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EQUILIBRIUM COMPARISON STUDIES OF METHANOL AND HCFC-123 ON ACTVATED CARBON FOR ADSORPTON REFRIGERATON

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ABSTRACT

In adsorption refrigeration, the adsorbent-adsorbate pair determines the behavior of the system. The knowledge of the equilibrium data between the adsorbent and adsorbate is very important for the design of an adsorber. In this study, the equilibrium adsorption of methanol and R123 on activated carbon has been studied using a thermobalance method for refrigeration and cooling systems. The relation of temperature, pressure and adsorbed mass of methanol and HCFC-123 in the activated carbon is determined using thermobalance. The equilibrium conditions were found at different levels of temperature and pressure, and the data were used to calculate the coefficients of Dubinin-Astakhov equations. Desorption equilibrium is also carried out; the cooling capacities of two refrigerants on activated carbon are evaluated. Finally a comparison is made between the two working pairs in order to find out which working is suitable for the adsorption refrigeration.

Keywords : *adsorption refrigeration, activated carbon, methanol, R123, thermobalance.*

RÉSUMÉ

Les études comparatives d'équilibre du methanol et du R123 dans le charbon actif pour la refrigeration par adsorption

En réfrigération par adsorption le couple adsorbent-adsorbat détermine le comportement du système. La connaissance des données d'équilibre entre l'adsorbent et l'adsorbat est très importante pour la conception de l'adsorbeur. Dans cette étude, l'équilibre d'adsorption de deux refrigerents dans le charbon actif a été étudié utilisant la méthode de la balance thermique, pour les systèmes de réfrigération et de refroidisseurs. La relation température, pression et masse adsorbée du méthanol, R-123 dans le charbon actif est déterminé en utilisant une balance. Les conditions d'équilibre ont été trouvées à des différents niveaux de température et de pression et les données ont été utilisées pour déterminer les paramètres de l'équation de Dubinin Astakhov. L'équilibre de désorption également a été étudiée afin de pouvoir calculer les capacités de froid des deux fluides dans le charbon actif. Finalement une comparaison est faite entre les deux pairs dans l'ordre de trouver lequel est meilleur pour la réfrigération par adsorption.

Mots-clés : *réfrigération par adsorption***,** *charbon actif, méthanol, R-123, thermobalance***.**

I - INTRODUCTION

Economizing energy, environmental protection and sustainable development are all the main themes of the contemporary world in the 21st century. In order to protect the ozonosphere in atmosphere and the ecological environment, the treaty system of ozone layer protection made of Vienna Convention for Protection of the Ozone Layer (1985), Montreal Protocol on Substances Depleting the Ozone Layer (1987) and five amendments of Montreal Protocol has provided the schedule to reduce the use of CFCs (chlorofluorocarbons). In other hand, Working pairs are the crucial parts in the adsorption refrigeration system. According to the basic principle and working characteristics of the adsorption refrigeration system, the adsorbent should have the characteristics of large adsorption capacity, large change of adsorption capacity with temperature variation, more flat desorption isotherm and good compatibility with refrigerant [1]. As for the refrigerant, as similar as that in vapor compression refrigeration systems, the requirements are large latent heat per volume, right freezing point and saturation vapor pressure, no toxicity, nonflammable, no corruption, good thermal stability, etc. [2]. Actually, there are no working pairs to completely meet the requirements mentioned above. But there are many commonly used working pairs which closely meet these requirements such as activated carbon–methanol [3, 4], activated carbon–ammonia [5], zeolite–water [6], silica gel–water[7], calcium chloride–ammonia and composite adsorbent–ammonia [8, 9], MaxsorbIII a an activated carbon on ethanol [10], activated carbon –R134a had been widely researched experimentally by many researchers [11, 12] , and activated carbon - n-butane by [13].

