Adsorption (2013) 19:997–1006
DOI 10.1007/s10450-013-9515-6

Selection and performance of adsorbents in an adsorption refrigeration cycle regenerated with water directly

Hai-jun Chen · Xiao-li Yao · Qun Cui · Yue-zhao Zhu · Ying Tang · Xiu-jun Chen · Juan Wu · Li-li Sheng · Hu-qing Yao

Received: 10 December 2011 / Accepted: 8 February 2013 / Published online: 20 February 2013

Abstract An adsorption refrigeration cycle regenerated with water directly (ARRD), which has the advantage of excellent heat transfer performance in the adsorbent bed with half-cycling time 3–5 min, and operates close to atmospheric pressure (0.1–0.5 MPa) with *n*-butane as a refrigerant, is developed. The purpose of this study is to find out advanced adsorbent/*n*-butane pairs for the ARRD system. Adsorption equilibrium performances of *n*-butane on the adsorbents were measured by positive pressure gravimetric method, and the adsorption equilibrium data were fitted by D-A equation. Desorption properties were determined through thermal analysis. The coefficient of performance and specific cooling power (SCP) were calculated. The results show that adsorption capacities of *n*-butane with activated carbon are all above 0.31 kg/kg and the highest can reach 0.43 kg/kg. Adsorption data are fitted well by D-A equation, with the correlative coefficients *R* above 0.93. Desorption temperatures of *n*-butane from carbons are between 110 and 130 °C, prospective for using low grade heat source. The quasi-equilibrium of *n*-butane on carbons can be achieved within 150–250 s, which benefits SCP of the ARRD system. The SCP of *n*-butane/AC-5 pair estimated in the ARRD systems is from 180 to 200 W/kg.

Keywords Adsorption refrigeration · Regenerated directly · *N*-butane · Activated carbon

Abbreviations

AC	Activated carbon
ACF	Activated carbon fiber
ARRD	Adsorption refrigeration cycle regenerated with water directly
BET	Brunauer-Emmett-Teller
COP	Coefficient of performance
D-A	Dubinin-Astakhov
DTA	Differential thermal analysis
GWP	Global warming potential
ODP	Ozone depletion potential
SCE	Specific cooling effect, kJ/kg
SCP	Specific cooling power, W/kg
TG	Thermogravimetry

List of symbols

$c_{p,a}$	Specific heat capacity of activated carbon, kJ/kg °C
$c_{p,ref}$	Specific heat capacity of liquid refrigerant, kJ/kg °C
E	Characteristic adsorption work, J/mol
L_e	Latent heat of *n*-butane, kJ/mol
n	Exponential constant of D-A equation
P	Adsorption equilibrium pressure of *n*-butane, kPa
P_c	Condensation pressure, kPa
P_e	Evaporation pressure, kPa
Q_{ad}	Adsorption heat, kJ/mol
Q_{cond}	Condensation heat, °C

H. Chen · Y. Zhu · J. Wu
Jiangsu Key Laboratory of Process Enhancement and New Energy Equipment Technology, School of Mechanical and Power Engineering, Nanjing University of Technology, Nanjing, China
e-mail: chenhj@njut.edu.cn

X. Yao
Sinopec Yangzi Petrochemical Company Ltd, Nanjing, China

Q. Cui (✉) · Y. Tang · X. Chen · L. Sheng · H. Yao
College of Chemistry and Chemical Engineering, Nanjing University of Technology, No. 5 Xin Mofan Road, Gulou District Nanjing 210009, Jiangsu, China
e-mail: cuiqun@njut.edu.cn

Q_{eva}	Cooling capacity, kJ/kg
Q_g	Desorption energy, kJ/kg
Q_h	Heat input of a cycle, kJ/kg
Q_p	Pumping energy, kJ/kg
R	Correlation coefficient; general gas constant
T_{a1}	The end of temperature precooling process, °C
T_{a2}	Adsorption temperature, °C
T_c	Condensation temperature, °C
T_e	Evaporation temperature, °C
T_{g1}	The end temperature of preheating process, °C
T_{g2}	Desorption temperature, °C
x	Equilibrium *n*-butane uptake, kg/kg
x_0	Maximum equilibrium *n*-butane uptake, kg/kg
x_{max}	Maximum *n*-butane uptake, kg/kg
x_{min}	Minimum *n*-butane uptake, kg/kg

Greek symbols

$\Delta\tau$	Adsorption time during a cycle, min
ε	Adsorption potential, J/mol
τ	Adsorption time, min

1 Introduction

The growing global non-renewable energy consumption has resulted in environment deterioration and energy resource depletion. In order to find a solution to these serious problems, more and more attention has recently focused on renewable energy and increasing the efficiency of energy systems. Thus, the technology utilizing waste heat or solar energy efficiently, such as adsorption refrigeration, can be one of the alternative methods (Wang and Oliveira 2006; Wongsuwan et al. 2001; Wang et al. 2009). Additionally, these systems have advantages of zero ozone depletion potential (ODP) and global warming potential (GWP), and are less sensitive to shocks. Nowadays, there are some small-scale adsorption machines available, such as solar adsorption refrigerator by Critoph (1994), silica gel-water adsorption chiller driven by low grade heat source by Liu et al. (2005) and adsorption ice maker for fishing boats by Cao et al. (2005) and by Li et al. (1999).

However, adsorption refrigeration systems have drawbacks of low coefficient of performance (COP), poor specific cooling power (SCP) and bulkiness of the equipments compared with traditional mechanical refrigeration systems, which block their large-scale industrialization and commercialization (Wang and Oliveira 2006). Most research on these adsorption systems are focused on searching or developing advanced working pairs, heat and mass transfer intensification in the adsorber, and heat recovery or heat regenerative adsorption cycles for full utilizing inner heat source. Adsorbent bed is the core part of adsorption systems. Since thermal conductivity of adsorbents is generally low, heat is transferred slowly through the adsorbent bed, which lengthens the periods of adsorption and desorption processes. Therefore, enhancement of heat and mass transfer in adsorbent bed is one of the key elements to improve performance of adsorption cycles. Since the indirect heat transfer method is adopted in the conventional adsorption systems, measurements such as adopting high thermal conductivity adsorbents by Lee et al. (2005) and by Chen et al. (2004), reducing heat resistance between adsorbent bed and adsorbents by Zhu and Wang (2002), extending heat transfer surface of adsorbent bed by Wang et al. (2007) and by Critoph and Metcalf (2004), and utilizing heat pipe in the bed by Vasiliev et al. (1995) and by Lu et al. (2006), are commonly applied to intensify heat transfer in adsorbent bed. Whereas, the methods mentioned above result in the degradation of mass transfer in the adsorber, or the increasing of metal mass of adsorbent bed which lowers the efficiency of adsorption cycles.

