Journal of Zhejiang University SCIENCE A
ISSN 1009-3095 (Print); ISSN 1862-1775 (Online)
www.zju.edu.cn/jzus; www.springerlink.com
E-mail: jzus@zju.edu.cn

Experimental adsorption equilibrium study and comparison of zeolite with water and ethanol for cooling systems

MAIGA Abdoulaye Siddeye*, CHEN Guang-ming†‡, WANG Qin
(*Institute of Refrigeration and Cryogenics, Zhejiang University, Hangzhou 310027, China*)
†E-mail: gmchen@zju.edu.cn

Received Mar. 14, 2006; revision accepted Aug. 10, 2006

Abstract: Two adsorption refrigeration working pairs of zeolite with water and ethanol were studied and the parameters of Dubinin-Astakhov model were regressed using the experimental data of equilibrium. The coefficient of heterogeneity varied from 1.305 to 1.52 for the zeolite-water pair and from 1.73 to 2.128 for zeolite-ethanol pair. The maximum adsorption capacity varied from 0.315 to 0.34 for zeolite-water and 0.23 to 0.28 for zeolite-ethanol, respectively. The results showed that the zeolite-water pair is suitable for solar energy cooling not only because of the high latent heat of vaporization of water but also because of the better equilibrium performance. On the other hand, zeolite-ethanol gives a high adsorption capacity at high regeneration temperature, which means it can be used in heat engine systems like buses and cars.

Key words: Adsorption refrigeration, Zeolite, Ethanol, Water, Equilibrium
doi:10.1631/jzus.2007.A0216 **Document code:** A **CLC number:** TB6; TK91

INTRODUCTION

In the past few decades, adsorption processes have been used exclusively for gas separation and purification purposes. It is only recently that this phenomenon has been exploited to produce cooling and heating. As regulations aiming at phasing out the CFCs are being implemented, thermally driven sorption refrigeration machines are emerging as an attractive alternative to electrical vapor compression machines that produce no harmful effect on the environment since their working fluids are generally characterized by zero ozone depletion potential (ODP) and zero global warming potential (GWP). Their additional advantage is that they can be driven by low grade heat energy.

The interest in solid sorption for heat transformation processes such as cooling, heating and heat storage is steadily increasing these years. Most of the solid sorbents available today were originally developed for other purposes such as gas separation instead of for cooling. They have not been optimized or even studied for cooling applications. In comparison with mechanical vapor compression systems, adsorption systems have the benefits of energy saving if powered by waste heat or solar energy. In addition, they are simple to control, have no vibration and lower costs. In comparison with liquid absorption systems, they have the advantage of being able to be powered by a large range of heat source temperatures and do not need a liquid pump or rectifier for the refrigerant and have no corrosion problems. Although adsorption systems have all the benefits listed above, they usually also have the drawbacks of low COP and low specific cooling power (SCP) which however, can be overcome by increasing the heat and mass transfer properties in the adsorber, by enhancing the properties of the working pairs and by better heat management during the adsorption cycle (Wang and Oliveira, 2005).

The working fluid is very important for adsorp-

---

‡ Corresponding author
* Ph.D student at Zhejiang University from Mali

tion cooling system. The types of adsorption mechanisms determine the theoretical aspects of approach and equating of the phenomenon. Since adsorption equilibrium is the most fundamental property, a number of studies have been conducted to determine first the amount adsorbed under a given temperature and pressure and second how selective adsorption takes place when two or more adsorbate components coexist. Many researchers investigated the adsorption of gases on microporous solids such as activated carbon (Marsh, 1987), charcoal (Gregg, 1986) and molecular sieves (Breck, 1974). They were originally for separation and purification processes, but are actually used very commonly in adsorption refrigeration and heat pump systems and gas storage (Rodrigez-Reinoso, 1997). The pairs studied include ammonia-carbon (Shelton *et al.*, 1990; Critoph, 1994), ammonia-salts (Spinner, 1992; Rockenfeller *et al.*, 1992), methanol-carbon (Douss and Meunier, 1989), zeolite-water (Cassioa *et al.*, 1992; Lu *et al.*, 2004), silica gel-water (Bidyut *et al.*, 1997), and ethanol-zeolite (Cui *et al.*, 2005). The two working fluids used in this study are environment friendly and safe and can be used in adsorption cooling and air conditioning driven by solar energy, waste heat of industries or heat engines.

