ADSORPTION REFRIGERATION RESEARCH IN SJTU

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Abstract

Various adsorption refrigeration cycles have been investigated, several prototype adsorption refrigeration systems have been developed and tested, typical examples are continuous heat regenerative adsorption ice maker using spiral plate adsorbers, adsorption heat pump using novel heat exchanger as adsorbers, solar powered adsorption ice maker, solar powered hybrid system of water heater and adsorption refrigerator, waste heat driven air conditioning system for automobiles. Reasonable experimental results have been obtained, It was found that with a heat source temperature of 100 ^{o}C, the refrigerator can obtain specific refrigeration power for 5.2 kg-ice/day per kg activated carbon in one adsorber, the heat pump can reach a specific cooling power for more than 150 W/kg-adsorbent with a COP close to 0.5, the adsorption solar ice maker yields 5-7 kg-ice per day per square meter solar collector, the hybrid solar water heater and ice maker is capable of heating 60 kg water up to about 90 ^{o}C and meanwhile yields ice making about 5 kg per day with a 2 square meter solar collector. This paper shows the various aspects researched in SJTU.

KEYWORDS

adsorption, heat pump, refrigeration, solar refrigeration

INTRODUCTION

As a good opportunity to replace CFCs or HCFCs refrigeration, adsorption refrigeration research has got enough attentions during these years, specially its potential applications in waste heat recovery, solar energy utilization and etc.. In recent years, various adsorption refrigeration cycles have been studied, however there are not enough verifications by prototype machines; not enough thermal -physical data measured; not enough consideration on adsorption mechanisms of adsorption refrigeration pairs; not much research on adsorption materials; not much considerations on the adsorption refrigeration applications.

Based upon the recent progress of adsorption refrigeration researches in Shanghai Jiao Tong University (SJTU), this paper concludes the various research aspects of adsorption refrigeration in SJTU, which includes adsorption mechanism, thermodynamic analyses of various adsorption refrigeration cycles, high performance prototypes of adsorption refrigerator and heat pump, application of adsorption systems in solar energy application and waste heat recovery.

ADSORPTION MECHANISM

Dubinin-Astakhov equation (D-A equation) is commonly used to describe the adsorption of activated carbon on methanol or ammonia, zeolite on water, which is expressed as

$$x = x_0 \exp\left(-\left(\frac{\varepsilon}{E}\right)^n\right) \tag{1}$$

where E is the characteristic adsorption work determined by the energy properties of adsorption system, x_0 is explained as limiting adsorption capacity, the reformed equation can be expressed as[1]

$$w = w_0 \exp[-D(T \ln \frac{p_s}{p})^n] \tag{2}$$

$$x = x_0 \exp[-K(\frac{T}{T_s} - 1)^n] \tag{3}$$

where w and x represent the volume adsorption and mass adsorption respectively at temperature T and pressure p that is the adsorbed liquid volume (l/kg) and the adsorbed liquid mass kg/kg) per unit mass of adsorbent. In the above equations, p_S is the saturated vapor pressure corresponding to the adsorption temperature T, p is the adsorption pressure which is the saturated pressure corresponding to the saturated refrigerant liquid temperature T_S, D,K and n are the adsorption parameters depending on the adsorption refrigeration pair, w_o,x_o are the maximum adsorbed liquid volume and adsorbed liquid mass per unit mass of adsorbent respectively. The co-relations of the above two equations are $x_0 = \rho w_0$ $K = DA^n$.

The above D-A equations are widely adopted in adsorption refrigeration research, but the physical meaning of w_o and x_o are not clearly defined, as in the application of the two equations w_o and x_o are treated as constants. It can be seen from D-A equation that when the temperature of adsorbent T equals to the saturated temperature of refrigerant T_S , we get $x=x_o$. As is known in an adsorption capacity measurement, the different saturated temperature of refrigerant liquid T_S (which corresponds to different adsorption pressure) yields different value of x_o thus the parameter of x_o as the maximum adsorbed mass is not well defined. It might be estimated that the higher the adsorption pressure, the larger the adsorbed mass, its maximum will be the refrigerant mass occupying the all pore volumes of adsorbent.