The forced convection adsorption cycle, a patented cycle originally suggested by Critoph (1994), is aimed to achieve both high efficiency and small size from a solid adsorption cycle by heat transfer intensification. In this cycle, thermally massive heat exchangers within the adsorbent beds are unnecessary. Despite the poor conductivity, the carbon (or other adsorbents) grains have a very high surface area which can be used for convective heat transfer. In the case of a carbon-ammonia bed, the ammonia vapor can exchange heat outside the bed in a conventional heat exchanger, and then pumped through the bed, where it rapidly exchanges heat with activated carbon there. As the surface area of the grains are so large, the heat transfer per mass of bed is higher than with conventional heat exchangers within the bed (heat transfer coefficient: 10^2–10^3 W/(m^2 K)). A thermodynamic model presented by the author predicted a COP of 0.95 when the evaporation temperature is 0 °C and a condensation temperature is 42 °C. Work funded by EPSRC and British Gas has been underway to test the concept in a laboratory scale system, a 10 kW water chiller, for air conditioning by Critoph (1999). Wang et al. (2011) proposed and designed a fluidized-bed adsorber/desorber which can be used in the adsorption refrigeration system in place of the conventional fixed-bed one. By way of the new approach, the poor heat and mass transfer in the conventional fixed-bed absorber/desorber can be overcome and the SCP of the adsorption refrigerator can be expected to be greatly improved accordingly. Difficulties in realizing these adsorption cycles lie in that the refrigerant cycling pump is required to provide high pressure (1.5–2.0 MPa) and be oil-free compressor.

In order to enhance heat and mass transfer in the adsorber, an adsorption refrigeration cycle regenerated with water directly (ARRD) was developed and patented (Cui et al. 2009). In this cycle, inner medium, such as water or water vapor is used to heat adsorbent bed directly and rapidly giving up its heat to the adsorbent during desorption phase, while in adsorption phase, refrigerant vapor is pumped to circulate through the beds and cool the adsorbent. Similar process has been commonly used in industrial process for organic vapor recovery (Salvador and Sanchez 1999). The diagram of this adsorption cycle and corresponding thermodynamic characteristics are sketched in Fig. 1.

Figure 1 shows that, a typical ARRD system in basic cycle mode mainly comprises an adsorber, an external cooler to cool the adsorber, a cycling pump, a vapor–liquid separator 1, a liquid reservoir, an expansion valve and an evaporator for adsorption refrigeration, as well as a hot water tank, a condenser, a water pump, and another vapor–liquid separator 2, for regeneration stage. In desorption phase (see Fig. 1a), hot water is pumped (by water pump) to the adsorber and releases its heat to the adsorbent directly (Q_h). The adsorbent temperature rises rapidly to inlet hot water temperature, typically 90–120 °C (T_{g2}) depending on operating conditions and the specific applications. The refrigerant (typically being *n*-butane or iso-butane) is dorbered from the adsorbent and enters the vapor–liquid separator 1 in combination with released water. Water is separated by the vapor–liquid separator 1 with refrigerant vapor. The refrigerant vapor and some water vapor releasing heat (typically 30–50 °C, Q_{cond}) in the condenser is condensed to saturated liquid and sent to the liquid reservoir, where water and liquid refrigerant is demixinged. Water from the vapor–liquid separator 1, as well as the lower lamination water in the liquid reservoir, is transferred back to the hot water tank, where they will be heated and pumped again to the adsorbent bed. Due to the presence of water vapor, condensation of refrigerant vapor might become more difficult compared with traditional adsorption cycles, thus to a higher residual refrigerant loading (x_{min}). During adsorption phase, cold *n*-butane vapor (near ambient temperature) is pumped (by cycling pump) through the adsorber, through the external cooler where it gives out adsorption heat of the adsorbent (Q_{ad}), through the vapor–liquid separator 2 rejecting little condensated water to the hot water tank, and back to the adsorber. The enthalpy of vaporization of the adsorbed refrigerant produces a cooling-effect at T_e by extracting heat (Q_{eva}) from a chilled medium. This phase is,

