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## **ΔΙΠΛΩΜΑΤΙΚΗ ΕΡΓΑΣΙΑ**

*Διερεύνηση σεναρίων για εφαρμογές  
προσρόφησης μέσω του ASPEN Adsorption*

*Case studies of adsorption applications using  
ASPEN Adsorption*

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## Περίληψη

Λόγω της αύξησης της θερμοκρασίας και ως συνέπεια της υπερθέρμανσης του πλανήτη η επιστημονική κοινότητα όπως και η αγορά προσπαθούν να βρουν μεθόδους ψύξης πιο φιλικές προς το περιβάλλον. Η ψύξη με προσρόφηση λόγω της εκμετάλλευσης ρευμάτων χαμηλής θερμοκρασίας, ώστε να μην απορρίπτονται στο περιβάλλον, μπορεί να θεωρηθεί μία από τις πιο φιλικές τεχνολογίες ψύξης. Στο πλαίσιο αυτό, αντικείμενο της παρούσας διπλωματικής εργασίας είναι η διερεύνηση υποψηφίων μέσων προσρόφησης για καινοτόμο αντλία θερμότητας με προσρόφηση νερού.

Για τα διάφορα μέσα προσρόφησης που μελετήθηκαν, μοντελοποιήθηκε η διεργασία της προσρόφησης του νερού από την κλίνη, που εντός της είναι το προσροφητικό μέσο, με τη βοήθεια του προγράμματος Aspen Adsorption, του οποίου το περιβάλλον παρουσιάστηκε σε γενικές γραμμές στην συγκεκριμένη διπλωματική εργασία. Η μοντελοποίηση έγινε για ένα εύρος θερμοκρασιών για τη διεργασία της προσρόφησης μόνο και όχι για όλο το σύστημα της αντλίας θερμότητας, μέσω της χρησιμοποίησης δεδομένων από μελέτες των συγκεκριμένων ζευγαριών προσροφητή-νερού που μελετήθηκαν στην παρούσα εργασία. Επιπλέον, σε κάποια ζευγάρια που χρησιμοποιούνται σε μεγάλη κλίμακα στον τομέα της ψύξης έγινε και μοντελοποίηση σε ένα εύρος πιέσεων εκτός από των θερμοκρασιών.

Ως αποτέλεσμα των μοντελοποιήσεων αυτών είναι η συσχέτιση των δύο βασικών θερμοδυναμικών μεγεθών, θερμοκρασίας και πίεσης, με ένα από τα πιο σημαντικά μεγέθη της προσρόφησης, το φορτίο της προσρόφησης. Μέσω αυτής της συσχέτισης μελετήθηκε στη συνέχεια ποιο είναι το σωστό ζεύγος θερμοκρασίας-πίεσης που θα επιλεγεί για τη μεγιστοποίηση του φορτίου της προσρόφησης αυτής της τεχνολογίας. Τέλος, από τα αποτελέσματα μπορούν επίσης να προκύψουν και ορισμένες εμπειρικές σχέσεις των παραπάνω μεγεθών ώστε να είναι πιο εύκολη η εύρεση του φορτίου της προσρόφησης χωρίς να χρειάζεται η μοντελοποίηση της διεργασίας μέσω του προγράμματος Aspen Adsorption.

## **Abstract**

Because of the increase of the temperature and as well the overheat of the planet, the scientific community and also the market try to find new methods and technologies for cooling which are friendlier for the environment. Cooling with adsorption can be one of the friendliest technologies because of the exploitation of streams of low temperatures in order not to be rejected to the environment. According to that, the topic of this thesis is about the research of candidate adsorbents for an innovative heat pump with the adsorption of water.

For the different adsorbents which were studied, the process of adsorption of the water from inside the bed where the adsorbent is, was modeled with the help of the program Aspen Adsorption whose environment was presented a bit in this thesis. The modeling was happened in a wide of temperatures only for the process of adsorption and not for the whole system of the heat pump, with the use of data from researches which include the pairs of adsorbent-water which were studied in this thesis. Moreover, for some pairs which are used widely for cooling, a modeling was also happened in a wide of pressures apart from the temperatures.

As a result of these modelings is the correlation of the two basic thermodynamic quantities, temperature and pressure, with one of the most important quantity of adsorption, the loading. According to this correlation, the best choice of pair temperature-pressure was studied in order to have the biggest loading of adsorption for this technology. Finally, from these results some empirical equations for the above quantities can be exported in order to be easier the calculation of the loading without the need of modeling the process with the use of Aspen Adsorption.

## **Preface**

When I was young, I was interested in science. This interest was continuing till the last years of school and I can easily say that this interest was change into love for the science. Moreover, I was also occupied with the environment and how to solve one of the biggest problems of our century. All of these make clear to me the choice of the university and the future which I would follow.

As it is obvious, I chose the Mechanical Engineering in order to learn more things about science, how to solve problems in our daily routine and how to make the conditions of living better both for us and environment. As it is evident, I started to be occupied with the environment and especially the sector of energy because it includes both of my interests. Except for my interests, to be a mechanical engineer needs to cooperate with others and I think that was the last thing which “told” me that I had taken the right decision about my future.

This thesis is the last part of my course in the university and it is also occupied with the sector of environment and especially a way to find technologies as friendlier as it is possible to it. According to this, this thesis is a small part of the research to save the environment from our civilization and especially our huge needs for energy. As I am finishing the university, I keep the knowledge, the background and the value of cooperation and the exchange of ideas with the people who I cooperated with.

At this moment, I want to thank the Professor and the supervisor of that thesis Dr. Karellas Sotirios for the assignment of this thesis.

I also want to thank a lot Mr. Roumpedakis Tryfonas for our perfect cooperation, support, guidance and exchange of ideas about this thesis but I want also to thank him about the time that he spent in order to help me finish successfully this thesis.

At the end, I want to thank my family and my close friends who help me and were next to me in the preparation of this thesis till it was complete, but also in the duration of my studies as a mechanical engineer in the university.

## Table of contents

Περίληψη.....	i
Abstract .....	ii
Preface.....	iii
Table of contents .....	iv
List of figures.....	v
List of Tables .....	vii
Nomenclature .....	viii
Chapter 1. Introduction .....	1
1.1 Introduction to refrigeration .....	1
1.2 Vapor Compression Cooling .....	3
1.3 Absorption cooling.....	5
1.4 Adsorption cooling.....	7
1.5 Bibliographic review and technology comparison.....	16
1.6 Thesis scope.....	21
Chapter 2. Case Studies on ASPEN Adsorption.....	23
2.1 Introduction to Aspen Adsorption .....	23
2.2 Topic of the thesis.....	24
2.3 Activated Carbon-Water .....	25
2.4 Zeolite-Water.....	35
2.5 Zeolite-Air.....	46
2.6 Silica gel-Water .....	50
Chapter 3. Conclusions.....	59
References .....	61

## List of figures

Figure 1.1 Working principle of a cooling machine [3].....	1
Figure 1.2 Ideal refrigeration cycle [4] .....	2
Figure 1.3 Schematic of a conventional vapor compression cycle system [3] .....	3
Figure 1.4 Refrigeration cycle of vapor compression [5].....	4
Figure 1.5 Schematic of a conventional single stage absorption cycle [3] .....	6
Figure 1.6 Double-bed adsorption process layout.....	8
Figure 1.7 Clapeyron diagram for the adsorption cycle. ....	8
Figure 1.8 Macroscopic image of silica gel. ....	10
Figure 1.9 Activated carbon.....	10
Figure 1.10 Zeolite.....	11
Figure 1.11 Working pair comparison based on work of Habib et al. [63].....	14
Figure 1.12 Working pair comparison. Adapted from San and Lin. [64] .....	15
Figure 2.1 The environment of Aspen Adsorption.....	23
Figure 2.2 Gas adsorption heat pump. ....	24
Figure 2.3 The parts of the process of adsorption.....	25
Figure 2.4 Chart of the loading subject to water concentration for 303K. ....	28
Figure 2.5 Chart of the water's concentration subject to time for 303K. ....	28
Figure 2.6 Chart of the loading subject to water concentration for 313K. ....	29
Figure 2.7 Chart of the water's concentration subject to time for 313K. ....	29
Figure 2.8 Chart of the loading subject to water concentration for 318K. ....	30
Figure 2.9 Chart of the water's concentration subject to time for 318K. ....	30
Figure 2.10 Chart of the loading subject to water concentration for 323K. ....	31
Figure 2.11 Chart of the water's concentration subject to time for 323K. ....	31
Figure 2.12 Chart of the loading subject to water concentration for 328K. ....	32
Figure 2.13 Chart of the water's concentration subject to time for 328K. ....	32
Figure 2.14 Chart of the loading in different temperatures. ....	33
Figure 2.15 Chart of the water's concentration in different temperatures. ....	34
Figure 2.16 Loading subject to water's concentration for 298K. ....	37
Figure 2.17 Loading subject to initial composition of water for 298K.....	38
Figure 2.18 Loading subject to water's concentration for 313K. ....	38

<i>Figure 2.19 Loading subject to initial composition of water for 313K.....</i>	<i>39</i>
<i>Figure 2.20 Loading subject to water's concentration for 323K. ....</i>	<i>39</i>
<i>Figure 2.21 Loading subject to initial composition of water for 323K.....</i>	<i>40</i>
<i>Figure 2.22 Loading subject to water's concentration for 333K. ....</i>	<i>40</i>
<i>Figure 2.23 Loading subject to initial composition of water for 333K.....</i>	<i>41</i>
<i>Figure 2.24 Loading in 4 different temperatures. ....</i>	<i>42</i>
<i>Figure 2.25 Loading subject to initial composition of the water in 4 temperatures. ....</i>	<i>43</i>
<i>Figure 2.26 Loading subject to water's concentration. ....</i>	<i>44</i>
<i>Figure 2.27 Loading subject to initial composition of mixture.....</i>	<i>44</i>
<i>Figure 2.28 Loading in 4 different temperatures. ....</i>	<i>45</i>
<i>Figure 2.29 Loading subject to initial mixture composition in 4 temperatures. ....</i>	<i>45</i>
<i>Figure 2.30 Zeolite-water heat pump [67].....</i>	<i>46</i>
<i>Figure 2.31 Loading subject to water's concentration. ....</i>	<i>48</i>
<i>Figure 2.32 Loading subject to pressure.....</i>	<i>49</i>
<i>Figure 2.33 Air drying with adsorption [68].....</i>	<i>50</i>
<i>Figure 2.34 Loading subject to pressure at 303K. ....</i>	<i>53</i>
<i>Figure 2.35 Loading subject to pressure at 308K. ....</i>	<i>53</i>
<i>Figure 2.36 Loading subject to pressure at 313K. ....</i>	<i>54</i>
<i>Figure 2.37 Loading subject to pressure at 318K. ....</i>	<i>54</i>
<i>Figure 2.38 Loading subject to pressure at 323K. ....</i>	<i>55</i>
<i>Figure 2.39 Loading subject to pressure at 328K. ....</i>	<i>55</i>
<i>Figure 2.40 Loading subject to pressure at 333K. ....</i>	<i>56</i>
<i>Figure 2.41 Loading subject to pressure at different temperatures.....</i>	<i>57</i>
<i>Figure 2.42 Loading subject to pressure at different pressures at constant loading. ....</i>	<i>57</i>
<i>Figure 2.43 Silica gel-Water adsorption chiller [70].....</i>	<i>58</i>



## List of Tables

<i>Table 1.1. Key features of two main working pairs for absorption chillers [8-12]</i> .....	6
<i>Table 1.2. Basic characteristics of most common refrigerants</i> .....	12
<i>Table 1.3. Comparison Between Various Solid Adsorbent Pairs</i> .....	15
<i>Table 1.4 List of experimental adsorption units in cooling [3]</i> .....	17
<i>Table 2.1 Constant parameters for Aspen Adsorption</i> .....	26
<i>Table 2.2 Types of the models</i> .....	26
<i>Table 2.3 Isotherm parameters</i> .....	27
<i>Table 2.4 Constant parameters for Aspen Adsorption</i> .....	35
<i>Table 2.5 Types of the models</i> .....	36
<i>Table 2.6 Isotherm parameters of water</i> .....	36
<i>Table 2.7 Composition-concentration of the mixture</i> .....	37
<i>Table 2.8 Additional parameters</i> .....	43
<i>Table 2.9 Parameters' values</i> .....	47
<i>Table 2.10 Initial composition</i> .....	47
<i>Table 2.11 Isotherm parameters</i> .....	47
<i>Table 2.12 Types of the models</i> .....	47
<i>Table 2.13 Constant parameters of Aspen Adsorption</i> .....	51
<i>Table 2.14 Types of the models</i> .....	51
<i>Table 2.15 Data for the isotherm parameters</i> .....	52
<i>Table 2.16 Isotherm parameters</i> .....	52

## Nomenclature

$B$	<i>Langmuir constant</i>	$[m^3/kg]$
$C$	<i>Molar concentration</i>	$[kmol/m^3]$
$COP$	<i>Coefficient of performance</i>	$[-]$
$COP_c$	<i>Carnot's coefficient of performance</i>	$[-]$
$H$	<i>Isosteric heat</i>	$[KJ/Kg]$
$K$	<i>Langmuir constant</i>	$[m^3/kg]$
$k_0$	<i>Equilibrium constant</i>	$[1/kPa]$
$P$	<i>Pressure</i>	$[kPa]$
$\dot{Q}$	<i>Power</i>	$[W]$
$Q$	<i>Solid loading</i>	$[kmol/kg]$
$q_0$	<i>Saturated amount adsorbed</i>	$[kg/kg]$
$R$	<i>Gas constant</i>	$[KJ/(kg*K)]$
$T$	<i>Temperature</i>	$[K]$
$W$	<i>Work</i>	$[W]$
$W$	<i>Solid loading</i>	$[kmol/kg]$
<u><i>Greek Symbols</i></u>		
$H$	<i>Efficiency</i>	$[-]$
<u><i>Subscripts</i></u>		
$C$	<i>Carnot</i>	
$C$	<i>Cold</i>	
$H$	<i>Hot</i>	
$Evap$	<i>Evaporator</i>	
$IN$	<i>In</i>	
$Des$	<i>Desorption</i>	
$Cond$	<i>Condenser</i>	
$0$	<i>Initial</i>	
$ads$	<i>Adsorption</i>	





# Chapter 1. Introduction

## 1.1 Introduction to refrigeration

According to the 2<sup>nd</sup> Thermodynamic Law, the natural heat flow is directed from a warm subject to a cold one. This flow is succeeded with 3 ways, either with conductivity, conduction or thermal radiation. Refrigeration, however, is the reverse process: the extraction of heat from a low temperature heat source and the rejection of this heat to a sink of higher temperature. Hence, in order to achieve this extraction, a work consumption is required.

The applications of refrigeration include commercial and industrial refrigeration and air-conditioning [1, 2]. These applications of cooling follow the reverse cycle of a thermal machine which has 4 phases:

- Work is provided in the cycle to compress the refrigerant and raise its temperature from the low temperature  $T_c$  to the high temperature of the cycle  $T_h$ .
- The refrigerant rejects heat at the high temperature  $T_h$ . The heat is rejected reversibly from the system by being in contact with a high temperature heat sink, with a temperature equal to or lower than the  $T_h$ .
- The refrigerant is expanded to the low temperature  $T_c$  of the cycle.
- The refrigerant evaporates, reversibly absorbing heat at a constant temperature  $T_c$  from a cold reservoir. This heat, transferred from the cold reservoir to the system, is the cooling load of the cycle, which results in the decrease of the cold reservoir's temperature. After the completion of phase 4, the refrigerant is led to the compressor for the restart of the cycle.

Underneath, is shown the principle of a cooling machine.

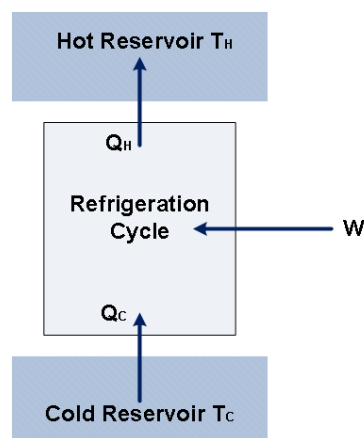


Figure 1.1 Working principle of a cooling machine [3]

Moreover, the underneath chart is shown the T-s diagram of an ideal cooling machine:

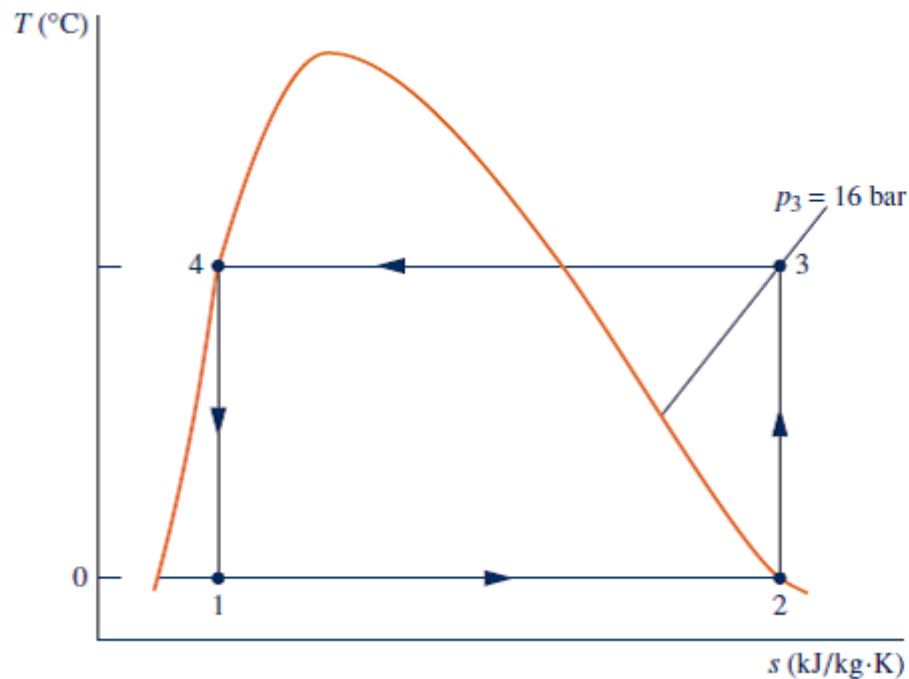


Figure 1.2 Ideal refrigeration cycle [4]

From all of the above, the performance level of a “Carnot” cooling machine is:

$$COP_C = \frac{T_c}{T_h - T_c} \quad (1.1)$$

As it is obvious, in correspondence to the Carnot cycle for thermal machines, the COP for the reverse Carnot cycle gives the maximum value of the COP for every cooling device working between temperatures  $T_H$  and  $T_C$ . The fact that expansion and compression are considered adiabatic and isentropic in the Carnot cycle, as well as the fact that both evaporation and condensation take place without any losses, ensure that the Carnot cycle achieves the maximum cooling output for a given work input. Hence, the Carnot cycle is an idealized cycle and is used as the performance limit for every cooling device operating under the same conditions [3].

At last, the basic refrigeration technologies can be distinguished based on the method for the production of the cooling effect. There are 3 main technologies can be identified:

- Vapor compression cooling
- Absorption cooling
- Adsorption cooling

Subsequently, these three technologies are going to be analyzed with particular focus on adsorption cooling, as it is the topic of this thesis.

## 1.2 Vapor Compression Cooling

This system is the most commonly applied cooling system and it is used in the industry in large scale such as the cooling of foods and the cooling of buildings. This system has a compressor in order to offer in the system the required work for the pressurization of the flow. The VCC has four key-processes namely the compression, the condensation, the expansion and the evaporation, as explained underneath:

- 1–2: Compression of the working vapor up to the condensation pressure. At the exit of the compressor, the refrigerant is superheated.
- 2–3: Condensation of the working medium. At the exit of the condenser, in the ideal vapor compression cycle, the stream is saturated.
- 3–4: Expansion of the condensed stream until evaporation pressure. At the exit of the throttling device, the refrigerant is inside the two-phase region.
- 4–1: Evaporation of the working medium. At the exit of the evaporator, in the case of the ideal vapor compression cycle, the stream is saturated.

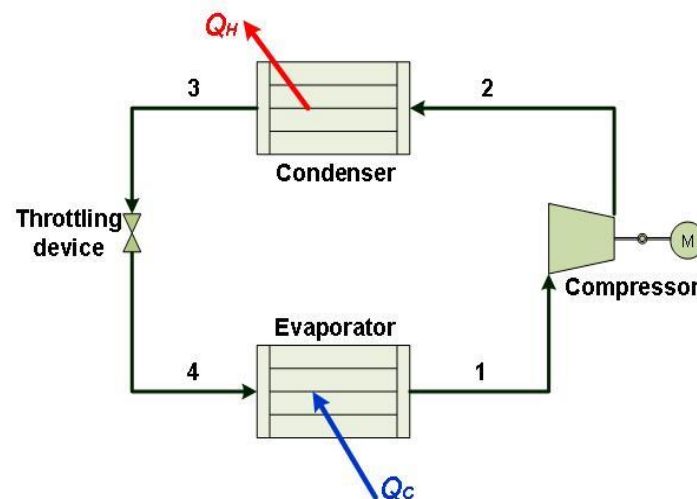


Figure 1.3 Schematic of a conventional vapor compression cycle system [3]

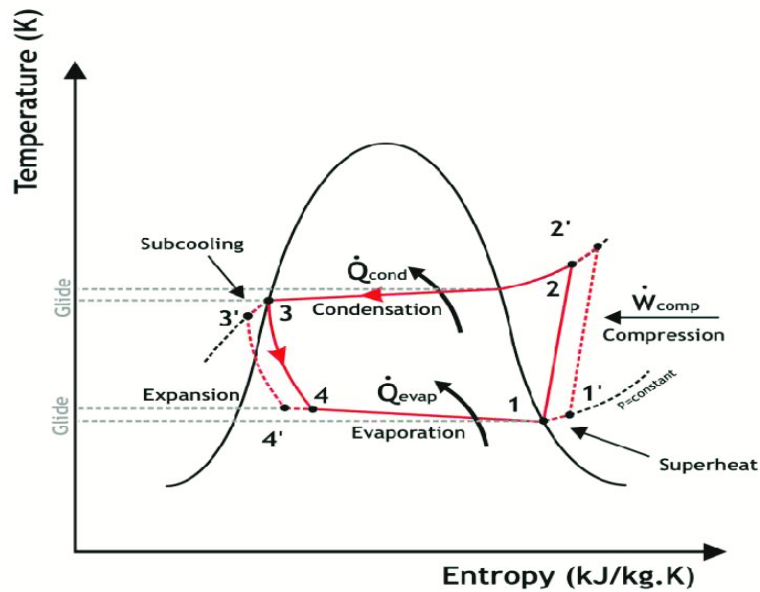


Figure 1.4 Refrigeration cycle of vapor compression [5]

In real-time applications, the vapor compression cycle deviates from the previously described behavior, mainly as a result of irreversibilities related to the compressor. Apart from deviation from isentropic compression, there are many other issues related to pressure drops across the components. Additionally, heat transfer toward and from the surroundings, should also be taken into consideration.