II - THEORETICAL DESCRIPTION AND REPRESENTATION OF ADSORPTION EQUILIBRIUM DATA

The description of the adsorption equilibrium is based on the fundamental works of Dubinin and his co-workers. The Dubinin-Radushkevich (DR) equation for adsorption on activated charcoal, based on the theory of volume filling in micropores by Polanyi was published in 1947. 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 [14] and can be expressed as :

$$x = x_0 \exp[-k(\frac{\varepsilon}{\beta})^2] \qquad (1)$$

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 ***Equation (1)*** can be expressed as

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

where *x* represents the mass adsorbed at temperature *T* and pressure *p*, in terms of the adsorbed vapor mass (kg/kg) per unit mass of adsorbent. *p* is the adsorption pressure which is the saturated pressure corresponding to the saturated refrigerant liquid temperature T_s only when the system is in equilibrium; x_0, *K*, *n* are the adsorption parameters depending on the adsorption refrigeration pair, in which *n* is the heterogeneity parameter varied from l to 3 [15], x_0 is the maximum adsorbed gas mass per unit mass of adsorbent. On the other hand, Figure 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. As adsorbent with low regeneration temperature, can use solar energy and low temperature waste heat; adsorbent with high regeneration temperature, can use for high temperature waste heat, e.g. heat from the exhausted gases of an engine. The mass difference Δq of adsorbate (refrigerant) utilized for absorbing heat in one cycle is :

$$\Delta q = q_A - q_B \tag{3}$$

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.

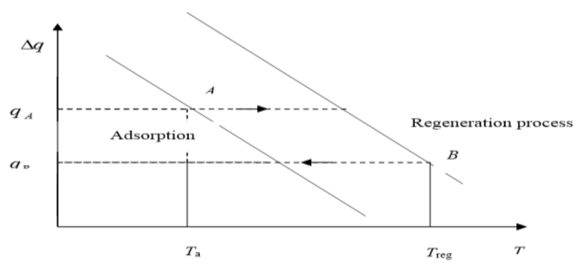

Figure 1 : *Adsorption - regeneration cycle shown in isobaric diagram*

With regard to Δq , as seen clearly from ***Figure 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 ***Figure 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 adsorption systems.

III - MATERIALS AND PROCEDURE

III-1. PCT-1A TG-T thermogravimetric analyzer

Figure 2 : *Photograph of thermobalance and accessories*

The PCT-1A provided a system for measuring weight changes on samples up to 1000 mg between room temperature and 1100°C with a sensitivity of $10\ \mu g$, from Beijing Instrument Industry. Constant computer control enabled the user to define a precise temperature profile that could be comprised of ramps and isotherms while controlling the gas environment with on/off switching in user specified preprogrammed methods. The computer data acquisition and control system obtained and stored time; weight and temperature at define time intervals. The maximum pressure of the system is atmosphere pressure. The temperature fluctuation in the thermobalance can be controlled within about 1°C. The experiment setup ***(Figure3)*** consists of a thermogravimetric balance type PCT-IA with an accuracy of 0.01mg when the sample mass is in the range between the maximum weight of 200 mg and the minimum of 1mg at a working room temperature varied from 10-35ºC. The maximum pressure of the system is atmosphere pressure. The temperature fluctuation in the balance can be controlled within about 1ºC. 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 an 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. 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.

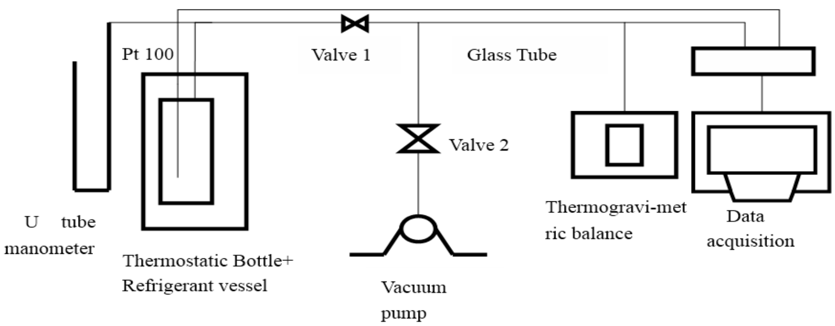

Figure 3 : *Experimental setup of the thermogravimetric balance system*

III-2. Activated carbon coconut shell

Activated carbon is a predominantly amorphous and microporous solid. Its physical properties are mainly dependent on the pore structure, namely, the surface area and pore size distribution. In this study a commercial activated carbon coconut shell produced from Shanghai Tangxin Active Carbon Co. Ltd by chemical activation with specific surface area 1000 m^2/g and an average grain diameter of 0.5 mm with density 1070 kg/m^3.