A clear definition of adsorption capacity is $x = x(T, p)$, which means the adsorbed mass in adsorbent is a function of adsorption pressure p and adsorbent temperature T. The above considerations have an assumption that the mini-pore sizes are nearly uniform in the adsorbent, a more generalized equation will be $x = x(T, p, B)$ in which B corresponds to the mini-pore sizes of adsorbent. The pore size distribution can be assumed as

$$f(B) = \frac{1}{B_2 - B_1} \tag{4}$$

for uniform pore volumes (size between B_1 and B_2) or

$$f(B) = \frac{1}{\sqrt{2\pi}\Delta} \exp\left[-\frac{(B - B_0)^2}{2\Delta^2}\right] \tag{5}$$

for assumed Gauss normal distribution size with a half width of Δ.

For mathematical convenience, we may postulate a continuous distributions $f(B)$ for the adsorption concentration x_{0j},and $x_{0j} = f(B_j)\delta B_j$. The sum is then replaced by the integral

$$\int_0^\infty f(B)dB = 1 \tag{6}$$

For a given size mini-pores characterized by B_j adsorption equation can be treated as

$$x_j = x(T, p, B_j) \tag{7}$$

For an adsorption surface, the total adsorption capacity can be integrated with the characteristic adsorption of mini-pores multiplied by its distribution, thus we get

$$x = \int_0^\infty x(T, p, B) f(B) dB \tag{8}$$

As limited in a very narrow range of pores $\Delta B \to 0$ we may take $x(T, p, B) = const = x_{B_i}$, $(B_1 \le B_i \le B_2)$ in this range, thus we get a simple form

$$x = x_i = x_{i0} \cdot \exp\left[-\left(\frac{RT \ln(f_0/f)}{E_i}\right)^{n_i}\right] \tag{9}$$

From a mathematical view point, the general expression for the pore size with a Gauss distribution yields a Gauss -based general equation for the filling of pores

$$x = x_0 \exp\left(-B_0 y\right)\cdot\exp\left(y^2\Delta^2/2\right)\cdot\left[1-erf(z)\right]/2 \tag{10}$$

This is the modified equation, where $z=\left(y-B_0/\Delta^2\right)\Delta/\sqrt{2}$, and erf(z) is error function. The variable $y=\left(T/\beta\right)^2\ln^2\left(f_0/f\right)$ already contains the adsorptive-dependent shifting factor β affinity factor), and therefore simplifies the overall graphical representation, f represents fugacity of refrigerant which is used to modify the pressure terms in D-A equation. This equation contains three parameters: x_0, B_0 and Δ,which can be determined by adsorption experiments.

Typical values based upon the data treatment of adsorption capacity measurement are shown in table 1 (activated carbon – methanol, zeolite-water) for heterogeneous distribution of adsorbent pore size and table 2 (activated carbon fiber-methanol) for that of homogeneous distribution.

Table 1 Adsorption parameters of three adsorption pairs [1]

Adsorption pair	x_0 kg/kg	B_0 $\times10^{-6}K^{-2}$	Δ $\times10^{-6}K^{-2}$
YKAC-methanol	0.294	1.033	0.289
SXAC-methanol	0.265	1.273	0.251
Zeolite-water	0.203	1.152	0.310

Table 2: Adsorption parameters of three ACF-methanol adsorption pairs

Adsorption pair	x_0 kg/kg	E kJ/mol	n
JIAACF-methanol	0.342	6.703	1.346
SYACF-methanol	0.606	3.904	0.904
NTACF-methanol	0.602	7.674	1.272

RESEARCHES ON HEAT RECOVERY ADSORPTION REFRIGERATION CYCLES

Adsorption refrigeration is based upon the processes of heating-desorption-condensation and cooling-adsorption-evaporation, the cooling-adsorption process needs heat dissipation both of sensible heat and heat of adsorption. For a two beds continuous adsorption refrigeration system, heat recovery is important to increase the cycle COP, the possible heat recovery for a two adsorption bed system will be some part of sensible heat and heat of adsorption shown as fig.1.

