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Chapter 2

CHEMISORPTION HEAT PUMPS FOR WATER HEATING AND STEAM PRODUCTION

Rogério Gomes de Oliveira^{1,2*}

¹Campus Araranguá, Universidade Federal de Santa Catarina (UFSC), Araranguá, Brazil

²Laboratory of Energy Conversion Engineering and Energy Technology (LEPTEN),
Department of Mechanical Engineering, UFSC, Florianópolis, Brazil

ABSTRACT

Chemisorption heat pumps are devices that can produce useful cooling or heating effects due to cyclic endothermic and exothermic reactions between the vapor of a working fluid and a salt. The cooling effect can be produced at temperatures as low as -40 °C, whereas the heating effect can occur at temperatures up to 350 °C. The level of operation temperatures depends on the working fluid and the salt used in the machines. Due to the intermittent nature of the heating and cooling productions, where the reaction can be halted for long periods, these machines have an inherent heat storage capability, without need of thermal insulation to prevent heat losses. Moreover, these machines have great energy saving potential because their main source of energy can be heat wasted in other processes or solar energy. Hence, this chapter starts with a description of the operation principle of these machines, followed by the presentation of the types of cycle that can be used for heat amplification, heat upgrade or for simultaneous production of useful heating and cooling effects. Then, the salts and working fluid usually employed are presented, together with the techniques that can be used to avoid salt agglomeration and the attenuation of the adsorption capacity, and the techniques that can reduce the thermal resistance of the sorbent bed. The chapter finishes with a discussion of the technical and economical feasibility of machines operating for heat upgrade, for production of simultaneous cooling and heating effect and for temperature lift. This last application is especially useful to consume industrial waste heat at low temperatures and lift its temperature to a level high enough to generate medium pressure steam.

* Corresponding author: Rogério Gomes de Oliveira, Email: rogerio.oliveira@ararangua.ufsc.br.

1. INTRODUCTION

Since the oil crisis in 1970s, the research about technologies that can enhance the efficiency of thermal conversion processes and reduce the dependency on fossil fuel increased considerably. Besides the use of renewable sources, like solar energy and wind energy, the effective use of waste heat can play an important role in the management of the energy consumption in the different sector of the world economy. Industrial waste heat occurs in various industrial sectors, and it can be considered as one of the five major conventional energy sources, together with coal, petroleum, natural gas and waterpower [1].

Based on the wasted heat produced in the Netherlands, Haije et al. [2] estimated that the worldwide industrial activities emission amounts to up to 8333 PJ/y. However, most of this heat is not used due to their relatively low temperature, which is in the range of 50 to 200 °C. If the temperature can be upgraded, the heat may be useful again in many fields, and result in enormous energy savings and reduction of CO₂ emission. For example, if waste heat is upgraded to above 200 °C, it can be used for production of medium pressure steam.

Usually, the temperature lift can be obtained at the expense of electrical means (mechanical vapor compression heat pump) and by thermal means (absorption, physical adsorption and chemical adsorption heat transformers). Although mechanical compression heat pumps have higher efficiency than thermal compression heat pumps, the former type still consumes high-grade electric energy. Thermal compressors can be directly driven by low- and medium-grade renewable energy or waste heat; hence, they can effectively accomplish the recovery of waste heat.

Among the heat pumps, chemisorption heat pumps have several advantages over the other types. Chemisorption heat pumps can provide compression ratio of more than 100, which is not feasible in mechanical compression systems, and can cause temperature lift higher than 100 °C, which is not possible with absorption systems [3].

According to Spinner [4], the reactive gas is usually ammonia or water, whereas the sorbent are alkaline, alkaline earth, or metallic halides, sulphates, nitrates and phosphates. The working temperatures of the heat pump will depend on the working pair chosen, but they usually range from cooling production at -40 °C to heat production at 350 °C [5].

Although the chemisorption heat pumps present the above advantages, they suffer from low specific heating power (SHP), low heating power density and low coefficient of amplification (COA). To overcome these limitations, the research related to these systems usually focuses on the thermodynamic characterization of working pairs [6-13], on advanced cycles [14-16], and on alternatives to enhance the heat and mass transfer in the reactors. The main technologies to reduce the external heat transfer resistance in the reactors are related to the use of heat pipes [17-18], and to the type of heat exchanger design of the reactor [19-20].

The latter approach can also help the reduction of the mass transfer resistance [21]. The internal heat transfer resistance can be reduced using coated adsorbents [22-23] and with composite or consolidated adsorbents [8, 24-28].

Hence, to show the possibilities and limitations of the chemisorption machines for water heating and production of medium-pressure steam, the next sections present the operation principle of these machines, the types of cycle that can be employed for heat amplification, heat upgrade or to produce simultaneous useful heating and cooling effects.

A brief description of the working pairs usually employed is also presented, together with the techniques that can be used to reduce the thermal resistance in the sorbent bed.

The last section discusses the performance results of some machines tested either as heat pump type I, which amplifies the amount of available heat, but not the temperature, or as heat pump II (a.k.a thermo-transformer), which upgrades the temperature level of the heat consumed. The last application is especially useful to lift the temperature of waste heat in more than 50 °C.