III-3. Refrigerents

The methanol with impurity less than 0.3 % is produced by Shanghai Zhenxing Chemical Factory China. It is an alcohol so flammable, with high latent heat of vaporization and almost stable and low specific volume. It can be used for freezing purpose because it freezing points are below zero. Methanol is used in solar refrigeration. Like water, it is considered as environmentally friendly fluid. The sub-atmospheric refrigerants such as water, methanol and ethanol have excellent thermodynamic properties but their specific cooling power (SCP) can be limited by low mass transfer rates from internal diffusion, pressure drops etc. The refrigerant R123 is HCFC produced by Zhejiang Chemical Industry Research Institute. The operating pressure is near to atmosphere pressure. It has a small latent heat than other working pairs used in this study, a high molecular weight; a high critical temperature with a boiling point of 27°C. But R123 is an HCFC, which might be phased out in the future. Compared to other refrigerants, it shows better from the environment view than many HFCs because its atmosphere lifetime is only as short as 1.3 year. The ODP is 0.012 and the GWP is only 76 while R134a, for example, its life time is 14 years and has a very high GWP of 1320 [16].

So R123 has a favorable overall impact on the environment that is attributable to some factors such as a short atmospheric lifetime, very low GWP, low ODP, low emissions of current design for R123 chillers and also offers exceptionally high efficiency. It is a safer refrigerant and its toxicity is very low, classified as a B1 refrigerant [17]. While long-term alternatives have been identified for most refrigerant needs, the search is going on for R123's replacement. For perspective, R134a has largely replaced R12 in appliances, commercial and transport refrigeration, mobile air conditioners, chillers, and other uses. These uses and the elusive R123 replacement are the plums of the refrigerant market. Despite all the activity for the plums, niche applications, and service fluids, the important successor to replace R123 has not emerged [18]. HCFC123 has been employed in a vapor compression chiller. If using it with activated carbon as working pair for gas solid refrigeration and heat pump systems, the compressor and its associated problems such as lubricant and electric power consummation problems are eliminated. Adsorption refrigeration has no moving part and also has the potential of a long life. In addition the pair activated carbon-R123 can use natural gas fired heat, waste heat or renewable energy such solar energy which all are environmentally friendly. The production cost of adsorption refrigeration is also lower than that of the traditional compressor one, since the activated carbon and the standard materials for the adsorber construction can be found at lower price. Activated carbon has the advantage to be regenerated easily than other adsorbents and can be produced easily, making it an excellent sorbent. The activated carbon–methanol would be one of most promising working pairs in the practical systems [19, 20]. Certainly, the activated carbon–methanol has many shortcomings. Firstly, the activated carbon would catalyze methanol to decompose into dimethyl ether especially at the temperature of more than 150 ºC. Therefore, the activated carbon–methanol is suitable for the desorption temperature no more than 120 ºC. Secondly, methanol should be used carefully due to its high toxicity. Thirdly, high vacuum is necessary for this system.

III-4. Procedure

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 300ºC and the temperature of the working fluid inside the vessel is fixed at 10, 20 and 25ºC. 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.

IV - RESULTS AND DISCUSSION

Table 1 gives the different weight of the activated carbon from saturated to the desorption state and the adsorption capacity.

Table 1 : *Drying weight and adsorption capacity of the activated carbon after desorption*

Mass of saturated activated carbon(mg)	Mass of adsorbed Impurity (mg)	Mass of drying activated carbon(mg)	Adsorption capacity (%)
50.00	8.24	41.76	19.73

Table 2 gives the finding parameters of Dubinin -Astakhov equation after the experiment, while the ***Figure 4, 5***. Gives the adsorbed capacity at different pressure of the two refrigerants on the activated carbon

Table 2 : *Finding Dubinin -Astakhov equations*

Working pairs	Finding Dubinin Astakov equation (DA)
Methanol-AC :	$x = 0.32 \exp\left(-17.23\left[\frac{T}{Ts}-1\right]^{2}\right)$
R123 – AC :	$x = 0.58 \exp\left(-1.98\left[\frac{T}{Ts}-1\right]^{1.37}\right)$

