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"Thermal Swing Adsorption Refrigeration (Heat Pump)"

F. Meunier
Centre National de la Recherche Scientifique
Lab. Informatique pour la Mécanique
et Sciences d'Ingenieur
B.P. 133
F-91403 Orsay
France

Thermal swing adsorption refrigeration (heat pump)*

F. Meunier

LIMSI CNRS, Orsay, France

A review of the possibilities of thermal swing adsorption processes for refrigeration and heat pumping is presented. Adsorbent-adsorbate pairs suited for such development are examined, and processes using adsorbers with or without temperature gradients are discussed. It is shown that these adsorption-based devices have significant potentials provided the heat and mass transfer rates of the adsorption/desorption steps can be enhanced. Possible ways of enhancing adsorber performances are explored.

Keywords: adsorption; refrigeration; heat pump; zeolite; activated carbon; water; methanol

Introduction

If adsorptive processes have been extensively studied for gas separation or gas purification and catalysis, very few studies did exist on adsorptive refrigeration before the 1970s. After the discovery by Faraday that cooling could be obtained by vaporizing liquid ammonia and absorbing the vapor on silver chloride in a closed system, works had been undertaken on solid-gas pairs. Two adsorptive systems studies have been published in the 1930s: silica gel SO_2[1] (for the purpose of cooling of trains) and activated carbon-methanol.[2] But, at that time those studies did not lead to commercialization because of the emergence, at the same time, of the chlorofluorocarbons (CFCs), which were much more efficient. It is only in the 1970s after the energy crisis that new studies in this field were undertaken with the objective of a rationnal use of energy; the objective being to use either solar energy or waste heat to fire refrigerators or heat pumps. Most of the studies in that field have been dedicated to open cycles or desiccant cooling, a topic that will not be discussed in this article; however, promising studies on closed cycles have also been performed. In this article, we are concerned only with closed cycles studies.

Two possibilities seem very attractive for heat management adsorptive processes.

1. Soft technology (e.g., solar technology[3–5] or use of waste heat). In that case, mechanical simplicity and high reliability will prevail over efficiency.
2. Advanced technology. Mechanical simplicity is no longer a requirement, and high efficiency is required.

Although successful from a technical point of view, those studies did not lead to a commercial product (solar powered active carbon-methanol refrigerators have been commercialized, but the commercialization has been stopped).

More recently, in the 1990s, a new chance, because of environment, has been given to adsorptive systems. Recent studies on the ecological impact of traces of halocarbons in the atmosphere have shown that the emission of CFCs affects the ozone layer around the globe and adds to the greenhouse effect, participating in the global warming. CFCs have been identified as major contributors to ozone depletion (they have a high ozone-depleting potential [ODP]), and their global warming potential (GWP) is thousands of times higher than that of carbon dioxide. Substitution fluids, hydrochlorofluorocarbons (HCFCs), and hydrofluorocarbons are a necessary step for the elimination of CFCs; nevertheless, it is only a temporary solution before the total elimination of chloride and floride products since their GWP is too high. After the Montreal protocol in 1987, severer regulations against CFCs and HCFCs have been taken recently in November 1992 in Copenhagen so that alternative solutions to compressors using CFCs is still more urgent.

Adsorption cycles are a possible response to that ecological problem. But, to become competitive, those adsorptive devices must be energy efficient and environmentally friendly. The three refrigerant fluids (water, methanol, and ammonia) presented in that study are environmentally friendly (zero ODP and zero

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Address reprint requests to Dr. F. Meunier at LIMSI CNRS BP 133, 91403 Orsay, France.

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GWP). How energy efficient must be the devices? The answer is very easy: to produce globally less CO_2 than an electrically driven refrigerator, an adsorptive refrigerator must have a global ratio between cooling energy and primary thermal energy higher than an electrically driven refrigerator. That means a cooling coefficient of performance (COP) higher than 1 for the adsorptive refrigerator (the electrically driven refrigerator has a COP of the order of 3 and the ratio to produce electricity from heat is about one third, which makes a global ratio of 1).

If those two goals (friendly fluids—zero ODP and zero GWP—and less CO_2 production than electrically driven compressors) are achieved, another requirement will be compactness: For example, to be able to accommodate an adsorptive air-conditioner under an automobile hood requires very efficient adsorbers.

In this article, we address the problems of pair selection and process selection; we also present some of the more significant realizations; and, finally, we say a few words about the objectives and challenges that make this field so exciting.

