with the middle parts with same manner as the previous step. This is the main reason for the opposite temperature change at the inner parts. In other words for r=0.05 up to 150 seconds within a 600 second step, the inner side of the bed behaves opposite of the process, which decreases system performance. On the other side, when radius is decreased to half, unlike the case for r=0.05 the temperature lines do not intersect. Therefore when r=0.025m all parts of the bed start heating or cooling before 150 s.

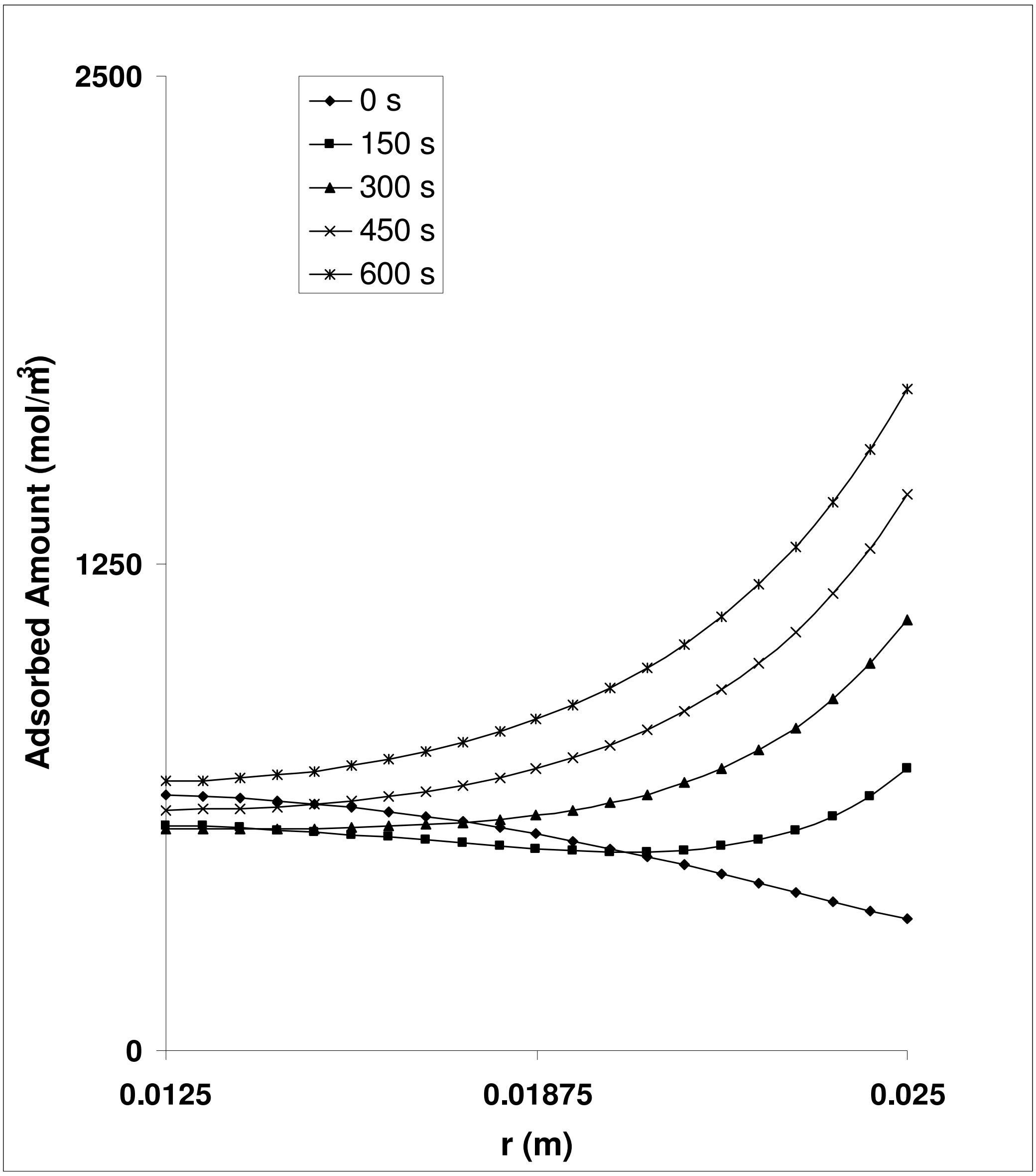

figure 6.8 : *Concentration profile with respect to time for 600 s adsorption stage for r=0.025m*

As the concentration plots are considered a pattern similar to temperature profile at r=0.5 m is observed and the first lines cross each other at the inner sides. The result for such phenomenon is that, as the temperature at the outer side is reversed during step change, it takes time for the inner parts to respond, that, the previous step continues on the inner part at the start of the next step. However, when radius is reduced this effect also decreases.