ADSORPTION EQUILIBRUM AND COOLING THEORY

When an adsorbent is in contact with the surrounding fluid (adsorbate), adsorption takes place and after a sufficiently long time, the adsorbent and the adsorbate reach equilibrium. The relation between the adsorbed amount and the temperature at a fixed saturation pressure is known as sorption isobar. Many methods can be used to determine the amount adsorbed like thermogravimetric (weight change) volumetric method (volume change) and chromatography.

As is known, in a closed system, the adsorption of gas onto solid can be measured by monitoring the decrease in adsorbate pressure within a known volume or by measuring the mass gain of the adsorbent due to the adsorbing gas molecules. Adsorption isotherms are useful for characterizing adsorbent with respect to different adsorbates. For describing adsorption isotherm of vapor at relative pressure, the Dubinin-Astakhov equation (D-A equation) is commonly used. The equation was modified by (Wang and Wang, 1999) and can be expressed as:

$$x=x_0\exp[-k(\varepsilon/\beta)^2], \tag{1}$$

where x_0 is limiting adsorption capacity, k is a constant determined by the structure of the adsorbent, β is affinity coefficient determined by the adsorbent-adsorbate pair, ε is the adsorption potential energy. The reformed equation of Eq.(1) can be expressed as

$$x=x_0\exp[-K(T/T_s-1)^n], \tag{2}$$

where x (kg/kg) represents the mass adsorbed at temperature T and the system pressure, in terms of the adsorbed vapor mass per unit mass of adsorbent; T_s is the saturated refrigerant under the system pressure; x_0, K, n are the adsorption parameters depending on the adsorption refrigeration pair, in which n is the heterogeneity parameter varied from 1 to 3 (Rudzinski and Everett, 1992), x_0 is the maximum adsorbed gas mass per unit mass of adsorbent.

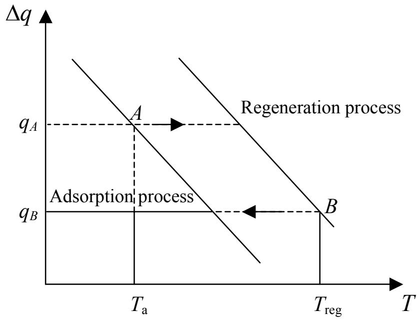

Fig.1 Adsorption-regeneration cycle shown in isobaric diagram

On the other hand, Fig.1's isobaric adsorption diagram shows that the higher the regeneration temperature, the greater the amount difference of mass absorbed. Therefore, for a given adsorbent, the regeneration temperature plays an important role in adsorption process. Adsorbent with low regeneration temperature can use solar energy and low temperature waste heat while adsorbent with high regeneration temperature can use high temperature waste heat, e.g. heat from the exhaust gases of an engine.

The mass difference Δq of adsorbate (refrigerant) utilized for absorbing heat in one cycle is:

$$\Delta q = q_A - q_B, \quad (3)$$

where q_A and q_B are the mass of adsorbate per unit mass absorbent at the end of the adsorption process and regeneration process, respectively.

With regard to Δq, as seen clearly from Fig.1, only regeneration temperature T_{reg} is the variable parameter because in the real situation for adsorption cooling or heat pump, the evaporation, condensing and adsorption temperatures are given. From Fig.1, it is clear that the higher the regeneration temperature, the larger the Δq will be. So from this point of view, the regeneration is an important parameter in the design of cooling or heat pump systems.