2. TYPES OF CYCLE

Chemisorption heat pumps operate under cycles that have at least one positive sorption (enrichment of the sorbent with sorbate), which is also known by adsorption or synthesis reaction, and one negative sorption (depletion of sorbate from the sorbent), which is also known as desorption or decomposition reaction. The heating effect can be obtained during the condensation of reactive gas in the condenser and during the adsorption of reactive gas in the reactor, or exclusively during the adsorption, when the system is designed for temperature lift, as in the case of the thermo-transformers.

The reaction during the cyclic operation of the system is described by equation 1.



where S is salt, $n+m$ is number of moles of working fluid initially adsorbed, n is the number of moles of working fluid desorbed, and ΔH_r is the reaction heat. The reaction is monovariant, and the equilibrium solid-gas is described by the Clapeyron equation (equation 2)

$$\ln(P_{Eq}) = -\frac{\Delta H_r}{RT} + \frac{\Delta S_r}{R} \quad (2)$$

Equation 2 can be modified to indicate the equilibrium temperature at a certain pressure as follows.

$$T_{Eq} = \frac{\Delta H_r}{\Delta S_r - R \ln(P)} \quad (3)$$

Figure 1 shows a Clapeyron diagram and the scheme of a machine for a single stage heat pumping cycle type I, with one reactor filled with salt and one reactor with saturated working fluid. The machine receives heat at a high temperature (T_H), and the salt inside the reactor desorbs working fluid to the condenser, which releases heat at a temperature T_{A+} , which is above the ambient temperature (T_A). The working fluid from the condenser is transferred to the evaporator, and once this period of the cycle finishes, the salt in the reactor can adsorb the working fluid back. The evaporation of the working fluid consumes heat at ambient temperature (T_A), and the adsorption of the working fluid releases heat at the same level of temperature that heat was previously rejected in the condenser.

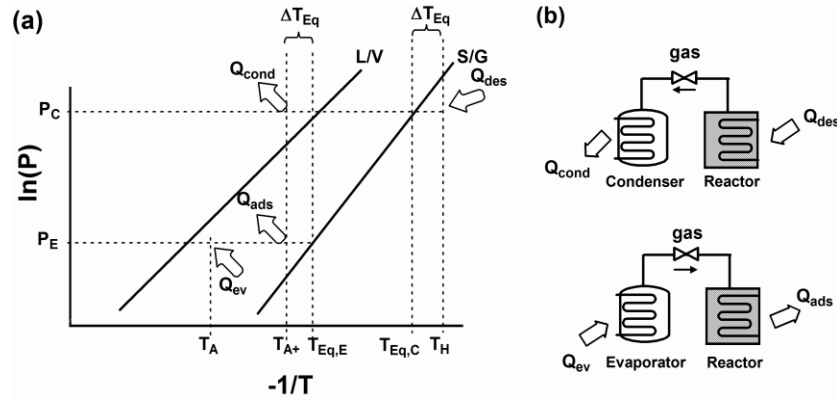


Figure 1. (a) Clapeyron diagram for a single stage heat pump type I; (b) scheme of a heat pump type I.

The maximum amount of refrigerant desorbed or adsorbed by a salt is defined by the stoichiometric coefficient m , according to equation 1, and which can be achieved if T_H is higher than the equilibrium temperature calculated with equation 3 at the condensation pressure ($T_{Eq,C}$), or if T_{A+} is lower than the equilibrium temperature at the evaporation pressure ($T_{Eq,E}$).

The difference between the equilibrium temperature and the thermal fluid temperature is known as equilibrium temperature drop (ΔT_{Eq}), and it is the driving force of the reaction. Small values of ΔT_{Eq} decrease the reaction rate; hence, reduce the output heating power. Moreover, reactions carried out too close to the equilibrium can last for so long that an adsorbed or desorbed amount equal to the stoichiometric coefficient cannot be achieved in a practical time. The performance of machine is usually expressed in terms of coefficient of amplification (COA), as shown in equation 4. Typical values for the COA_I are in the range of 1.4 to 1.6.

$$COA_I = \frac{Q_{ads} + Q_{cond}}{Q_{des}} \quad (4)$$

One problem of this kind of heat pump type I is related to the extremely high pressure inside the system, depending on the working fluid. For a system using ammonia, a heat production at 110 °C would result in working pressures above 7.5 MPa.

An alternative to solve this problem is the use of the resorption cycle [3, 5], where the reactor with the saturated working fluid is replaced by a reactor with another salt.

By combining two salts that have different equilibrium temperature at the same pressure, it is possible to obtain two heating effects at middle temperature T_{A+} , using one heat input at higher temperature T_H . The salt that has the lower equilibrium temperature is known as low-temperature salt (LTS), whereas the other salt is named high-temperature salt (HTS).

The proper choice of the salts enables the reduction of the working pressure, and increases the COA because the adsorption heat of the salt is higher than the latent heat of condensation. The COA for the resorption system is defined as shown in equation 5.

$$COA_I = \frac{Q_{ads.HTS} + Q_{ads.LTS}}{Q_{des.HTS}} \quad (5)$$

Touzain [29] presented an extensive list of reaction enthalpy for different reactions using ammonia as working fluid. For heat production at 110 °C using $\text{CaCl}_2/2$ as LTS and $\text{MgCl}_2/2$ as HTS, the working pressure is limited to about 2.0 MPa, and the COA_I is about 1.75. In case the LTS is $\text{ZnCl}_2/6/4$ and the HTS is $\text{NiCl}_2/6/2$, the working pressure is reduced to 1.0 MPa, and the COA_I can reach 1.79.