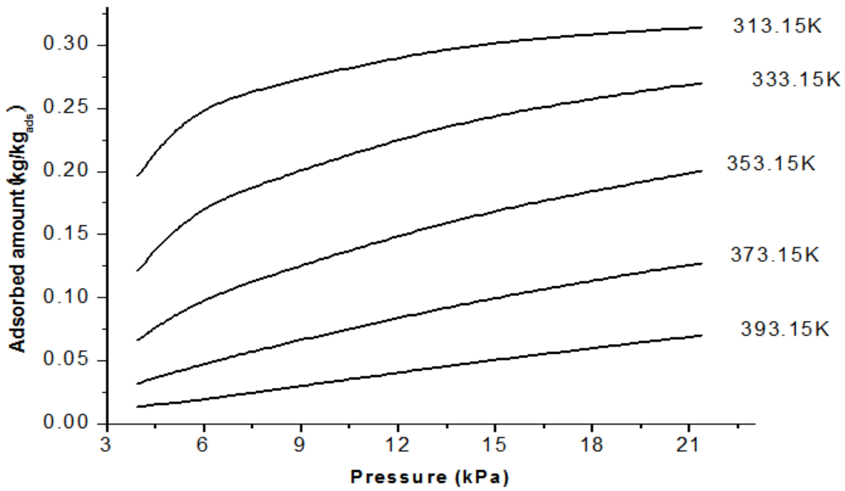

Figure 4 : *Calculated adsorption capacity vs. pressure of methanol- AC*

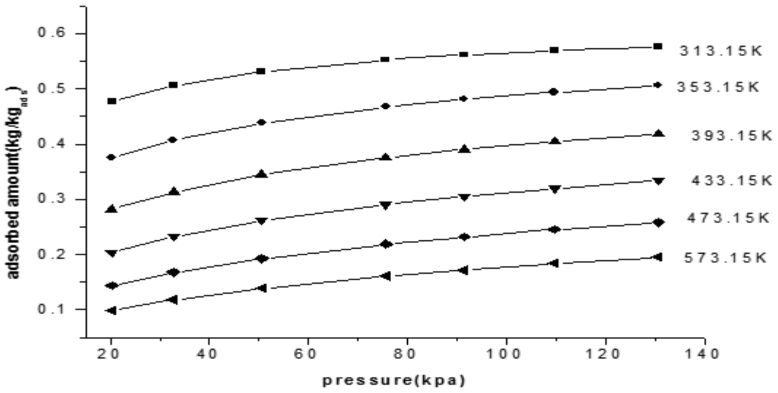

Figure 5 : *Calculated adsorption capacity vs. pressure of R123-AC*

Table 3 : *Desorption and cooling capacity of methanol-AC*

Desorption temperature (C)	**Methanol-activated carbon**	
	Desorbed capacity (kg/kg_{ads})	cooling capacity (kJ/kg_{ads})
60	0.082	90.20
80	0.104	114.40
100	0.121	133.10
120	0.136	149.6
140	0.152	167.2

Table 4 : *Desorption and cooling capacity of R123-AC at different desorption temperature*

Desorption Temperature (°C)	**Desorbed capacity(kg/kg_{ads})**	**cooling capacity(kJ/kg_{ads})**
80	0.153	27.05
100	0.21	37.13
130	0.307	54.28
160	0.420	74.26
200	0.543	96.00
230	0.639	113.00
250	0.686	121.30

From the ***Table 3*** and ***Table 4*** it can be seen that the R123 has the highest desorbed capacity but has the low cooling capacity due to it lower latent heat also the methanol cannot be used at high temperature while the R123 can be.

V - CONCLUSION

The physical adsorption of gases is a very useful technique for the characterization of porous solids and especially, microporous solids. An important problem in the characterization of microporous solids is the parameters that characterize the microporous solids structure. One of the most equations used for the description of the experimental data is Dubinin - Astakhov equation. Also in adsorption refrigeration, one of the key factors that influence the characteristics of the system is the working pair. Therefore, the adsorption and desorption equilibrium data of a working pair are very useful for designers and also for the analysis of thermodynamic performances. In this paper, the adsorption and desorption equilibrium for methanol and an HFC named R123 with activated carbon as adsorbent are investigated. The results show that, the combination working pair of R123-activated carbon has the highest adsorption and desorption capacities at all temperatures than that of methanol-Activated carbon and especially at low desorption temperatures. But the cooling capacity of methanol is higher than that of R123 dues to the high latent heat of methanol. From these initial results it can be seen that R123-activated can be a good working pair which can replace at high desorption temperature around 200ºC where alcohols can be very dangerous. To determine which of these working pairs are suitable for use in adsorption refrigeration and heat pump, a more detailed thermodynamic study is necessary.

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