EXPERIMENTAL SETUP

The experiment setup (Fig.2) consists of a thermogravimetric balance type PCT-IA with accuracy of 0.01 mg when the sample mass is in the range between the maximum weight of 200 mg and the minimum of 1 mg at a working room temperature varied from 10 °C to 35 °C. The maximum pressure of the system is atmosphere pressure. The temperature fluctuation in the balance can be controlled within about 1 °C. A thermostatic bottle with an adsorbate vessel containing refrigerant is submerged in a thermostatically controlled bath of liquid water, so that the pressure within the system is kept at the saturation pressure corresponding to the bath temperature. The temperature of the bath is measured by a Pt 100 thermometer with accuracy of ±0.1 K after calibration. A 10 mm diameter glass tube is used for the connection between the balance, the adsorbate vessel contained in the thermostatic vessel, two glass vacuum valves and the vacuum pump. In order to obtain temperature and mass adsorbed data, a data acquisition system model Hewlett Packard Agilent 34970A and a remote microcomputer were used. U tube Hg manometer is used to monitor the vacuum of the system.

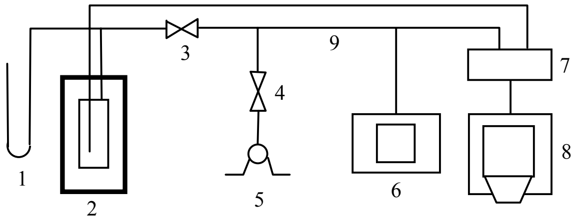

Fig.2 Experimental setup of the thermogravimetric balance system

1: U tube manometer; 2: Thermostatic bottle+refrigerant vessel; 3: Valve 1; 4: Valve 2; 5: Vacuum pump; 6: Thermogravimetric balance; 7: Data acquisition; 8: Computer; 9: Glass tube

Room temperature is also controlled so that there is no danger of any condensed liquid in any part of the glass tube, which might give an erroneous adsorption capacity measurement.

In the thermogravimetric balance, the weight of the sample is measured as a function of the sample's temperature and the saturated pressure of the refrigerant.

Isobaric and isothermal measurements can be carried out to obtain the entire field of equilibrium state of the working pair. Isobaric regeneration measurement can also be carried out. In an isobaric regeneration procedure, the pressure of the vapor is fixed by setting the working fluid in the vessel at a fixed temperature. During the experiment, the sample temperature is increased from 50 to 300 °C and the temperature of the working fluid inside the vessel is fixed at 10, 20 and 25 °C. For each adsorption temperature step, one equilibrium point consisting of temperature, saturated pressure and adsorbed amount is obtained. To calculate the adsorbed amount, the dry mass is needed. In the thermogravimetric balance, the temperature and the mass of the adsorbent is given in millivolt (mV) so that we standardize with standard weight to find the relation between the milligram and millivolt for eventual conversion. The temperature can be converted by the catalogue given by the thermogravimetric balance manufacturer. To obtain the dry mass, the zeolite was first weighed by an electric balance with accuracy of 0.1 mg and the obtained value is then put into the thermogravimetric balance. After that the regeneration of the zeolite was carried out at about 400 °C. In this phase, the valve connected to the thermogravimetric balance via the vacuum pump was kept open until the adsorbent temperature reached 400 °C and the vacuum pump was turned on to remove formed vapor for about an hour. After that equilibrium adsorption was carried out. At each adsorption process, the sample is heated at the regeneration temperature which is about 400 °C for zeolite, under vacuum condition for about an hour to see if the drying weight has any change.

RESULTS AND DISCUSSIONS

The zeolite used in our study was 13× powder with specific surface 1.73 m^2/g and with average diameter of 4 μm. The distilled water with estimated impurity of less than 0.1% is a commercial product from Hangzhou Wahaha Group Co., Ltd., China and the ethanol with impurity less than 0.3% from Shanghai Zhenxing Chemical Factory.

The mass of zeolite is first weighed and immediately put into the thermogravimetric balance and then the heating will start from ambient temperature close to 400 °C. At the same time, the vacuum pump is turned on to take out all formed vapors for about an hour. The obtained results are given in Table 1.

After the above process, adsorption experiment was carried out for different saturation temperatures at different regeneration temperatures.