Moreover, in order to ensure the efficient operation of the throttling device, it is common practice to apply a certain level of subcooling at the condenser. By exiting the refrigerant at a subcooled liquid state, it is ensured that no vapor bubbles will be entering the throttling device, disrupting the flow regulation and thus not allow the full expansion of the stream, creating non-ideal conditions at the evaporator inlet [6]. On the other hand, in order to prevent the entrance of liquid droplets in the compressor, a certain level of superheating is applied in the evaporator. Superheating leads to higher cooling load; however, the compression work is increasing at the same time, thus careful design must take place for each case.

To calculate the efficiency of this technology, as in every cooling machine, the COP is used, as it was mentioned before, which is the ratio of the  $Q_c$  (cooling load) divided by  $W$  (work of the compressor) in this case.

$$COP = \frac{Q_c}{W} \quad (1.2)$$

Based on the application, the cycle can be modified by having more than one compressor or evaporator or valve. Such cooling machines are very popular in the industry because of the wide range between the low and the high temperature they can reach.



### 1.3 Absorption cooling

Absorption cycles have similarities to vapor compression cycles in that both use an evaporator, a condenser, and an expansion device. The main difference lies in the fact that absorption machines are thermally driven, using heat to increase the pressure of the fluid exiting the evaporator and to deliver it to the condenser. Absorption chillers are commonly powered by waste heat, solar energy, geothermal sources, or the combustion of biomass or natural gas.

The cooling effect is, as in mechanically driven chillers, produced in the evaporator. Apart from the condenser and the expansion device, absorption chillers, in their simplest configuration, implement two more heat exchangers, the generator, and the absorber. By adding heat to the generator, the refrigerant, which is volatile and dissolved in a carrier, is separated from the carrier solution. The refrigerant is then re-dissolved in the carrier at the absorber. Absorption is an exothermic process, resulting in the need for heat rejection in the absorber. Between the absorber and the generator, a pump is installed to elevate the pressure of the solution. However, the impact of the pump from an energy point of view is minor, and in typical cases does not exceed the 1% of the chiller's nominal cooling output.

On the other hand, to reduce the pressure of the solution exiting the generator before it enters the absorber, an expansion device is implemented. In order to enhance the system's energy utilization, a heat recovery unit is installed between the absorber and the generator to transfer heat from the hot (and weak in terms of concentration) solution exiting the generator to the cold (and strong in terms of concentration) solution exiting the absorber [7].

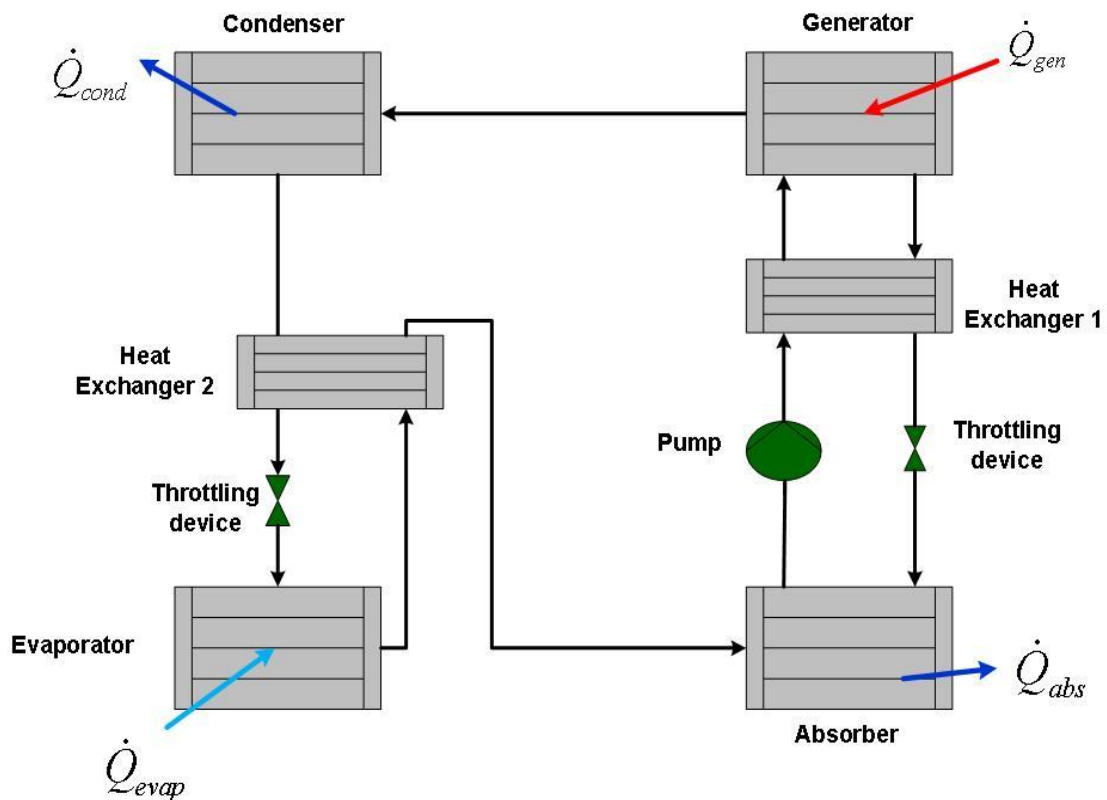


Figure 1.5 Schematic of a conventional single stage absorption cycle [3]

The two main working pairs which are dominant in the market are water (H<sub>2</sub>O)-lithium bromide (LiBr) and ammonia (NH<sub>3</sub>)-water (H<sub>2</sub>O). In the first one the water is the refrigerant and in the latter is the ammonia. There are also several other working pairs but they are not so popular in the market mainly due to the poor efficiency and/or their availability.

Table 1.1. Key features of two main working pairs for absorption chillers [8-12]

NH <sub>3</sub> -H <sub>2</sub> O	H <sub>2</sub> O-LiBr
COP: 0.4-0.6	COP: 0.5-0.7
Temperature minimum as low as -60 °C	Temperature minimum 5 °C (freezing issues)
-	Crystallization issues
More compact design	Less compact
Ammonia toxic, corrosive and volatile	Non-toxic and non-flammable working pair
High pressures	Partial vacuum pressure

In terms of working range, the commercially available absorption chillers extend from small domestic units, with a cooling capacity of few hundred W, to large industrial chillers, with capacities as high as tens of MW [13]. The long lifetime and the efficient part load operation are the main advantages of the commercial absorption chillers.

The temperature restrictions relative to the available working pairs, the large weight in comparison to conventional compression chillers and the crystallization issues are the main drawbacks of the absorption technology. In fact, the low COP of the absorption cycle is a main obstacle to the expansion of the market [14].

On the other hand, the low energy consumption enables the application of absorption in remote areas, turning the technology in the most distributed in worldwide basis cooling system.

#### 1.4 Adsorption cooling

Adsorption involves the distribution of molecules between two phases, one of which is a solid and the other either a liquid or a gas. Adsorption is a well-known and applied technology in water treatment, in the purification of liquids, and in gas cleaning processes. However, in the 1990s researchers started to investigate the use of adsorption in a refrigerant cycle for cooling purposes [15, 16].

The two main phases of an adsorption cycle are the desorption and the adsorption. The adsorption cycle has 4 stages:

- At the start, the adsorbent is saturated of refrigerant at the adsorber bed, at a low pressure and temperature. Heat is added to the system in order to start the desorption process and regenerate the adsorbent. With the heat the pressure of the refrigerant increases.
- Secondly, high pressure refrigerant condenses in the system's condenser, by rejecting heat to a medium temperature secondary stream.
- Moreover, the low-pressure stream flashes and evaporates in the evaporator.
- Lastly, the vapor is being adsorbed in the second sorption bed with the help of a stream of cold water which generate the adsorbent.

In order to have a continuous process, the adsorption chillers have at least two beds. While the one bed adsorbs the vapor from the evaporator the other bed desorbs the vapor, which is in high pressure, flowing to the condenser of the system. The COP of this technology is defined as the ratio of the power of the evaporator ( $Q_{EVAP}$ ) and the driving heat which is used for the generation of adsorbent ( $Q_{IN}$ ):

$$COP = \frac{Q_{Evap}}{Q_{IN}} \quad (1.3)$$

On the other hand, the ideal COP,  $Cop_{Carnot}$ , is determined by the following equation:

$$COP_C = \frac{T_{Evap} * (T_{Des} - T_{Cond})}{T_{Des} * (T_{Cond} - T_{Evap})} \quad (1.4)$$

As a result of the aforementioned equations, the exergetic efficiency of an adsorption cycle is defined as:

$$\eta = \frac{COP}{COP_C} \quad (1.5)$$

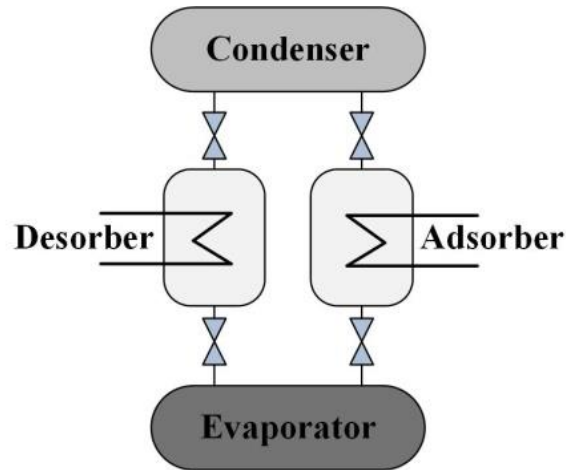


Figure 1.6 Double-bed adsorption process layout.

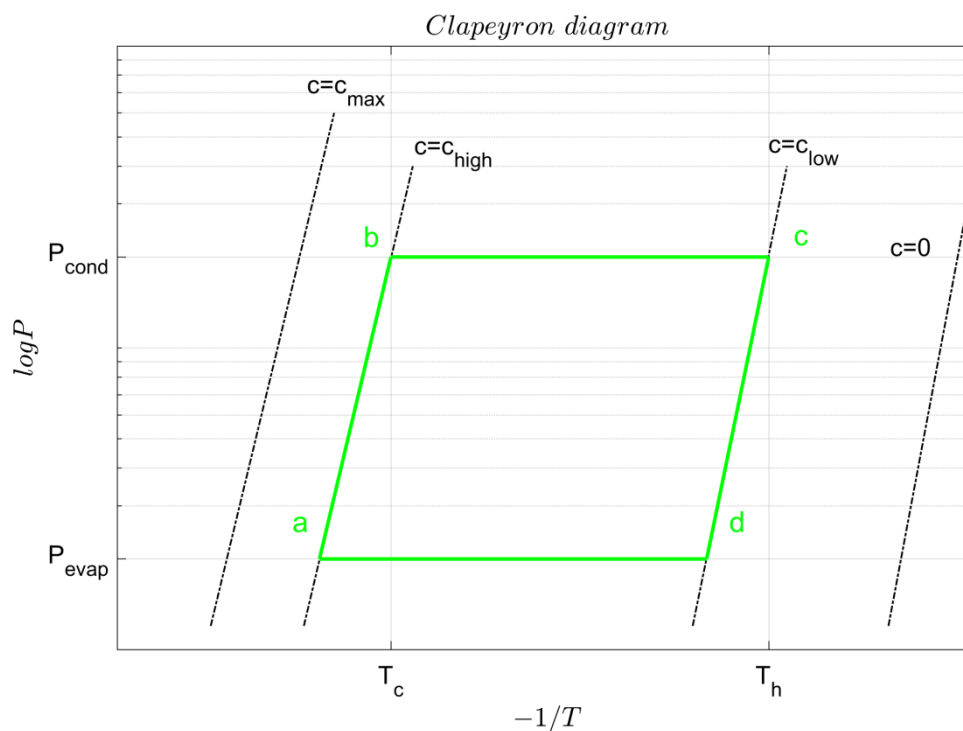


Figure 1.7 Clapeyron diagram for the adsorption cycle.

Adsorption cooling has advantages both over absorption and over technologies of vapor compression cycle. First of all, adsorption is powered by low grade heat sources and has simple equipment compared to absorption. Furthermore, adsorption allows the use of heat

sources with very low temperatures, while absorption systems require heat sources with at least 70°C. Compared to conventional vapor compression, adsorption systems enable the utilization of waste heat or solar energy, and have lower operational costs, no moving parts, and no vibrations [17-19]. The main drawback of adsorption technology is the limited adsorption capacity of the adsorbents, resulting in a low COP and low specific cooling power (SCP); hence, this is the main reason of the restricted use of adsorption technology in cooling applications [20].

However, these disadvantages can be overcome via the intensification of heat and mass transfer properties in the adsorber, by increasing the adsorption properties of the working pairs and via a better heat management during adsorption cycle.

There are many ways to categorize adsorption applications. Firstly, it can be divided into two types based on the nature of surface forces: physical adsorption and chemical adsorption. Physical adsorption is caused by relatively weak van der Waals forces that hold the adsorbate at the surface. Multiple layers may be formed since physical adsorption is not selective. For most adsorbents, the adsorption heat released during adsorption of the refrigerant is similar to the condensation heat of the refrigerant [19]. Due to the small heat of adsorption, this type of adsorption is stable only at temperatures below 150°C [21].

In terms of kinetics, physical adsorption is fast and does not require any energy input to be initiated, whereas chemical adsorption may need a certain level of energy in order to be activated [22]. As a result of the weak forces applied, physical adsorption is a reversible process, unlike chemical adsorption [20]. In chemical adsorption much greater forces are applied. The adsorbent reacts chemically with the adsorbate producing new types of molecules. A certain level of electron exchange is also involved [23]. One of the most important differences between the two types of adsorption is that chemical adsorption is confined to a monolayer, unlike physical adsorption [24].

The adsorbents which are used in the adsorption cooling have different effects in the COP and generally in the cycle of adsorption per application. There are three main types of adsorbents: physical, chemical, and composite adsorbents. In general, the desired features for an adsorbent include a large internal surface area, regeneration capability, and slow aging in order to preserve adsorptive capacity despite continuous recycling.

First of all, the physical adsorbents are used the most in the applications of cooling and especially the silica gel, the activated carbon and the zeolite. The first one, silica gel, is one of the most popular adsorbents. Silica gels owe their wide use to their large capacity, low cost, market availability, and their ease of regeneration at approximately 150°C, in contrast to zeolites, which require 350°C [25, 26]. This type of adsorbent is appropriate for low grade waste heat sources [27]. Silica gel is a porous, granular form of silica with small particle size of 2–5 nm and a large surface-to-volume ratio [28]. Silica gel is synthesized either from polymerization of  $\text{Si}(\text{OH})_4$  or from aggregation of colloidal silica.

As a water adsorbent, silica gel is characterized by average adsorptive capacity [29]. However, the silica gel loses its ability of adsorption if it is overheated. As a water adsorbent, silica gel is characterized by average adsorptive capacity [29]. Adsorption systems with silica

gel-water working pairs have been widely investigated either in single or multiple stage systems [30-32].

In order to enhance the properties of silica gel, various modifications have been investigated. Fang, Liu [33] investigated the influence of metallic ions doped on silica gel and found that the mean pore size, the total pore volume, the thermal stability, and the adsorptive capacity were enhanced. Tangkengsirisin, Kanzawa [34] studied the influence of the addition of activated carbon in silica gel and found that it enhanced the desorption rate and regeneration temperature.



*Figure 1.8 Macroscopic image of silica gel.*

The activated carbon is the most known adsorbent and it is used widely in cooling applications. It is produced by materials such as wood, coal, and fossil oil. The microcrystal of the activated carbon is a six element carboatomic ring. The spaces between the individual microcrystallites are called pores. Most of the adsorption takes place in these micropores. Depending on the nature of the application, different pore volumes and pore size distributions in activated carbons are desired. Hence, for liquid adsorption, relatively large pores in a few nanometer sizes are preferable [35]. Activated carbon materials are divided into three categories: powder activated carbon (PAC) with a particle size of 1–150 nm, granular activated carbon (GAC) with a particle size of 0.5–4 mm, and the extruded activated carbon (EAC) with a particle size of 0.84 mm [36]. In general, activated carbons are a competitive solution given their high surface area and their low cost.



*Figure 1.9 Activated carbon.*

The last one known adsorbent is the zeolite. Zeolite is a crystalline aluminosilicate with a three-dimensional framework structure of  $AlO_4$  and  $SiO_4$  that forms uniformly sized pores at a size of a molecule [37]. The reason of the investigation of this type of adsorbent is the lower temperature that it needs for its regeneration than the corresponding temperature which the activated carbon needs. However, this temperature is higher than the silica gel's temperature. Till December 2018 there are 245 types of physical zeolite [38]. The main reasons for the steady increase in the use of zeolites include the large number of commercially available structures, their high structural ability, and safety and environmental considerations [39].

Apart from Si and Al, other elements can be introduced, resulting in what is known as zeotypes, including, among others, aluminophosphates (AlPOs) and silicoaluminophosphates (SAPOs). In general, based on the synthesis technique, different properties can be achieved from zeotypes.

Apart from adsorption, zeotypes can be used for catalysts, ion exchange, and other applications. However, there is currently no commercial product due to the fact that their procedure synthesis and the employed raw materials are quite expensive, which leads to high final product costs [40]. One more restriction in their use is the high affinity for water vapor that zeolites have [41].



*Figure 1.10 Zeolite.*

Another type of sorbents is the metal organic frameworks (MOFs) which belong to a recently developed class of adsorbents that show attractive features for adsorption chillers. Indeed, since they are characterized by huge specific surface area as well as the low temperature requirements for desorbing their water content, MOFs have drawn much scientific interest in recent years [42]. Nevertheless, at their current stage of development, the main issues are (1) their hydrothermal cycling stability, which is really limited and results in a significant drop in their adsorption capacity, and (2) their production cost, which is still too high for practical applications [43, 44].

The second type of adsorbents is the chemical-based adsorbents. Chemical adsorbents have been developed to enhance the adsorption system's performance and make them competitive with respect to conventional vapor compression units [45]. The large adsorption capacity and low evaporating temperature are the main advantages of chemical adsorbents. The main disadvantages of chemical adsorbents are a low thermal conductivity that results

in slower reaction, and the durability of the chemical adsorbents with repeated reaction cycles [46, 47].

However, chemical adsorbents are going to be addressed briefly due to their limited use. Chemicals adsorbents include:

- Calcium chloride
- Lithium chloride
- Metal oxides

The last category of adsorbents is the composites which are also are not used in large scale in cooling applications. Composite adsorbents have been developed and investigated recently in the search for improved heat transfer rates that will eventually allow for more efficient cooling systems. Composite adsorbents are made from porous media and a combination of one or more physical and chemical adsorbents, such as silica gel, expanded graphite, metal chlorides, and zeolite [19].

Depending on the adsorbent, there are refrigerants that can be used and have better properties for the adsorption cycle. The most known refrigerants are water, ammonia, methanol, and ethanol. These refrigerants have to have some desired abilities such as:

- High latent heat of vaporization
- Thermal stability
- Environmentally friendly
- Non-flammable
- Non-toxic
- Non-explosive

Table 1.2 summarizes some key properties of the four aforementioned refrigerants that are used in cooling applications.

*Table 1.2. Basic characteristics of most common refrigerants*

	Water	Ammonia	Methanol	Ethanol
<b>Boil point (°C)</b>	100	-34	65	79
<b>Molecular mass (g/mol)</b>	18	17	32	46
<b>Latent heat of vaporization (kJ/kg)</b>	2258	1368	1102	842
<b>Density (kg/m<sup>3</sup>)</b>	958	681	791	789

Water was the first adsorbent to be used thanks to its availability, cost, and its absence of environmental impact [48]. On the other hand, the main disadvantage of water is that it cannot be used for ice making or refrigeration below 0°C applications.

Ammonia is extensively used in adsorption cooling systems, especially with metal chloride or metal chloride composite adsorbents [49-51]. The main advantages of ammonia include the high enthalpy of vaporization, thermal stability, no ozone depletion, low global warming potential, and a low freezing point. The main disadvantage of ammonia is the fact that it is toxic [52].



Ethanol is another widely used refrigerant thanks to its low freezing point (-114°C), non-toxicity, high thermal stability, and good latent heat of evaporation [53, 54]. Brancato et al. [55] performed theoretical calculations on the performance of ethanol adsorption chillers with carbonaceous and composite adsorbents.

Methanol is also used as refrigerant in adsorption applications. The main advantages of methanol include its high latent heat of vaporization and its non-toxicity [56]. On the other hand, methanol is corrosive, leading to the need for corrosion-resistant materials and an increase in cost of equipment.

As a result, in the industry there are some working pairs of adsorbent-refrigerant which are used in large scale. The pair zeolite-water is one of the first which was used in adsorption cooling applications [57, 58]. The zeolite-water pair requires regeneration temperatures that exceed 200°C, with an adsorption-evaporation temperature lift up to 70°C or more. This pair remains stable at high temperatures, and the latent heat of water is much higher than those of methanol or other classical refrigerants. However, a system operating with the zeolite-H<sub>2</sub>O pair is more suitable for A/C applications due to the solidification temperature of water, which restrains the freezing process. The maximum adsorption capacity was approximately 12%. Furthermore, it was proved that the level of adsorption increased with water vapor pressure and with a decrease in zeolite temperature.

The second pair which is used the most in industry is silica gel-water. Silica gel-water is ideal for solar energy applications due to its low regeneration temperature, thus only requiring low-grade heat sources, commonly below 85°C. Moreover, water has the advantage of having a greater latent heat than the other conventional refrigerants. However, this pair has a low adsorption capacity as well as a low vapor pressure, which can hinder mass transfer. Furthermore, this working pair requires vacuum conditions in the system [59]. Main applications for this working pairs are refrigeration, water cooling, and ice making.