Pair selection

Pairs most commonly used

Most significant criteria for the pair selection are the following:

- Temperature lift capability of the pair
- Boiling temperature of the fluid
- Adsorption capacity of the fluid by the adsorbent

To exemplify the concept of temperature lift, let us present for the pairs zeolite-water and active carbon-methanol, a set of isosters in a diagram in which the coordinates are the following:

- Temperature of the liquid in equilibrium with the vapor at the pressure, P, in the adsorber
- Temperature of the adsorbent

This corresponds to a simple case when the adsorbent is at a uniform temperature and no pressure drop exists.

Figure 1 shows the isosters for Zeolite NaX-water. A typical cycle is represented in this diagram. Let us define two temperature lifts DT1 (corresponding to the temperature difference between adsorption and evaporating temperatures) and DT2 (corresponding to the temperature difference between regenerative and condensing temperatures). Taking DT1 = 55°C and DT2 = 195°C, it is possible to adsorb/desorb 195 g of water per kg of zeolite and per cycle (*Figure 1*). Evaporation of water provides a cooling energy equal to 390 kJ; for a cycle time equal to 30 minutes, that would correspond to a cooling rate equal to 216 W per kg of zeolite. This is one of the characteristics of the NaX-water pair to be able to operate cycles with high temperature lifts.

Figure 2 shows isosters of the Active Carbon (AC35)-methanol pair. It can be noted that the situation is completely different from that for NaX-water. In this case, the evaporating temperature lift has to be limited to 40°C, but the regenerating temperature can be quite low. For example, it is possible to adsorb/desorb 180 g of methanol per kg of activated carbon and per cycle with a regenerative temperature as low as 100°C (*Figure 2*). Evaporation of methanol will provide 212 kJ; for a 30-min cycle, this would correspond to a cooling rate equal to 118W per kg of active carbon. With active carbon, the regenerating temperature must be low because a methanol decomposition occurs for temperatures higher than 150°C.

As a criterion to choose a pair, in general, we require a strong affinity between the gas and the adsorbent: This excludes all the macroporous or mesoporous adsorbents. But, on the other hand, we do not want this affinity to be too high, because, if this was the case, the regeneration would be very difficult: It is the reason why NaX zeolite is preferred to 4A or 5A zeolites.

Because of those selection criteria, at present, three working fluids and three adsorbents dominate adsorp-

Notation

AlPO	aluminophosphate
CFC	chlorofluorocarbon
COA	coefficient of amplification (equal to the heating coefficient of performance)
COP	coefficient of performance
GWP	global warming potential
HCFC	hydrochlorofluorocarbon
ODP	ozone depleting potential
TSA	temperature swing adsorption
VIP	18-membered ring pore aluminophosphate
p	pressure
T	temperature
Q	heat
q	adsorbate loading
$\rho_0(T)$	liquid density of the adsorbate

Indices

liq	liquid
min	minimum
max	maximum
ev	evaporator
cond	condenser
abc, cda, ea	operating lines in a (p,T) diagram