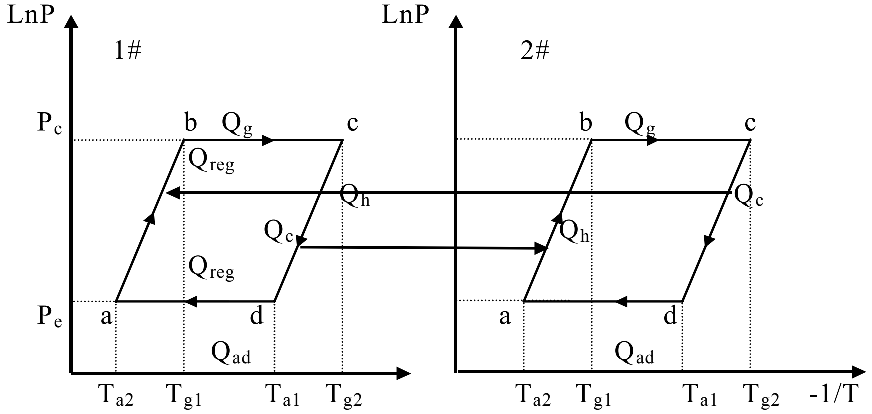

Fig.1 Two-bed adsorption system with heat recovery.

The COP for basic type adsorption refrigeration cycle (one bed or two beds without heat recovery) is

$$COP_B = \frac{Q_{ref}}{Q_h + Q_g} \tag{11}$$

The COP for a two-bed heat recovery cycle can be expressed as

$$COP = \frac{Q_{ref}}{Q_h + Q_g - Q_{reg}}$$

Where Q_{reg} is the heat recovered. In the above equations, Q_h and Q_g are the heat for generation corresponding to the two processes (isostersis and isobars). The refrigeration effect (12)

$$Q_{ref}=\Delta x \cdot L \qquad (13)$$

is the latent heat L multiplied by the cycle concentration change Δx.

The cycle COP will be increased more than 25% by heat recovery process[2], but the COP for a single effect air conditioning system is still low, possibly in the range of 0.4 – 0.6. Multi-beds system will be good to recover more heat, thereby increase COP, however the real system will be very complicated.

For a real heat recovery adsorption system, the heat capacity of metallic adsorber and also the thermal fluid will have strong influence on system COP[2]. If R_m is defined as the heat capacity ratio of adsorber material to adsorbent, and R_f that of thermal fluid to adsorbent, the total heat capacity ratio $R=R_m+R_f$ will have strong influence on system COP. A typical example of the heat capacity ratio effect on system COP is when R=10, the COP will decrease by 30-50% if compared with the ideal COP_0 (COP corresponding to R=0) . When R=5, the COP decreases about 20-30%.

In real design of an adsorption system, good heat transfer should be considered, in order to shorten cycle time and increase specific cooling power (SCP), which may need to increase heat transfer area by finned tubes etc.. But the heat capacity ratio should be controlled, the ideal value of R should be limited below 5, possibly below 3. Oil should be used as thermal fluid to decrease the heat capacity ratio R_f, also the flow volume of thermal fluid should be controlled.

Plate-fin heat exchanger and spiral plate heat exchanger have been applied as adsorbers because of very good heat transfer performance, the SCPs have been obtained as 150 W/kg-adsorbent for air-conditioning and 5.2 kg-ice/day/kg-adsorbent for ice-making, but the COPs are low due to the high values for both of R_f and R_m values. In the two systems, R is high than 10, which causes the COP value relatively low[3].