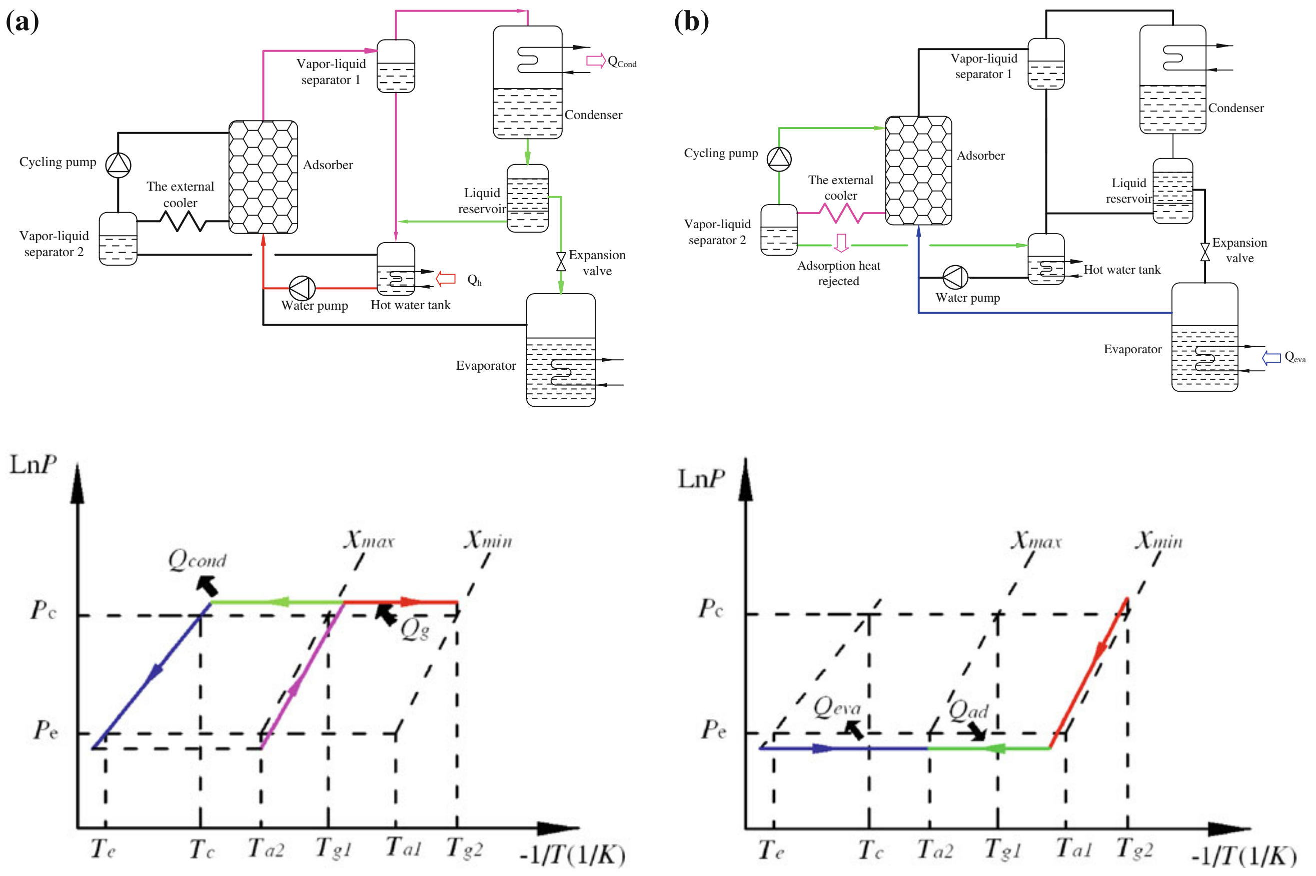

Fig. 1 Diagram of the novel ARRD system in basic cycle mode

to some extent, similar to that of the forced convection adsorption cycle by Critoph (1994), except for the attendance of water vapor. The circulation flow rate of *n*-butane vapor during adsorption phase may be 10–20 times the desorption hot water flow rate. Co-adsorption of water vapor will lower *n*-butane adsorption uptake on the adsorbent (x_{max}), as shown in Fig. 1b. Continuous refrigeration can be available through alternative operating with two or more beds. The presence of water vapor will affect both of desorption and adsorption, resulting in a lower COP compared to traditional adsorption cycles. Moreover, the pumping energy will, to some extent, decrease COP of the ARRD cycle.

To date, the adsorption pairs mostly used include water–silica gel, water–zeolite, methanol–carbon, ammonia–carbon and ammonia-metal salts. For the traditional refrigerants in the adsorption heat pump, the system pressure is too low (high vacuum) for water or methanol, or too high for ammonia. Thus, adsorption refrigeration systems which operate surrounding atmospheric pressure are considered to be the orientation of their commercial industrialization by Meunier (1998). In the ARRD system, *n*-butane, commonly used as refrigerant in mechanical refrigerator in Europe (Fatouh and Kafafy 2006), is adopted as the refrigerant, which works at near atmospheric pressure.

Preliminary studies on the ARRD system (Sheng et al. 2009; Rui et al. 2010) have shown that: (1) Due to enhancement of heat and mass transfer in adsorbent bed, half-cycling time can be shorten to 3–5 min, which will benefit SCP of adsorption systems. (2) Operation pressure is 0.1–0.5 MPa, slightly higher than atmospheric pressure, which is effective to maintain steady performance of adsorption systems and relieve pressures of *n*-butane cycling pump.

The objective of this study is to find out advanced working pairs for ARRD systems, which may be suitable for the applications to the new adsorption cycles and offer new concept for adsorption refrigeration. In the study, adsorption performance of *n*-butane on adsorbents were determined with self-proposed positive pressure gravimetric method, desorption performance by thermal analysis, and COP and SCP of these pairs were estimated.

2 Experimental tests

2.1 Main materials

Main activated carbons (AC) were used in this experiment are represented in Table 1. Besides the ACs, two kinds of hydrophobic zeolites, pure-silica Silicalite-I and high-silica (Si/Al higher than 500) HZSM-5, supplied by Nanjing Heyi Inorganic Chemical Co., Ltd., were also used for adsorption of *n*-butane, which was purchased from Nanjing Weize Science and Technology Co., Ltd., with the purity of 99.15 %.

2.2 Adsorption of *n*-butane on adsorbents

In order to determine adsorption performance of *n*-butane on the adsorbents, a positive pressure gravimetric device was established by Chen et al. (2007), referring to the vacuum gravimetric method by Cui et al. (2005) and by Chen et al. (2008), and experimental apparatus proposed by Wang et al. (2009). The main measurement steps of this device are similar to that previously reported for vacuum gravimetric method by Cui et al. (2005) and by Chen et al. (2008). Before measurements, carbon adsorbents were firstly activated at 150 °C (300 °C for zeolites) for 3 h in an oven, and then were vacuumized at 80 °C for 2 h in the measurement apparatus. Adsorption equilibrium between *n*-butane vapor and the adsorbents was determined under vapor pressures 0–0.2 MPa and in the temperature ranging from 30 to 70 °C. Adsorption rate of *n*-butane on the adsorbents was measured at 30 °C and 0.14 MPa.

2.3 Thermal analysis

The desorption behavior of *n*-butane from carbons was investigated by thermogravimetry (TG)-differential thermal analysis (DTA) analysis. The TG-DTA measurements were performed on a WCT-1 type TG-DTA equipment at 15 °C with a heating rate of 10 °C/min to the temperature of 250 °C in static air atmosphere. Before the TG-DTA measurement the adsorbents were saturated with *n*-butane at ambient temperature under 0.15 MPa.

3 Results and discussion

3.1 Adsorbent selection

To screen out the adsorbents for ARRD cycles, adsorption equilibrium data (x, kg/kg) of *n*-butane on them in 30 °C and vapor pressure 0–0.2 MPa were determined and the isotherms are shown in Fig. 2.