Other pairs which were investigated for cooling applications include pairs with adsorbent activated carbon. The two main working pairs which are investigated are activated carbon-methanol and activated carbon-ammonia. Activated carbon-methanol is one of the most common working pairs in adsorption refrigeration systems. It also operates at low regeneration temperatures, while its adsorption-evaporation temperature lift is limited to 40°C. This pair is also characterized by its large cyclic adsorption capacity, low freezing point, low adsorption heat, and the high evaporation latent heat of methanol. However, activated carbon has a low thermal conductivity, which decreases the system's COP. Additionally, methanol has a high toxicity and flammability [60].

The activated carbon-NH<sub>3</sub> pair requires regeneration temperatures that can exceed 150°C. Its adsorption heat is similar to that of activated carbon-methanol, but it requires higher operating pressures, which prevents the infiltration of air into the system and reduces the cycle time the main disadvantage of this pair [61]. These factors help to increase the specific cooling capacity of the system. Main applications for this working pairs are ice making and refrigeration.

One last pair used in the industry is calcium chloride-methanol. The potential use of a CaCl<sub>2</sub>-methanol working pair in an adsorption chiller has been investigated for either standalone operation or for implementation in a CHP. It was concluded that since the CHP operation

resulted in an increased regeneration temperature, a significant increase in the COP was identified [62].

Apart from the aforementioned working pairs, there are more pairs which may be used in cooling applications. Below, there are some charts which show two key performance parameters (COP and specific cooling power) of different pairs.

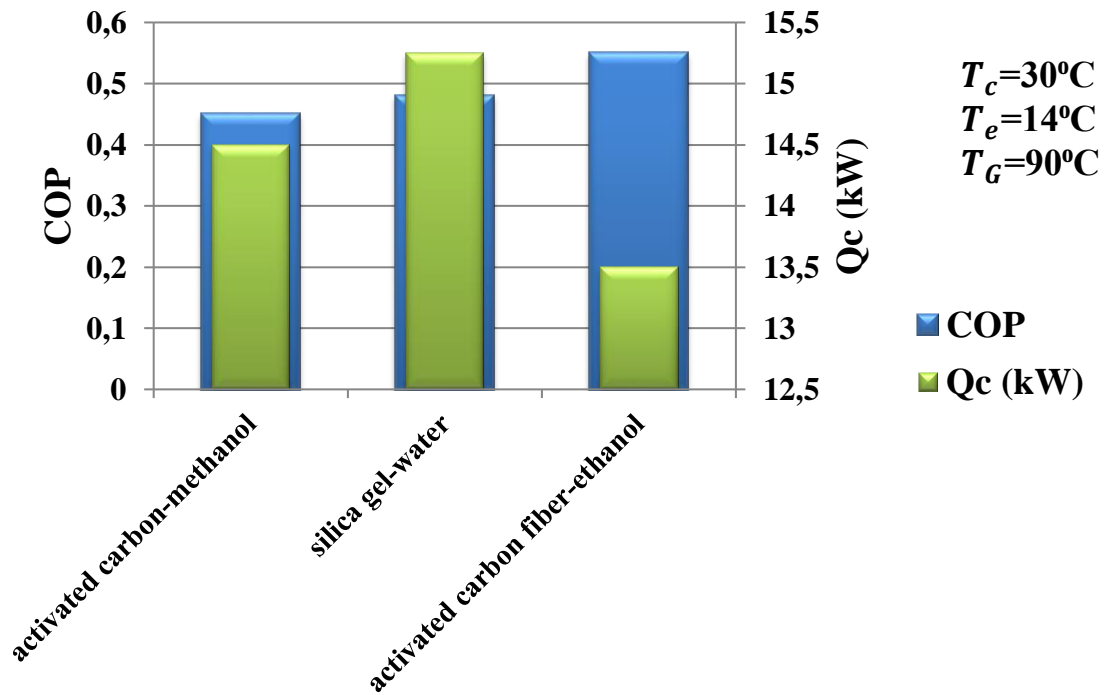


Figure 1.11 Working pair comparison based on work of Habib et al. [63]

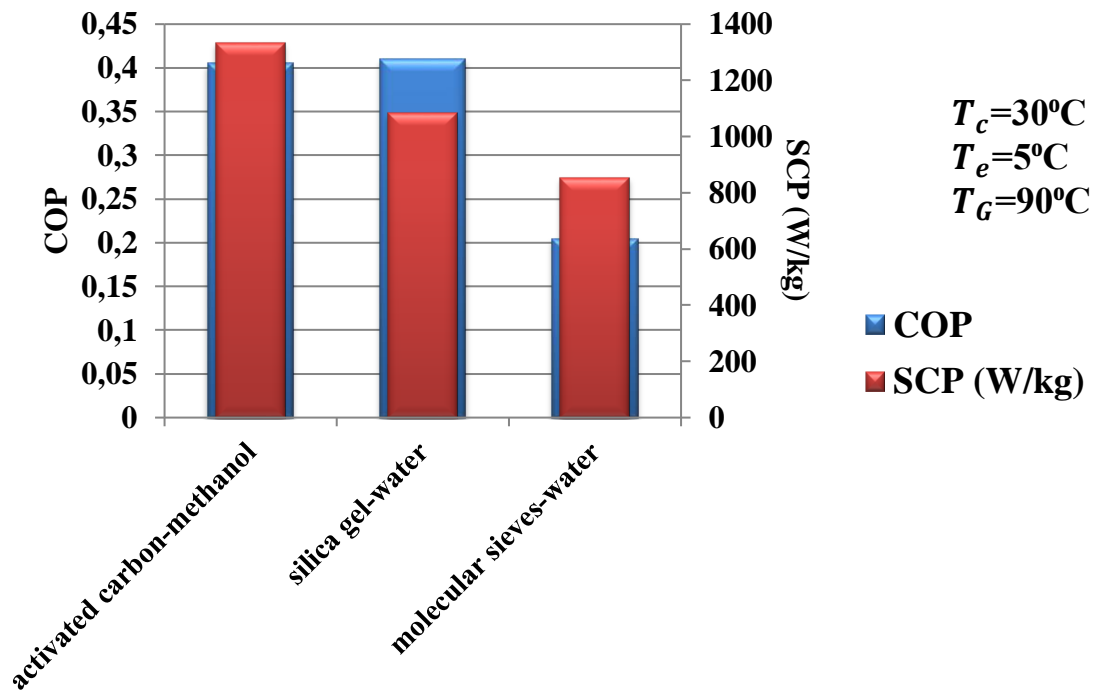


Figure 1.12 Working pair comparison. Adapted from San and Lin. [64]

On the other hand,

Table 1.3 presents an overview of some key working pairs and compares some of their adsorption related characteristics.

Table 1.3. Comparison Between Various Solid Adsorbent Pairs

Absorbent	Refrigerant	Adsorption heat (kJ/kg)	Density of refrigerant (kg/m <sup>3</sup> )	Considerations
Activated carbon	H <sub>2</sub> O	3000	1000	Water is applicable except for very low operating pressure
Zeolite	H <sub>2</sub> O	3300-4200	1000	Natural zeolite has lower values than synthetic zeolite
Zeolite	NH <sub>3</sub>	4000-6000	681	
Zeolite	CH <sub>3</sub> OH	2300-2600	791	
Silica gel	CH <sub>3</sub> OH	1000-1500	791	Suitable for temperature less than 200°C
Silica gel	H <sub>2</sub> O	2800	1000	Used mostly for descent cooling
Calcium chloride	CH <sub>3</sub> OH	1800-2000	791	Used for cooling

## **1.5 Bibliographic review and technology comparison**

The adsorption cooling technology has been significantly developed in the last decades and because of its advantages it is used in large scale in industry. Especially, thanks to the highly exothermic adsorption process, an adsorption cycle can be used for heat pump applications.

Table 1.4 presents a non-exhaustive list of applications of adsorption cooling till 2018. As shown, silica gel-water is the most commonly investigated working pair in experimental studies, due to its competitive performance and high availability.

In conclusion, at this time, there are only a few manufacturers across the world that produce commercial adsorption chillers. These manufacturers include Bry-Air, Fahrenheit AG, Weatherite Manufacturing Limited, Mayekawa USA, and GBU. The aforementioned companies focus mostly on single-stage adsorption chillers with either silica gel-water or zeolite-water as the working pair. Companies that focus on the use of water as an adsorbent are also justified by Table 1.4, which shows that, according to the reports from literature, experimental water adsorption cooling systems have the highest second law efficiency.

Table 1.4 List of experimental adsorption units in cooling [3]

Refrigerant	Adsorbent	$\Theta_{des}$ (°C)	$\Theta_c$ (°C)	$\Theta_\epsilon$ (°C)	COP	$\eta$ (%)	SCP (W/kg)	Remarks	Source
<b>Ammonia</b>	BaCl <sub>2</sub> /vermiculite	90	30	10	0.52 – 0.55	22.2– 23.5	300–680	single bed	(Veselovskaya et al. 2010)
	CaCl <sub>2</sub> /activated carbon	144	29	-21	0.26	18.70	474	two beds with two condensers and a single evaporator	(Lu and Wang 2013)
	CaCl <sub>2</sub> /activated carbon	130	25	5	0.23	6.35	230	two beds	(Pan et al. 2014)
	CaCl <sub>2</sub> /BaCl <sub>2</sub>	95	30	0	0.20 1	12.50	220.3	trigeneration system with an ORC and a two-stage adsorption chiller	(Jiang et al. 2014)
	CaCl <sub>2</sub> /expanded graphite	140.3	25	-15	0.27	15.00	422.2	two beds	(Li et al. 2010)
	CaCl <sub>2</sub> /Silica gel	125	27–35	-2.5	0.2	8.86– 12.26	364	two stage/cogeneration system	(Bao et al. 2014)
	Activated carbon	80	28	7	0.12	6.11	n/a	fin-plate adsorption bed	(Shu Xu 2012)
<b>Water</b>	LiNO <sub>3</sub> /vermiculite	90	35	10	0.66	38.48	230	single adsorber	(Sapienza et al. 2012)
	MIL-101(Cr)/graphene oxide(2%GrO <sub>syn</sub> ) (composite)	90	n/a	20	0.17	n/a	140	two fin-tube bed	(Eman Elsayed, Raya AL-Dadah et al. 2017)

AQSOA (zeolite)	90	35	11	0.37	20.63	410.625	One adsorber in a vacuum chamber	(Lingbao Wang, Xianbiao Bu, Weibin Ma 2018)
MOF-801	80-85	n/a	5	0.67	n/a	2000		(M.V.Solovyeva et al. 2018)
SWS-8L	90	30	15	0.3	9.45	389	single bed	(Freni et al. 2012)
composite microporous activated carbon/silica gel/CaCl <sub>2</sub>	115	27	5	0.7	24.42	378	single bed	(Tso and Chao 2012)
Activated carbon	115	27	5	0.37	12.91	65		
SAPO-34 (silica gel)	60	31–35	15	0.12	7.78–2	169.74	solar powered (PTC)/ single bed	(Du et al. 2016)
Silica gel RD-2060	95	30	10	n/a	n/a	460	newly designed packed bed	(Ramy H.Mohammed et al. 2018)
Silica gel	80	30	14	0.45	17.7	176	single bed/common heat exchanger for evaporation-condensation	(Chang et al. 2007)
Silica gel	65-85	38	11.5	0.15	17.4	n/a	two-bed	(Sourav Mitra et al. 2016)
Silical gel	55-95 (water)	30	9	0.7-	9-26.5	30-120	four bed-double effect	(Marlinda et al. 2010)
	90-150 (hot fluid)			1.2	31.5			
Silica gel	80	30	14	0.37	13.8	72	two bed/solar	(Chang et al. 2009)
Silica gel	82.1	31.6	12.3	0.49	23.31	n/a	two adsorption chambers	(Chen et al. 2010)

<b>Methanol</b>	Silica gel	85	32	20	0.33 1	9.16	n/a	solar adsorption chiller with two single-bed adsorption units and mass recovery	(Luo et al. 2006)
	Silica gel	80	30	15	0.53	19.49	68	single bed	(Vodianitskaia et al. 2017)
	Silica gel	84.4	30.5	16.3	0.43	13.79	104.6	two chambers/mass recovery	(Xia et al. 2009)
	Zeolite/CaCl <sub>2</sub>	85	28	14	n/a	n/a	377	compact dual adsorber	(Ka ChungChan et al 2017)
	Zeolite	174	34	12	0.4	9.86	n/a	single bed adsorption system	(Mohamed. H. Ahmed et al 2018)
	Zeolite	80-90	41	18	0.42	24.59 - 30.04	n/a	Stirling engine coupled with two-bed adsorption chiller	(Flannery et al. 2017)
	ZSM-5 (zeolite)	100	n/a	n/a	0.06	n/a	91.2	solar powered (PTC)/ single bed	(Du et al. 2016)
	Silica gel/ LiCl	85.2 88	31.4 25	15.2 -4	0.41 0.13	15.34 8.03	225 n/a	solar powered/ single stage/ two bed	(Lu and Wang 2014)
	Silica gel/ LiCl	96	31	15	0.41	12.93	244	two beds	(Lu and Wang 2013)
	LiCl/SiO <sub>2</sub>	85	30	10	0.32 -0.4	14.71 - 18.40	2500	single bed	(Gordeeva and Aristov 2011, Gordeeva et al. 2009a, Gordeeva et al. 2009b)
	CaCl <sub>2</sub> /silica gel	84.8	29.8	15.3	0.41	13.41	n/a	two beds/mass recovery	(Gong et al. 2012)
	Activated carbon	70-100	25	7-10	0.30 1	7.93- 14.74	353.2	two beds	(Abdual Hadi N. Khalifa et al. 2011)
	Activated carbon	38-116	20.4	-1.1	0.09 6solar	3.09 solar	n/a	solar powered (CPC)/single bed	(González and Rodríguez 2007)
	Activated carbon	90	17	-8.4	0.07 8 solar	71	n/a	single bed	(Lemmini and Errougani 2007)
	Activated carbon	72.6 (opt)	n/a	n/a	0.33 4	26.9	68.2	two stage	(Baiju and Muraleedharan 2011)

<b>Ethanol</b>	Olive waste	120	25	8	0.75 gross 0.18 -0.2 solar	18.77	n/a	solar powered (PTC)/single bed	(Abu-Hamdeh et al. 2013)
	SG/LiBr composite	90	30	7 -2	0.64 0.72	31.8 51.43	n/a n/a	single bed	(Brancato et al. 2015)
<b>Glycol</b>	Activated carbon cloth	100	30	14	0.23 6	7.01	59-181	possible to utilize solar irradiation/single stage	(Tierney et al. 2017)
	SWS-1L composite	95- 100	35	7-12	0.25	11.58 - 15.33	150-200	single bed	(Freni et al. 2007)



## 1.6 Thesis scope

As indicated by previous sections, the adsorption phenomena of innovative working pairs has not yet been thoroughly investigated, thus there is significant room for improvement. This study aims to evaluate the potential of ASPEN Adsorption on being used to investigate novel working pairs and assess their potential on further implementation in adsorption cooling cycles.

In the next chapters, the main questions to be addressed are the following:

- How is an adsorption characteristic calculated in ASPEN Adsorption?
- How accurate are the available in literature models in comparison to the predictions from ASPEN Adsorption?
- How are the adsorption characteristics of the considered working pairs affected by variations in the working conditions?
- Which is the optimal built-in model of ASPEN Adsorption for the simulation of the considered working pairs?
- Is eventually ASPEN Adsorption trustworthy on evaluating without prior experimental results novel working pairs?



## Chapter 2. Case Studies on ASPEN Adsorption

### 2.1 Introduction to Aspen Adsorption

In order to study the different pairs of adsorbents-adsorbates before they will be used in industry, it is essential the use of the program, Aspen Adsorption, in order to modeling the cooling circle. With this program, the results which are received can show a lot of key-factors about this technology such as the loading, the pressure drop in the adsorbent bed and others. This program is very useful because of the incorporated libraries of the properties of adsorbates and of the parts to 'build' the cooling cycle such as different adsorbent beds.

However, Aspen Adsorption has not incorporated libraries for the adsorbents and we have to 'fix the bed' so it will have the right adsorbent inside. For this procedure, we need some isotherms parameters and also the mass transfer coefficient of adsorbate. So, for this reason, Aspen Adsorption is a bit difficult to modeling the adsorption cycle.

There will not be an analyzing report how the Aspen Adsorption is used in this thesis but it is important to be shown the parts of it. There is a picture of the environment underneath.

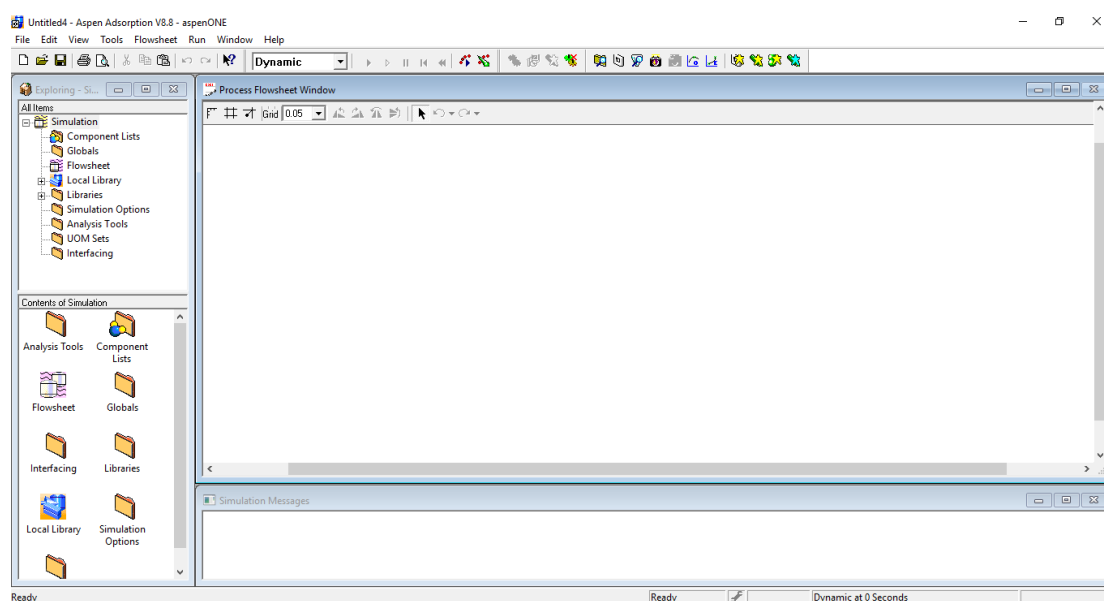


Figure 2.1 The environment of Aspen Adsorption.

At the beginning, the big white area above is the Flowsheet where are placed the parts of this technology such as the adsorbent bed. Under this, is Stimulation Messages area where messages show if any change is current or not. Moreover, there are two others areas in the left where there are the libraries of the parts which are placed in the Flowsheet.

At this moment, it is useful to explain the steps in order to make the Aspen runs. First of all, from the Aspen Plus the component list or set is chosen. Namely, the components and the property option are chosen in this step. There are all the components and different options of the property to choose in every case. This step is completed when the list is configured.

After that, it is time to build the cycle in the Flowsheet. From the libraries which are mentioned above, the bed and the other parts are chosen in order to build the refrigeration cycle. In this thesis only the process of adsorption is needed to be build. When the cycle is ready, it is about time to specify the parts which are used, in this case the bed the product and the feed.

At last, the final step in order to make Aspen Adsorption ready for running, is to specify how long the run will last and also the step of the repetition. After all of this the program is ready.

## 2.2 Topic of the thesis

The heat pumps are one of the most common technologies which are used for cooling and especially domestic cooling. They also have a big use in industry. The heat pumps differ from each other in the method of cooling which is used. There are heat pumps with vapor compression and with the use of adsorption or other method.

In this thesis the study is about heat pumps which adsorption is used. Moreover, the adsorbate which is going to be utilized is water or a mixture of water and some other components such as ethanol. Plus, there is an example with adsorption of water from the air for cooling.

Generally, this thesis is going to be a study of different pairs of adsorbents with water adsorption with the results of some key-factors such as the loading in different temperatures or pressures. The data for the runs will be taken from papers in order to have correct results. From these results, it is easy to study the different adsorbents and export some conclusions. From these results it is also easy to make some equations in order to measure the loading with the use of the temperature or pressure and not with the use of Aspen Adsorption.



*Figure 2.2 Gas adsorption heat pump.*

## 2.3 Activated Carbon-Water

The first pair which is going to be studied is activated carbon-water. This type of adsorbent is not very common in cooling with water as adsorbate, but with the activated carbon, ammonia is usually used. However, it is also important the study of this pair in order to observe some key-factors such as the loading and how it is changed according to the temperature in order to have an idea for the other type of adsorbents which are going to be studied.

At the beginning, the parts which are used in order to construct the process are the “liquid” bed, the “liquid” feed and the “liquid” product. These three parts are connected by the “stream liquid connection”. These parts, as it is said above, are taken from the libraries of Aspen Adsorption. The choice of ‘liquid’ parts instead of gas or ionx parts models better the pure water feed and this is the reason which they have been chosen. Underneath is the flowsheet of the process in order to be clear which components were used in the example.