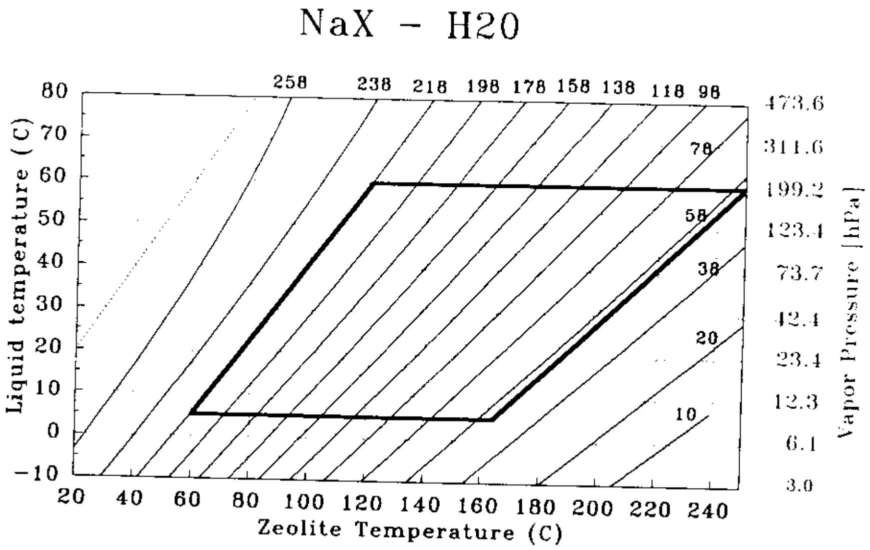

Figure 1 Set of isosters for the zeolite-water pair (numbers indicate adsorbate loading in g per kg of adsorbent). The equation of the isotherm is given by a Dubinin correlation: $m(p,T) = 0.269\ \rho_0(T)\ \exp[-1.8.10^{-7}\ (T\ln(\rho_0(T)/p)^2]$. In this equation, m is expressed in kg of adsorbate per kg of adsorbent and $\rho_0(T)$ is the density of the adsorbate assumed to be equal to the liquid density. A typical refrigerating cycle is depicted. The saturation line corresponds to the liquid/vapor equilibrium.

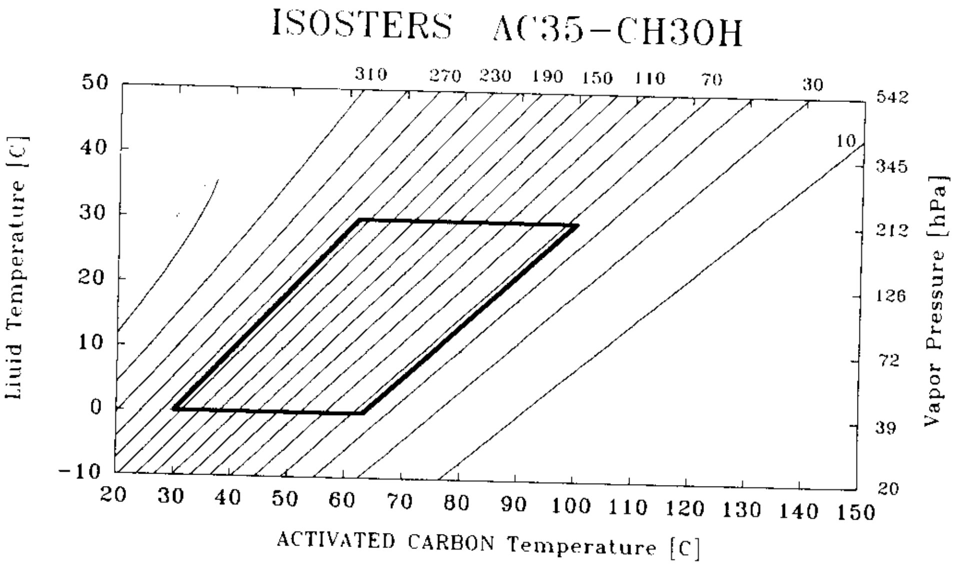

Figure 2 Set of isosters for the activated carbon-methanol pair (numbers indicate adsorbate loading in g per kg of adsorbent). The equation of the isotherm is given by a Dubinin correlation: $m(p,T) = 0.407\ \rho_0(T)\ \exp[-3.22.10^{-7}\ (T\ln(\rho_0(T)/p)^2]$. In this equation, m is expressed in kg of adsorbate per kg of adsorbent and $\rho_0(T)$ is the density of the adsorbate assumed to be equal to the liquid density. A typical refrigerating cycle is depicted. The saturation line corresponds to liquid/vapor equilibrium.

tive heat pumps: water, methanol, and ammonia for the fluids and zeolite, activated carbon and silica gel (ultramicroporous silica gel) for the adsorbents. Nevertheless, this does not mean that all the pairs have been screened; new adsorbents with large micropores (about 10 A) could be very attractive.

Two pairs have been studied in detail at LIMSI: zeolite-water and activated carbon-methanol. The zeolite-methanol pair has been rejected because it is not stable, because catalysis occurs and results in the production of dimethylether.

The physical chemical properties of the two pairs are quite different: activated carbon easily desorbs methanol when heated, whereas zeolite retains much more water. For that reason, the activated carbon-methanol pair is well adapted to operate cycles with small evaporating temperature lifts (up to 40°C), whereas the zeolite-water pair is capable of operating cycles with large evaporating temperature lifts (70°C or even more).

Two other characteristics of these pairs are important.