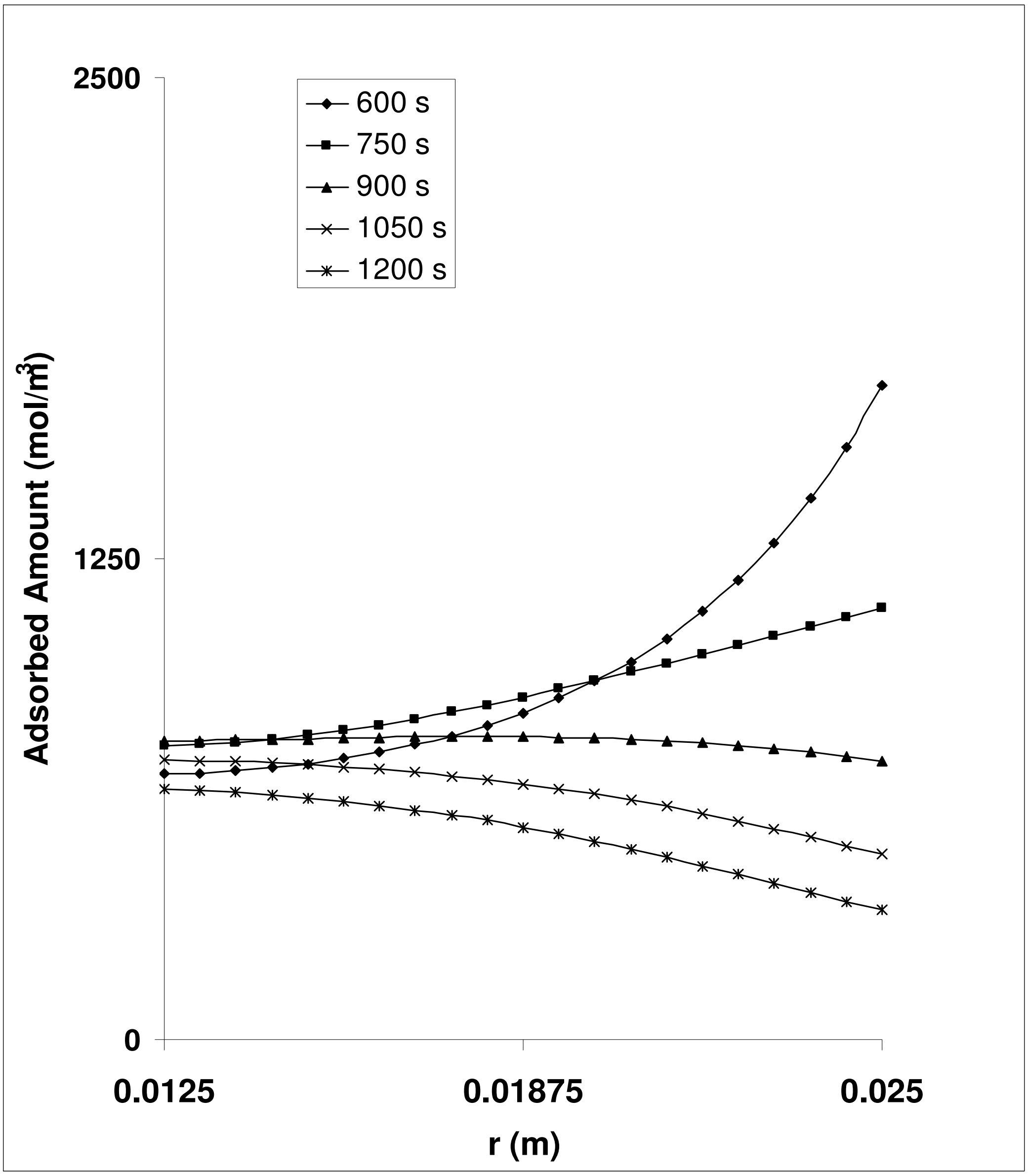

figure 6.9 : Concentration profile with respect to time for 600 s desorption stage for r=0.025m