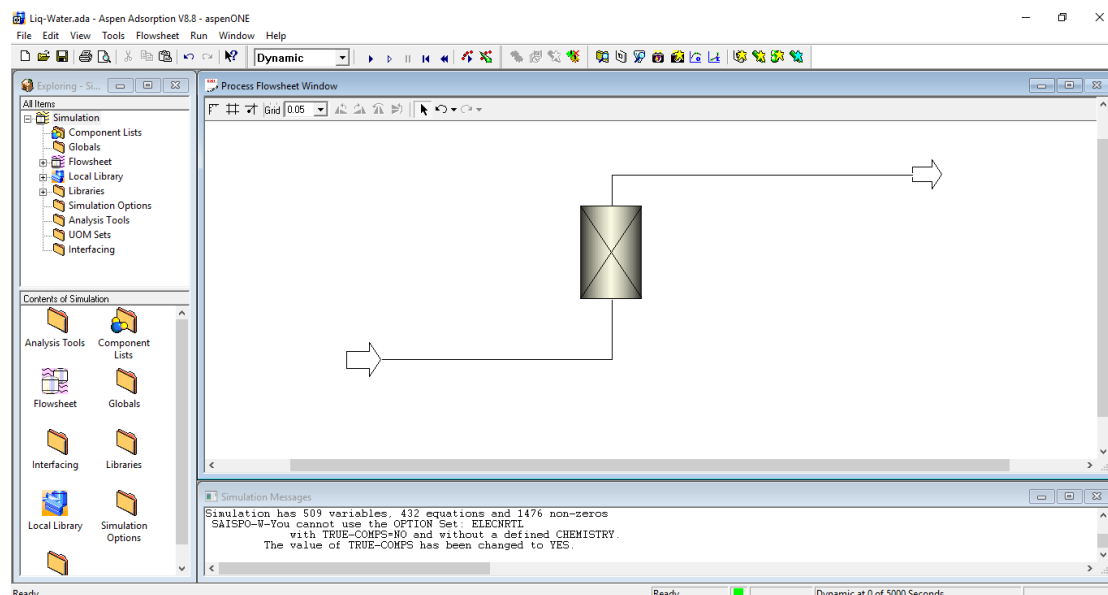


Figure 2.3 The parts of the process of adsorption

Furthermore, it is important to separate the parameters which are going to be specified to two categories, the constant ones and these which are changed. The parameters which are going to be changed are the isotherm parameters and the temperature only in this example. The other parameters are going to be the same and are presented in the table below.

Table 2.1 Constant parameters for Aspen Adsorption

Parameter	Value
Feed flowrate	1*10 <sup>-6</sup> m <sup>3</sup> /sec
Water concentration	55,5 kmol/m <sup>3</sup>
Pressure	1,1 bar
Height of adsorbent layer	0,35 m
Internal diameter of adsorbent layer	35 mm
Inter-particle voidage	0,4
Solid density	1000 kg/m <sup>3</sup>
Water constant dispersion coefficient	1*10 <sup>-5</sup> m <sup>2</sup> /sec
Water constant mass transfer coefficient	0,05 sec <sup>-1</sup>
Specified flow direction	0

The above parameters concern the adsorbent bed and with them specified, the adsorbent is also specified, in that case activated carbon. The values of some of these parameters are random because in this example the key-factor which is studied is the loading subject to temperature and these parameters do not have an impact to the loading in the Aspen Adsorption. The only parameter which is a bit important is the mass transfer coefficient and for this reason its value is taken for Matlab after some search.

Except for these constant parameters, it is also useful to present some other parameters such as the kinetic model and the isotherm model which also are constant and present in the below table.

Table 2.2 Types of the models

Parameter	Type
Material balance assumption	Convection with constant dispersion
Kinetic model	Solid linear lumped resistance
Isotherm model	Langmuir 1
Energy balance	Isothermal

These parameters concern the process of the adsorption. The other parameters which are not presented here are the default. The most important of the above parameters is the isotherm model. "Langmuir 1" was selected because is one of the simplest isotherm methods and also a lot of papers has the correlation between this method and the corresponding equation in Aspen Adsorption, especially the correlation of the isotherm parameters. For this reason, in this example and also in the next ones it is preferred the use of "Langmuir 1" as the isotherm model.

The equation of the isotherm model "Langmuir 1" in the Aspen Adsorption has the underneath form:

$$w = \frac{IP_1 * c_1}{1 + IP_2 * c_2} \quad (2.1)$$

The above equation was taken from a study between activated carbon and ethyl acetate because of the lack of papers which include this specific rare pair, activated carbon-water [65]. So, if it is compared with the equation of the model in theory for the loading, it will be

obvious the similarity of these two equations and the easy correlation between them. The theoretical equation is:

$$\frac{q}{q_0} = \frac{b \cdot c}{1 + b \cdot c} \quad (2.2)$$

All of the above are remained constant through the runs. The three parameters which are changed are the isotherm parameter 1 (IP1), isotherm parameter 2 (IP2) and the temperature. Underneath there is a table with the values of these three parameters.

From the two equations above it is easy to export the isotherm parameters which are underneath.

$$IP_1 = \frac{q_0 \cdot b}{M} \quad (2.3)$$

$$IP_2 = \frac{b}{M} \quad (2.4)$$

The values of  $q_0$  and  $b$  have been taken from the above paper and  $M$  is the value of molar molecular weight of water.

Because the isotherm parameters were only for 3 temperatures, it was useful to do a linear interpolation for 2 more temperatures in order to have better results. Finally, as it is obvious, the process is going to be the adsorption and not the desorption because of the values of the temperature which have the range of 303K-328K.

*Table 2.3 Isotherm parameters*

Temperature (K)	IP1	IP2
303	2,063337	2,8264895
313	1,632381	2,553388
318	1,361187	2,3307992
323	1,304089	2,2203374
328	1,069951	1,1070239

At last, it is useful to explain the initial values which are selected. In the tab "Initials" the initial concentration of water inside the bed is 0 kmol/m<sup>3</sup> in every run.

At this moment, some charts are going to be present to illustrate the results better. The underneath charts show the loading subject to concentration of the water which is adsorbed and the water's concentration subject to time. The charts are for 5 temperatures between 303K-328K.

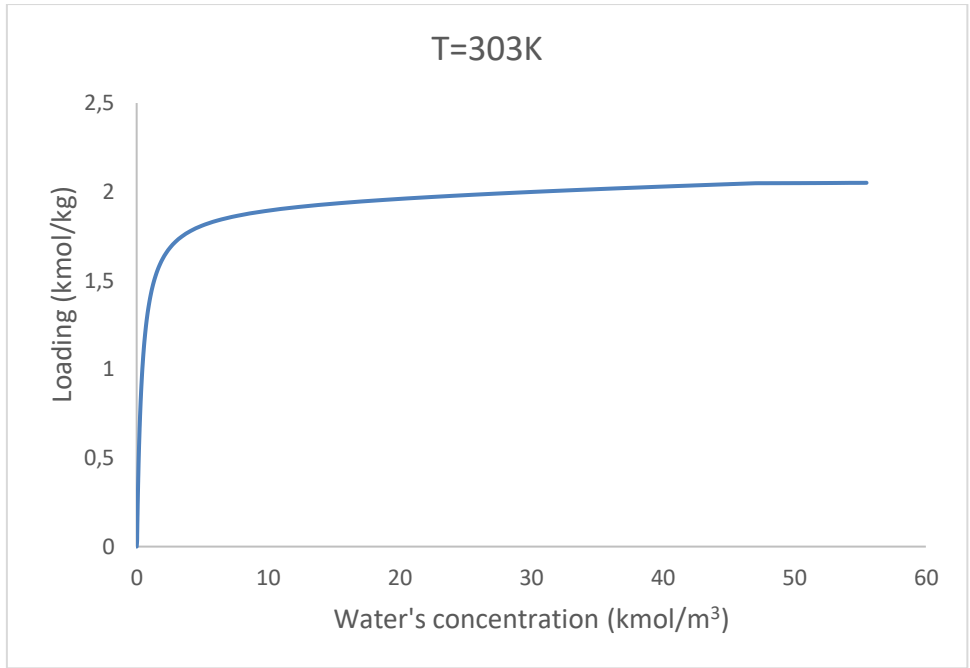


Figure 2.4 Chart of the loading subject to water concentration for 303K.

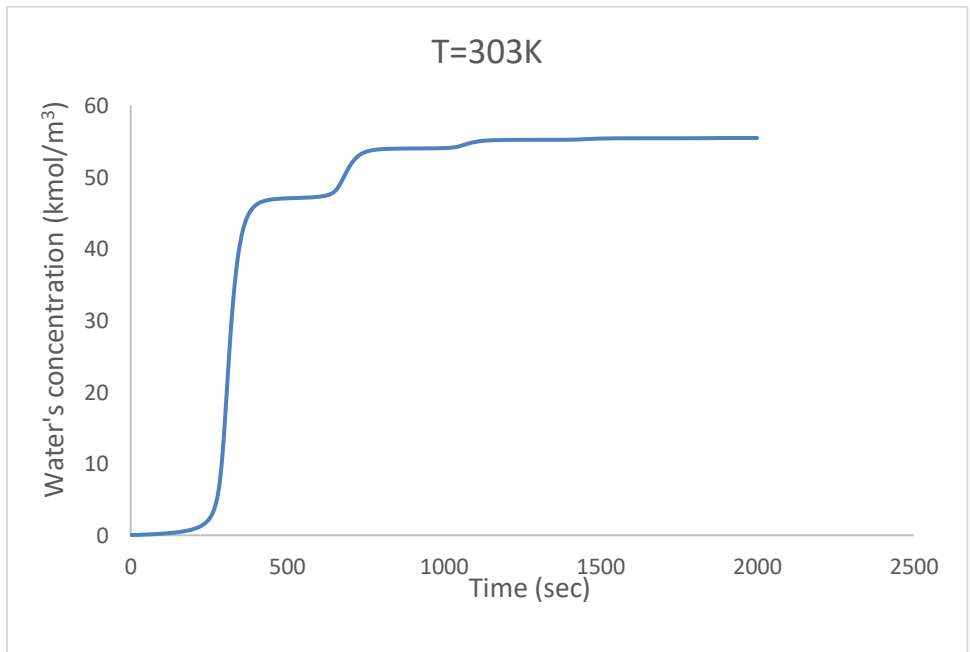


Figure 2.5 Chart of the water's concentration subject to time for 303K.



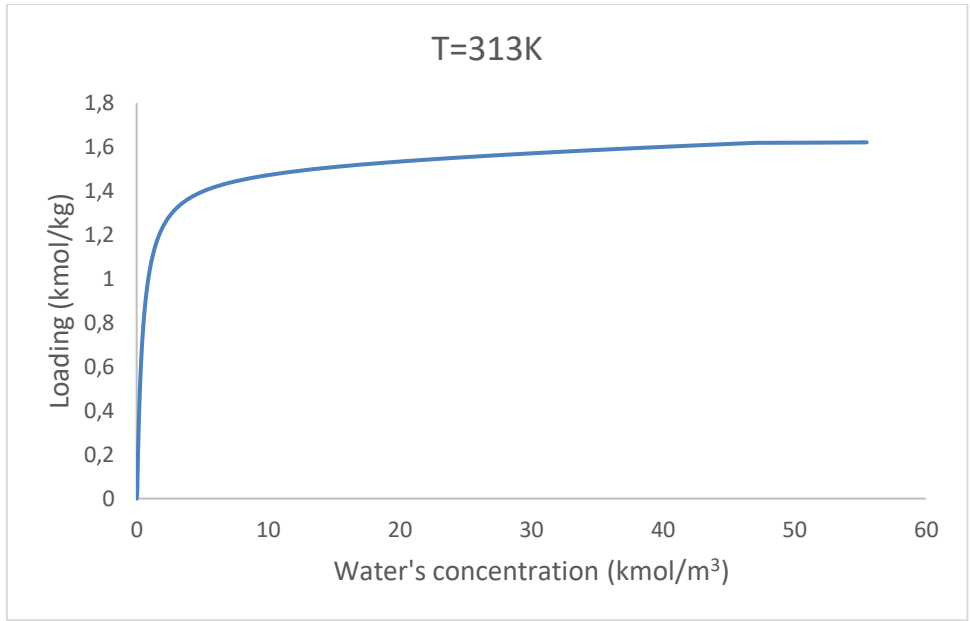


Figure 2.6 Chart of the loading subject to water concentration for 313K.

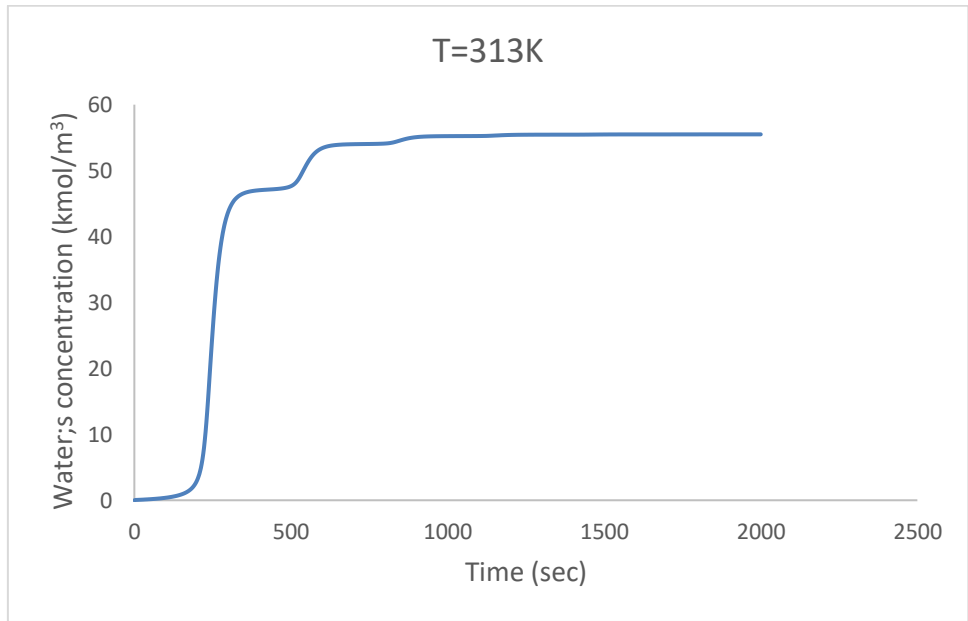


Figure 2.7 Chart of the water's concentration subject to time for 313K.

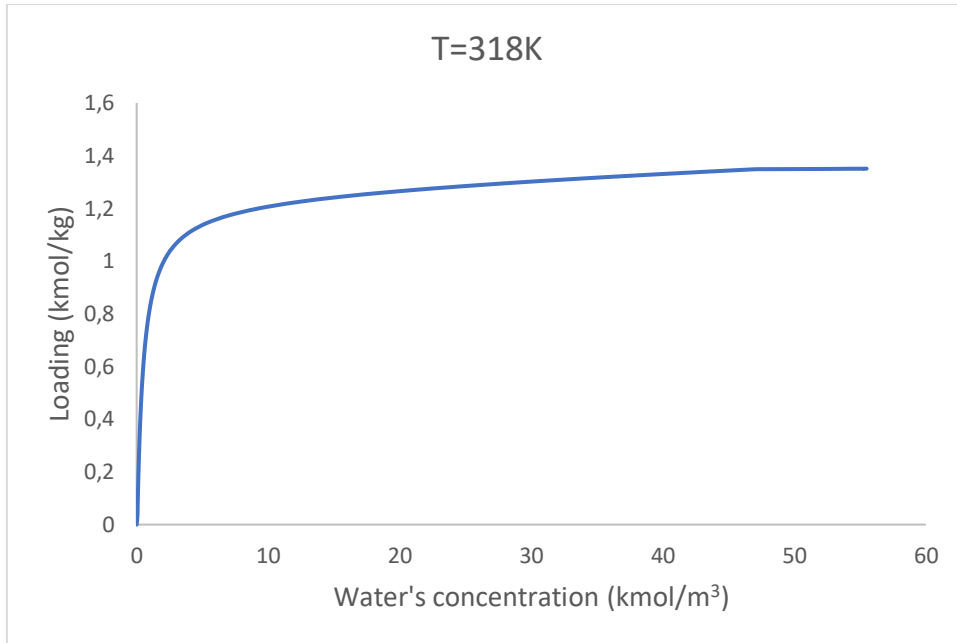


Figure 2.8 Chart of the loading subject to water concentration for 318K.

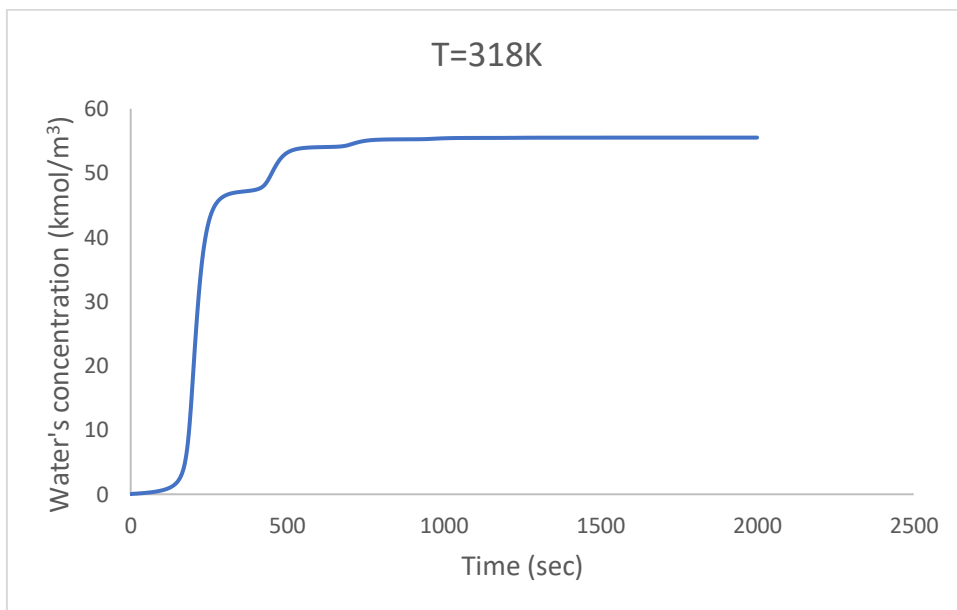


Figure 2.9 Chart of the water's concentration subject to time for 318K.

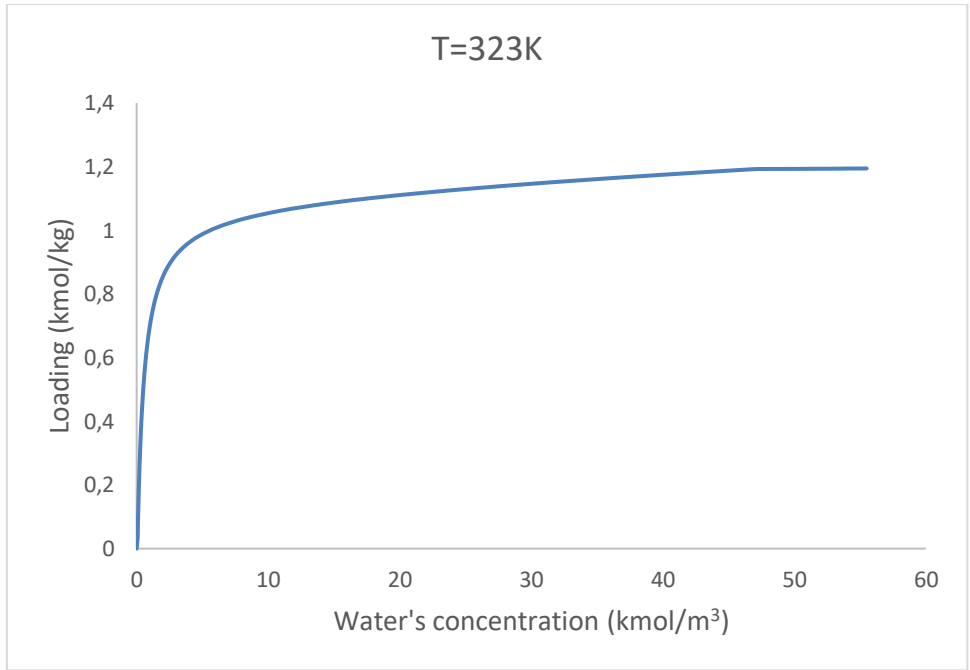


Figure 2.10 Chart of the loading subject to water concentration for 323K.

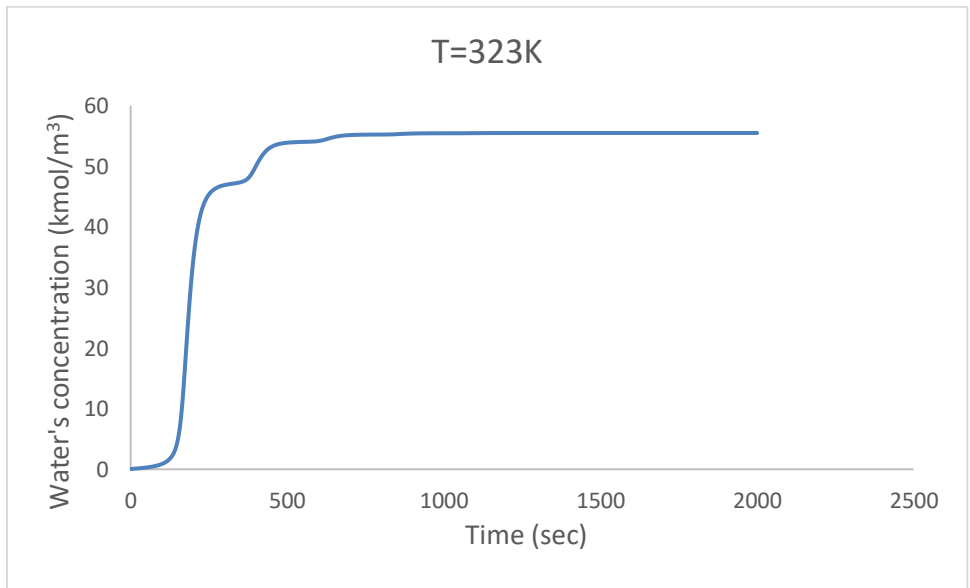


Figure 2.11 Chart of the water's concentration subject to time for 323K.