Table 1 Operating conditions and values of relative pressure in two phases for a cycle with water as a working fluid

Phase	T_{liq}	P	T_{ads}	P_0	P/P_0
Evap	5°C	870 Pa	40°C	7,370 Pa	0.11
Cond	40°C	7370 Pa	250°C	39.8 10^5 Pa	0.0018

1. To avoid ice formation, the zeolite-water pair should operate at evaporating temperatures higher than 0°C. An antifreeze agent may be used for this purpose, but the resulting low operating pressure becomes a drawback to achieving high cooling rates at low temperatures.
2. The activated carbon-methanol pair is limited to regenerating temperatures of 150°C because of methanol instability, whereas the zeolite-water pair may be regenerated at high temperatures (250–300°C).

Specially designed adsorbents?

At the moment, only commercially available adsorbents have been tested. It should certainly be possible to find other adsorbents leading to higher performances. As an example, let us indicate what could be an ideal adsorbent for water adsorption in view of an air-conditioner. In *Table 1* are presented the operating conditions in the two phases: adsorption and regeneration for a zeolite-water pair.

In *Table 1*, T_{liq} is the temperature of the evaporating or condensing water depending on the phase, P is the corresponding pressure. T_{ads} is the adsorbent temperature, and P_0 is the saturating pressure of the liquid at the temperature T_{ads}. P/P_0 is the relative pressure.

As depicted in *Figure 3*, an ideal adsorbent would be the adsorbent showing a type-V isotherm (according to IUPAC[6] classification after Brunauer et al.[7]) with a large step at a relative pressure in the range of 10^{-1} so that evaporation and condensation could occur at relative pressures respectively higher and lower than the pressure step. Aluminophosphate adsorbents like 18-member ring pore aluminophosphates (VIPs) or aluminophosphates (AlPOs) could be a solution although in the case of AlPO's, important irreversibilities have been reported[8] as is usual with type V isotherms.

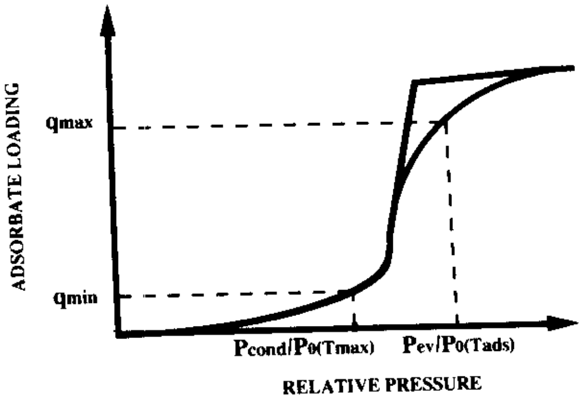

Figure 3 Type V ideal isotherm corresponding to a specific application: The regenerative temperature has to be high enough so that $P_{cond}/P_{0(Tmax)}$ be smaller than the relative pressure of the step.

Process selection for refrigeration or heat pumping

The basic cycle is a thermal swing adsorption (TSA) cycle. A TSA cycle is a cycle in which desorption takes place at a higher temperature than adsorption. *Figure 4* depicts the two isotherms corresponding to the regeneration temperature (T_{max}) and the adsorption, or feed, temperature (T_{min}). This refrigeration TSA cycle is quite different from a usual TSA separation cycle. In a separation cycle (*Figure 4a*), the feed partial pressure (during adsorption) is higher than the purge partial pressure (during desorption), whereas in a refrigeration cycle (*Figure 4b*), it is the opposite. The consequence is important because, for the same given operating temperatures, the adsorbate concentration swing is higher in a separation cycle than in a refrigeration cycle: It is the reason why it is more difficult to fire a refrigeration TSA cycle than a separation TSA cycle. Another important difference between a TSA refrigeration cycle and a TSA separation cycle comes from the nature of the heat transfer. In a separation TSA cycle, the heat transfer is generally a direct heat transfer: Heating

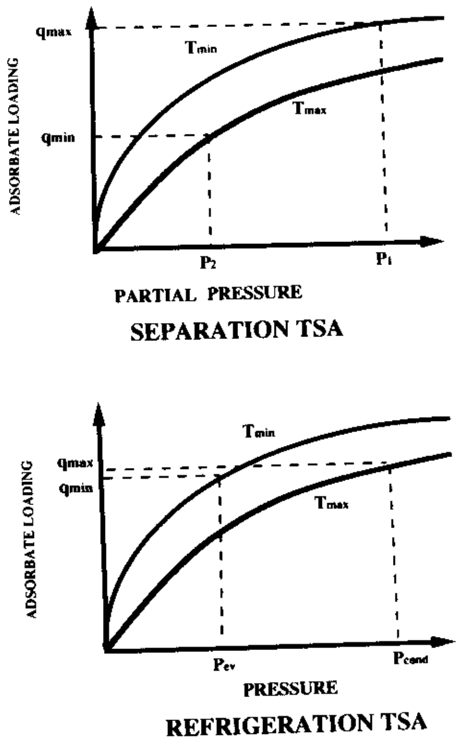

Figure 4 Schematic of the separation and refrigeration TSA processes in a diagram showing the two isotherms corresponding to the minimum and maximum temperatures of the adsorbent during the temperature swing.