6.3 System Simulation With Varying Cycle Time And Radius

As explained previously, in order to improve the performance of the adsorption heat pump, adsorption bed geometry is an important parameter. However, within this study as the proposed system geometry and assumptions are considered, the main parameter of geometry to vary is the bed radius. On the other side, as factors other than geometry are concerned the cycle time is another important parameter. Moreover, since the main drawback of the adsorption heat pumps are the large volumes, the most important performance to improve is the cooling power per asorbent amount. Therefore, several simulations were done, with varying cycle time and radius. Results are as given in Table 6.4.

Table 6.4: *Average power with respect to cycle time and bed radius*

Cycle time	r = 0.10 m	r = 0.05 m	r = 0.025 m
1200 s	277	177	55
1800 s	288	124	60
2400 s	282	125	61
3000 s	272	122	59

6.3.1 System Power With Respect To Radius For A Cylindrical System

The system radius is an important parameter for system power per weight of adsorbent. In order to predict the affect of adsorbent bed radius, on system power per activated carbon, several simulations were carried out for different system radius values. The results are as shown in Table 6.4. As seen from this table, decreasing the adsorbent bed radius has less decreasing affect on the system power compared to the decrease in the adsorbent amount. Decreasing the adsorbent radius to half only decrease the power approximately to half although the adsorbent amount deceases to one fourth. This means, the system power per unit amount of carbon doubles.

6.3.2 System Power With Respect To Cycle Time

As cycle time changes, the system performance considerably changes since it determines how efficient the capacity of the adsorbate is used. From Table 6.4 it is seen that increasing, cycle time makes more of the adsorption capacity, but as the cycle time is increased, the average system power stats to decease. This shows that, increasing the cycle time increases the capacity, but as time is increased too much, since significant amount of capacity is already used, and increase in capacity is less compared to increase in cycle time that, the average power during the whole cycle decreases. As a result there exists a certain cycle time value for a given system that makes the power maximum.

6.3.3 The Optimal Cycle Time With Respect To Radius

Table 6.4 shows the affect of cycle time to performance with respect to radius. As mentioned in part 6.3.2 for any radius value, there exist a certain cycle time value for maximum average system power. The optimum cycle time can be seen from Table 6.4 and it depends on radius.

CHAPTER 7

CONCLUSIONS

This study deals with modeling of adsorption based chemical heat pumps mainly dealing with the adsorption properties and improvement of the adsorption process inside the adsorption bed. The following conclusions can be drawn based on the results of the calculations.

1. The internal temperature profile for the adsorbent bed during either cooling or regeneration period is highly non-homogeneous due to the significant thermal resistance of the packing. This is the main drawback against complete use of adsorption bed capacity, thus have high performances. Highly non homogeneous temperature profile results in the situation that, temperatures of some parts of the adsorbate material change very little between adsorption and regeneration cycles that the capacity of these portions are not utilized.

2. The main reason for adsorption or desorption and resulting concentration profile difference inside the bed arises from the change in temperature profile inside the adsorbent bed.

3. The non homogeneous temperature profile is caused by the poor heat transfer property of the porous medium and as the radius of the bed is decreased, temperature profile becomes more homogeneous.

4. The total adsorbed amount of material at a certain point of the adsorbent, during adsorption or desorption step, is determined by the temperature at the point and time elapsed for the adsorption to proceed.

5. Increasing the cycle time increases the degree up to which the capacity of the bed is used. However increasing the cycle time up to a certain value increases the average system power but if the cycle time is increased too much, the increase in the capacity per cycle is less that the increase in cycle time that, as cycle time is increased further the average power decreases. Then, there exists a certain cycle time for optimum average system power.