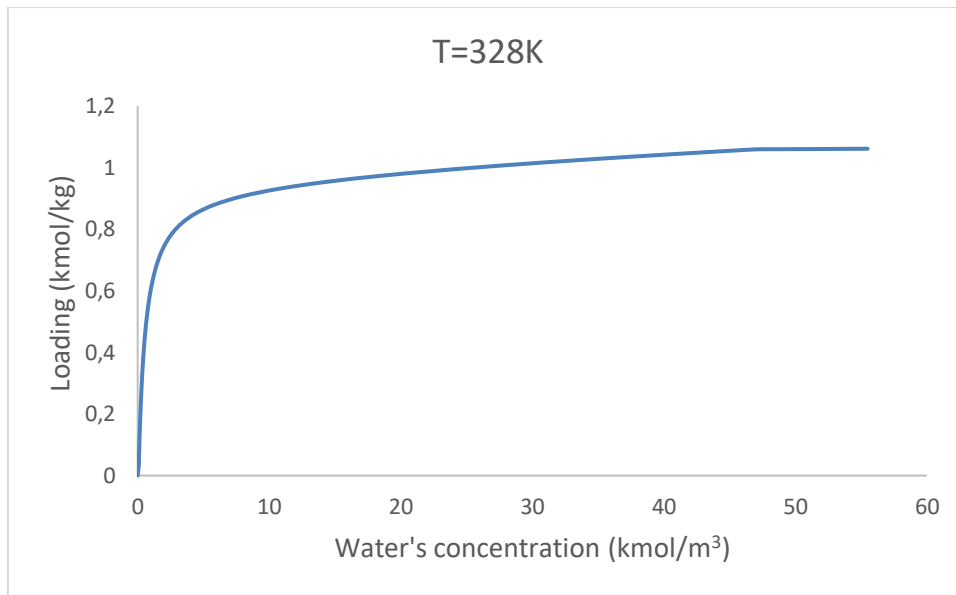


Figure 2.12 Chart of the loading subject to water concentration for 328K.

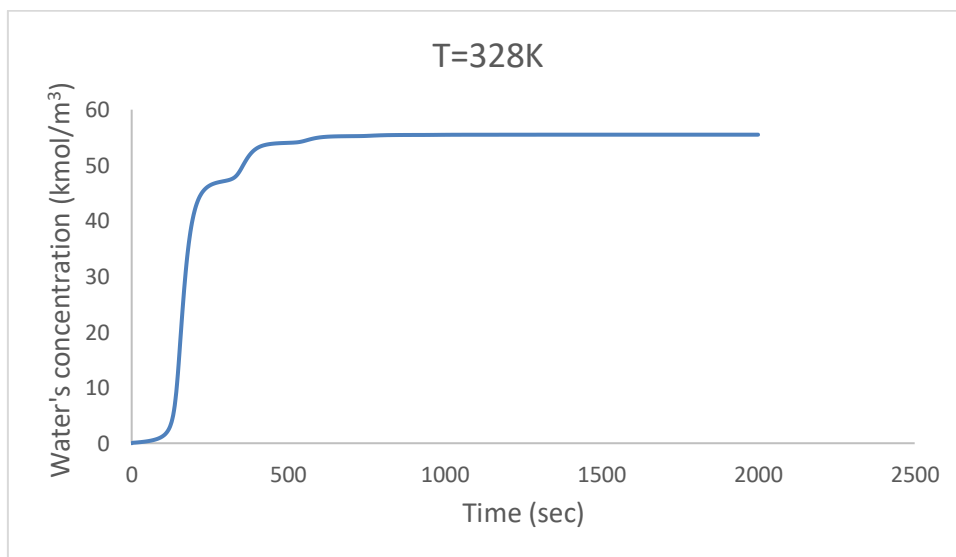


Figure 2.13 Chart of the water's concentration subject to time for 328K.

From the charts of loading subject to concentration for the five different temperatures, it is evident that the loading increases very quickly in the beginning of the adsorption process and after when it reaches the maximum value is constant. This early increase can be interpreted as the result of the value of the mass transfer coefficient.

Moreover, the loading reaches first his maximum value and after the concentration of water does. Again, the reason of this is the value of the mass transfer coefficient. Namely, the mass transfer coefficient plays a significant role in the form of the curve. The bigger the value is, the faster the loading reaches its maximum value. So, the curve of the first chart can be also linear or it can have the hollow reversely. At last, when the loading and the concentration reach the maximum values the process continues with these constant values.

The maximum value is a result of the temperature and the isotherm parameters and it is going to be analyzed underneath.

The other five charts show the concentration of water which is adsorbed subject to time for the 5 temperatures. As it is evident, the concentration increases till it reaches a maximum value. However, the curve is not so smooth such as the curve of the loading subject to water's concentration. In the beginning, the process of adsorption is slow because as it is said before, the loading needs also some time to reach its maximum value, so the concentration of water increases slowly. After that, when the loading is maximum, the concentration increases faster till it maximizes. In this phase, the curve has some anomalies in order to reach as smooth as it can the maximum value. That is happening because the increase is very fast. Finally, when it is maximum at the value of  $55,5 \text{ kmol/m}^3$ , it maintains constant.

These charts show a lot of how the adsorption is happening and also make easy the comparison of the charts in different temperatures.

At this moment, the next two charts will present the different runs in order make a comparison between the different temperatures. The charts are a combination of the 10 charts above for a better comparison.

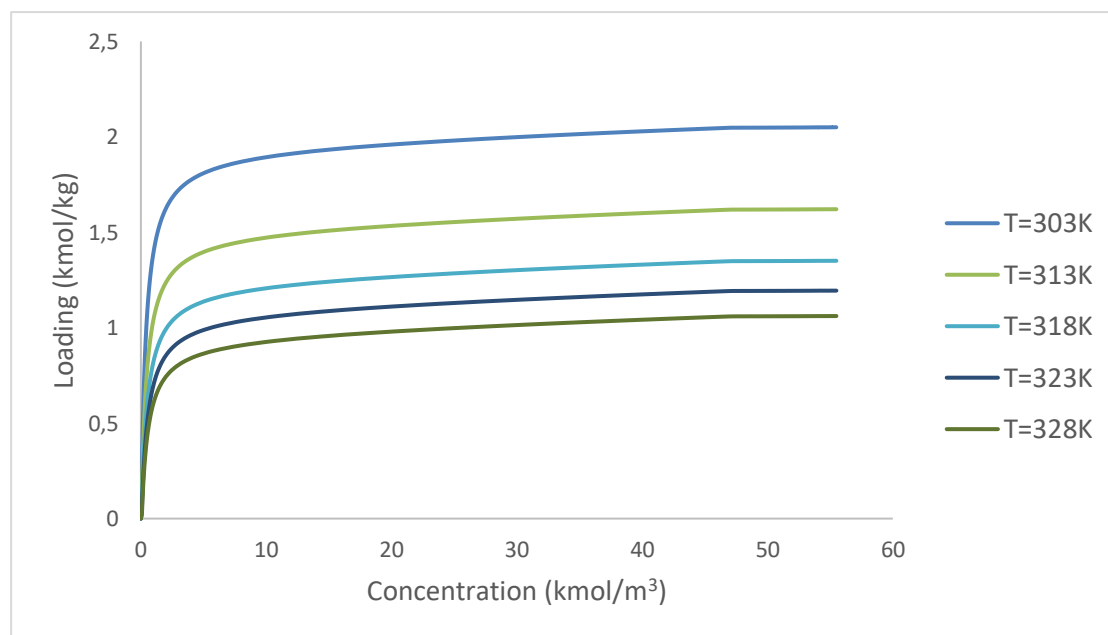


Figure 2.14 Chart of the loading in different temperatures.

The above chart presents the loading subject to concentration of water again but in different temperatures. The range of the temperature is 303K-328K.

However, the important part of this chart is the different values according to the different temperatures. The bigger the value of the temperature is, the smaller the loading is, namely, these two magnitudes are in reverse proportion. With the increase of the temperature, the loading decreases, and this is evident from the maximum value of the loading. This decrease

is not laminar but as it is apparent, this decrease is getting smaller with the increase of the temperature.

Moreover, the reason of this difference is result of the isotherm parameters. These parameters have a connection with the temperature so, the change of the temperature leads to a change of these parameters. Especially, the change is reverse than the change of the temperature. For this reason, the loading has the same fluctuation as the isotherm parameters.

The scientific reason of the decrease of the loading is that the bed and especially the adsorbent has a better comportment in low temperature. As a result of this, adsorption cooling uses lower temperatures than the others methods of cooling. So, the “not so hot” product of every process in industry can be used in order to regenerate the adsorbent for adsorption and not be totally useless.

From the above chart except for the above conclusions, it is important that an equation can be exported. This equation can simplify the process of adsorption with the help of Aspen. It can use only the temperature in order to calculate the loading and it is not compulsory to find all the data for the Aspen such as the isotherm parameters or the mass transfer coefficient.

One last chart that can be shown is the next one in order to understand even better this example.

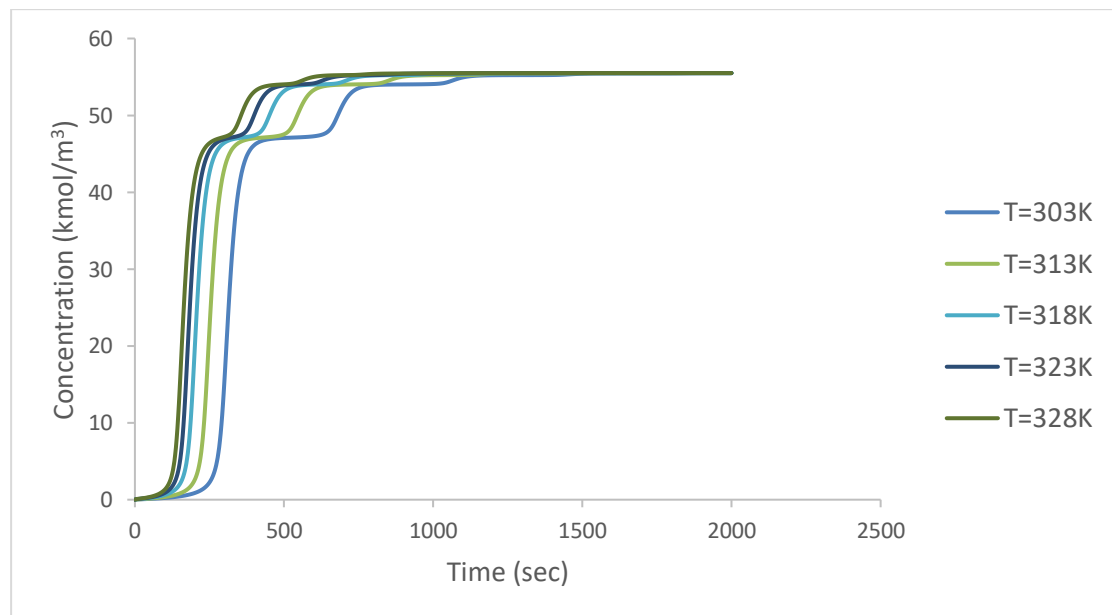


Figure 2.15 Chart of the water's concentration in different temperatures.

From the above chart, the curves have also the same form. However, there are some spotted differences. The first one is that the smaller the temperature is, the most time is needed in order to start the fast period of reaching the maximum value of concentration. The second one which is result of the first one is that the time of reaching the maximum value is bigger when the temperature is lower. The reason of these two differences between

the 5 curves are related to the loading. Because the loading in the low temperature is bigger, it needs more time to maximize so it starts later the fast period of reaching the maximum value of the water concentration.

So, in low temperatures, the loading is bigger but the water is adsorbed slower. However, if the dimensions of the bed or the feed increases the bigger loading is clearly better for the process of adsorption with the exact pair.

## 2.4 Zeolite-Water

The zeolite-water is the one of the first pairs which is studied for adsorption cooling and especially in heat pumps. It can be used in industry and for domestic cooling because of the low temperatures which is used for the regeneration of the zeolite as it was mentioned before. However, the low efficiency and the high cost are two drawbacks of this technology in order to be used widely.

The specific pair many times instead of pure water, it has a mixture of water and ethanol. So, the runs in this part of the thesis is going to be with the mixture and not with pure water because in the papers the isotherm parameters are used for a mixture as well.

In the beginning, it is important to choose the appropriate type of bed, “liquid” or “gas”. In this example, both types were used but the results, which resemble with the ones of the paper from which the isotherm parameters were taken, are these ones with the use of the “liquid” bed and parts, so, the procedure of the “liquid” type is going to be explained more thoroughly. For the above reason in order to study this pair, is better to use “liquid” parts.

For the “liquid” bed and all the other parts, “liquid” feed, “liquid” product and “liquid” connection. The Flowsheet in Aspen Adsorption is the same with the previous example so it does not be shown again.

The parameters which are constant in every run are presented in the tables underneath. The first table presents the parameters which specify the bed and the type of adsorbent which is inside it and the second these ones which specify the process of the adsorption.

*Table 2.4 Constant parameters for Aspen Adsorption*

Parameter	Value
Feed flowrate	$5 \cdot 10^{-6} \text{ m}^3/\text{sec}$
Pressure	1,2 bar
Height of adsorbent layer	34,3 mm
Internal diameter of adsorbent layer	24 mm
Inter-particle voidage	0,321
Intra-particle voidage	$1 \cdot 10^{-10}$
Solid density	$770 \text{ kg}/\text{m}^3$
Ethanol constant mass transfer coefficient	$1 \cdot 10^{-10} \text{ sec}^{-1}$
Water constant mass transfer coefficient	$2,0 \text{ sec}^{-1}$
Darcy's pressure drop coefficient	$1 \cdot 10^{-3}$
Specified flow direction	0

Table 2.5 Types of the models

Parameter	Type
Material balance assumption	Convection only
Pressure drop assumption	Darcy's law
Kinetic model	Fluid linear lumped resistance
Isotherm model	Langmuir 1
Energy balance	Isothermal

As it is obvious, in these two tables there are some differences with the corresponding tables of the previous pair. The reason is that the parameters have been taken from papers which has as the working pair the zeolite-water/ethanol and because of this they are preferred. Moreover, it is important to specify the type of the zeolite and according to the parameters the zeolite is 3A.

The isotherm model is again "Langmuir 1" because only this model is specified and have a correlation between the theory and the Aspen Adsorption as it was mentioned. The equation in this example about the loading is the underneath.

$$q = \frac{q_0 * K * c}{1 + K * c} \quad (2.5)$$

The isotherm parameters according to the above equation are the following,

$$IP_1 = q_0 * K \quad (2.6)$$

$$IP_2 = K \quad (2.7)$$

The values of the  $q_0$  and  $K$  are taken from the paper [66].

Plus, the isotherm parameters which are changed are in the table underneath. There are only for water because ethanol is not adsorbed. For this reason, the value of isotherm parameters of ethanol is  $1 * 10^{-10}$  and constant through the runs.

Table 2.6 Isotherm parameters of water

Temperature (K)	IP1	IP2
298	0,073987	0,307
313	0,03404	0,148
323	0,01806	0,086
333	0,00931	0,049

It is useful to explain the procedure of the runs first. For every temperature, the mixture of the water/ethanol is changing, namely the concentration of the two components is fluctuated. The values of the of the pure concertation of water and ethanol are 55,5 kmol/m<sup>3</sup> and 17,12 kmol/m<sup>3</sup> respectively. The pure values of the concentration have been calculated in matlab for constant temperature of 273K and pressure of 1 atm. These two values are multiplied with the composition of the mixture. The table underneath presents the different composition and the concentration of the two components



Table 2.7 Composition-concentration of the mixture

Composition of water(%)	Concentration of water(kmol/m <sup>3</sup> )	Composition of ethanol(%)	Concentration of ethanol(kmol/m <sup>3</sup> )
0	0	100	17,12
10	5,55	90	15,408
25	13,875	75	12,84
50	27,75	50	8,56
75	41,625	25	4,28
100	55,5	0	0

At last, in the tab “Initials” the initial values of the concentration of the two components are 17,12 kmol/m<sup>3</sup> for the ethanol and 0 kmol/m<sup>3</sup> for water. Generally, inside the bed it is good not to have any of the adsorbate and have full of the second component which is not adsorbed.

About this example the charts, which are going to present in order to understand a bit better the adsorption of water/ethanol with zeolite, differ from the charts of the previous pair. The results are going to show the difference in the loading subject to the initial composition of the mixture and the temperature again. There are two charts for each temperature.

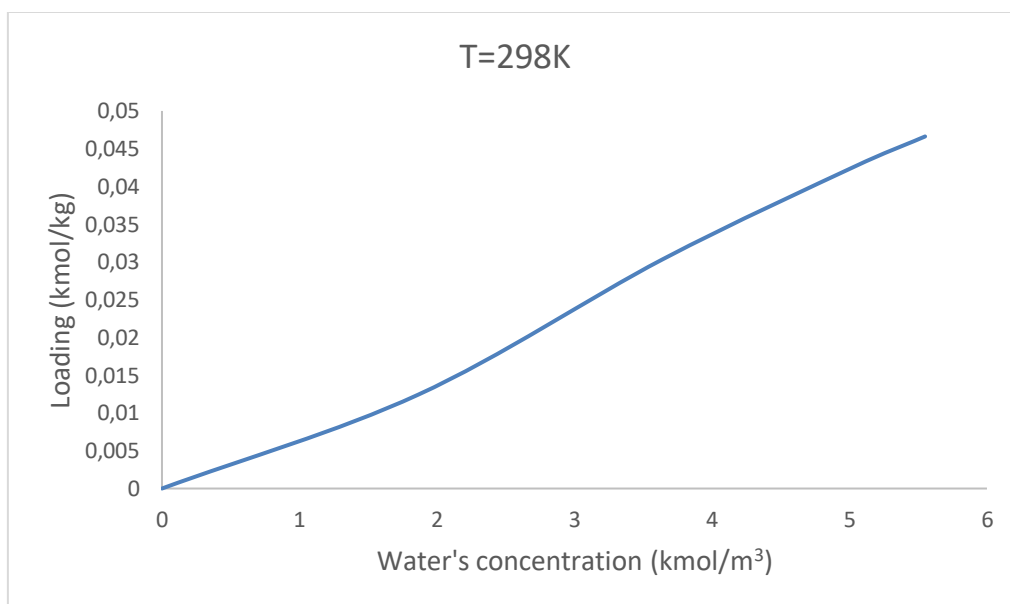


Figure 2.16 Loading subject to water's concentration for 298K.

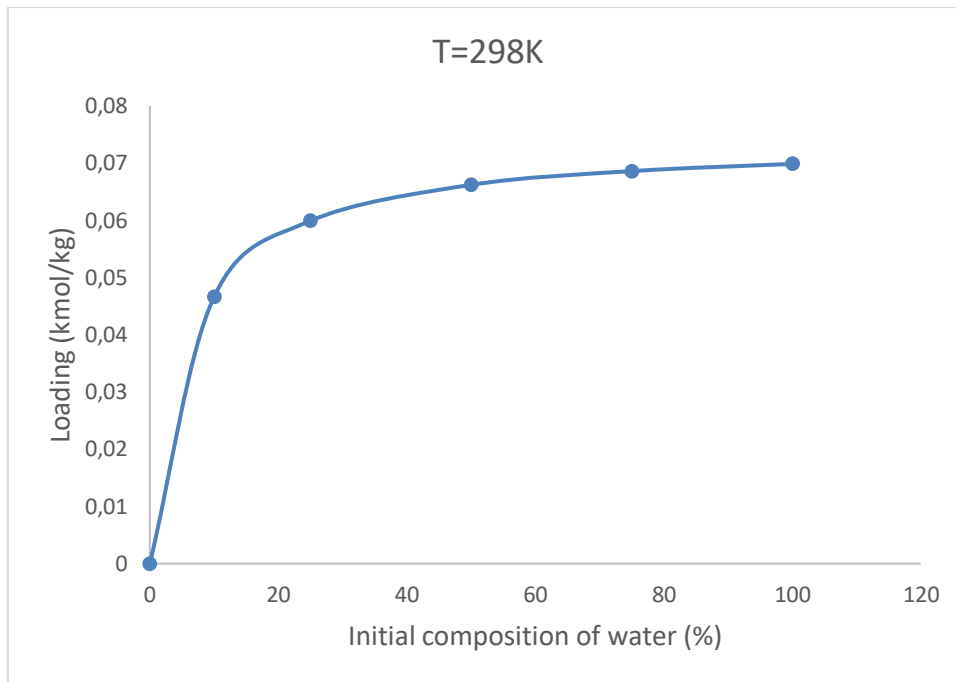


Figure 2.17 Loading subject to initial composition of water for 298K.

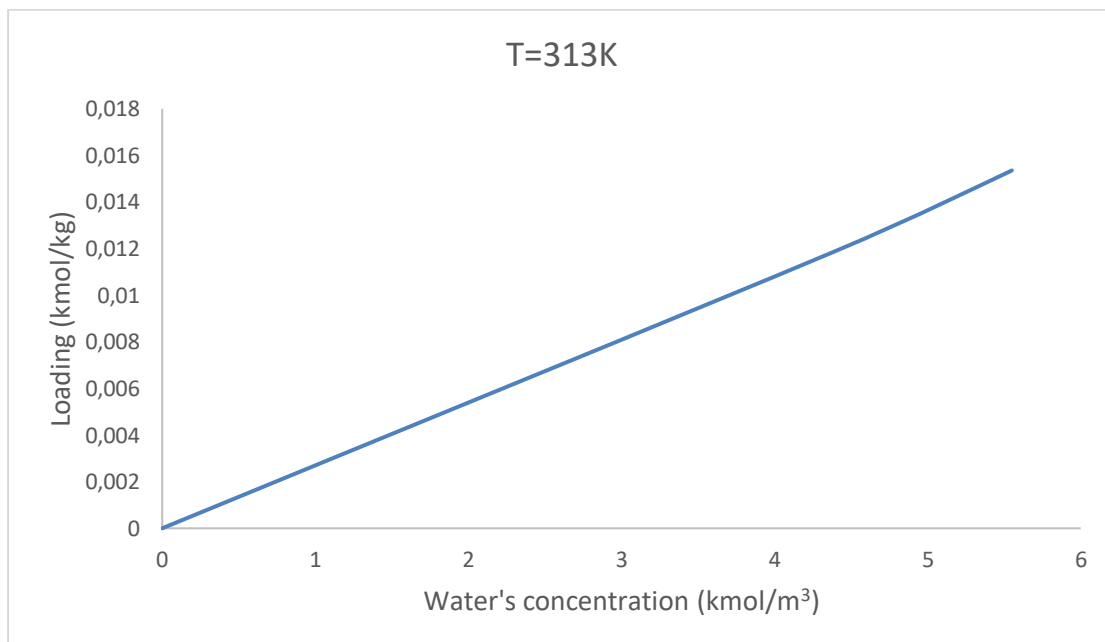


Figure 2.18 Loading subject to water's concentration for 313K.