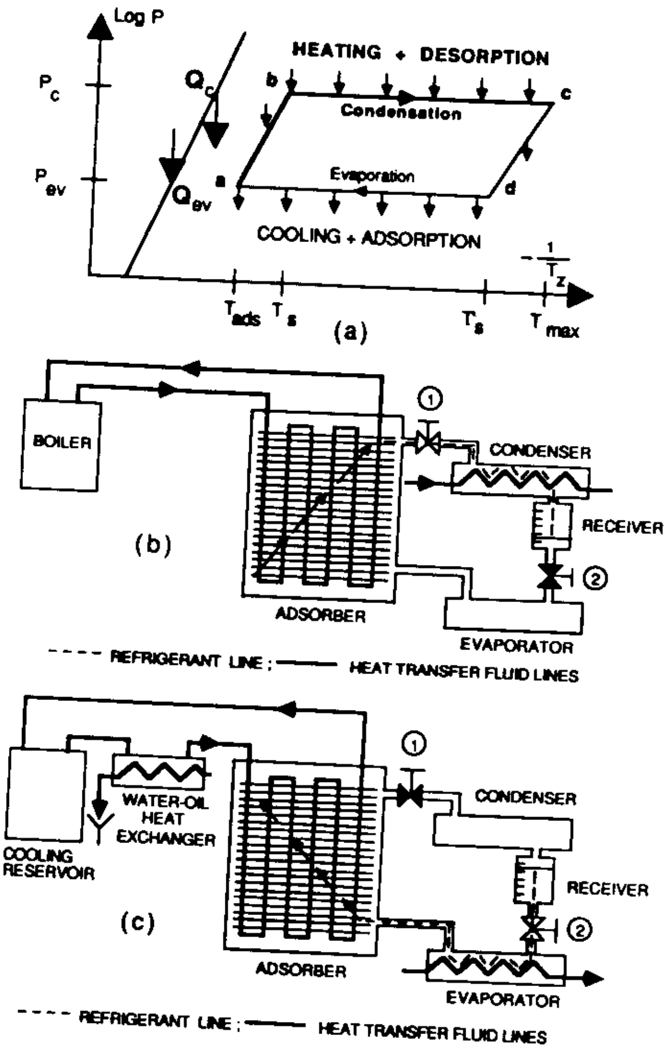

Figure 5 (a) Single-adsorber cycle in a Clapeyron diagram. (b) Schematic of the unit in sequence 1 (heating of the adsorber, condensation). Valve 1, closed; valve 2, open. (c) Schematic of the unit in sequence 2 (cooling of the adsorber, evaporation). Valve 1, open; valve 2, closed.

(cooling) is provided by the gas flowing in the adsorber. On the opposite, in a refrigeration TSA cycle, heat transfer is indirect: Heating (cooling) is generated by the transfer through a heat transfer fluid to a metallic heat exchanger and then to the adsorbent bed.

Basic cycle: single adsorber cycle

The solid adsorption heat pump consists of an adsorber filled with adsorbent (zeolite or active carbon), connected to an evaporator and a condenser. The working fluid flows between the adsorber and the condenser (evaporator) depending on which valve is open. As there is no carrier gas, the driving force for this working fluid flow is the pressure difference. The three units—adsorber, evaporator, and condenser—are linked to external heat sources as follows: heating phase (*Figure 5b*), adsorber-boiler and condenser–intermediate temperature heat sink; cooling phase (*Figure 5c*), adsorber–intermediate temperature heat sink and evaporator–low temperature heat source.

In *Figure 5a*, the intermittent cycle is shown in a Clapeyron diagram (log *p* vs. *T*).

Heating phase (abc). As the adsorber is heated, pressure increases from the evaporating pressure to the condensing pressure. The valve between the adsorber and the condenser is open when the pressure in the adsorber reaches the condensing pressure constrained by the intermediate heat-source temperature; then condensation starts. The heat input to the adsorber during this first sequence is *Q*abc, whereas the heat output from the condenser is *Q*cond. At the end of this phase, the valve between adsorber and condenser is closed.