6. Decreasing the system radius makes the internal temperature profile more homogeneous which improves the capacity use of adsorbent material, thus, increase the average power per absorbent

CHAPTER 8

RECOMMENDATIONS

The study done up to here, manly include a general approach to adsorption heat pumps through modeling concept manly focusing on the affect of system radius on the average power for cylindrical adsorption bed. The choice of cylindrical system is proper due to the fact that cylindrical beds are common for real applications. However, in such a system since the heat transfer is important, more complex geometries that consider use of fins or cooling/heating coils are considerable and worth studying.

The research done for this thesis includes some experimental work that was used for determining rate of adsorption. However, the found results were not compared with any experimental data. Therefore, in order to check the accuracy of the computation, several experiments can be done on proposed geometries and compared with the theoretical results.

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APPENDIX A

ACTIVATED CARBON DATA

(Analyzed at METU Central Laboratory)

AREA-VOLUME-PORE SIZE SUMMARY

SURFACE AREA DATA

Multipoint BET	1.446E+03 m²/g
Langmuir Surface Area	1.481E+03 m²/g
BJH Cumulative Adsorption	1.049E+04 m²/g
BJH Cumulative Desorption	7.877E+02 m²/g
DH Cumulative Adsorption	1.085E+04 m²/g
DH Cumulative Desorption	8.288E+02 m²/g

PORE VOLUME DATA

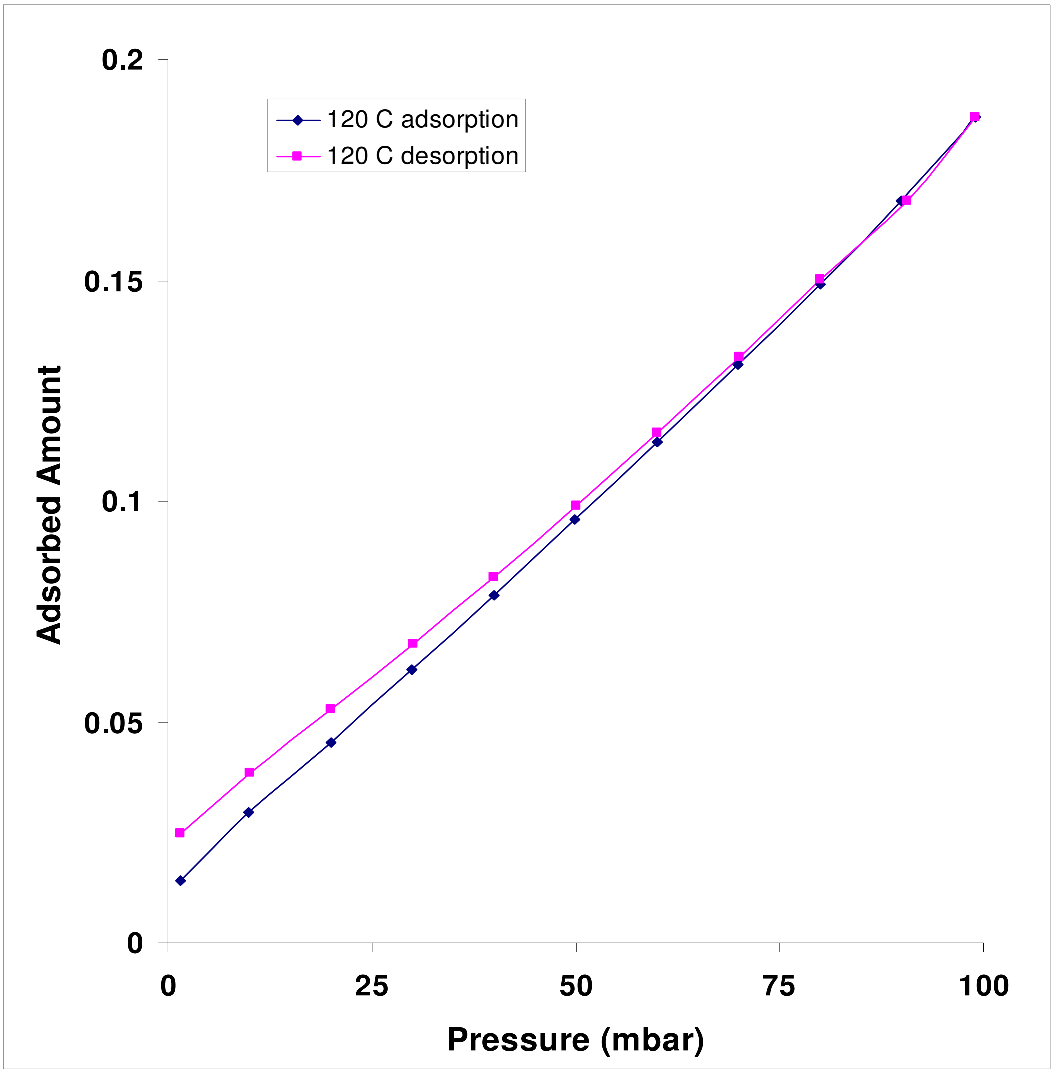
BJH Cumulative Adsorption	2.124E+00 cc/g
BJH Cumulative Desorption	5.422E-01 cc/g
DH Cumulative Adsorption	2.107E+00 cc/g
DH Cumulative Desorption	5.425E-01 cc/g
DR Method Micro Pore Volume	8.879E-01 cc/g