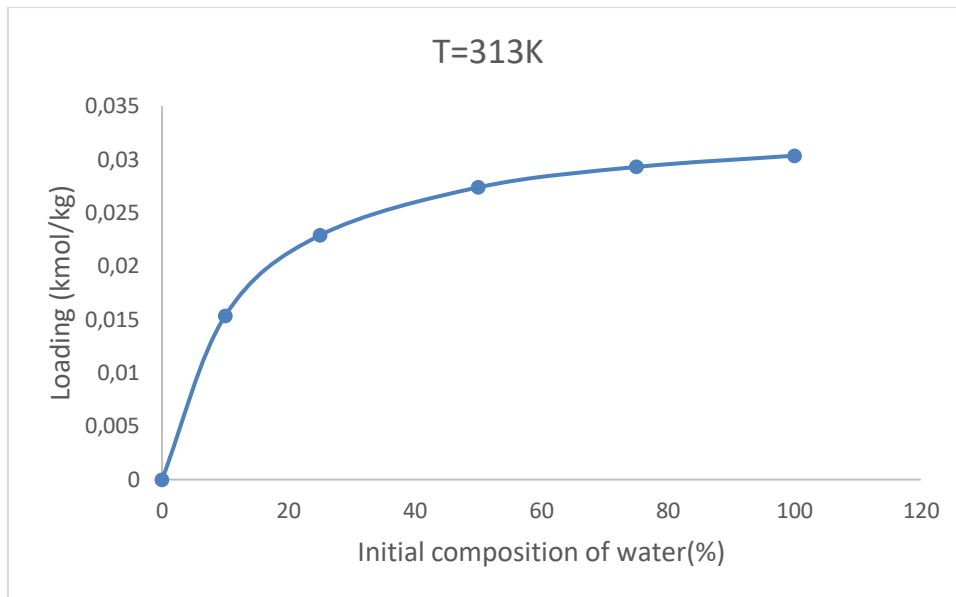


Figure 2.19 Loading subject to initial composition of water for 313K.

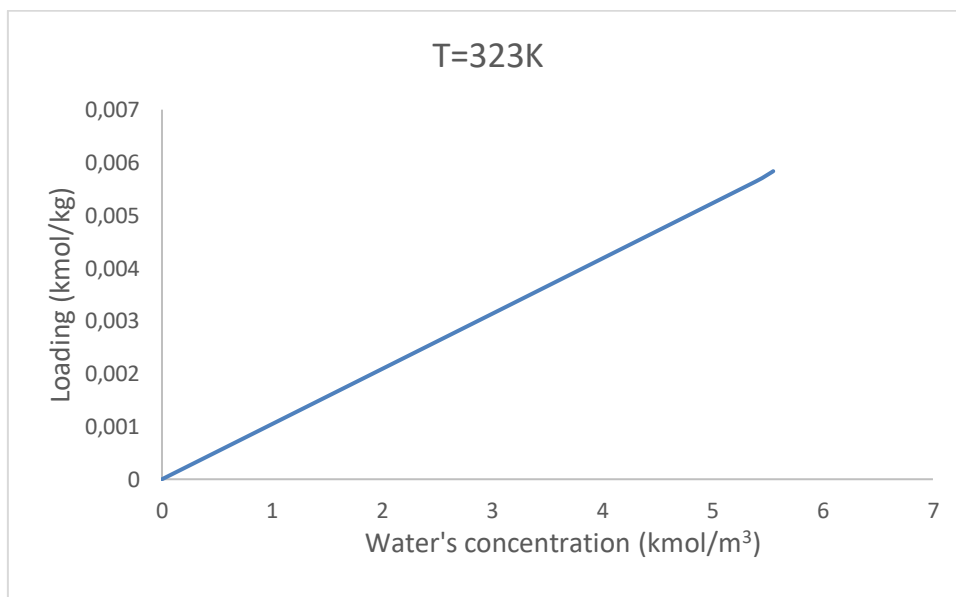


Figure 2.20 Loading subject to water's concentration for 323K.

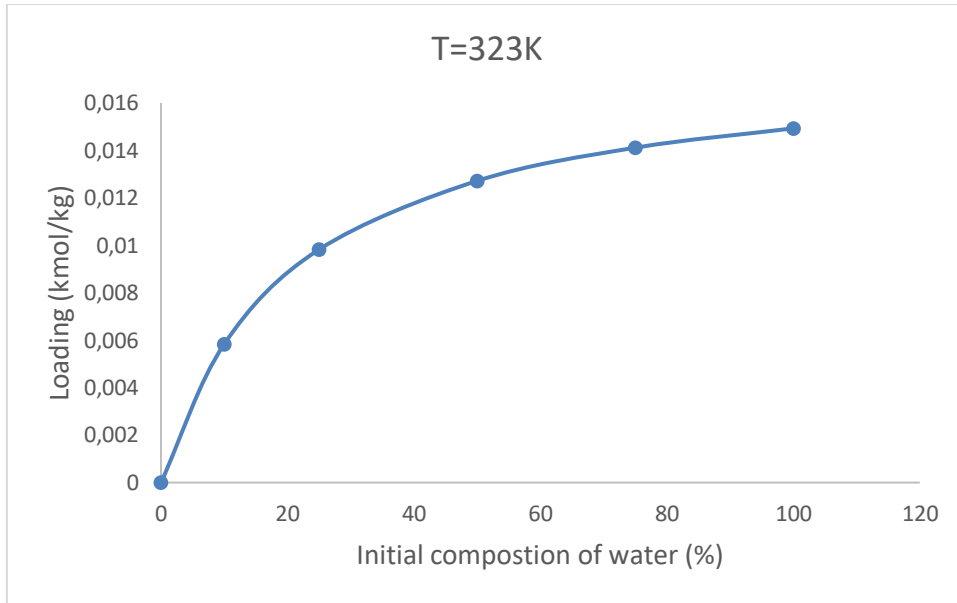


Figure 2.21 Loading subject to initial composition of water for 323K.

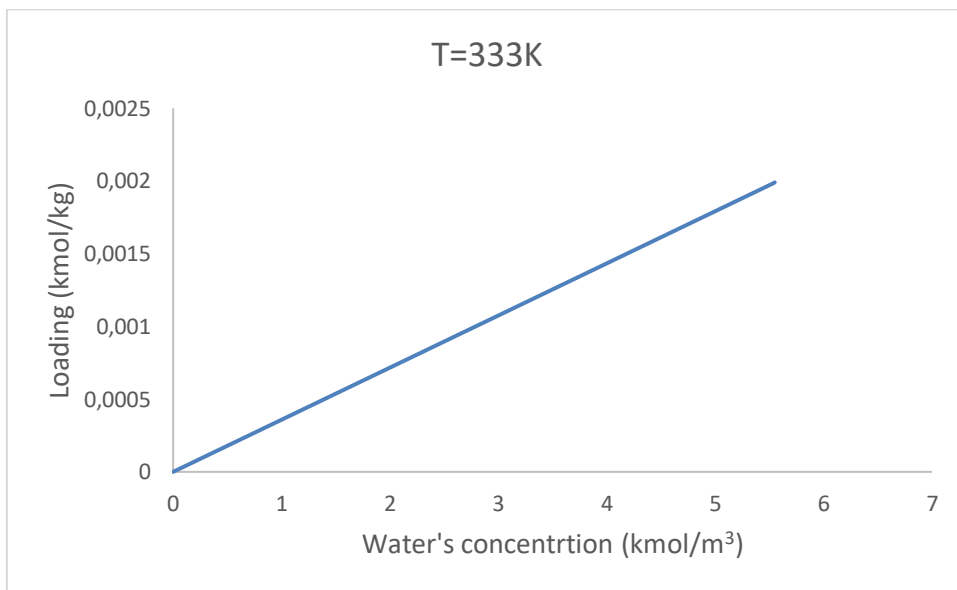
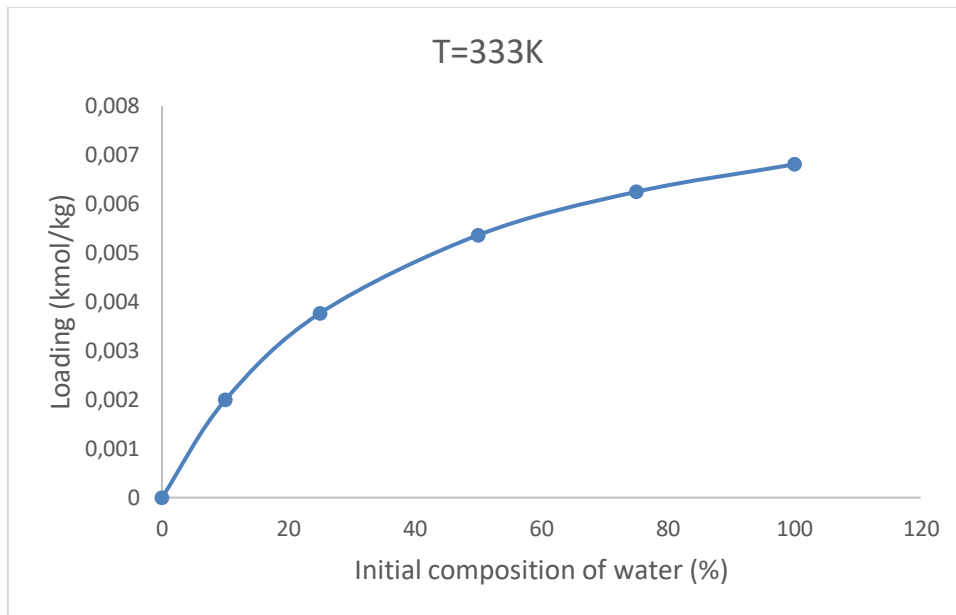


Figure 2.22 Loading subject to water's concentration for 333K.



*Figure 2.23 Loading subject to initial composition of water for 333K.*

In order not to be a misunderstanding the concentration in x axe in the charts of loading subject to water's concentration is the concentration of water which is adsorbed and not the initial concentration/composition of water. The maximum value of 5,55 kmol/m<sup>3</sup> is different from the pure concentration which is used in the previous example because of the use of mixture. As it is evident in those charts, the curves do not have the same form as the corresponding curve of the pair of activated carbon-water. These curves are almost linear and the loading with the concentration are increasing together. This difference may be due to the different adsorbent which is used in this case. So, about this pair the loading and the concentration reach almost together their maximum value. Also, it is obvious that the maximum value of the loading is smaller of the corresponding value of activated carbon-water and the main reason is the isotherm parameters. The isotherm parameters have a narrow bond with the temperature and also with the adsorbent. The initial mixture composition for these curves is 90% ethanol and 10% water.

According to the others charts, the maximum value of the loading increases when the initial composition of water also increases. However, this raise is not linear. It is obvious that loading increases more in the smaller compositions of water than in the big ones. So, above 50% of water in the mixture the maximum value of loading does not have a big change. As a result of this, the use of mixture does not have a big difference in the maximum loading value and it is preferred from pure water because of some advantages such as smaller corrosion in the pipes.

At this moment, it is important the comparison of these two charts for the 4 temperatures. For this reason, underneath there is a combination of the above charts in order to be more obvious the differences. The first one is the loading subject to the water's concertation for the initial composition of mixture, 90% ethanol and 10% water.

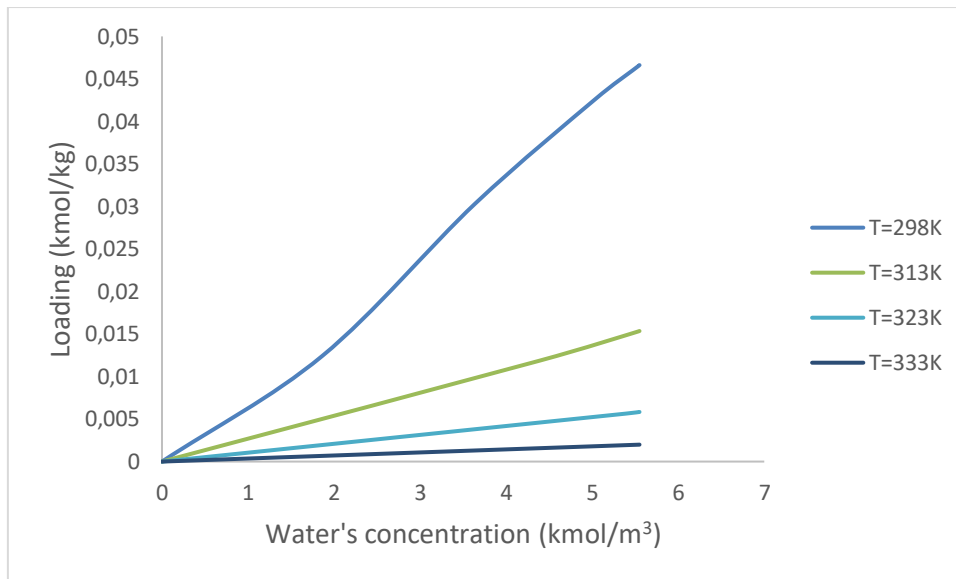


Figure 2.24 Loading in 4 different temperatures.

From the above chart it is evident that the lower the temperature is, the smaller the loading is. This chart has the same result as the corresponding one for the previous pair. The result is that with smaller temperature the bed can adsorb more water and as it is mentioned previously is the reason why adsorption cooling uses low temperatures. The different values of the 4 curves in constant concentration is due to the isotherm parameters which are used. The isotherm parameters as before are proportionate with the loading but invert analog with the temperature.

It is important to make a comparison between the two pairs and especially about the maximum value of the loading. As it is overt, the different form of the curves is the result of a lot of parameters such as the mass transfer coefficient, the kinetic model, the isotherm parameters, the use of a mixture and not pure water etc. The most important part, however, is the maximum value of the loading. It is obvious that in the pair of zeolite-water/ethanol the loading is smaller of the corresponding value of the first pair. The main reason is the isotherm parameters which are used in the two examples. However, the use of mixture or the dimensions of the bed also play a role. So, it cannot be a further comparison between these two pairs because of many different values in parameters.

The next chart presents the curve of maximum value of the loading subject to the initial composition of the mixture for 4 temperatures.

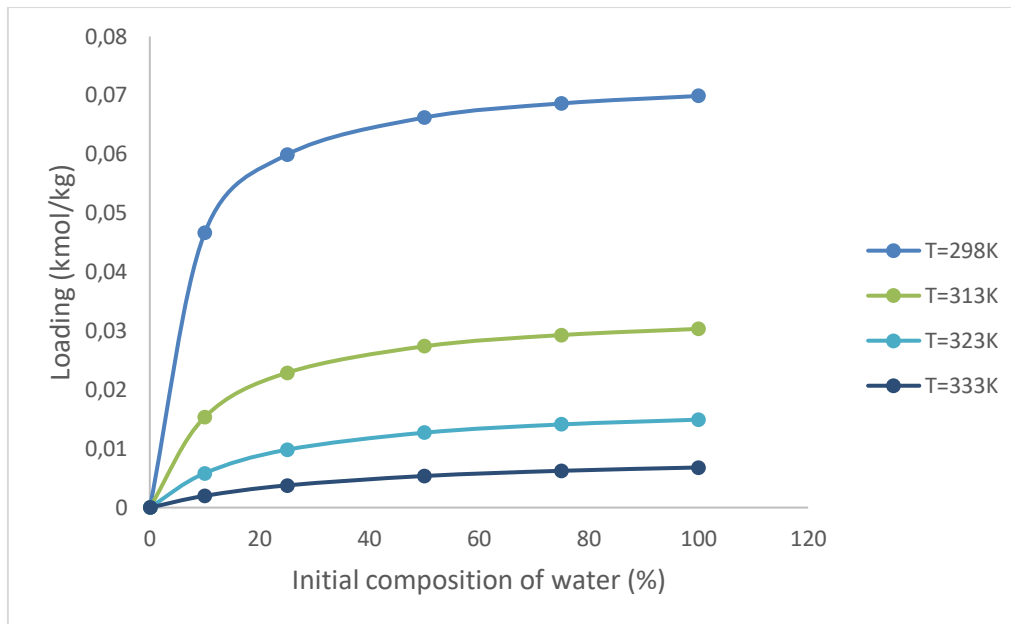


Figure 2.25 Loading subject to initial composition of the water in 4 temperatures.

This chart is very similar with the corresponding chart from the paper from which the isotherm parameters have been taken. The similarity is only in the form of the curve and not in the results. The reason of this is the lack of data that the paper has. So, it was necessary the use of random values for the parameters such as the dimensions of the bed. However, the same form of the chart shows that in the paper the liquid form of bed has been used.

According to the chart, it is apparent again that the lower the temperature is, the higher the maximum values of the loading are. And this is happening for each initial composition of the water.

As on the previous example, for the last two charts two equations can be exported in order to use only the temperature as data to calculate the loading.

At that moment, it will be presented shortly the same example but with the use of 'gas' parts in order to build the process. First of all, it is good to present the extra parameters in a table. The other parameters are the same as before.

Table 2.8 Additional parameters

Parameter	Type/Value
Flowrate	$8,75 \cdot 10^{-6}$ kmol/sec
Adsorbent particle radius	0,65 mm
Water's constant mass transfer coefficient	$110 \text{ sec}^{-1}$
Momentum balance assumption	Ergun equation
Isotherm dependency	Concentration

The procedure of each run is the same as before when the "liquid" parts were used. At last, as it was mentioned before, inside the bed there is only ethanol, so in the tab "Presets/Initials" for the two components the mole fraction is 1,0 for the ethanol and 0,0 for water.

Underneath, the 4 corresponding charts are going to be presented of “gas” parts in order to observe the differences.

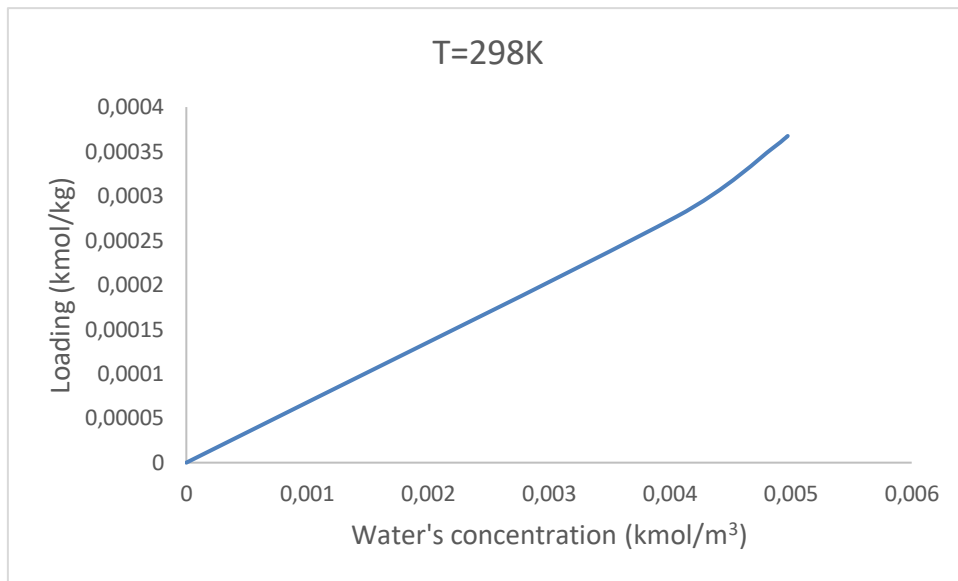


Figure 2.26 Loading subject to water's concentration.

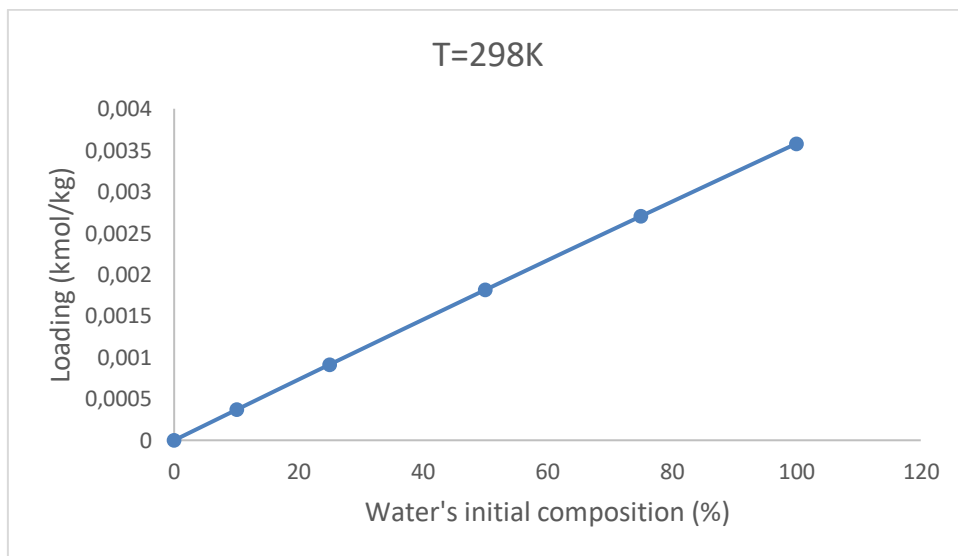


Figure 2.27 Loading subject to initial composition of mixture.



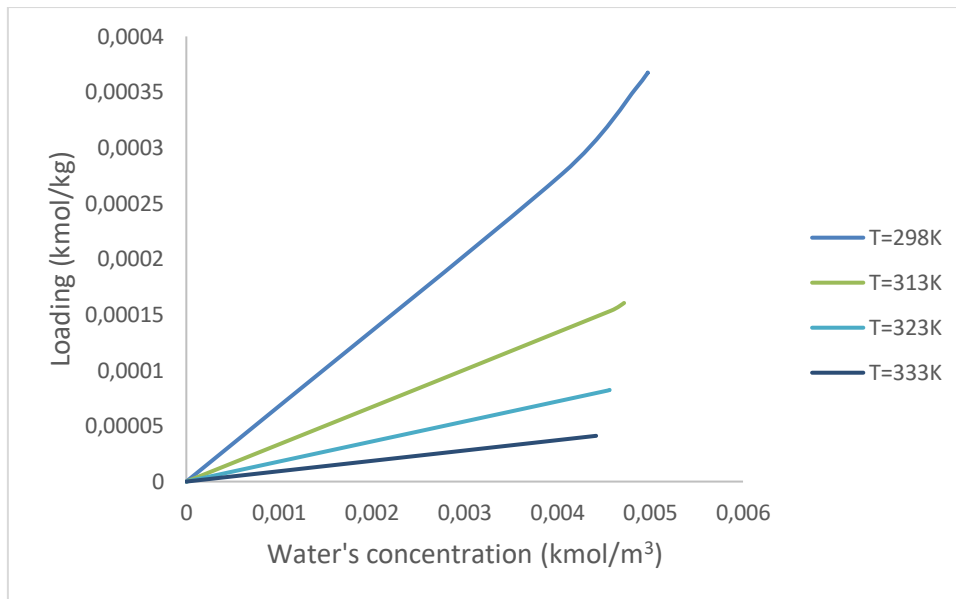


Figure 2.28 Loading in 4 different temperatures.