From Fig. 2, it can be seen that the shape of isotherms belong to type I according to the Brunauer classifications, which exhibits signs of monolayer saturation at higher pressures (Ruthven 1984). Under lower pressures of 0–0.02 MPa, the amount of *n*-butane loading on carbons increases rapidly, while under the pressures higher than 0.02 MPa, the amount absorbed changes slightly and there emerges a platform on the isotherm curve. For Silicalite-I or ZSM-5/*n*-butane pair, the turning pressure might shift to lower pressures, which show stronger reaction of *n*-butane

Table 1 Characteristics of main AC

Code	Specification	Iodine value (mg/g)	Manufacturer
AC-1			Institute of Chemical Industry of Forest Products, Nanjing, China
AC-2	Cocoanut shell	1,200	Nanjing Mulinsen Charcoal Co., Ltd., China
AC-3	Apricot shell	1,100	Nanjing Mulinsen Charcoal Co., Ltd., China
AC-4	Cocoanut shell	1,500	Nanjing Mulinsen Charcoal Co., Ltd., China
AC-5	Cocoanut shell	1,550	Nanjing Mulinsen Charcoal Co., Ltd., China
AC-6	Cocoanut shell	1,500–1,550	Nanjing Mulinsen Charcoal Co., Ltd., China
AC-7	Cocoanut shell	1,443	Nanjing Mulinsen Charcoal Co., Ltd., China
AC-8	For Pd loading		Nanjing Mulinsen Charcoal Co., Ltd., China
AC-9	Cocoanut shell	>1,500	Nanjing Mulinsen Charcoal Co., Ltd., China

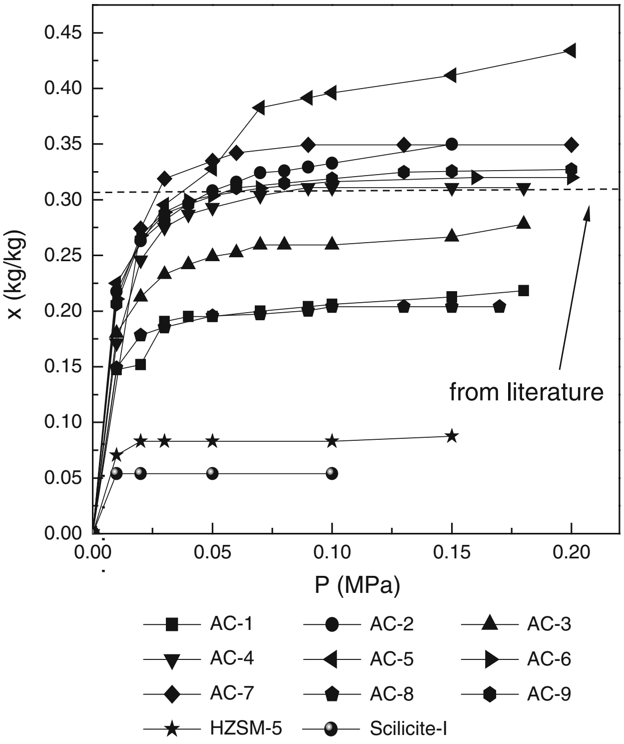

Fig. 2 Adsorption isotherms of *n*-butane on the adsorbents

on them than on the carbons. Figure 2 also shows that, adsorption capacities of AC-2, AC-5, AC-9 are all above 0.31 kg/kg, the highest of which can reach 0.43 kg/kg, 3–43.3 % higher than that reported in the literature by Fiani et al. (1999). From Table 1, it can be seen that the three-carbons all have higher iodine adsorption value (>1,200 mg/mg) because of rich micro-pores (<2 nm). Therefore, the three-carbons of abundant micro-pores are chosen for further investigations.

Activated carbon fiber (ACF) and pitch based carbon, or named as super-AC, which have a high surface area (BET, Brunauer-Emmett-Teller) surface area higher than 3,000 m^2/g) and larger adsorption capacity than granular AC, are the promising candidates for adsorption process applications as reported by Saha et al. (2008), by Wang et al. (1997) and by Zhou et al. (2004), though for their high cost and low apparent density. Consequently, super-AC will be considered to be applied in the ARRD systems in our future work.

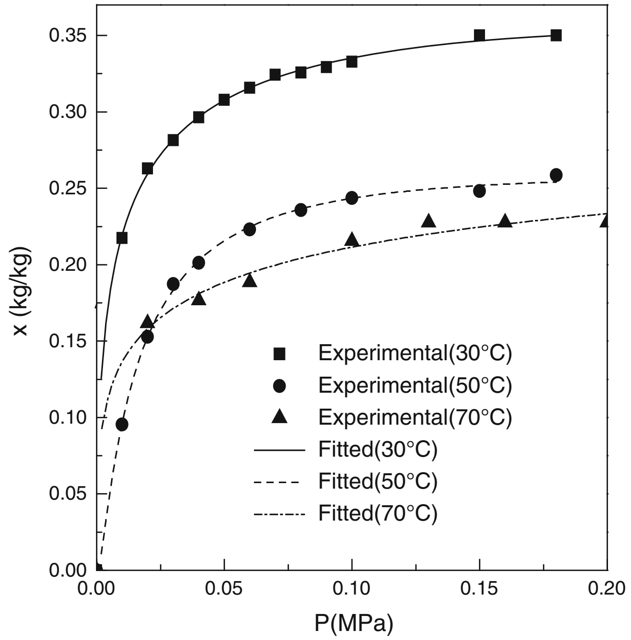

Fig. 3 Adsorption isotherms and fitted value of *n*-butane on AC-2

3.2 Adsorption equilibrium performance of *n*-butane on carbons

3.2.1 *Adsorption isotherms*

The equilibrium curves of *n*-butane on the three carbons at 30, 50 and 70 °C, and under vapor pressures 0–0.2 MPa are shown in Figs. 3, 4, and 5 respectively.

From Figs. 3, 4 and 5, it can be seen that, at 30 °C (typical adsorption temperature), the amount of *n*-butane loading on AC-5 is the highest of all, which can reach to 0.43 kg/kg. With adsorption temperature increasing,