Cooling phase (cda). As the adsorber is cooled, pressure decreases. The valve between the adsorber and the evaporator is open when the pressure in the adsorber reaches the evaporating pressure constrained by the low-temperature heat source; then evaporation starts. The heat input to the evaporator during this second sequence is *Q*ev, whereas the heat output from the adsorber to the intermediate heat exchanger is *Q*cda.

The cooling coefficient of performance of a single adsorber cycle, COP_{cl}, is equal to the heat load in the evaporator per unit heat load in the adsorber under regeneration.

$$COP_{cl} = Qev/Qabc \tag{1}$$

The heating coefficient of performance, COP_{hl}, (or coefficient of amplification: COA_l) is

$$COA_l = (Qcond + Qcda)/Qabc = 1 + COP_{cl} \tag{2}$$

Both COP_l and COA_l depend on the values of the four operating temperatures. A systematic study of the effect of the operating temperatures on an activated carbon/methanol cycle was conducted by Douss and Meunier.[9]

With the activated carbon/methanol pair, experimental COP ranges from 0.2 (Tev = −20°C)–0.58 (Tev = 5°C) when the adsorber temperature swings between 14.5°C and 80°C, and the condensing temperature is equal to 14.5°C.

Intermittent cycles have two disadvantages: the cooling effect obtained being intermittent, and that large thermal swing may cause significant irreversibilities.[10]

To overcome these disadvantages, regenerative cycles using several adsorbers have been proposed. The simplest regenerative cycle is a two-adsorber cycle.

Two-adsorber cycles

Two types of regenerative cycles have been proposed.

- TSA cycles with homogeneous temperature adsorbers
- TSA cycles with traveling temperature fronts

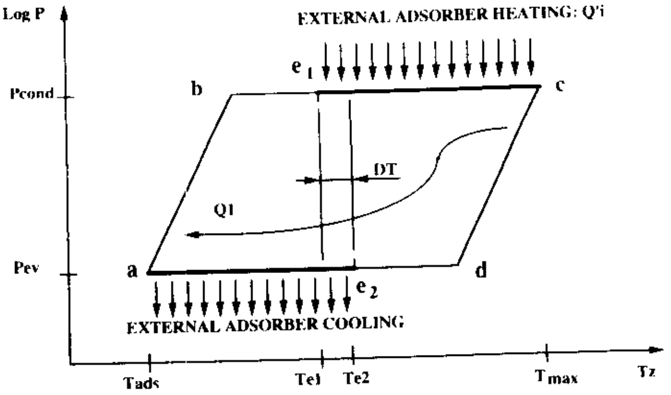

Figure 6 Ideal two-adsorber cycle in a Clapeyron diagram.

Two-adsorber TSA cycles with homogeneous temperature adsorbers. The following section discusses homogeneous temperature adsorbers.

1. *Heat recovery*: The basic idea of such a cycle is to use part of the heat discarded by an adsorber to preheat the other adsorber. Two heat-recovery phases are introduced in the cycle. At a particular time, adsorber 1 is at low temperature, whereas adsorber 2 is at high temperature; adsorber 1 is then preheated using heat coming from adsorber 2, which is precooled. During this phase, no heat is exchanged between the adsorbers and external heat sources.

An ideal two-adsorber cycle may be represented in a *p-T* diagram (*Figure 6*). The thermodynamic path of the sequences are represented as (abe_1, cde_2) heat recovery, (e_1c) external heating, and (e_2a) external cooling.

During the heat recovery step, heat exchange between the two adsorbers is effected through the heat transfer fluid (oil) with adsorber 1 being heated from T_{ads} to T_{e1} and adsorber 2 being cooled from T_{max} to T_{e2} (*Figure 6*).

The efficiencies of the two-adsorber cycle are given by

$$\mathrm{COP}_2 = (Q_{ev1} + Q_{ev2})/Q'_1 + Q'_2) \tag{3}$$

$$\mathrm{COA}_2 = (Q_{cond1} + Q_{cond2} + Q_{e2a1} + Q_{e2a2})/(Q'_1 + Q'_2) = 1 + \mathrm{COP}_2 \tag{4}$$

where Q_{evi} (Q_{ci}) is the evaporating (condensing) heat corresponding to the evaporation (condensation) related to adsorber i, and Q_{e2ai} is the heat released by adsorber i under adsorption during the external cooling phase.