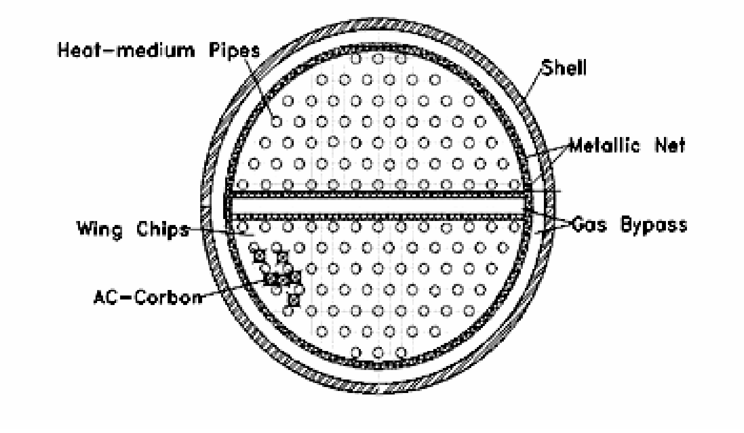

Fig.2 A newly designed plate-finned tubes adsorber.

An improvement has been made in activated carbon-methanol adsorption air-conditioning system, the newly designed plate-finned tubes adsorber is successful both for heat transfer and also the heat capacity control. The adsorber heat capacity ratio is R_m=1.36, while the thermal fluid heat capacity ratio R_f=1.5 for water and R_f=0.53 for oil. The total heat capacity ratio is thereby controlled as R=1.89 if oil is used as thermal fluid[4].

HEAT AND MASS RECOVERY ADSORPTION REFRIGERATION CYCLE [5]

Mass recovery could be initiated followed by heat recovery. As is clear, when adsorber 1 (as generator) is desorbed, it is at the generation temperature T_{g2} and condensing pressure P_c, which is to be cooled to serve as adsorber (temperature from T_{g2} to T_{a1}, pressure from P_c to P_e), while adsorber 2 (currently as adsorber) has adsorbed refrigerant, and is hoped to be heated to serve as generator (temperature from T_{a2} to T_{g2}, pressure from P_e to P_c). A go-between connection between two adsorbers will speed up the pressure changes to reach equilibrium pressure $P_m=(P_e+P_c)/2$. This process will cause more desorption in the generator.

The combined mass and heat recovery procedures will contribute COP significantly. In the real system operation, heat recovery may have two kinds. One of which is sensible heat recovery, the other is sensible heat recovery followed by adsorption heat recovery. Fig.3 shows the COPs of various operation procedures compared with basic type cycle and mass recovery cycle. It is seen that mass recovery followed by heat recovery (sensible & heat of adsorption) is of the best performance, and for activated carbon-methanol air –conditioning system, COP over 0.6 can be achieved with a generation temperature of 80 °C. If the generation temperature reaches 120 °C, COP will be close to 0.8.

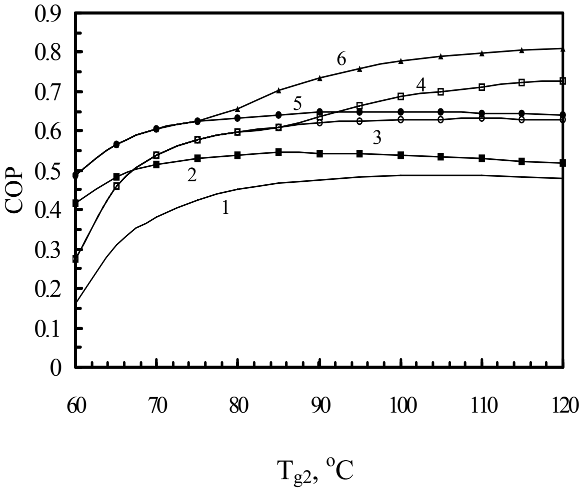

Fig.3 Comparison of COPs for various operation procedures of heat and mass recovery cycle. $T_e=5°C, T_c=T_a=30°C$. R=0. 1: Basic type cycle; 2: Mass recovery cycle;3: Sensible heat recovery; 4: Sensible + adsorption heat recovery;5: Sensible heat & mass recovery;6: Sensible + adsorption heat & mass recovery.