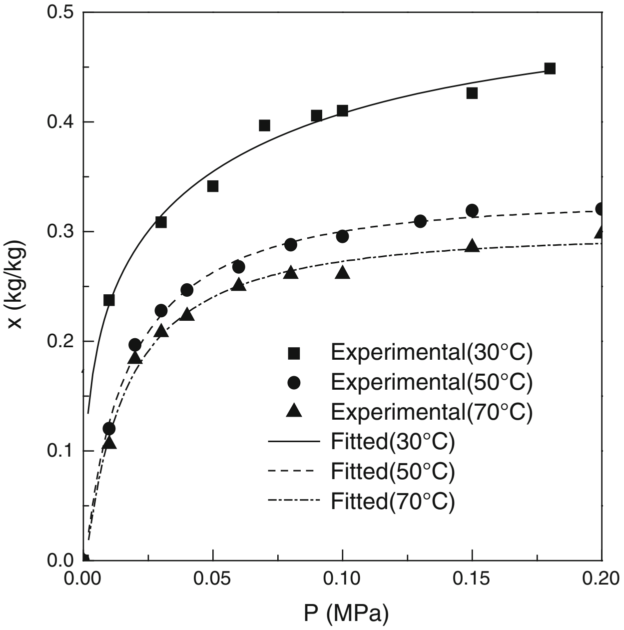

Fig. 4 Adsorption isotherms and fitted value of *n*-butane on AC-5

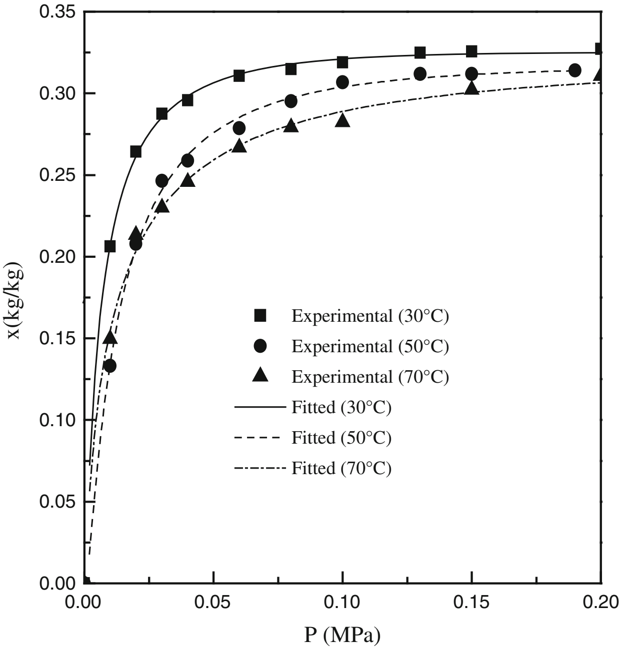

Fig. 5 Adsorption isotherms and fitted value of *n*-butane on AC-9

adsorption capacities of carbons decrease. The decrease rate of *n*-butane adsorption capacity with increasing of temperature goes down from that of AC-5/*n*-butane pair, to AC-2/*n*-butane pair and to AC-9/*n*-butane pair, which might imply that *n*-butane can be desorbed from AC-5 easier than from AC-2 or AC-9.

3.2.2 *Adsorption thermodynamic model*

For design purposes, the experimental data should be expressed as a function of temperature and pressure. In the literature, several thermodynamic models (Ruthven 1984) have been proposed to describe adsorption equilibrium properties on AC: the Langmuir model, the Freundlich model, the Dubinin-Astakhov (D-A) model and the Toth equation etc. Among these models, D-A equation, based on Polanyi potential theory and micro-pore filling theory, is more preferred by Richard et al. (2009) and by Critoph (1996) for alkanes on AC. Accordingly, D-A model was adopted to fit adsorption equilibrium data of *n*-butane on carbons. The equation of D-A model is as follows:

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

$$\varepsilon = RT \ln\left(\frac{P_s}{P}\right) \quad (2)$$

where n is an exponential constant usually varies between 1 and 3; x is adsorption equilibrium capacity, kg/kg; x_0 is maximum equilibrium adsorption capacity, kg/kg; ε is adsorption potential, J/mol; E is characteristic adsorption work (or as the activation energy), J/mol; P is adsorption equilibrium pressure of *n*-butane, MPa; P_s is saturation pressure of *n*-butane corresponding to adsorption temperature, MPa.

Table 2 Regression parameters of D-A equation

Carbon	x_0	E (J/mol)	n	R	Q_{ad} (kJ/mol)
AC-2	0.400	9838.7	1.21	0.9338	21.81
AC-5	0.543	9125.8	0.79	0.9606	19.32
AC-9	0.332	15456.6	1.77	0.9905	22.44

The experimental adsorption data were regressed using D-A equation and the fitted parameters and isotherms are given in Table 2 and Figs. 3, 4 and 5, respectively. The approximation of Figs. 3, 4 and 5 shows a good accuracy of fitting. Also, from Table 2, it can be seen that correlative coefficients R are all above 0.93 which shows that these adsorption data are fitted well with D-A equation. Thus, the D-A equation provides a good analytical description of the whole set of experimental data and can be used to perform mathematical modeling of the ARRD system based on these carbons/*n*-butane pairs. The isosteric heat tends to approach 22 kJ/mol, the latent heat of vaporization of *n*-butane at saturation temperature 5 °C, which is in a good agreement with physical adsorption nature for *n*-butane on carbons.

Figure 6 shows the pressure–temperature–uptake diagram of *n*-butane on AC-2 carbons.

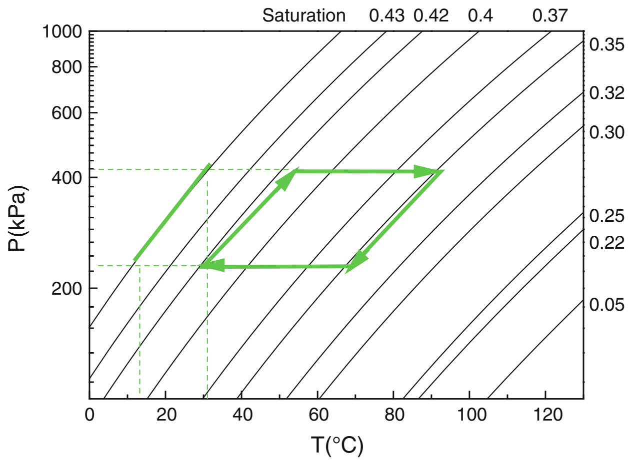

Fig. 6 Pressure–temperature–uptake of *n*-butane/AC-2 diagram for a cycle

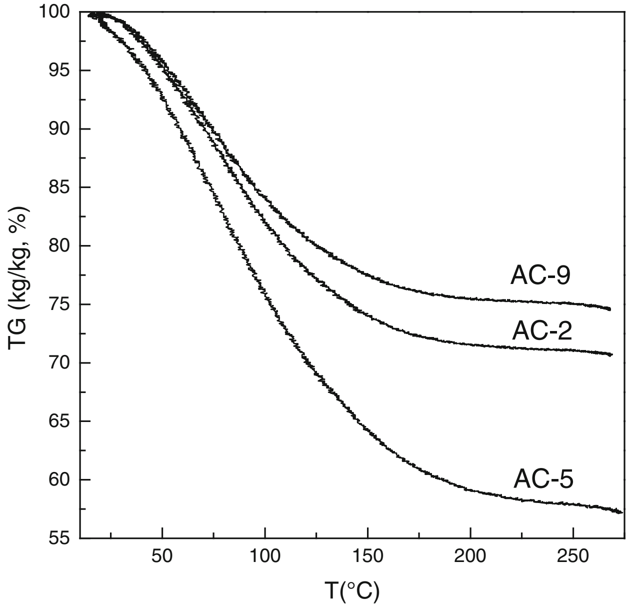

Fig. 7 TG-curves for the desorption of *n*-butane from carbons

3.3 Desorption performance of *n*-butane from carbons

Desorption temperature is one of the main parameters of judging regenerating performance of the adsorbents. Generally, the lower the desorption temperature, the easier the regeneration, which means low grade waste heat can be sufficiently utilized for adsorption cycle. Based on screening of the carbons, desorption properties were investigated by TG-DTA analysis and the results are shown in Fig. 7.