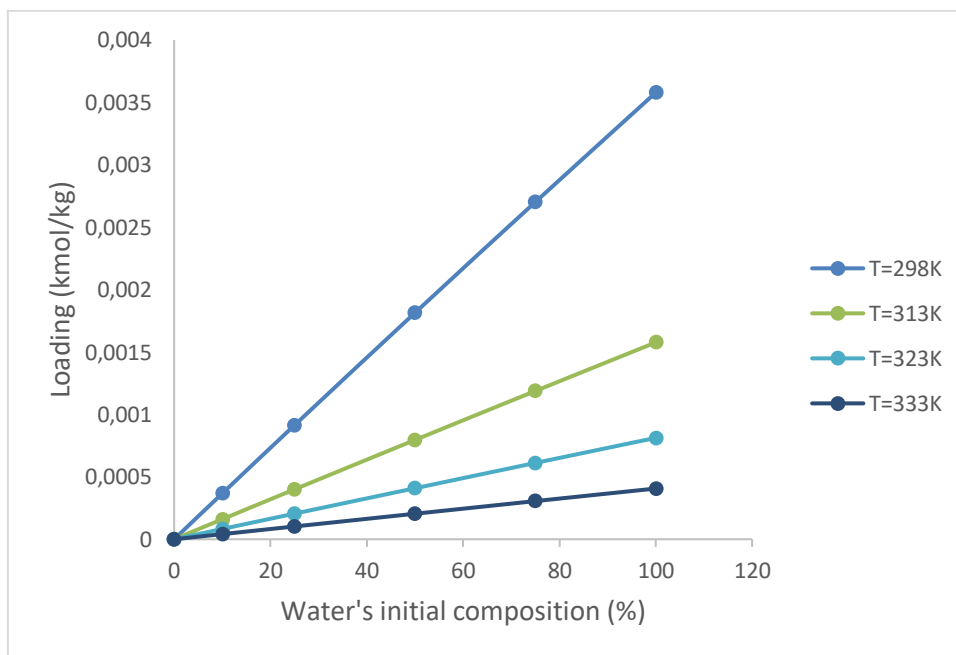


Figure 2.29 Loading subject to initial mixture composition in 4 temperatures.

For the runs with “gas” parts the individual charts for the 4 different temperatures are not presented but only the two of temperature 298K are.

From the above charts, it is obvious that there are some differences with the corresponding ones in liquid bed. First of all, the loading is a lot smaller in the case of gas bed. The reason of this difference is the parts which are used. In the gas phase the water which is adsorbed may be less and so the loading.

One more difference is that with the change of temperature the maximum value of water's concentration also changes. This was not happened with the liquid bed. The reason of this is that with the increase of temperature the concentration of water reduces for the same composition. As the composition stays constant (10% of water) the concentration will change.

One last difference and the most important is the form of the curve of the chart with loading subject to initial composition of the mixture. As it is evident, the curve is linear. This may happen because in gas phase the selection of "Langmuir 1" as isotherm method is not the appropriate.

In conclusion, both types of bed have the same result. When the temperature raises, the loading reduces. Plus, the purer the mixture with water is, the bigger the loading is. However, the values are different.

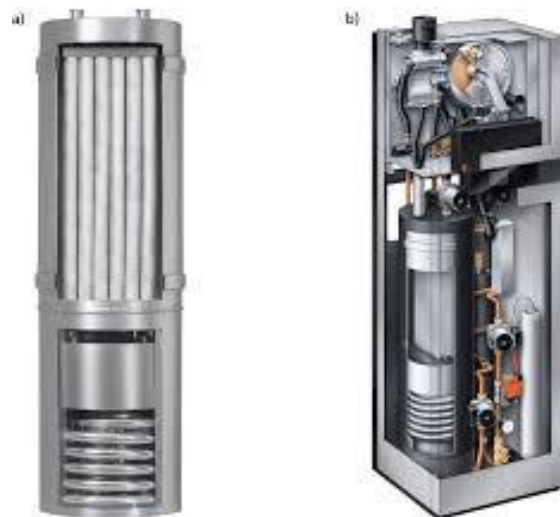


Figure 2.30 Zeolite-water heat pump [67].

## 2.5 Zeolite-Air

The zeolite is a very common adsorbent as it was mentioned. For this reason, it is useful to study another pair with the zeolite for cooling. The adsorbate is not water but air and the cooling procedure happens with the method of air drying. Namely, the zeolite adsorbs the water which is in the air. With this process, the air which is became colder and that is how the cooling happens. Except for the water, the zeolite adsorbs also carbon dioxide in order to clean the air. However, the adsorption of water is important and it is going to be study.

First of all, as in the previous examples, it is useful to present the data which are used. The first table is about the values of parameters in order to specify the bed and they remain constants.

*Table 2.9 Parameters' values*

Parameter	Value
Feed flowrate	$8,75 \cdot 10^{-6} \text{ m}^3/\text{sec}$
Pressure	1,2159 bar
Height of adsorbent layer	34,3 mm
Internal diameter of adsorbent layer	24 mm
Inter-particle voidage	0,321
Intra-particle voidage	$1 \cdot 10^{-10}$
Solid density	$760 \text{ kg}/\text{m}^3$
Carbon dioxide constant mass transfer coefficient	$70 \text{ sec}^{-1}$
Water constant mass transfer coefficient	$110 \text{ sec}^{-1}$
Nitrogen constant mass transfer coefficient	$1 \cdot 10^{-10} \text{ sec}^{-1}$
Oxygen constant mass transfer coefficient	$1 \cdot 10^{-10} \text{ sec}^{-1}$
Specified flow direction	0

As it is obvious, the components which are used are the four which are in the air. From this table is also evident that only water and carbon dioxide are adsorbed. Moreover, with the above data the type of zeolite which is used is 4A in this example.

Because in this example the key-factor which is going to be studied is the loading subject to the pressure, the initial composition of the air and the isotherm parameters are constant and are presented in the next two tables.

*Table 2.10 Initial composition*

Parameter	Value(%)
Oxygen	0,209834
Nitrogen	0,789375
Carbon dioxide	0,0003955
Water	0,0003955

*Table 2.11 Isotherm parameters*

Component	IP1	IP2
Oxygen	0	0
Nitrogen	0	0
Carbon dioxide	168,409	93349
Water	10504,6	795511

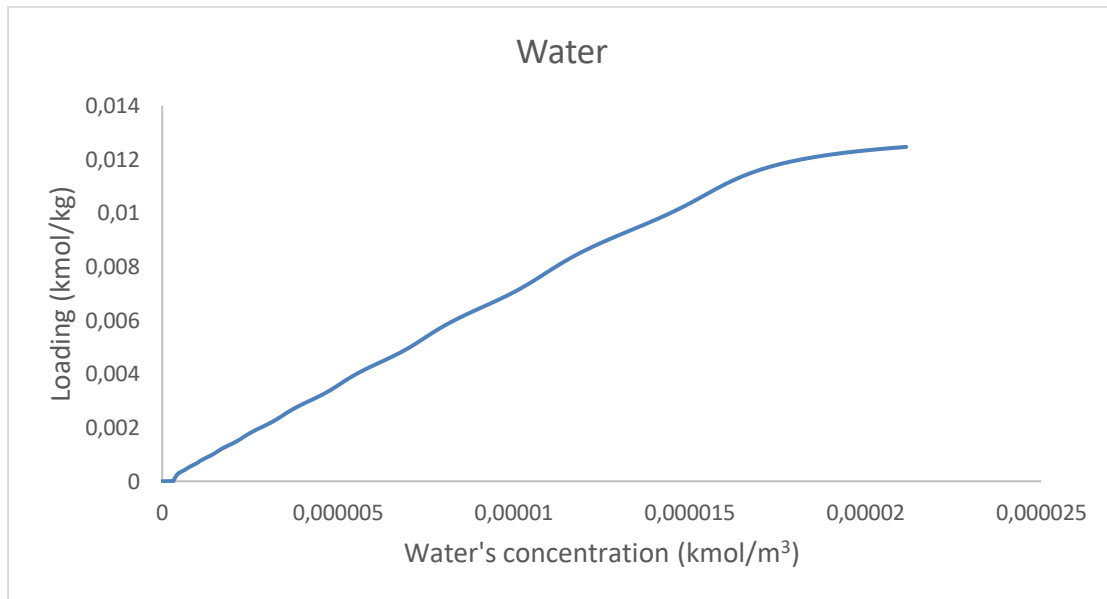
Moreover, it is important to specify the parameters for the process of adsorption. The constant values are presented in the next table.

*Table 2.12 Types of the models*

Parameter	Type
Material balance assumption	Convection only
Momentum balance assumption	Ergun equation
Kinetic model	Fluid linear lumped resistance
Isotherm model	Langmuir 1 (concentration dependency)
Energy balance	Isothermal

These are the constant parameters for this example. At last, in the tab “Presets/Initials” the values of the mole fractions of the components are for nitrogen 0,79 and for oxygen 0,21. For the other two components the mole fraction is 0 because as it was mentioned, the bed has to be free from the components which are going to be adsorbed.

First of all, for the constant parameters it is useful to present a chart of the loading of the water which is adsorbed subject to the concentration as in the previous examples. This chart is underneath.



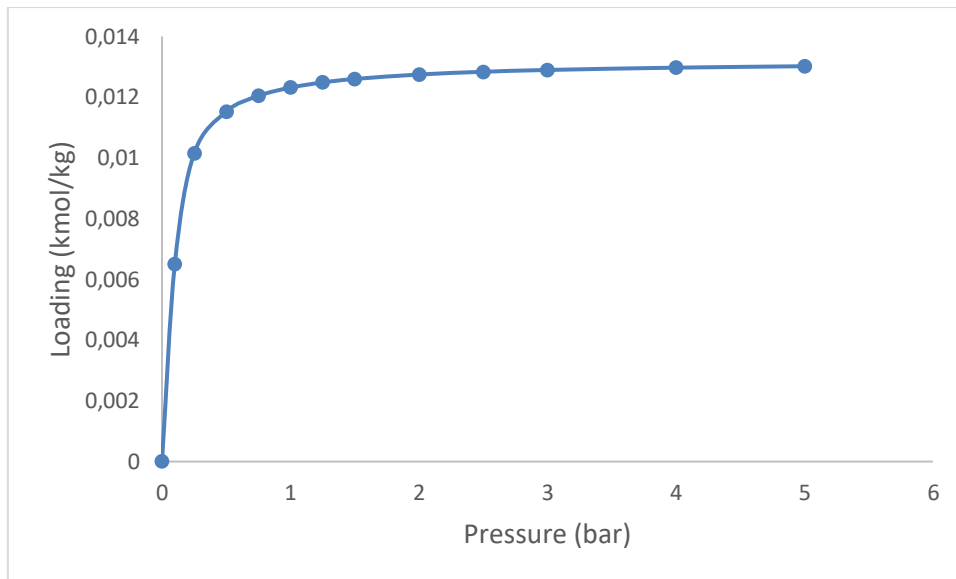
*Figure 2.31 Loading subject to water's concentration.*

From the above chart it is apparent that in this case the loading is not exactly linear with the concentration of water which is adsorbed. Moreover, the curve is not smooth but there are some anomalies. These anomalies may be due to the simultaneous adsorption of carbon dioxide.

The last part which “destroy” the linear curve is like that in order to reach smoothly the maximum value of the loading like in the example of activated carbon. One last observation, in the beginning of the curve it is evident that the water's concentration does not increase till the loading starts to increase.

One last conclusion is that the loading is big relative with the water's concentration in this example. The reason is the big value of the isotherm parameters for this example which are used.

At this moment, it is time to present the loading subject to pressure. For this reason, the choice of “gas” parts is forced because only with these parts the loading change with the change of the pressure. Firstly, underneath is the chart in order to have a first look of the correlation between the loading and the pressure.



*Figure 2.32 Loading subject to pressure.*

From the above chart, it is overt that with the increase of pressure, the loading also increases. It is useful to make a comment about the loading so, there will not be a misunderstanding. The values of the loading for each pressure is the maximum value which the loading reaches in every run.

The increase is not linear and that is important. In low pressures, the loading increases rapidly but after a value of pressure, the loading stays “constant”. At this example, this value is 1,25 bar approximately. That is important because in cases in which big loading is needed, the pressure is not needed to be too high to reach the value of loading. This means lower cost of the equipment because it is smaller. However, the form of the curve shows that there is an above limit from the loading.

At last, it is important to make an observation about the difference between the correlation of the loading with the pressure and the temperature from the previous examples. With the increase of the temperature the loading, as it is overt, decreases but with the increase of the pressure it also increases.

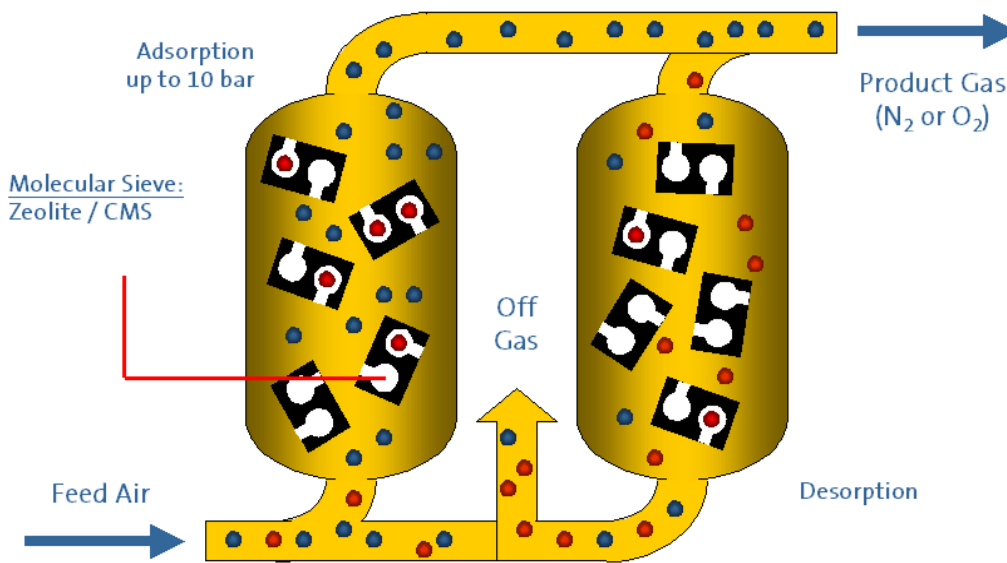


Figure 2.33 Air drying with adsorption [68]

## 2.6 Silica gel-Water

At this moment, the pair which is going to be studied is one of the most common and the one which is used widely in the industry for cooling and for domestic cooling. Silica gel-water is used for adsorption cooling and it is one of the most important pair for this technology. For this example, the study is about how the pressure and the temperature change the loading of the process.

At the beginning, it is good to explain the utilization of “gas” parts in the Aspen Adsorption. The “gas” parts can model better the change of the pressure because in Aspen Adsorption in the “liquid” parts there is not any change of the loading with the change of pressure. The parts which are used are the “gas” bed, the “gas” feed, the “gas” product and the “gas” connection. These parts can be taken from the libraries of the Aspen Adsorption. The Flowsheet of the process is the same as in the previous examples and it is not presented again.

As in the previous examples, there are some constant parameters and some which are changed. Firstly, the constant parameters are going to be presented. The parameters which are presented in the table underneath are the ones which specify the type of the adsorbent inside the bed and the dimensions of the bed.

Table 2.13 Constant parameters of Aspen Adsorption

Parameter	Value
Feed flowrate	$5 \cdot 10^{-6}$ kmol/sec
Height of adsorbent layer	34,3 mm
Internal diameter of adsorbent layer	24 mm
Inter-particle voidage	0,321
Intra-particle voidage	$1 \cdot 10^{-10}$
Solid density	850 kg/m <sup>3</sup>
Water constant mass transfer coefficient	110,0 sec <sup>-1</sup>
Adsorbent particle radius	0,015 mm
Specified flow direction	0

From the above table, it is obvious that some parameters are the same with the ones of the other examples such as the dimensions of the bed because the paper [69] from which the isotherm parameters were taken does not have these parameters. However, some parameters such as the density and the adsorbent particle radius have been taken from the paper which the isotherm parameters were taken in order to have better and as possible same results. After of the specification of these parameters, the adsorbent is specified and it is silica gel type A+++.

The next table is about the models which are used for the process of the adsorption and mostly the models are the same as in previous examples.

Table 2.14 Types of the models

Parameter	Type
Material balance assumption	Convection only
Momentum balance assumption	Ergun equation
Kinetic model	Fluid linear lumped resistance
Isotherm model	Langmuir 1
Energy balance	Isothermal

These parameters have not any difference from the corresponding ones in previous example and there will not be any explanation.

At this moment, it will be important to explain the parameters which are not constant and especially the isotherm parameters. As it was mentioned, the isotherm parameters are taken from the above paper. This paper has an equation (2.3) for the isotherm parameters subject to temperature. Because of that, it was easy to study a lot of temperatures.

$$C = \frac{q_0 * k_0 * \exp\left(\frac{H_{ads}}{R * T}\right) * P}{1 + k_0 * \exp\left(\frac{H_{ads}}{R * T}\right) * P} \quad (2.8)$$

From the above equation and the model of the “Langmuir” it is obvious which are the IP1 and IP2.

$$IP_1 = q_0 * k_0 * \exp\left(\frac{H_{ads}}{R * T}\right) \quad (2.9)$$

$$IP_2 = k_0 * \exp\left(\frac{H_{ads}}{R*T}\right) \quad (2.10)$$

The data for the equation is inside the paper and the only change which happened is in the measurement units. Because in the paper the loading is in “kg/kg” and in the Aspen the loading is in “kmol/kg” it was necessary to convert the units. This was happened with the division of the quantities which has in its units the unit “kg” with the molecular weight of the water, 18,01528 kmol/kg. The data is presented in the table underneath.

Table 2.15 Data for the isotherm parameters

Quantity	Value
C <sub>0</sub> (kg/kg)	0,4999
C <sub>0</sub> (kmol/kg)	0,027748667
K <sub>0</sub> (kPa <sup>-1</sup> )	0,00000543
H <sub>ads</sub> (KJ/kg)	2288,896
H <sub>ads</sub> (KJ/kmol)	41235,10233
R (KJ/(kmol*K))	8,314

At the next table the isotherm parameters are presented for every temperature.

Table 2.16 Isotherm parameters

Temperature (K)	IP1	IP2
303	1,920279557	69,20258833
308	1,472564959	53,06795368
313	1,138848848	41,04157007
318	0,887903473	31,99805897
323	0,697606677	25,14018726
328	0,552138202	19,89782817
333	0,440081919	15,85956991

It is evident that with the increase of the temperature the isotherm parameters decrease and that it will have an impact to the loading.

The runs in this example follow the next “plan”. For each temperature and as well for each pair of isotherm parameters, the pressure changes for 5kPa to 20kPa in order to observe the correlation of loading and pressure. Moreover, in temperatures above 303K in order to reach the value of the loading in 20kPa of temperature of 303K, the pressure increases till the loading reaches this value. The charts are going to explain better the results.

At this moment is good to present some charts in order to explain the results. First of all, the first charts are about the maximum value of the loading subject to several values of pressure for 7 temperatures.



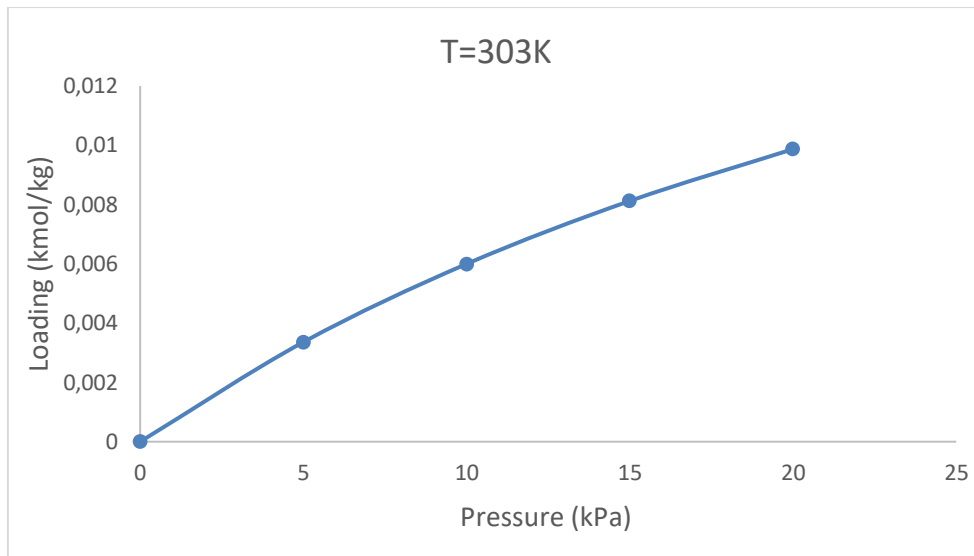


Figure 2.34 Loading subject to pressure at 303K.

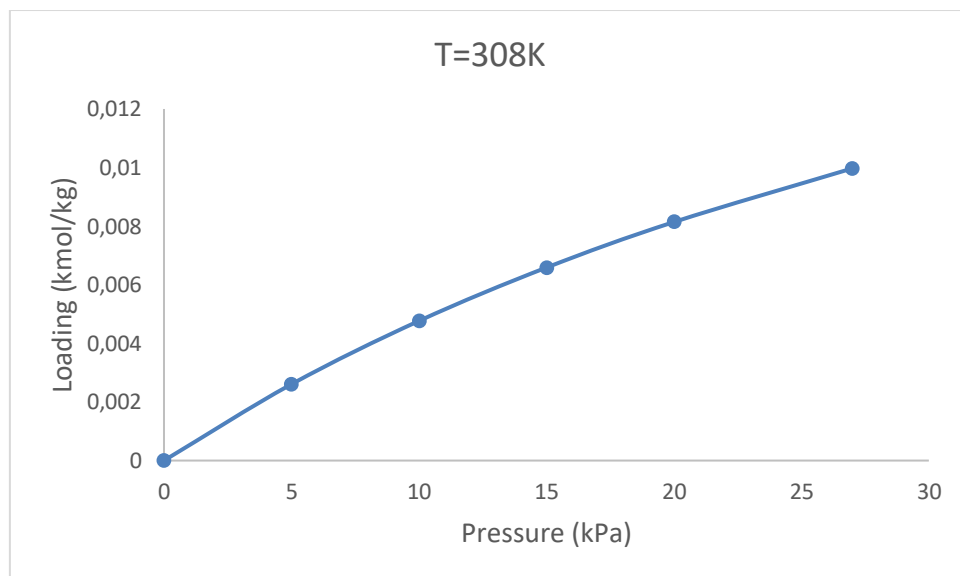


Figure 2.35 Loading subject to pressure at 308K.