HYBRID HEATING AND COOLING CYCLE [6]

A solar powered ice-maker using activated carbon-methanol has been developed in SJTU, in which two 0.75 m^2 plate solar collector-adsorbers are connected in parallel. With a heat radiation of 20 MJ/m^2 per day, the ice-making performance is 5-7 kg-ice/m^2 solar collector, and the solar COP is 0.12 – 0.15. The solar collector-adsorber needs good thermal insulation (except the face of thermal radiation receiving, in which radiation heat should be absorbed) to yield enough desorption during the day, but needs good cooling in the night to get enough adsorption. This contradiction can be solved by a hybrid system of solar powered water heated and ice-maker.

The schematic design of a hybrid solar powered water heater and refrigerator is shown in figure 4. The system consists of a solar collector, a water tank, an adsorber /generator, a condenser, an evaporator, a receiver and a ice box.

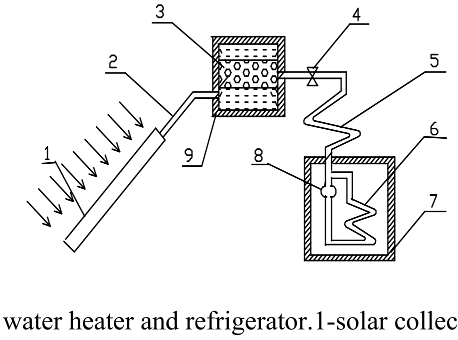

Fig.4 Schematic of the solar water heater and refrigerator.1-solar collector; 2-water pipe; 3-adsorber; 4-valve; 5-condensor; 6-evaporator; 7-refrigerator (with cold storage); 8-receiver; 9-hot water container

The working principle is just a combination of a solar water heater and adsorption refrigeration. Heating of the water tank is started in the morning through evacuated tube type solar collector. With the increasing of the water temperature, the temperature in the adsorbent bed rises. In an ideal process, the adsorbent temperature could be very close to the water temperature in the tank. When the temperature in the adsorbent rises up to a temperature (T_{g1}) which causes the vapor pressure of the desorbed refrigerant up to the condensing pressure (Pc), desorption at constant pressure is initiated, the desorbed vapor is condensed in the condenser and collected in the receiver. This liquid flows to the evaporator via an flow rate regulating valve. The temperature of the water and the adsorbent bed continues rising due to solar heating, a maximum temperature (T_{g2}) for 80-100° could be achieved at the end of the process. The high temperature water is used in the evening for the family, also the hot water in the tank could be drained out and moved into another tank at home, thus hot water can be used very flexibly.

With the refilling of the water tank with cold water, the temperature of the adsorbent bed is reduced rapidly ($T_{g2} \rightarrow T_{a1}$), and the pressure in the adsorber drops to a value below evaporation pressure (P_e). Evaporation could happen if the connecting valve is open, and ice will be made in the refrigeration box. The cooling of the adsorber and the rejection of adsorption heat may cause the temperature of cold water in the tank to rise several degrees ($T_0 \rightarrow T_{a2}$), however this energy is not wasted. Several degrees high than cold water temperature (T_0) will not influence much the adsorption refrigeration, this might be even better than normal cooling to the adsorption bed by natural convection. Refrigeration will continue for the whole night until the next morning.

The features of the hybrid system include (1) It has two purposes: water heating and refrigeration with one solar collector, which is suitable for household applications; (2)Adsorber/Generator is separated from collector, thus high efficiency vacuum collector can be used for water heating, thereby heating the adsorber at same time. The high efficiency heating does not mean a bad cooling of the adsorber through the night, as by draining the hot water from the tank, cold water is refilled to the tank, thus the adsober is cooled and refrigeration will take place; (3) Energy efficiency is high for the use of the total solar energy collected; (4) There is no danger of methanol disintegration as the maximum temperature of adsorbent bed cannot exceed 100 ^{o}C , due to the water tank.