As Fig. 7 shows, desorption temperature of *n*-butane from carbons chosen ranges from 110 to 130 °C, which is similar as that of silica gel-water pair, AC-methanol pair and strontium chloride-ammonia pair, markedly lower than that of zeolite-water pair (Wang and Oliveira 2006). Since it can be regenerated with low grade heat source, ARRD systems adopting *n*-butane/carbons pairs chosen have a promising prospect.

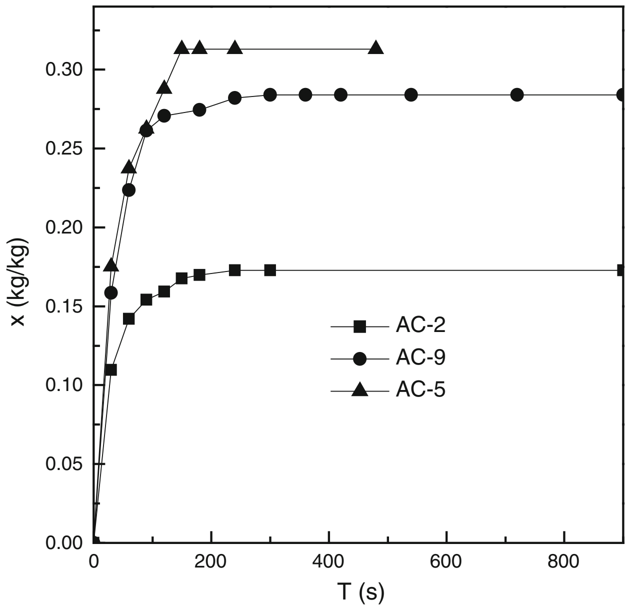

Fig. 8 The kinetics of *n*-butane on AC (30 °C)

3.4 Kinetics of *n*-butane on carbons

The adsorption kinetics of *n*-butane on AC is of great importance to dynamic operation and simulation of an adsorption system, as well as the ARRD system. The amount of *n*-butane loading on AC as a function of time was determined and is shown in Fig. 8. Due to its physical adsorption nature, the *n*-butane adsorption occurs within a few minutes, and it only takes about 400 s to reach mass and thermal equilibrium. Therefore, the quasi-equilibrium of the adsorption system can be achieved within 150–250 s, which will benefit SCP of the ARRD system a lot.

3.5 Application in ARRD system of *n*-butane/carbon pair

Specific cooling effect (SCE) and COP of the ARRD system in the study are simplified calculated from the adsorption equilibrium parameters without consideration of the cycle time adopting the calculation procedure proposed by Hamamoto et al. (2006). For the simplicity of the calculation, the pumping energy is estimated (Q_p) as 20 kJ/kg adsorbent according to the ARRD experiment under test. However, due to the complexity of influence of water vapor on adsorption and desorption of *n*-butane, its negative effect on cycling *n*-butane adsorption capacities is not

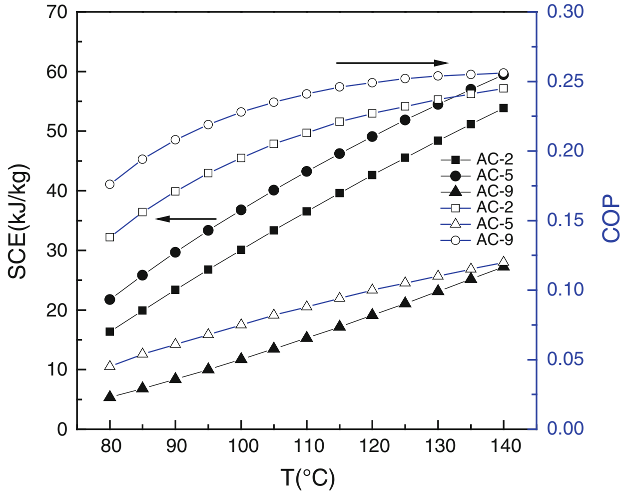

Fig. 9 Influence of regeneration temperature on SCE and COP in an ARRD cycle

under consideration in this paper. Corresponding influences are now being carried out and will be reported.

The amount of n-butane on AC can be expressed by the D-A equation Eqs. (1–2). Characteristic temperatures can be calculated from T_c, T_e, T_{g2} and T_{a2}, as follows (Wang et al. 2007):

$$T_{g1} = T_c \times T_{a2}/T_e \tag{3}$$

$$T_{a1} = T_e \times T_{g2}/T_c \tag{4}$$

where T_{g1} is the end of preheating process, T_{a1} is the end of precooling process, respectively.

The cooling capacity of each ARRD cycle can be calculated from the following expression:

$$SCE = (x_{\max} - x_{\min})(L_e - \int_{T_e}^{T_c} c_{p,ref}\mathrm{d}T) \tag{5}$$

where x_{max} is the maximum adsorption uptake, kg/kg, x_{min} is the minimum adsorption loading, kg/kg, L_e is vaporization heat of n-butane at T_e, respectively.

The heat input for each ARRD cycle can be estimated from the following expression:

$$Q_h = \int_{T_{a1}}^{T_{a2}} c_{p,a}\mathrm{d}T + x_{\max}\int_{T_{a1}}^{T_{g2}} c_{p,ref}\mathrm{d}T + \int_{T_{g2}}^{T_{a2}} xc_{p,ref}\mathrm{d}T + \int_{x_{\min}}^{x_{\max}} Q_{ads}\mathrm{d}x + Q_p \tag{6}$$

where Q_p is the pumping energy consumed by water pump and vapor circulating pump; $c_{p,a}$ is the specific heat capacity of AC estimated as 1.2 kJ/kg K; $c_{p,ref}$ stands for the specific heat capacity of liquid refrigerant, referring to (Lu 1982).