Q_i is the heat supplied directly by the boiler to adsorber i during the external heating phase.

The heat recovery step is very important, because it is responsible for the enhancement of the efficiencies. In the search for more advanced regenerative cycles, several solutions have been proposed. Meunier[10] has shown that, using an infinite number of adsorbers with ideal heat recovery between homogeneous temperature adsorbers and using a single evaporator and a single condenser, it was possible—with given conditions of operating temperatures—to get a cooling COP much higher than 1 (1.85), equal to 65% of the ideal Carnot COP corresponding to the operating temperatures.

2. *Pressure equalization*: Another idea, first proposed in Munich,[11] is to perform a pressure equalization between the two adsorbers at the end of the phase when one adsorber is at the higher temperature and higher pressure, whereas the other adsorber is at the lower temperature and lower pressure. This strategy has been successfully tested at LIMSI,[12] resulting in a COP improvement around 25% and an enhancement of the cooling capacity around 35% or a reduction of the regenerative temperature of the order of 10–15°C for the same cooling capacity. This could be very important in the competition between liquid absorption (LiBr-water pair) and solid adsorption (silica gel-water pair) for air conditioning systems fired with low-grade heat rejected from cogeneration gas fired engines because in that case, waste heat is generally available at 70°C only, temperature too low for liquid absorption systems when solid sorption systems using the pressure equalization cycle could be more efficient. This could be an excellent solution for Japan.[13] Obviously, the heat recovery and the pressure equalization strategies could be combined to still improve the cycle performance.

Two-adsorber TSA cycles with traveling temperature fronts. The following section discusses traveling temperature fronts.

The basic idea of the traveling temperature concept as adapted to refrigeration TSA cycles is that in a homogeneous temperature TSA cycle, the limitation to the regenerative efficiency comes from the fact that heat can be transferred from adsorber 1 to adsorber 2 only if adsorber 1 is at a higher temperature than adsorber 2. With the concept of traveling fronts, it would be possible to transfer heat from adsorber 1 to adsorber 2 even if the mean temperature of adsorber 1 is lower than the mean temperature of adsorber 2 as long as the outlet temperature of adsorber 1 is higher than the outlet temperature of adsorber 2 (*Figure 7*). Therefore, it is conceptually possible to get much more effective regeneration efficiency than with a homogeneous temperature adsorber process as soon as one is able to promote sharp traveling temperature fronts in adsorbers: This is the key point of this process invented by Shelton[14] and Tchernev.[15]

Unfortunately, dispersion effects, which contribute to get a ramp or a smooth curve rather than a sharp front may come from axial heat transfer, low heat-transfer coefficient between heat-transfer fluid and adsorbent, mass-transfer limitations (owing to kinetics of adsorption as well as from vapor flow), etc. For these reasons, at the moment, it has not been demonstrated that a good temperature front shape was obtainable in the operating conditions of a refrigerating cycle with the adsorber designs currently used. Nevertheless, it does not look like that for any scientific reason, such a

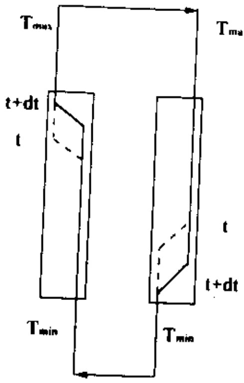

Figure 7 Schematic of the temperature front process concept: high temperature fluid out from the left adsorber is used to heat the right adsorber, whereas low temperature fluid out from right adsorber is used to cool down the left adsorber. Fronts propagate in both adsorbers between times *t* and *t* + *dt*.

process would not be possible, but it certainly requires conceiving new adsorbers, which seems to have been recently achieved by Shelton's group.[16]

Cascading cycles

It is well known by mechanical engineers that cascading cycles may be very effective to get either higher efficiencies or higher temperature lifts. The same concept of cascading cycles (as used with compressors or with liquid absorption[17]) can be also applied to adsorptive cycles.

At LIMSI, this concept has been adapted using two different pairs.[18]

An active carbon-methanol intermittent cycle with low regenerative temperature is boosted by a two-adsorber zeolite-water cycle (*Figure 8*).

In this cycle, only two temperature levels are used for the working fluids (the same evaporating temperature and the same condensing temperature are used for water and methanol). Low-temperature adsorptive heat of the zeolite cycle is used as regenerative heat for the active carbon cycle.[19]

Results of studies carried out at LIMSI

A brief summary of the most relevant results obtained from studies conducted at LIMSI in recent years is given subsequently.