PORE SIZE DATA

BJH Adsorption Pore Diameter	5.485E+00 Å
BJH Desorption Pore Diameter	1.689E+01 Å
DH Adsorption Pore Diameter	5.485E+00 Å
DH Desorption Pore Diameter	1.689E+01 Å

APPENDIX B

120 °C ISOTHERM



APPENDIX B

PROGRAM CODE

```
# Written for Octave Platform

# Clearing Any Existing Data
 Clear

#=================================================
##       C O N S T A N T S
#=================================================

# Avagadro Number
 Na=6.02e23;

# Gas Constant  [m^3 Bar K^-1 mol^-1]
 Rg=8.3e-5;

# Gas Constant  [j/m K]
 Rg_e=8.314 ;

# Boltzman Constant [in m'2 kg s^-2 K^-1]
 Boltz=1.38e-23;
```

```
#============================================
##      P H I S I C I C A L   D A T A
#============================================

#------------------------------------------
## Properties of Cooling Water
#------------------------------------------

# Convection Coefficient
 h_c
# Temperature For Cooling The Adsorptin Bed
 T_w(1)
# Temperature For Cooling The Adsorptin Bed
 T_w(2)

# Dubinin-Rad. Constants
 D_R_W0
 D_R_D
 D_R_n
 F0Ds0Rp2
 Ea

#------------------------------------------
## Properties of Carbon
#------------------------------------------
#       (taken from several sources among
#       the ones given in references)
#------------------------------------------

Cliq=3000000000;

# Specific Heat of Carbon [ J / gr K ]
 Cpc

# Molecule Weight of Ethanol
 Mwe
```

```
# Specific Weight of Carbon
 rhc

#Void Fraction  of Carbon
 eps
 d_p
 emmis



#------------------------------------------
## Properties of Vapor
#------------------------------------------
#         (taken from several sources among
#         the ones given in references)
#------------------------------------------

# Latent Heat of Vapor [ J / mol K ]
 Hlatent

# Specific Heat of Vapor [ J / mol K ]
 Cpv

# Heat of adsorption [ J / mol ]
 Hads



#=============================================
##        S Y S T E M   V A L U E S
#=============================================

#System Properties
 Diff_resist_neigligable

# Whether to Load Initial Condition From External File
 loadinitdata
```

```
# Nuber Of Cycles
 c_n

# Time for adsorption
 time(1)

# Time for regeneration
 time(2)

#Determine Whether There Is Constant Vapor Feed
 vapor_limited



#--------------------------------------------
## Characteristic Measures
#--------------------------------------------

# Characterisitic Lenght
 R0=1;

# Characterisitic Temperature
 T0=1;

# Characteristic Pressure [
 P0=1;

# Characteristic Time [ s ]
 t0=1;

# Specific Adsorbed Amount [ mol / m^3 ]
 C0=1;
```

```
#--------------------------------------------
## Dimensionless Values
#--------------------------------------------

# Dimensionless Length of Bed
 L0

# Initial Dimensionless Temperature
 Tb0

# Initial Dimensionless Pressure
 Pb0

# Dimensionless Outer Radius
 R

# Dimensionless Length
 L

# Boundary Pressure
 Pbb

# Initially Adsorbed Concentration
 Cads0


#--------------------------------------------
## Computational properties
#--------------------------------------------

# Mesh Number In Outer Radial Direction
 n=40;

# Mesh Number In Length Direction
 m=2;
```

```