The COA_I of the heat amplification heat pumps can be increased in a multiple effect cycle, as presented by Sun [30], and depicted in the Clapeyron diagram of Figure 2.

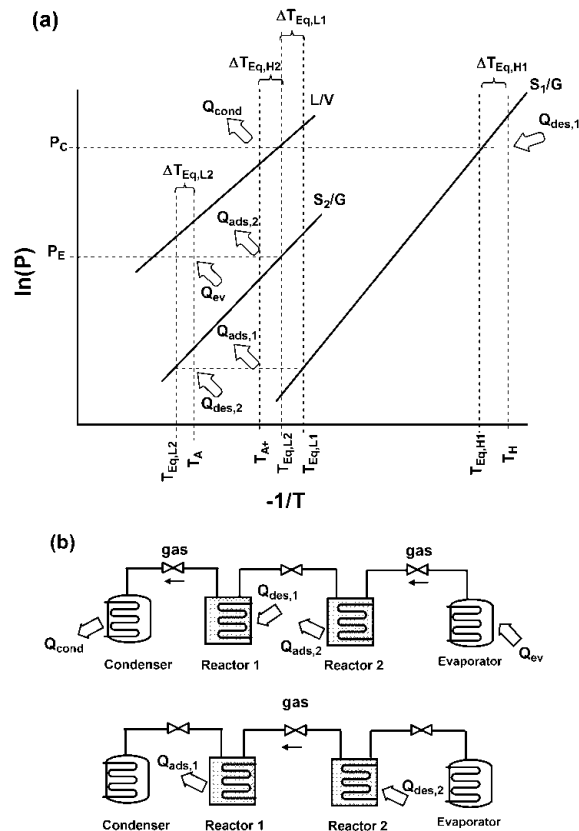


Figure 2. (a) Clapeyron diagram for a double stage and multiple effect heat pump type I; (b) scheme of a double stage and multiple effect heat pump type I.

From the data compiled by Touzain [29], it was possible to calculate that a cycle using $\text{CaCl}_2/2$ as LTS, $\text{FeCl}_2/6/2$ as HTS, and ammonia as working fluid could achieve a COA of 2.27. The heat production would be in the range of 75 to 90 °C, the heat supply at temperature T_H should be above 245 °C, whereas the heat supply at ambient temperature T_A should be above 25 °C.

In the heat pump type II, which is designed for temperature lift instead of heat amplification, there are two heat inputs at middle temperature T_{A+} , which result in heat

rejection at a higher temperature T_H . Such a cycle is depicted in the Clapeyron diagram of Figure 3, and besides the reactor with a HTS, the system needs either one reactor with saturated working fluid or a reactor with a LTS. The use of LTS instead of saturated working fluid can reduce the working pressure of the system, but will decrease the COP.

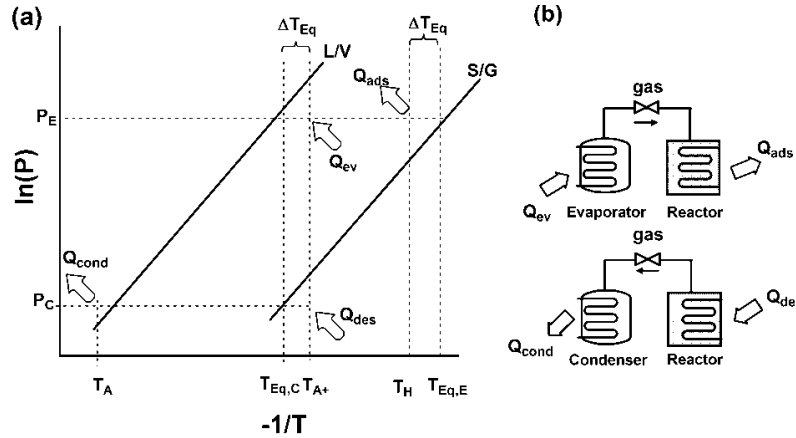


Figure 3. (a) Clapeyron diagram for a single stage heat pump type II; (b) scheme of a heat pump type II.

In the first period of this cycle, heat is supplied at T_{A+} to the reactor with the LTS. Such a level of temperature can be obtained with waste heat or in solar collectors. The working fluid is desorbed from the LTS and adsorbed by the HTS, which releases heat at T_H . In the second period of the cycle, the reactor with the HTS receives heat at T_{A+} to desorb the working fluid towards the reactor with the LTS. The adsorption process in the LTS reactor releases heat at ambient temperature, and the cycle can start again.