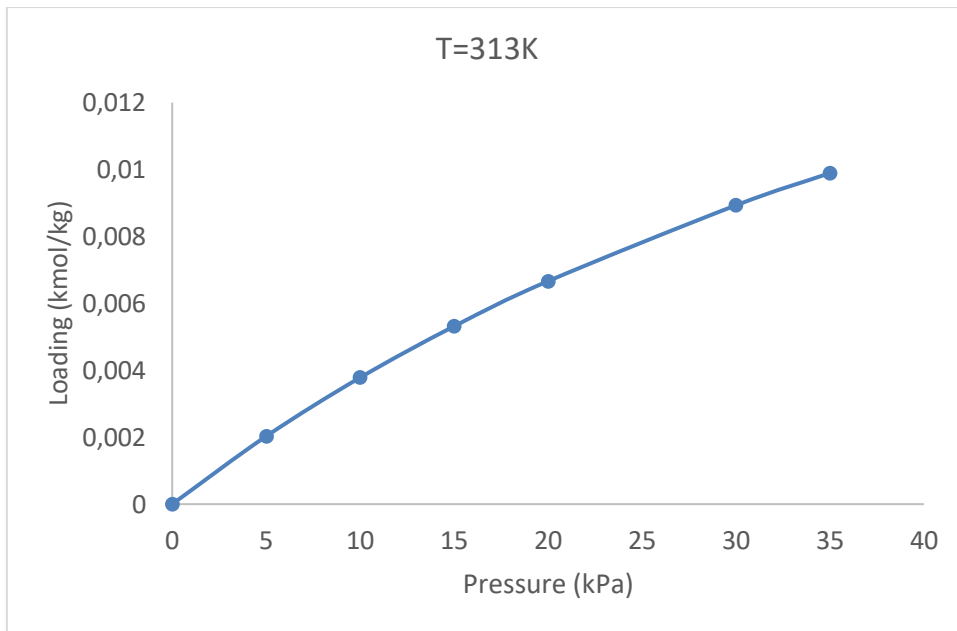


Figure 2.36 Loading subject to pressure at 313K.

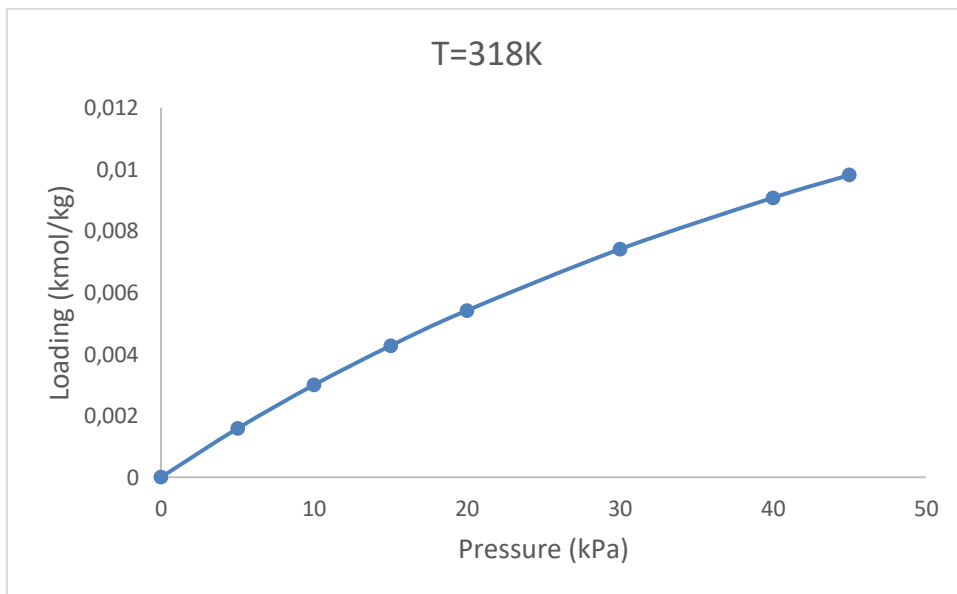


Figure 2.37 Loading subject to pressure at 318K.

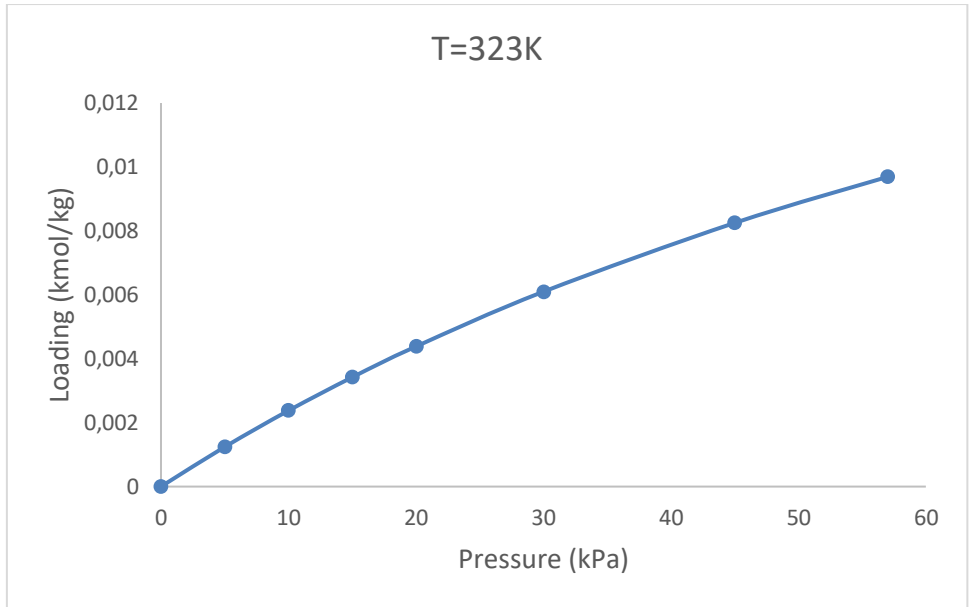


Figure 2.38 Loading subject to pressure at 323K.

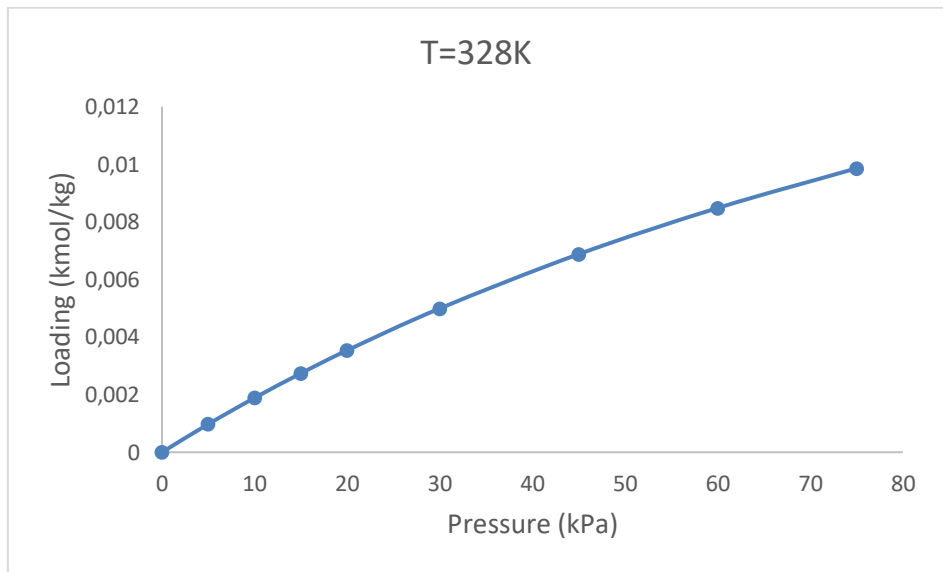


Figure 2.39 Loading subject to pressure at 328K.

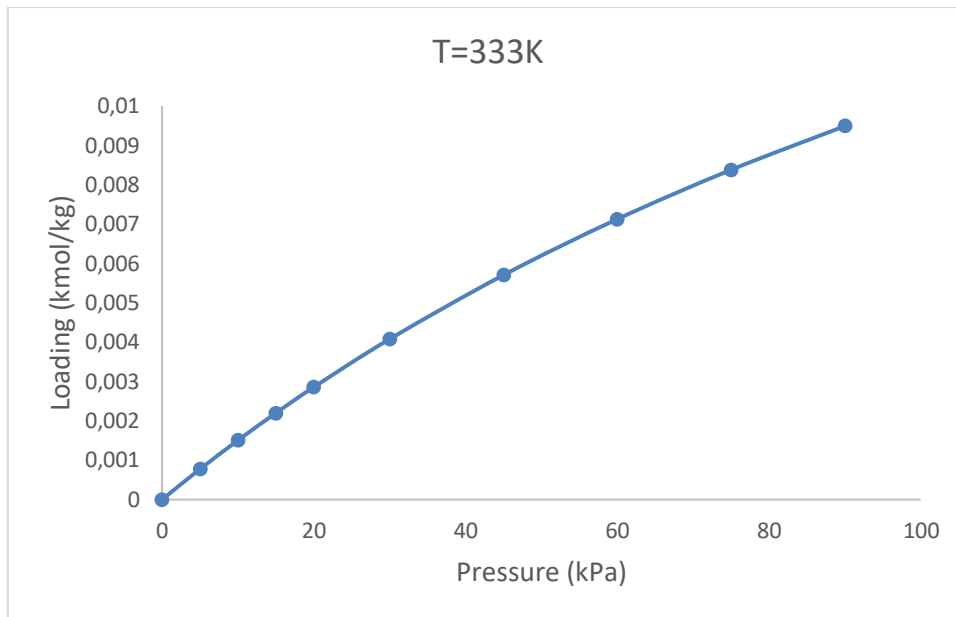


Figure 2.40 Loading subject to pressure at 333K.

The above charts present the loading of the adsorption process subject to pressure for 7 different temperatures. All of them have the same form as it is evident. The curve is almost linear but as it is obvious the increase of the loading is bigger than the corresponding of the pressure.

The most important result of these charts is the difference from the corresponding chart in the previous example with zeolite-air. In the chart of zeolite-air, the loading increases very fast and after a value of a pressure the increase is minimal. On the other hand, in these 7 charts the increase as it was mentioned is almost linear.

The above statement is due to three possible reasons. The first one is the difference of the adsorbent. The silica gel may be more sensible with pressure's changes so it may not have an upper limit such as the zeolite. The second one may be the difference in the adsorbate as well. The air differs from the water so the difference in the charts may be due to this.

The last but not least may be the values of the pressure in which the runs took place. For the zeolite-air the values of the pressure reach 10 bars. However, for the pair silica gel-water the values are smaller and the maximum value through the runs is approximately 1 bar.

According to that, the loading may not increase as much as when the pressure stays below a value-limit. This value may be the value of the atmospheric pressure of 1 bar. As it was mentioned for the pair of zeolite-air the pressure in which the increase of the loading is very small is 1,25 bar. So, above this value-limit, the charts of the pair silica gel-water may have the same form with the corresponding one of zeolite-air.

As it is obvious in the above 7 charts the values of the pressure differ from each other. That will be explained underneath in one chart.

The next chart presents a summary of the 7 charts in order to have a better conclusion to the loading subject to pressure and temperature.

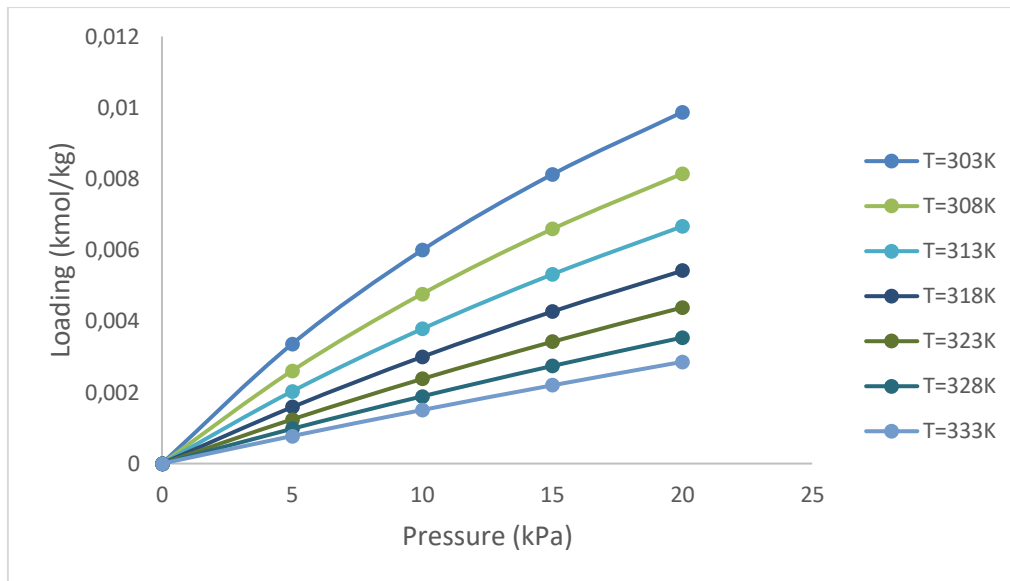


Figure 2.41 Loading subject to pressure at different temperatures.

As in the previous examples, it is evident that also in this one the loading has the same correlation with the temperature. Namely, the loading is bigger when the temperature drops and at the same time the pressure is constant in each temperature. Because of that, the cooling with the method of adsorption uses feeds with small temperatures for the regeneration of the adsorbent inside the bed. This is one of the most important advantage of this method as it was also mentioned above.

From the above chart except for the correlation of the loading and the temperature it is obvious the difference in the decrease of the loading in every pair of temperature. According to this, the loading decreases more in small temperatures when the pressure is constant. The less decrease is observed from 328K to 333K.

The next chart is again about the loading subject to pressure but there is a difference.

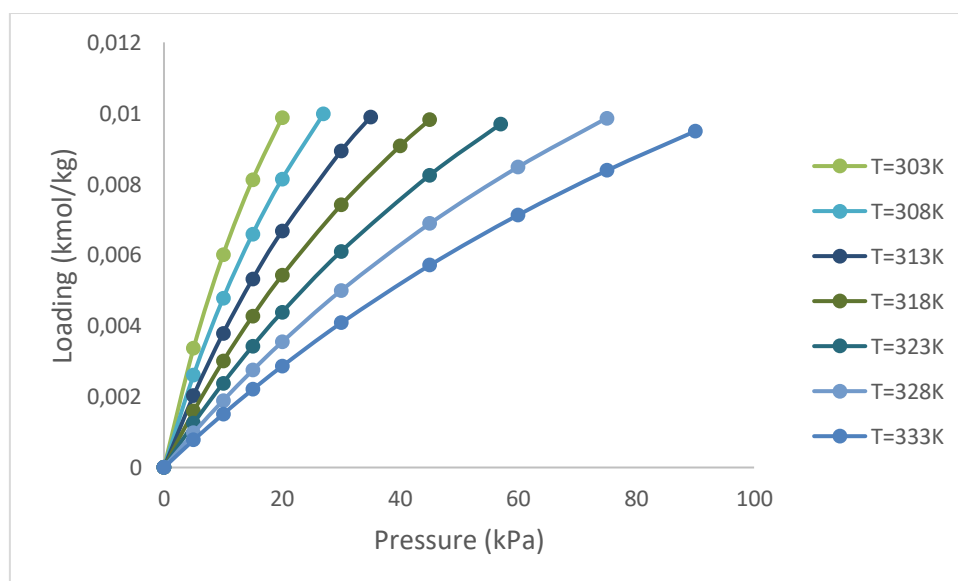


Figure 2.42 Loading subject to pressure at different pressures at constant loading.

According to the above chart, it is apparent that the loading was kept “constant” in order to illustrate the impact of the pressure and the temperature. As it is obvious in order to have the same loading in different temperatures, it has to increase the pressure in high temperatures. For example, in order to have the same loading in temperature of 303K and in temperature of 333K the pressure have to be 20kPa and a bit higher of 90kPa respectively.

Moreover, it is apparent that the bigger is the value of the loading the bigger the value of the pressure is in order to reach it. For example, for the value of the loading of 0,004 kmol/kg for the temperatures 303K and 333K the pressure has to be approximately 7kPa and 30 kPa respectively. On the other hand, for the maximum loading of this example, the pressure has to be 20kPa and a bit higher of 90kPa for the two above temperatures respectively. So, as it is evident for bigger loadings the pressure has to be very high when the temperature is also high and that may have some disadvantages such as huge equipment to reach these values of pressure and temperature.

According to the above results, it is obvious that the adsorption cooling is more efficient in smaller temperatures and this confirms the use of small temperature in this method of cooling as it was also mentioned in the previous examples.

At last, for the two charts above it is very useful to export two equations in order to calculate the loading with the use of temperature and the pressure and not with the use of isotherm parameters and the other data which Aspen adsorption needs.

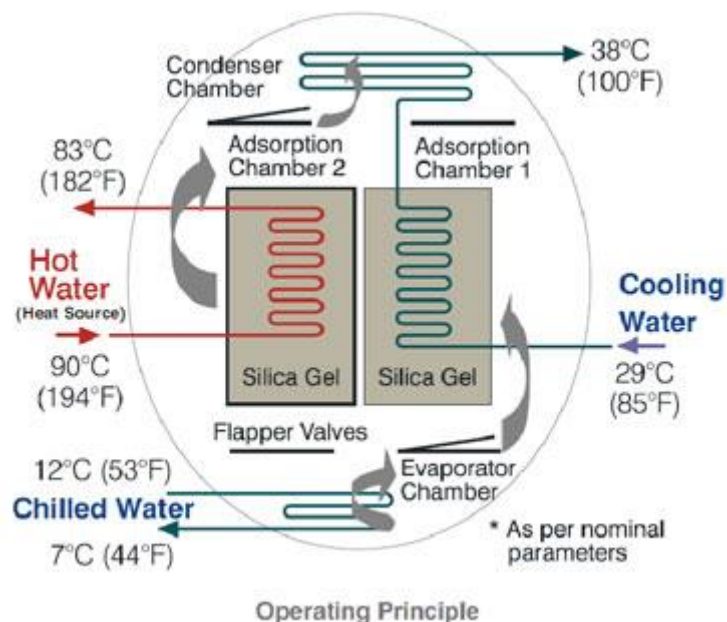


Figure 2.43 Silica gel-Water adsorption chiller [70]

## Chapter 3. Conclusions

According to the above modelings and the charts which were exported from them the results which have been also exported are the expecting ones. At this moment, it is good to make a more concentrated list with the results and also suggest some further researches.

First of all, the first pair which was studied, was the activated carbon-water. As it was said before this pair is not used in the market but with activated carbon ammonia is used. The results about this pair are underneath:

- The smaller the temperature of adsorption is, the bigger the loading is.
- Mass transfer coefficient has a huge role because the bigger its value, the faster the adsorption happens.

The second pair which was studied was the zeolite-water/ethanol and it is one of the first pair which studied for adsorption. The results which were exported are:

- As in the previous pair the smaller the temperature is, the bigger the loading is.
- In this pair the adsorbate is a mixture, so the more water is in the mixture, the bigger the loading is. However, after a value of the percentage of water in the mixture, the increase of the loading is small.

The third pair was zeolite-air. The adsorbate is not water as it was mentioned, but the water is adsorbed from the air in order to have cooling. The results are:

- The bigger the pressure of adsorption is, the bigger the loading also is. The temperature and the pressure have opposite correlation with the loading. However, the loading after a value of the pressure reach a limit and it does not increase further. That means smaller equipment and smaller cost.
- In this pair the isotherm parameters (IPs) which are used, have big values and apart from the small value of the concentration of water, the loading is also big. So, the IPs play a big role how big the loading is going to be.

The last but not least pair which was studied is the silica gel-water. This pair is the pair which used widely in the industry and the market as it is also said before. The results are the next ones:

- For constant pressure, the smaller the temperature is, the bigger the loading is. This result is the same as in the first two pairs.
- For constant value of loading, the bigger the temperature is, the bigger the pressure have to be in order to reach this value.

From all the above results, two are the most important and these two can be exported generally from the process of adsorption, so they will be presented a bit more. According to this, the first one is the correlation of temperature and loading. As it was mentioned before, the smaller the temperature is the bigger the loading is. That happens because when the temperature is high, the molecules on the adsorbent surface leave the surface more easily

than when there is a low temperature, for the same density. This leads to the lower loading for high temperature than for low temperature with the same pressure.

The second result which is the same in every pair of adsorbent-adsorbate is the correlation between the pressure and the loading when the temperature is constant. As it is obvious from above, the higher is the pressure the higher the loading is. That happens because when the gas phase pressure is high, there are more chances for molecules to adsorb onto the adsorbent surface.

From all the above, it is easy to conclude that the “perfect” pair of temperature-pressure for the adsorption process is that one with the low temperature and the high pressure. However, that is not possible because both have a limit, under and upper respectively.

As a general remark for this study, the main goal was the evaluation of ASPEN Adsorption for potential use to assess the performance of innovative working pairs for implementation on adsorption cycle. The main weakness identified was the fact that the software requires precise experimental data for the adsorption characteristics of the proposed pair per case, thus only previously experimentally validated pairs could be evaluated.

Finally, some suggestions for further research according to this thesis are presented underneath:

- The study of the process of desorption for different adsorbents with the same adsorbate
- The study of whole system of heat pump with water as adsorbate
- The study of whole system of heat pump with different adsorbate from water
- The study of different pairs in a heat pump in the same conditions



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