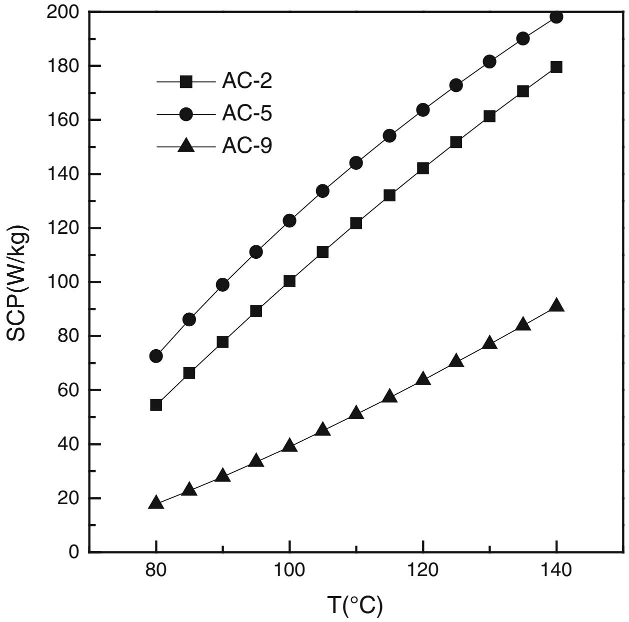

Fig. 10 Influence of regeneration on SCP in an ARRD cycle

The SCE and the COP are estimated by the following expressions:

$$COP = SCE/Q_h \tag{7}$$

In this calculation the adsorption temperature and cooling temperature are set as 30 °C, respectively, and the evaporation temperature is set as 10 °C. And the calculated COP and SCE are shown in Fig. 9.

There is an optimum condition for COP to reach at maximum for AC/n-butane pairs. At 130 °C, the COP of AC-5/n-butane pair in ARRD can reach 0.25, which is relatively low. The COP can be improved with heat regeneration between the cooler and the hot water tank. With increasing of the heat source, the SCE increases for the three pairs, especially for AC-5/n-butane and AC-2/n-butane working pairs due to their isotherm sensitive to temperature. In general, the SCE is lower adopting n-butane as the refrigerant compared with ammonia adsorption cycles because of its lower latent heat.

For adsorption cycles, the SCP is an important parameter. The higher the SCP is, the smaller the adsorption system in size is. Here, a simplified method is used to estimate the SCP as follows:

$$SCP = SCE/\Delta\tau \tag{8}$$

where $\Delta\tau$ is time needed for the adsorption phase. According to preliminary ARRD system test, $\Delta\tau$ is set as 5 min, which can be further optimized. The SCP was estimated using Eq. (8) and is given in Fig. 10.

By comparing the estimated results with those in the literature (Wang and Oliveira 2006; Wongsuwan et al. 2001), it is found that SCP of *n*-butane/AC-5 pair is 180–200 W/kg, lower than those of ammonia/AC pair, $CaCl_2$ based composite adsorbent/ammonia pair and zeolite/water pair. This is mainly due to a low latent heat of *n*-butane. Also, due to the complexity of the real ARRD system, and heat leakage of real process, the SCP of *n*-butane/carbon pairs may be lower than these estimated data. With such a consideration, further experimental investigations are required. At present, a laboratory scale ARRD system for refrigeration, with 200–300 g carbon in the adsorber, is underway to test this adsorption cycle.

The presence of water vapor (after regeneration with hot water) can have a severe negative influence both on the adsorption and desorption behavior of *n*-butane on carbons as reported by Marban and Fuertes (2004), as well as the SCP of ARRD system. Therefore, it is necessary to specify this influence so that appropriate measures can be made to minimize its impact. Further work on equilibrium and dynamic properties of water/*n*-butane co-adsorption on AC is being carried out.

4 Conclusions

The ARRD developed for cooling and air conditioning applications, has obvious advantages of excellent heat transfer performance in the adsorbent bed (half-cycling time being 3–5 min), and appropriate operating conditions (0.1–0.5 MPa) with *n*-butane as refrigerant.

Experiments and analysis on advanced working pairs for the ARRD system shows that the adsorption equilibrium capacity of *n*-butane on AC preferred are all above 0.31 kg/kg, the highest of which can reach 0.43 kg/kg. Adsorption equilibrium data are fitted well by D-A equation, with the correlative coefficients R above 0.93, and the modeled parameters are obtained. Isosteric heat of *n*-butane on carbons tends to approach 22 kJ/mol, similar to its latent heat of vaporization. The carbons preferred can be regenerated between 110 and 130 °C, which has a promising prospect. The quasi-equilibrium of *n*-butane on carbons can be achieved within 150–250 s, which is a good benefit for SCP of the ARRD system. The COP and SCP were calculated with simplified method. The SCP of *n*-butane/AC-5 pair estimated is 180–200 W/kg.

It is also found that the presence of water vapor can have a severe negative influence both on the adsorption and desorption behavior of *n*-butane on carbons in the ARRD cycle. The data concern merely pure *n*-butane and do not concern co-adsorption data as required by the cycle. Further work on equilibrium and dynamic properties of water/*n*-butane co-adsorption on AC is necessary.

Besides, the cycle performances in terms of both COP and SCP are low. Moreover, the SCP estimation based on a 5 min cycle time is very optimistic. In our future work, developing advanced pairs and optimizing the ARRD cycle, are being carried out to improve both COP and SCP of the ARRD system.

Acknowledgments This work was supported by National Natural Science Fundation of China under contracts 20876074 and 50806032. This work was also supported by the Natural Science Foundation of Jiangsu Higher Education Institutions of China under contracts 11KJA480003.

References

Cao, X.S., Wang, G.X., Wang, Y.T.: Adsorption refrigeration machines for fisher boats. Chinese patent, ZL200410075543.6 (2005)

Chen, X.J., Chen, H.J., Cui, Q., Tang, Y., Yao, H.Q.: Adsorption performance of domestic activated carbon for ammonia refrigeration applications. In: 22nd IIR International Congress of Refrigeration, p. 55. Chinese Association of Refrigeration, Beijing (2007)

Chen, H.J., Cui, Q., Gu, C.H., Yao, H.Q.: Heat conduction enhancement of adsorbents in adsorption refrigeration. J. Nanjing Univ. (Nat. Ed.) **26**, 13–18 (2004). (in Chinese)

Chen, H.J., Cui, Q., Tang, Y., Chen, X.J., Yao, H.Q.: Attapulgite based LiCl composite adsorbents for cooling and air conditioning applications. Appl. Therm. Eng. **28**, 2187–2193 (2008)

Critoph, R.E.: An ammonia carbon solar refrigerator for vaccine cooling. Renew. Energy **5**, 502–508 (1994a)

Critoph, R.E.: Forced convection enhancement of adsorption cycle. Heat Recovery Syst. CHP **14**, 343–350 (1994b)

Critoph, R.E.: Evaluation of alternative refrigerant—adsorbent pairs for refrigeration cycles. Appl. Therm. Eng. **16**, 891–900 (1996)