The COA of the heat pump type II is calculated with equation 6. A system designed to upgrade heat from 140 °C to 240 °C can have a COA of 0.34 if uses $\text{MnCl}_2/2$ as LTS and $\text{NiCl}_2/2$ as HTS [31].

$$COA_{II} = \frac{Q_{ads.HTS}}{Q_{des.HTS} + Q_{des.LTS}} \quad (6)$$

Goetz et al. [5] analyzed several combinations of salts that can be used to increase the temperature of a heat transfer fluid, and they found that this increase can vary between 35 °C to 70 °C, when the machine operates in an ambient at 15 °C. These salt combinations and operation conditions are shown in Table 1. The difference between the equilibrium temperature of the LTS and the heat transfer fluid was assumed 10 °C, whereas this difference for the HTS was assumed 20 °C. Higher temperature lifts can be obtained in the double stage cycle presented by Goetz et al. [5], which is shown in the Clapeyron diagram depicted in Figure 4. The utilization of $\text{CaCl}_2/2$ as LTS and $\text{MnCl}_2/2$ as HTS enables an upgrade of the temperature of the heat transfer fluid from 90 °C to 175 °C, whereas in the single stage cycle, the temperature of the heat transfer fluid is lifted to only 125 °C. Besides the reactors with the LTS and the HTS, the cycle needs a condenser and an evaporator. The

drawback of the double stage cycle when compared to the single stage cycle is the reduction of the COA_{II} , which in this case, drops its maximum value from 0.53 to 0.42. The utilization of an evaporator and a condenser also increases the maximum operation pressure, which reaches values around 4.2 MPa.

Table 1. Working pairs and operation conditions for thermo-transformers

| LTS | HTS | Temperature lift |
|--------------|--------------|--------------------|
| $CaCl_2/2$ | $MnCl_2/6/2$ | from 90 to 125 °C |
| $BaCl_2/8/0$ | $CaCl_2/4/2$ | from 95 to 120 °C |
| $CaCl_2/8/4$ | $MnCl_2/6/2$ | from 100 to 135 °C |
| $CaCl_2/8/4$ | $FeCl_2/6/2$ | from 120 to 185 °C |
| $MnCl_2/6/2$ | $NiCl_2/6/2$ | from 130 to 195 °C |
| $CaCl_2/4/2$ | $MgCl_2/6/4$ | from 145 to 215 °C |

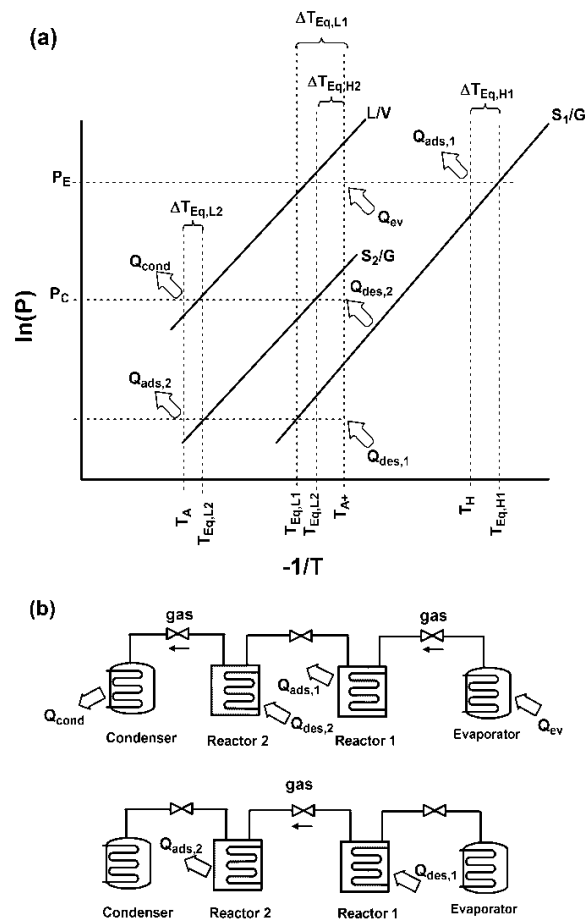


Figure 4. (a) Clapeyron diagram for a double stage heat pump type II; (b) scheme of a double stage heat pump type II.

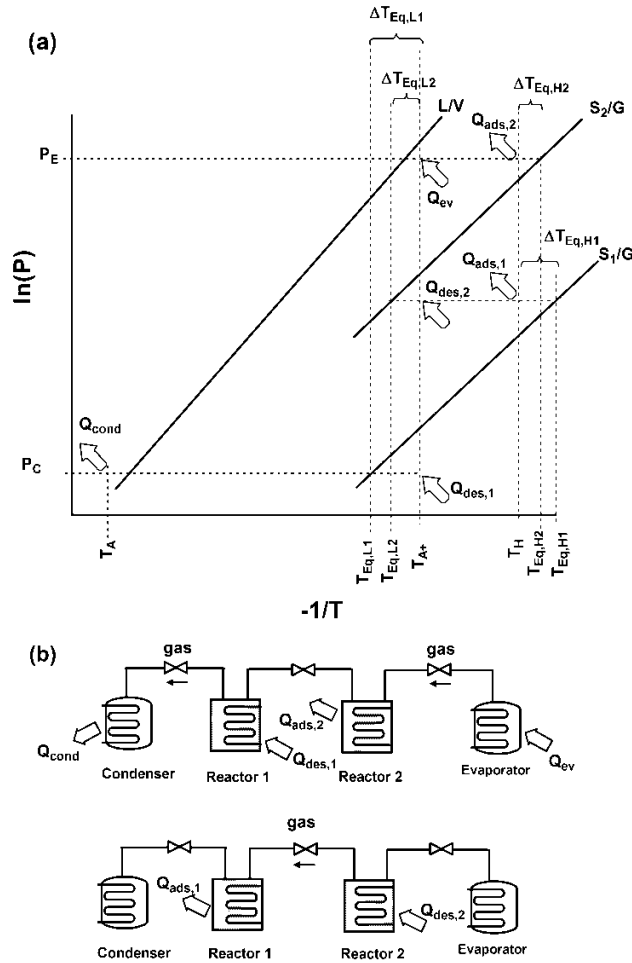


Figure 5. (a) Clapeyron diagram for the second type of double stage heat pump type II; (b) scheme of the second type double stage heat pump type II.