# Mesh Number In Inner Radial Direction
 l=20;

# Mesh Length in Radial Direction
 dr=R/n;

# Mesh Length in Length Direction
 dz=L/m;

# Sample Interval Steps
 n_t_step=time/dt/t0
 s_n_t_step=ceil(n_t_step/n_sample)*2;

# Time Step
 dt=.1/t0*2;

# Nuber Of Sample Steps
 n_sample=8;


#-------------------------------------------
# Applying the Initial Conditions And Creating The Value Array
#-------------------------------------------


 for i=1:n+1
         for j=1:m+1
                 if(i>l)
                         Cads(j,i)=Cads0;
                 endif
                 Pb(j,i)=Pb0;
                 T(j,i)=Tb0;
         endfor
 endfor



 for i=1:l+1
         for j=1:m+1
```

```
                    Pb(j,i)=Pbb;
            endfor
    endfor

    for i=l+1:n+1
            r_p(i-l)=(i-1)*dr*R0;
    endfor

    Cadsl=0;
    q_convt=0;
#--------------------------------------------
# Preparing the Temporary Arrays for the Time Step Iteration
#--------------------------------------------

    if(loadinitdata)
            load insdata
    endif
    Pbn=Pb;
    Tn=T;
    Cadsn=Cads;

    fid_s_p_c=fopen("sample_plot_C","w");
    fid_s_p_t=fopen("sample_plot_T","w");
    fid=fopen("s_no","w");
                                    fid_s_p_c=fopen("sample_plot_C","a");
                                    fid_s_p_t=fopen("sample_plot_T","a");
                                    fprintf(fid_s_p_c,"r" );
                                    fprintf(fid_s_p_t,"r" );
                                    for i=l:n+1
                                            fprintf(fid_s_p_c,",%f",(i-1)*dr );
                                            fprintf(fid_s_p_t,",%f",(i-1)*dr );
                                    endfor
                                    fprintf(fid_s_p_c,"\n");
                                    fprintf(fid_s_p_t,"\n");
                                    fprintf(fid_s_p_c,"%d",0 );
                                    fprintf(fid_s_p_t,"%d",0 );
```

```
                                        for i=l:n+1
                                                  fprintf(fid_s_p_c,",%f",Cads(2,i));
                                                  fprintf(fid_s_p_t,",%f",T(2,i));
                                        endfor

                                        fprintf(fid_s_p_c,"\n");
                                        fprintf(fid_s_p_t,"\n");
                                        fclose(fid_s_p_c);
                                        fclose(fid_s_p_t);
                                        fclose(fid);



#==================================================
##STARTING TIME ITERATION
#==================================================

 k=1
 Nads(1)=0;
 t_s=1;
 P_s(1,1)=0;

 for c=1:c_n
          for s=1:2
                    kl=k;
                    q_conv=0;
                    T_inf=T_w(s);
                    Nads_s0=Nads(t_s);
          for k=kl:kl+n_t_step(s)
```

```
#-------------------------------------------
# This Part Has Nothing About Computation.
#-------------------------------------------

# Putting Values to Plot File

            if(mod(k,s_n_t_step(s))==0)

                c_time=k*dt;