Critoph, R.E.: Forced convection adsorption cycle with packed bed heat regeneration. Int. J. Refrig. **22**, 38–46 (1999)

Critoph, R.E., Metcalf, S.J.: Specific cooling power intensification limits in ammonia-carbon adsorption refrigeration systems. Appl. Therm. Eng. **24**, 661–678 (2004)

Cui, Q., Chen, H.J., Tao, G., Yao, H.Q.: Performance study of new adsorbent for solid desiccant cooling. Energy **30**, 273–279 (2005)

Cui, Q., Chen, H.J., Yao, H.Q.: Novel adsorption refrigeration cycle regenerated with water directly. Chinese patent, ZL200710132939.3 (2009)

Fatouh, M., Kafafy, M.E.: Assessment of propane/commercial butane mixtures as possible alternatives to R134a in domestic refrigerators. Energ. Convers. Manage. **47**, 2644–2658 (2006)

Fiani, E., Perier-Camby, L., Thomas, G., Sanalan, M.: Calorimetric and gravimetric measurements of hydrocarbon adsorption on a granulated active carbon. J. Therm. Anal. Calorim. **56**, 1453–1459 (1999)

Hamamoto, Y., Alam, K.C.A., Saha, B.B., Koyama, S., Akisawa, A., Kashiwagi, T.: Study on adsorption refrigeration cycle utilizing activated carbon fibers. Part 2. Cycle performance evaluation. Int. J. Refrig. **29**, 315–327 (2006)

Lee, C.H., Park, S.H., Choi, S.H., Kim, Y.S., Kim, S.H.: Characteristics of non-uniform reaction blocks for chemical heat pump. Chem. Eng. Sci. **60**, 1401–1409 (2005)

Li, D.Y., Liu, X.J., Li, L., Liu, X.C., Li, H.W., Liu, X.D.: Adsorption refrigeration machine of dual generator. Chinese patent, ZL99115216.6 (1999)

Liu, Y.L., Wang, R.Z., Xia, Z.Z.: Experimental study on a continuous adsorption chiller with novel design. Int. J. Refrig. **28**, 218–230 (2005)

Lu, H.Z.: Shiyou Huagong Jichu Shuju Shouce. Chemical Industry Press, Beijing (1982) (in Chinese)

Lu, Z.S., Wang, R.Z., Wang, L.W., Chen, C.J.: Performance analysis of an adsorption refrigerator using AC in a compound adsorbent. Carbon **44**, 747–752 (2006)

Marban, G., Fuertes, A.B.: Co-adsorption of *n*-butane/water vapor mixtures on activated carbon fiber-based monoliths. Carbon **42**, 71–81 (2004)

Meunier, F.: Solid sorption heat powered cycles for cooling and heat pumping applications. Appl. Therm. Eng. **18**, 715–729 (1998)

Richard, M.A., Bénard, P., Chahine, R.: Gas adsorption process in activated carbon over a wide temperature range above the critical point. Part 1: modified Dubinin-Astakhov model. Adsorption **15**, 43–51 (2009)

Rui, Z.Q., Sheng, L.L., Cui, Q., Wang, H.Y., Chen, H.J., Yao, H.Q.: Heat transfer characteristics of adsorbent bed of adsorption refrigeration system regenerated directly. Environ. Sci. Technol. **33**, 332–335 (2010). (in Chinese)

Ruthven, D.M.: Principles of adsorption and adsorption processes. Wiley, New York (1984)

Saha, B.B., Chakraborty, A., Koyama, S., Yoon, S.H., Mochida, I., Kumja, M., Christopher, Y., Kim, CNg: Isotherms and thermodynamics for the adsorption of *n*-butane on pitch based activated carbon. Int. J. Heat Mass Transf. **51**, 1582–1589 (2008)

Salvador, F., Sanchez, J.C.: Effect of regeneration treatment with liquid water at high pressure and temperature on the characteristic of three commercial activated carbons. Carbon **37**, 577–583 (1999)

Sheng, L.L., Cui, Q., Chen, H.J., Tang, Y., Yao, H.Q.: An adsorption refrigeration cycle regenerated with water directly using activated carbon-alkane pair. In: The 13th Asian Chemical Congress, Shanghai (2009)

Vasiliev, L.L., Kanonchik, L.E., Antuh, A.A., Kulakov, A.G., Kulikovsky, V.K.: Waste heat driven solid sorption coolers containing heat pipes for thermo control. Adsorption **1**, 303–312 (1995)

Wang, R.Z., Oliveira, R.G.: Adsorption refrigeration—an efficient way to make good use of waste heat and solar energy. Prog. Energy Combust. **32**, 424–458 (2006)

Wang, R.Z., Jia, J.P., Teng, Y., Zhu, Y.H., Wu, J.Y.: A potential solid adsorption refrigeration pair-active carbon fiber methanol. Acta Energiae Solaris Sinaca **18**, 222–227 (1997). (in Chinese)

Wang, D.C., Shi, Z.X., Yang, Q.R., Tian, X.L., Zhang, J.C., Wu, J.Y.: Experimental research on novel adsorption chiller driven by low grade heat source. Energ. Convers. Manage. **48**, 2375–2381 (2007a)

Wang, R.Z., Wang, L.W., Wu, J.Y.: Adsorption refrigeration theory and applications. China Science Press, Beijing (2007b). (in Chinese)

Wang, L.W., Wang, R.Z., Oliveira, R.G.: A review on adsorption working pairs for refrigeration. Renew. Sustain. Energy Rev. **13**, 518–534 (2009a)

Wang, L., Chen, L., Wang, H.L., Liao, D.L.: The adsorption refrigeration characteristics of alkaline-earth metal chlorides and its composite adsorbents. Renew. Energy **34**, 1016–1023 (2009b)

Wang, Q., et al.: Experimental investigation on a fluidized-bed adsorber/desorber for the adsorption refrigeration system. Int. J. Refrig. (2011). doi:10.1016/j.ijrefrig.2011.05.020

Wongsuwan, W., Kumar, S., Neveu, P., Meunier, F.: A review of chemical heat pump technology and applications. Appl. Therm. Eng. **21**, 1489–1519 (2001)

Zhou, L., Zhou, Y.P., Sun, Y.: A comparative study of hydrogen adsorption on superactivated carbon versus carbon nanotubes. Int. J. Hydrogen Energy **29**, 475–479 (2004)

Zhu, D.S., Wang, S.W.: Experimental investigation of contact resistance in adsorber of solar adsorption refrigeration. Sol. Energy **73**, 177–185 (2002)