An alternative to enhance the COA_{II} of the double stage cycle is the use of a larger pressure difference between the condenser and the evaporator than that used in the salts [30]. Such a cycle, which is shown in Figure 5, can reach a COA_{II} up to 0.70, when the heat lift occurs between 85 and 115 °C, and $BaCl_2/8/0$ is the LTS, $CaCl_2/8/4$ is one of the HTS and $ZnCl_2/6/4$ is the other HTS. Similar COA_{II} can be obtained for a heat lift between 115 and 155 °C, if $BaCl_2/8/0$ is the LTS, $CaCl_2/4/2$ is one of the HTS and $MnCl_2/6/2$ is the second HTS. One of the drawbacks of employing such a scheme to increase the COA is the high working pressure. In the former case, it would reach almost 3.5 MPa, whereas in the latter case, it would reach about 7.5 MPa.

Another alternative to enhance the COA of the heat pumps type II is the utilization of an internal heat recovery between two pairs of working salts, as suggested by Neveu and Castaing [14], and shown in Figure 6. In this case, four reactors are necessary, and two of these reactors have the salt with the lowest equilibrium temperature.

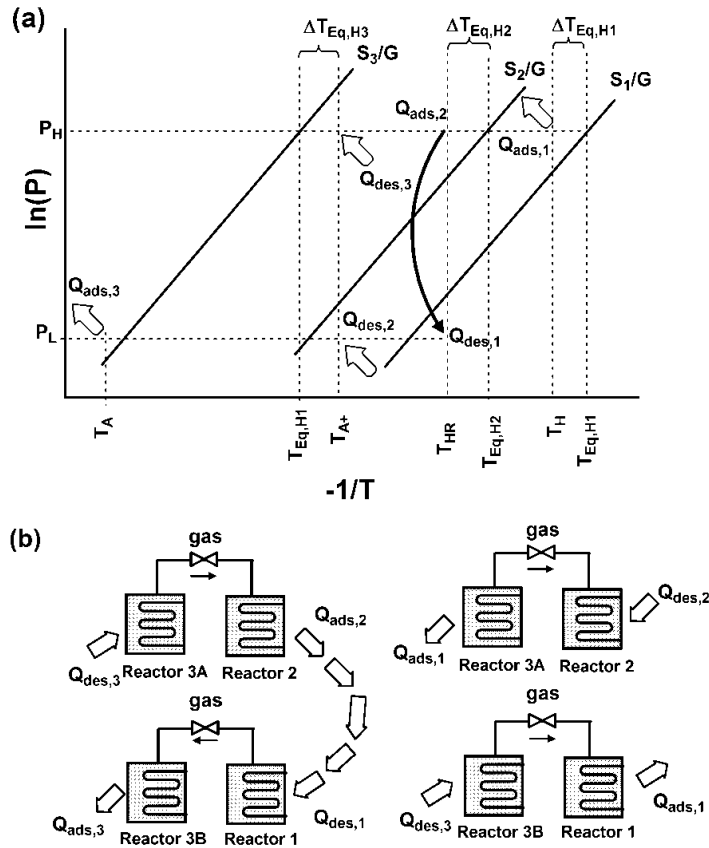


Figure 6. a) Clapeyron diagram for a single stage heat pump type II, with internal heat recovery; b) scheme of a single stage heat pump type II, with internal heat recovery.

In the cycle with heat recovery, the heat output at T_{HR} of the HTS with the lowest equilibrium temperature is used to regenerate the HTS with the highest equilibrium temperature.

The COA_{II} can reach values close to 0.55, for a temperature lift between 75 and 120 °C, if $BaCl_2/8/0$ is the LTS, $CaCl_2/4/2$ is one of the HTS and $ZnCl_2/6/4$ is the second HTS. The working pressure for this operation condition would be less than 2.0 MPa.

Slightly higher COA_{II} of up to 0.57 can be achieved if $SnCl_2/4/2.5$ is the LTS, $ZnCl_2/6/4$ is one of the HTS and $MnCl_2/6/2$ is the second HTS. In this case, the temperature lift can be from 65 to 125 °C, and the working pressure would be less than 1.0 MPa.

Some types of cycle can also be used for simultaneous heating and cooling effect production, and they are of special interest in places with demand of both cooling and heating, like some process in the food industry.