The amount of water or ethanol adsorbed by zeolite is determined for each regeneration temperature from low to high regeneration temperatures. After obtaining the adsorbed amount at all regeneration temperatures, the adsorbent must be regenerated again to see if there are any changes of the sample drying weight. With the drying weight and the amount of adsorbed water or ethanol at each regeneration temperature known, it was possible to calculate the adsorption capacity, which equals the adsorbed amount divided by the drying weight. In order to find many equilibrium data, a series of experiments are carried out at some saturated pressure corresponding to the saturation temperature of 10, 20 and 25 °C of the adsorbate (water or ethanol) and the regeneration temperature of the adsorbent (zeolite) varied from 50 to 300 °C; the found values are plotted in Fig.3.

Fig.3, shows that regeneration temperature was less than about 100 °C and that the adsorption capacity of the zeolite-water is greater than that of zeolite-ethanol, but at temperatures higher than about 100 °C the tendency changes, the adsorption capacity of the zeolite-ethanol pair is greater than that of the zeolite-water. We can conclude that zeolite-ethanol is not suitable for low temperature heat energy such as solar energy utilization, but can be used for high temperature heat recovery such as for the heat from an engine. On the other hand, this situation can be known also from the heterogeneity coefficient *n* of Dubinin-Astkhov of the two pairs. The greater the value of *n* of a working pair, the higher the regeneration temperature.

By the experimental results, it is possible to calculate the parameters x_0, *K* and *n* of Eq.(2). The obtained results for the two adsorbates are given in Table 2.

From the results, the adsorption capacity of zeolite 13×-water is about 0.33 kg/kg while Ramos *et al.*(2003) found it to be 0.3 kg/kg while Lu *et al.*(2004) reported it to be 0.264 kg/kg under the same condi-

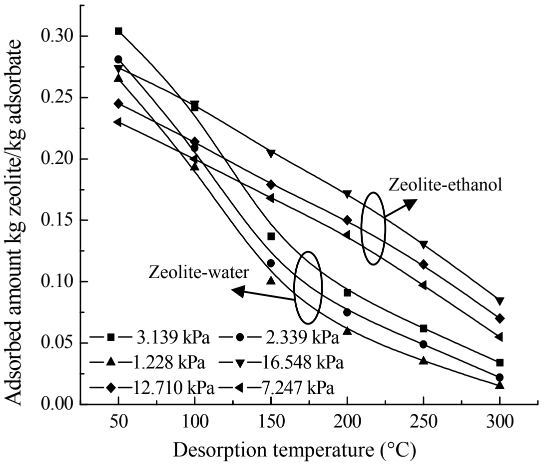

Fig.3 Adsorption capacity at different regeneration temperatures and saturated pressures

Table 1 Amount of drying mass and the adsorption capacity of the sample after regeneration

Mass of saturated zeolite (mg)	Mass of adsorbed water (mg)	Mass of dry zeolite (mg)	Adsorption capacity (%)
57.2	13.32	43.88	30.36

Table 2 The parameters of Dubinin-Astakhov equation at different saturation temperatures

Working pair	x_0			*K*			*n*		
	25 °C	20 °C	10 °C	25 °C	20 °C	10 °C	25 °C	20 °C	10 °C
Water-zeolite	0.340	0.330	0.315	2.552	2.685	2.968	1.358	1.305	1.520
Ethanol-zeolite	0.280	0.250	0.230	1.292	1.276	1.276	1.730	1.750	2.128

tions. Our result is a little higher than their results. This can be explained by the accuracy of the thermogravmetric balance and also the quality of the adsorbent used in each experiment. In our method the amount adsorbed is measured directly (thermogravimetric), while other authors used the volumetric method that is, in general, of less accuracy than the former one.

CONCLUSION

In the design of adsorption refrigeration, one of the key factors is the choice of the adsorbent-adsorbate pair, because the characteristics of both adsorbent and adsorbate play an important role in the adsorption cycle. From the experimental results reported in this paper, the coefficient of heterogeneity of the zeolite-ethanol is higher than that of zeolite-water but the adsorption capacity of the last one is higher than that of the first one. From these results, we can conclude that zeolite-water is more convenient for the low grade heat source such as solar energy while zeolite-ethanol is better for high temperature waste heat recovery such as heat from engines. Another point is that the maximum adsorption capacities of the zeolite-water are very close for different saturation temperatures while zeolite-ethanol is not. At regeneration temperature less than 100 °C the zeolite-water adsorption capacity is greater than that of the zeolite-ethanol but at the temperature higher than 100 °C the zeolite-ethanol is higher than that of the water-zeolite. On the other hand, water is convenient in adsorption cooling because of its high latent heat of vaporization but for an application below 0 °C it cannot be used while ethanol can be.