A prototype hybrid system for water heating and ice-making has been developed[6], the adsorber is consisted of 28 ϕ50×1×750mm stainless steel tubes, in which 22 kg activated carbon was filled, the adsorber mass is about 25 kg. The water tank is filled with 120-150 kg water. A 1500 W electric heater is used to simulate a 3 m^2 evacuated heat pipe type solar collector.

Table 3. The experimental results of the hybrid system[6]

Experimental date	Energy accepted	Hot water output		Ice output		COP_{system}	COP_{cycle}	η_{system}
	MJ	^{0}C	*kg*	^{0}C	*kg*			
Dec. 9-10, 1998	54	98	150	-2.5	10.5	0.067	0.386	0.906
March 10-11, 1999	49	91.3	112	-1.8	10	0.064	0.431	0.758

Table 4. Calculated performance of the hybrid system based upon experimental results[6]

Experimental date	Energy accepted	Hot water output		Ice output		COP_{system}	COP_{cycle}	η_{system}
	MJ	^{0}C	*kg*	^{0}C	*kg*			
Dec. 9-10, 1998	24.6	98	60	-2.5	10.5	0.143	0.386	0.795
March 10-11, 1999	22	91.3	60	-1.8	10	0.144	0.431	0.797

Table 3 shows the two experimental results of hot water and ice output in two typical seasons: winter and spring. The water bath is relatively big, in which 150 kg water and 112 kg water were filled for testing. In order to get the designed value in which hot water output is about 60kg with a 2 m^2 solar collector heat input, calculations based upon the above tests shown in table 3 were done, table 4 shows the results. Here 60 kg water is assumed in the water bath, the energy accepted is about 22-24 MJ per day, which is a simulation to a 2 m^2 solar collector. The calculated results show that a 2 m^2 solar collector is capable of heating 60 kg water to about 90 ^oC and producing ice for about 10 kg.

Attention should be made that the demonstration prototype system of water heating is in an open tank, in which the cover of the tank is not sealed, which caused about several percent heat dissipation by evaporation of water. The value of η_{system} is thus smaller than the ideal system, so is the COP_{system}.

PERFORMANCES OF AN ADSORPTION REFRIGERATOR AND A HEAT PUMP

A prototype of continuous heat regenerative adsorption refrigerator using spiral plate adsorber[7,8], and an adsorption heat pump usuing newly configured adsorber[9] shown as fig.2, have been developed, in which activated carbon - methanol is used as adsorption refrigeration pair. In the adsorption systems, two adsorbers are independently operated for heating or cooling along with the intermediate heat recovery process. Each of the system has two adsorbers, one condenser and one evaporator, and a receiver is installed for the observation of refrigerant flow in the system. There are 6 kg activated carbon in each adsorber of refrigerator and 26 kg activated carbon in each adsorber of heat pump.

With a generation temperature less than 100 ^oC, the ice-making test for the refrigerator has obtained a specific cooling power of 5.2 kg-ice/adsorber kg-adsorbent per day. Its COP is about 0.13 , this value is mainly caused by big heat capacity ratio R, which is close to 10[8].

The adsorption heat pump has reached a specific cooling power of about 150 W/adsorber kg-adsorbent with a desorption temperature of about 100 ^oC, meanwhile its COP is over 0.4 with a heat capacity ratio R=2.86 (water as thermal fluid), it is estimated that the COP for air conditioning will reach about 0.5 if R=1.89 (oil as thermal fluid) [9] .