Xu et al. [32] presented an experimental study that showed that a machine operating under a resorption cycle, as shown in Figure 7, can produce cooling effect at 0 °C simultaneously to a heating production of 80 °C, with a coefficient of performance (COP, in equation 7) of 0.24, and a combined coefficient of performance and amplification (COPA, in equation 8) of 1.16.

$$COP = \frac{Q_{des, LTS}}{Q_{des, HTS}} \quad (7)$$

$$COPA = \frac{Q_{des, LTS} + Q_{Ads, HTS}}{Q_{des, HTS}} \quad (8)$$

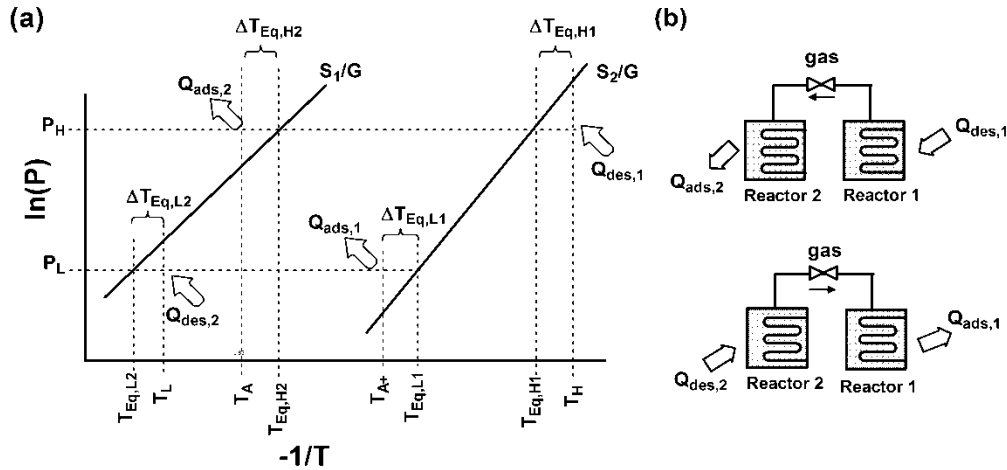


Figure 7. (a) Clapeyron diagram for a resorption cycle with simultaneous heating and cooling effects; (b) scheme of a resorption cycle with simultaneous heating and cooling effects.

The necessary temperature for the heat supply at T_H was 140 °C, and heat rejection occurred at 35 °C. Among the studied conditions, the best performance was achieved when the cooling effect occurred at 0 °C, the heating effect occurred at 80 °C, but the heat rejection occurred at 30 °C. In this case, the COP was 0.35 whereas the COPA was 1.30.

Higher COP and COPA can be obtained in a cycle with multiple effects similar to the double effect cycle presented by Li et al. [33]. The cycle presented by these authors aimed two cooling productions at the expense of a single heat input at high temperature. However, it is also possible to obtain besides the two cooling effects, multiple useful heating effects, depending on the high temperature heat input T_H and the salts employed. In Figure 8 it is possible to see that the third useful heating production will depend on the temperature level that heat is supplied at high temperature T_H .

If ammonia is used as working fluid, $\text{CaCl}_2/2$ is the LTS, and $\text{CoCl}_2/6/2$ is the HTS, it is possible to achieve cooling production at 5 °C and heating production between 65 and 75 °C, with a COP above 1.0 and a COPA around 2.9 when heat is supplied from an external source at temperatures above 220 °C. If the temperature of the heat supply is increased to values above 265 °C, the COPA can be close to 3.3.

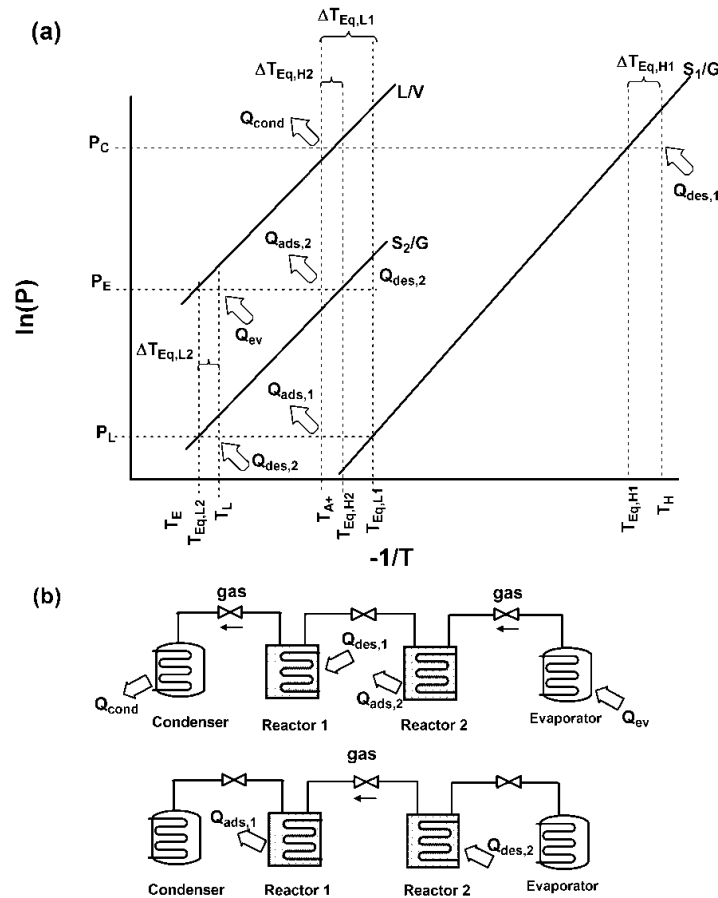


Figure 8. a) Clapeyron diagram for a multi effect cycle with simultaneous heating and cooling production; b) scheme of a multi effect cycle with simultaneous heating and cooling production.

3. WORKING PAIRS

Ideally the working fluid for chemisorption heat pumps should have the following characteristics:

- 1 low ozone layer depletion potential (ODP);
- 2 low global warming potential (GWP);
- 3 operation pressure close to atmospheric pressure;
- 4 high molar mass;
- 5 high condensation enthalpy;
- 6 low toxicity;
- 7 non-flammability.