                fid_s_p_c=fopen("sample_plot_C","a");
                fid_s_p_t=fopen("sample_plot_T","a");
                fprintf(fid_s_p_c,"%d",c_time);
                fprintf(fid_s_p_t,"%d",c_time);

                for i=l:n+1
                    fprintf(fid_s_p_c,",%f",Cads(2,i));
                    fprintf(fid_s_p_t,",%f",T(2,i));
                endfor

                fprintf(fid_s_p_c,"\n");
                fprintf(fid_s_p_t,"\n");
                fclose(fid_s_p_c);
                fclose(fid_s_p_t);

            endif

            if(mod(k,100)==0)
                cl1=clock;
                fid=fopen("s_no","a");
                n_t=c_n*(n_t_step(1)+n_t_step(2));
                fprintf(fid,"%d/%d %d %d/%d
\t%d:%d:%f\n",c,c_n,s,k,n_t,cl1(4),cl1(5),cl1(6));
                fclose(fid);
            endif

#       - - - - - -
```

```
            if(mod(k,100 )==0 )
                t_s=k/100;
                Nads(t_s)=0;
                q_ads(t_s)=0;
                q_sens(t_s)=0;
                q_ads(t_s)=0;
                Cadsl_p(t_s)=Cadsl;
                q_convt_p(t_s)=q_convt;
                q_conv_p(t_s)=q_conv;
                t_p(t_s)=k*t0*dt;

                for i=l+1:n+1

                    Nads(t_s)=Nads(t_s) + Cads(2,i)*2*pi* dr*
dr*i*L*R0^2;
                    P_s(t_s)=(Nads(t_s)-Nads_s0)*Hlatent/((k-
kl)*dt*t0);
                    Pw_s(t_s)=(q_conv)/((k-kl)*dt*t0);
                    Cpeff=Cpc*rhc*(1-eps)+Cpv*Pb(2,i)*P0/
(Rg*T(2,i)*T0)*eps;
                    q_sens(t_s)=q_sens(t_s)+ T0*T(2,i)*2*pi*dr*dr*I
* L*R0^2;
                    q_ads(t_s)=q_ads(t_s)+ 2*Cads(2,i)*C0*
Hads*pi*dr*dr*i*L*R0^2;
                    Pb_p(t_s,i-l)=Pb(j,i);
                    Cads_p(t_s,i-l)=Cads(j,i);
                    Rads_p(t_s,i-l)=Rabs(j,i);
                    Lmbd_p(t_s,i-l)=Lmbd(j,i);
                    T_p(t_s,i-l)=T(2,i);
                endfor
                save data
                save insdata Cads T Pb
            endif

            if(Cadsl>Cliq && vapor_limited==0)
                k
```

```
                vapor_limited=1
            endif

#------------------------------------------
# Lenght Direction
#------------------------------------------

            for j=1:m+1

#------------------------------------------
# Radial Direction
#------------------------------------------

                for i=l+1:n+1

                        DerdrdC=0;
                        DerdzdC=0;

                    if (T(j,i)>365)
                    Ant_A=4.92531;
                    Ant_B=1432.56;
                    Ant_C=-61.819;
                    else
                    Ant_A=5.24667;
                    Ant_B=1598.673;
                    Ant_C=-46.424;
                    endif
                    P_sat(j,i)=10^(Ant_A-(Ant_B/(T(j,i)+Ant_C)));

# Calculating Adsorption Rate  [ mol / m^3 / s ]

                    W(j,i)=D_R_W0*exp(-D_R_D*(T(j,i)*
log(P_sat(j,i)/Pb(j,i)))^ D_R_n);
                    ksalv(j,i)=F0Ds0Rp2*exp(-Ea/(Rg_e*T(j,i)));
                    w(j,i)= (Cads(j,i)*46)/(rhc*(1-eps));
                    dwdt(j,i)=ksalv(j,i)*(W(j,i)-w(j,i))/60;
                    Rabs(j,i)=dwdt(j,i)/(46)*(rhc*(1-eps));
```