1. *For solar cooling*: A small domestic refrigerator (using zeolite/water)[20] and a 12 m^3 store house fired with zeolite/water pair[21] were constructed. In addition, demonstration[5,22,23] and commercial[24] ice-making units (using activated carbon/methanol) have also been successfully developed.
2. *Heat pump*: A 200 kW heat pump was designed, constructed and used to provide hot water in a slaughter house.[25]
3. *Laboratory units*: The following experimental apparatus were designed, constructed, and successfully operated:

- One and two-adsorber zeolite-water units[26]
- One and two-adsorber active carbon-methanol units[9,12]
- A three adsorber unit[19]

Some of the important conclusions from the experimental studies of these units are as follows

- Depending on the operating temperatures, the COP for one-adsorber cycles was found to range from 0.2–0.5.
- In contrast, the cooling COP for a two-adsorber cycle may be as high as 0.75.
- A value of greater than unity was achieved for the COP of a three-adsorber cycle.

The cooling rates obtained in these units were relatively low; with a maximum value of 50W/kg of adsorbent. There were two reasons for this relatively poor performance. The low heat transfer rates within the adsorber, and the relatively large pressure drop be-

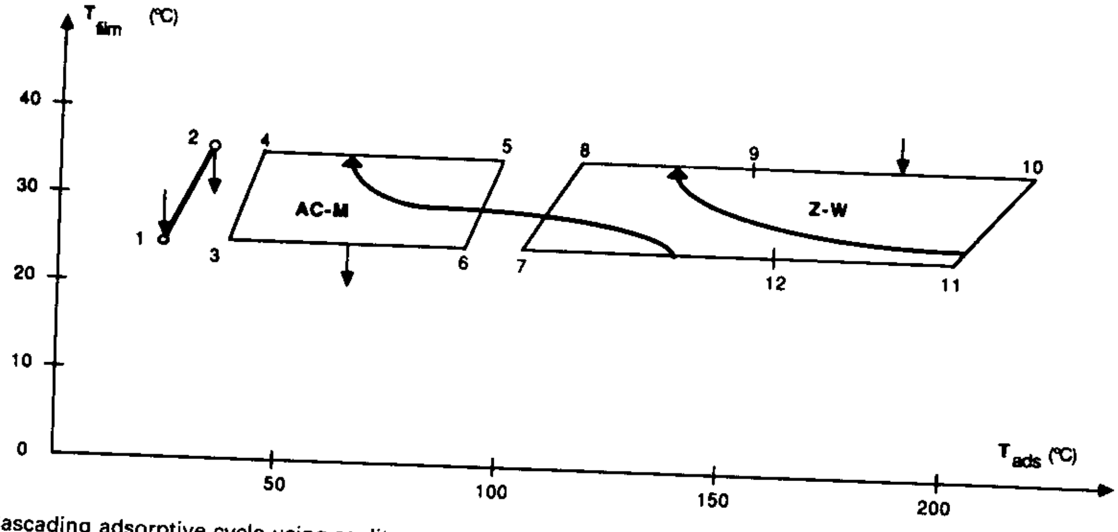

Figure 8 Cascading adsorptive cycle using zeolite-water and active carbon-methanol pairs.

tween the evaporator and adsorber, and hence the low evaporation efficiency. Both of these factors call for development of different types of adsorber and evaporator as well as new kinds of adsorbents.

Conclusions

For the adsorptive processes to become competitive with compression systems, three conditions have to be met.

1. To achieve an evaporating temperature on the order of −30°C
2. To enhance cooling rates per unit mass of adsorbents up 200W/kg and possible 1,000W/kg
3. To obtain a COP greater than 1

To meet the first condition, it is probable that new adsorbent/adsorbate pairs must be developed or identified. For example, both Critoph and Turner[27] and Shelton et al.[28] claimed that ammonia as a candidate adsorbate may meet this requirement. It is also likely that different adsorber configurations may be required to enhance cooling rates. To satisfy the last conditions, devising more efficient schemes for heat recovery and regeneration may also be required.

In light of the preceding remarks, it becomes obvious that the key to a successful development of adsorption-based cooling cycles is the availability of new kinds of adsorbents with the required adsorption and heat-transfer characteristics. For the purpose of improving the heat transfer characteristics, we have initiated studies on the preparation of composite adsorbents,[29] which, when completed, should at least provide a partial answer to the problems mentioned previously.

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