The first two characteristics aim avoiding environmental problems. The third characteristic is related to manufacturing costs, which increase if vacuum technology is

employed, or if the system must bear extremely high pressures. The high molar mass and high condensation enthalpy are important because the heating effect is produced in batch operation; hence high heating capacity per cycle leads to more compact machines.

Low toxicity and non-flammability are especially important characteristics if the working pressure is above atmospheric pressure, because any leak could put in danger those around the machine.

Unfortunately, no working fluid suitable to be used in chemisorption heat pumps has all desirable characteristics, and the most employed ones are water and ammonia.

Water meet all the requirements listed above except for its sub atmospheric saturation pressure at temperatures below 100 °C. Water is mostly used in adsorption and absorption chillers, where the sorbent is usually zeolite, silica-gel or LiBr [34]. However, there are few reports in the literature about the use of this refrigerant in chemisorption heat pumps. Boer et al. [10] suggested the use of NaS and water as working pair for chemisorption system, and they reported values of enthalpy, entropy, equilibrium pressure and melting point. Spinner et al. [15] described the combination of a system with a hydrate of MnCl_2 and a system with an ammoniate of NiCl_2 for cold production at -30 °C, from a heat source at 130 °C. Heat at this level of temperature was supplied to evaporate water, which was adsorbed by MnCl_2 . Such a process, released heat at 250 °C, which was used to desorb ammonia from NiCl_2 to a condenser at 20 °C. The adsorption of ammonia at -30 °C by NiCl_2 release the necessary heat to desorb water from MnCl_2 to another condenser.

One possible reason to the existence of few studies using water as working fluid in chemisorption heat pumps may be related to the fact that the system must be designed to withstand both vacuum and high pressure, in case there is heat production above 100 °C, and also, to the fact that low operation pressures can cause problems related to mass transfer resistance. Poor mass transfer reduces the reaction rate, and the heating power of the machine.

Ammonia does not have condensation enthalpy as high as water, and is incompatible with copper and its alloys, but it can react with several salts (alkaline, alkaline earth or metallic halides, nitrates, phosphates or sulphates). Touzain [15] compiled from more than 80 references, the enthalpy and entropy of about 350 reactions between inorganic salts and ammonia. Goetz et al. [5] also presented a list which contained the enthalpy and entropy for the reaction between ammonia and chlorides of Ca, Mn, Mg, Fe, Ni, Ba, Sr. The information from these references can be used to calculate the equilibrium pressure and temperature, as shown in equation 2, and can aid in the choice of the appropriate salts for a certain working condition. Moreover, once the salts are chosen, the utilization of the reaction enthalpy can give an indication of the expected COA.

Different from the physical adsorption, where the working fluid is adsorbed within the adsorbent structure (in the micro or meso pores), in the chemical adsorption the working fluid attaches to the external surface of the salt. Hence, the salts experiment swelling and shrinking during the reaction. Moreover, after successive cycles, they tend to agglomerate. These problems can attenuate the adsorption performance after few cycles and compromise the heat and the mass transfer, which will affect the reaction rate and the heating power.

An option to avoid this type of problem is the mixture of the salt to another material, or the impregnation of the salt in an inert matrix. Wang et al. [35] mixed CaCl_2 with activated carbon to avoid salt agglomeration and to keep the adsorption capacity constant. Vasiliev et

al. [17] developed a solar-electric heat pump where the salt was mixed with carbon fibers to reduce the heat and mass resistance and to avoid the salt agglomeration.

The impact of the swelling and shrinking on the heat transfer resistance can be minimized when the salt is mixed or impregnated in an inert matrix. Several researchers [8, 36-39] impregnated salts in carbon fiber to reduce the thermal and mass transfer resistances. Vasiliev et al. [39] mentioned that the impregnation of metallic salt on carbon fiber creates a thin film of the salt through the whole volume of the sorbent bed, which is beneficial to the adsorption process. These authors studied a heat pump with two reactors, where one of them was filled with a carbon fiber impregnated with BaCl_2 , whereas the other reactor was filled with carbon fiber impregnated with NiCl_2 . This system achieved a COA of 1.43 with a temperature lift around 100 °C.

According to Delloero et al. [40], the impregnation or intercalation of salt in carbon fibers avoids salt agglomeration and provides faster reaction rates. The drawback of the former method is that the adhesion of the salt on the fiber decreases after few reactions, whereas in the latter one, the preparation period is very long and it is difficult to control the amount of salt intercalated. Moreover, the length of the carbon fibers play an important role in the heat transfer process inside the reactor as demonstrated by the experiments conducted by Delloero and Touzain [36]. These authors compared composite sorbents of MnCl_2 impregnated in fibers 3 and 30 cm long, and observed that the reaction in the composite with short fiber was completed in one quarter of the period of the reaction in other composite. The authors explained that the faster reaction observed with the composite that had short fibers was due to the fact that the fibers remained positioned normal to the heat transfer direction, differently from the composite with long fiber, where the fibers wound inside the reactor.