Table 5 Adsorption heat pump performance for heating in winter time

Cycle Time (min)	Heat source temp. (^oC)	Heat pump power (kW)	COA	Heating temp. (^oC)	SHP (W/kg)
30	7.21	12.669	1.47	37.92	487
40	9.18	9.946	1.41	33.49	382
50	6.22	8.28	1.35	28.66	318
60	1.51	7.314	1.33	22.30	281
60	9.76	9.56	1.54	37.93	368

The reversed operation for heating with the adsorption heat pump was carried out, and found very attractive. In the winter time, when the environmental temperature is about 0 –10 ^oC, and the temperature lift is about 20 –30 ^oC, the system heat pumping efficiency COA=1.3 – 1.5, while the specific heating power SHP=280 –500 W/adsorber kg-adsorbent. Table 5 shows some experimental results.

The heat pump research shows that adsorption heat pump is capable of cooling and heating, the heating performance is attractive. It will be of much better performances if the bed thermal conductivity is increased significantly.

CURRENT WORK WITH THE APPLICATION POTENTIALS OF ADSORPTION SYSTEMS

A lot of researches regarding to adsorption refrigeration or heat pump systems have been performed in SJTU, the main work now is focused on solar adsorption refrigeration and air conditioning, the waste heat driven adsorption air conditioning for automobiles.

Solar adsorption ice maker seems to be attractive, 5-7 kg ice/day has been achieved with 1 m^2 plate type adsorber as solar collector, in which activated carbon-methanol is adopted. An improved hybrid solar water heater and refrigerator has been installed, in which 2 m^2 solar collector is adopted, 54 kg water is heated for hot water supply and 4 kg ice can be made which served as ice storage for refrigerator, a 120 liter box is used as refrigerator box, the temperature in the box can be kept for 40 hours at temperature below 5 ^oC. A potential application of solar adsorption refrigeration is for air-conditioning, such as household air conditioning and air conditioning for grain storage. It is expected to use solar plate type adsorber to assure low cost, the expected 1 m^2 adsorber will be less than 100 US$, which will be of commercial interests. With 6-8 m^2 adsorber, it is possible to establish a 20 m^2 room air conditioner, which has a running time of 8 hours. The obvious benefits of solar adsorption system is that the solar energy is used for desorption during the day, the adsorption air-conditioning system can be used when needed. In such applications, both zeolite-water and activated carbon-methanol can be used.

Automobile air conditioning driven by the exhausted gas is really very attractive, however it is very difficult to be realized. The research in SJTU now includes (1)adsorption bus air-conditioning with a cooling capacity of about 20 kW, in which activated carbon-ammonia is adopted, continuous operation will be achieved with the operation phase change of two adsorbers, the two adsorbers for 20 kW air conditioning will be constrained in one cubic meter space. (2)adsorption air conditioning system for train locomotive driver with a cooling capacity of 5 kW, in which zeolite-water is adopted. Continuous cooling is achieved by cold storage though only one adsorber is used in the system. This design is based upon simple operation, and easy maintenance. Zeolite-water is of the best performances for adsorption air conditioning driven by the exhausted gas from an engine, its COP can reach 0.4, however reliability is critical as it is operated in vacuum system. Activated carbon –ammonia is of good reliability, but its COP is only half that of zeolite-water. Waste heat recovery and refrigeration capacity should be matched in the design besides the adsorption system itself.

Acknowledgements

This work was supported by the Training Program for the Talents of State Ministry of Education, and Shanghai Commission of Science and Technology. The supports from Carrier Corporation and UTRC are specially appreciated. The author thanks a lot to Ms. Wu J. Y., Mr. Xu Y.X., Dr.Li M., Dr. Wang W. for their contributions in the research work.

Nomenclature

A	Constant of Clausius-Clapeyron equation	B	Pore size (m)
COP	Refrigeration COP	D	Characteristic parameter of adsorption pair
E	The characteristic adsorption work(kJ/mol)	f	Fugacity (Pa)
K	Characteristic parameter of adsorption pair	n	Characteristic parameter of adsorption pair
P	Pressure (Pa)	Q	Heat (J)
R	Gas constant (J/mol·K)	T	Temperature (^{o}C)
W	Volume adsorption capacity (l/kg)	x	Mass adsorption capacity (kg/kg)

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