 # Applying Rate to Bulk Pressure

```
if(!Diff_resist_neigligable)
    Pbn(j,i)=Pb(j,i)+(DerdrdC+DerdzdC-Rabs(j,i))*Rg*T(j,i)*T0*dt*t0/eps;
endif
```

 # Applying Rate to Adsorbed Concentartion

```
Cadsn(j,i)=Cads(j,i)+(Rabs(j,i))*dt*t0/C0/(1-eps);
Cadsl=Cadsl+(Rabs(j,i))*dt*t0*2*pi*dr*i*dr*dz;
```

#Calculating the Heat Flux

```
k_s=120*0.58;
k_p=10^(-1.76+0.0129*0.5/eps);
k_r=4*emmis/(2-emmis)*d_p/0.3048*(0.173)*(T(j,i)*T0*9/5)^3/(1e8);
h_g=7;

h_r=(k_r*(2*k_s+h_g*d_p/0.3048)/(d_p/0.3048*k_s));

h_p=(k_p*(2*k_s+h_g*d_p/0.3048)/(d_p/0.3048*k_s));
Lmbd(j,i)=k_r*eps+(1-eps)*((h_r+h_p)*k_s*d_p/0.3048/(2*k_s+(h_r+h_p)*d_p/0.3048));
Lmbd(j,i)=Lmbd(j,i)/0.58;
```

 # Calculating the Dervative at the Back Mesh Node

```
if(i<l+2)
    rdTdR0(j,i)=0 ;
else
    rdTdR0(j,i)=(T(j,i)-T(j,i-1))/(dr)*(i-2)*dr;
endif
```

```
# Calculating the Dervative at the Next Mesh Node

                                                if(i>n)
                                                        rdTdR1(j,i)=h_c*(T_inf-
T(j,n+1))/Lmbd(j,i)*R*R0;
                                                else
                                                        rdTdR1(j,i)=(T(j,i+1)-T(j,i))/(dr)*(i)*dr;
                                                endif



# Calculating the second Dervative at the Next Mesh Node

                                                if(i<=n)
                                                        lmbdrdrdT(j,i)=Lmbd(j,i)/(R0^2*(i-
1)*dr)*(rdTdR1(j,i)-rdTdR0(j,i))/(dr);
                                                else
                                                        lmbdrdrdT(j,i)=Lmbd(j,i)/(R0^2*(i-
1)*dr)*(rdTdR1(j,i)-rdTdR0(j,i))/(dr/2);
                                                endif

# Calculating the Dervative at the  lenght directon

# Calculating the Dervative at the Next Mesh Node

                                                if(j<=2)
                                                        rdTdz0=0;
                                                else
                                                        rdTdz0=(T(j,i)-T(j-2,i))/(2*dz);
                                                endif



# Calculating the Dervative at the Next Mesh Node

                                                if(j>=m)
                                                        rdTdz1=0;
                                                else
                                                        rdTdz1=(T(j+2,i)-T(j,i))/(2*dz)*(i)*dz;
```

```
                    endif

# Calculating the second Dervative at the Next Mesh Node

                    if(j>2&&j<m)
                        lmbdzdzdT(j,i)=Lmbd(j,i)/ (L0^2)*(rdTdz1-rdTdz0)/(2*dz);
                    else
                        lmbdzdzdT(j,i)=Lmbd(j,i)/(L0^2)*(rdTdz1-rdTdz0)/(dz);
                    endif



# Efective Cp

                    Cpeff=Cpc*rhc*(1-eps)+Cpv*Pb(j,i)*P0/(Rg*T(j,i)*T0)*eps;



# Change in T

                    Tn(j,i)=T(j,i)+(lmbdrdrdT(j,i)+lmbdzdzdT(j,i)+Hads/T0*Rabs(j,i))*dt*t0/Cpeff;

                endfor

            endfor



            Pb=Pbn;
            Cads=Cadsn;
            T=Tn;

            q_conv=q_conv+h_c*(T_inf-T(2,n+1))*2*pi*R*R0*R0*L*dt*t0;
            q_convt=q_convt+h_c*(T_inf-T(2,n+1))*2*pi*R*R0*R0*L*dt*t0;
```

 # Since P bulk in uniform

```
                        if(Diff_resist_neigligable)
                                Pbt=0;
                                for j=1:m+1
                                        for i=l+1:n+1
                                                Pbt=Pbt+Pb(j,i);
                                        endfor
                                endfor

                                Pba=Pbt/((m+1)*(n+1-l));
                                for j=1:m+1
                                        for i=l+1:n+1
                                                Pb(j,i)=Pba;
                                        endfor
                                endfor

                        endif
                endfor
        endfor
endfor
```