Expanded graphite is another inert material that had been used to avoid salt agglomeration and to enhance heat and mass transfer [24, 41-42]. Han and Lee [43] measured the thermal conductivity of several ammoniates impregnated in expanded graphite blocks. The thermal conductivity varied between 10 and 49 $\text{W m}^{-1}\text{K}^{-1}$, depending on the ammoniate, the mass fraction of expanded graphite and the density of the blocks. These researchers also measure the gas permeability in expanded graphite blocks impregnated with some chlorides [44]. The permeability varied between 5.0×10^{-16} and $1 \times 10^{-12} \text{ m}^2$, and also depended on the ammoniate, the mass fraction of expanded graphite and the density of the blocks. Usually, blocks with higher thermal conductivity have lower permeability, and the proper block for a certain application can be obtained by controlling the block density and the mass ratio between the adsorbent and the inert material.

Lee et al. [45] presented another concept to create consolidated expanded graphite block and improved both the mass and the heat transfer within the sorbent bed. The blocks had variable density, which increased gradually from 165 to 394 kg m^{-3} in the radial direction. The highest density occurred near the reactor wall. Experimental results showed that these blocks had much better heat transfer characteristics, since the temperature gap between the inner and outer sides of the bed was smaller than that observed in the blocks with uniform density.

4. TECHNICAL AND ECONOMICAL FEASIBILITY

Spoelstra et al. [31] investigated the economical and the technical feasibility of heat upgrade by thermochemical heat pump using $\text{MnSO}_4 \cdot 6/2$ as LTS, $\text{NiCl}_2 \cdot 6/2$ as HTS and ammonia as working fluid. A system designed to consume 5 kW of waste heat at 140 °C and deliver about 2 kW of heating at 240 °C would need a total capital investment of € 1,271k. The authors calculated that it would have a mean internal rate of return of 14 %, which indicated that it is economically viable. The calculated COA, which the authors named enthalpic efficiency, was 0.348, and the energy in the electricity consumed for the heat upgrade was about 1% of the energy of the heat delivered at high temperature.

Vasiliev et al. [3] and Mauran et al. [46] investigated the experimental performance of machines that could be used as heat pump and as refrigerator, depending on the necessity. The machine studied by the former authors had NiCl_2 as HTS and BaCl_2 as LTS, both impregnated in carbon fiber. Ammonia was the working fluid. The peak output heating, which was around 1400 to 1500 W, occurred at temperatures between 120 and 130 °C, whereas the cooling production occurred at temperature around 3 to 5 °C. The latter authors presented one of the few studies reported in the literature with heat pump machines using water as working fluid. The hydrate was $\text{SrBr}_2 \cdot 6/1$, and it was impregnated in an expanded graphite block. The system proposed was designed to produce cooling in the summer and heating in the winter through the use of flat plate solar collectors. These authors justified their choice for this hydrate instead of $\text{Na}_2\text{S}_5/0$, which had much higher energy density, because the dehydration of $\text{Na}_2\text{S}_5/2$ and $\text{Na}_2\text{S}_2/0$ cannot occur at temperatures above 35 °C if the heat source temperature is below 80 °C.

The total volume of the prototype was 1 m³, and it was capable to store up to 60 kWh of heating at 35 °C or up to 40 kWh of cooling at 18 °C, with mean heating and cooling powers of 2.5 and 4 kW, respectively.

In Netherlands, Haije et al [2] and Pal et al. [47] developed thermal transformers with LiCl as LTS and MgCl_2 as HTS. In both cases, ammonia was the working fluid. In the machine studied by Haije et al. [2], the reactor was a flat plate sandwich heat exchanger where the heat transfer fluids flew through the fins. According to the authors, the heat exchanger consisted of two parallel stainless steel plates vacuum brazed together, where the space between the plates was filled with a metallic wire mesh through where the heat transfer fluid passed. In the external side of the plate, there was a metallic foam impregnated with the salt. The system was used to upgrade heat from 155 to 200 °C and achieved a mean output heating power of 400 W. The experimental COA_{II} was 0.11, which was 40 % of the expected theoretical. The authors attributed the attenuation of the COA_{II} to the large thermal capacity of the reactor. Further improvements of the above mentioned prototype were reported by Pal et al. [47]. These authors mentioned that the machine developed by Haije et al. [2] had low performance due to salt degradation and leakage of salt from the metallic foam matrix, and also due to the fact that the proposed design had low heat and mass transfer. In the new prototype, these problems were avoided through the use of a new method, where the salts were deposited into the metallic foam in a way to increase the heat transfer while maintaining proper mass transfer. The mean heating power output was 300 W, and the system was capable to provide a temperature lift of at least 50 °C, upgrading heat from 130 °C to 180°C.

CONCLUSION

Chemisorption heat pumps and heat transformers can play an important role for energy saving. These machines can amplify the amount of heat in 30 to 60 % when operating in single stage or to more than 100 % when operating under double stage cycles. The temperature lift provide by these machines can be higher than 50 °C, with an efficiency of 30 to 70 % depending on the number of heating production effects and on the magnitude of the temperature lift.

In order to guarantee reasonable output heating power, the salt must be impregnated on an inert matrix which is usually a metallic foam or consolidated blocks of expanded graphite. Special attention should also be devoted to the heat capacity of the heat exchangers employed in the system. It should be kept to a minimum value in the thermo-transformer systems because when the heat capacity is too large, the real coefficient of amplification can be one third of the theoretical value.

Although ammonia is the most used working fluid, the utilization of water as working fluid has also been reported, especially for residential application of solar powered heat pumping and air conditioning system.

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