References

Bidyut, B.S., Atsushi, A., Takao, K., 1997. Silica gel water advanced adsorption refrigeration cycle. *Energy-The International Journal*, **22**(4):437-447.

Breck, D.W., 1974. Zeolite Molecular Sieves. John Wiley, New York.

Cassioa, G., Cammarata, G., Fichera, A., Restuccia, G., 1992. Advances on Innovative Heat Exchangers in Adsorption Heat Pumps. Proc. Symp. le Froid a Sorption Solide, Paris.

Critoph, R.E., 1994. Forced convection enhancement of adsorption cycles. *Heat Recovery System and CHP*, **14**(4):343-350. [doi:10.1016/0890-4332(94)90038-8]

Cui, Q., Tao, G., Chen, H.J., Guo, X.Y., Yao, H.Q., 2005. Environmental benign working pairs for adsorption refrigeration. *Energy*, **30**(2-4):261-271. [doi:10.1016/j.energy.2004.05.005]

Douss, N., Meunier, F., 1989. Experimental study of cascading adsorption cycles. *Chem. Eng. Sci.*, **44**(2):225-235. [doi:10.1016/0009-2509(89)85060-2]

Gregg, S.J., 1986. Sixty years in the physical adsorption of gases. *Colloids and Surfaces*, **21**(1):109-124. [doi:10.1016/0166-6622(86)80086-5]

Lu, Y.Z., Wang, R.Z., Jianzhou, S., Zhang, M., Xu, Y.X., Wu, J.Y., 2004. Performance of a diesel locomotive waste-heat-powered adsorption air conditioning system. *Adsorption*, **10**(1):57-68. [doi:10.1023/B:ADSO.0000024035.57025.97]

Marsh, H., 1987. Adsorption methods to study microporosity in coals and carbons. *Carbon*, **25**(1):49-57. [doi:10.1016/0008-6223(87)90039-X]

Ramos, M., Rafael, L.E., Manfred, J.H., 2003. Evaluation of a Zeolite-Water Solar Adsorption Refrigerator. ISES Solar World Congress 2003, Sweden.

Rockenfeller, U., Kirol, L.D., Sarkisian, P., Ryan, W., 1992. Advancing Heat Pump Staging for Complex Compound Chemisorptions System. Proc. Symp. le Froid a Sorption Solide, Paris.

Rodrigez-Reinoso, F., 1997. Activated Carbon Structure, Characterization, Preparation and Applications. *In*: Marsh, H., Heintz, E.A., Rodrigez-Reinoso, F. (Eds.), Introduction to Carbon Technologies. Edward Arnold, Great Britain, p.35-101.

Rudzinski, W., Everett, D.H., 1992. Adsorption of Gases on Heterogenous Surfaces. Academic Press Inc., San Diego, CA.

Shelton, S.V., Wepfer, W.J., Miles, D.J., 1990. Ramp wave analysis of the solid-vapor heat pump. *J. Energy Res. Technol.*, **112**:69-77.

Spinner, B., 1992. Les Transformations Thermochimiques a Ammoniac. Proc. Symp. le Froid a Sorption Solide, Paris.

Wang, R.Z., Oliveira, R.G., 2005. Adsorption Refrigeration—An Efficient Way to Make Good Use Waste Heat and Solar Energy. International Sorption Heat Pump Conference, Denver, CO, USA.

Wang, R.Z., Wang, Q.B., 1999. Adsorption mechanism and improvements of adsorption equation for adsorption refrigeration pairs. *International Journal of Energy Research*, **23**(10):887-898. [doi:10.1002/(SICI)1099-114X(199908)23:10<887::AID-ER527>3.0.CO;2-N]