

METHANOL ADSORPTION ON ACTIVATED CARBONS FOR ADSORPTION HEAT PUMP APPLICATIONS

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Introduction

Interest in adsorption heat pumps has been renewed in recent years, primarily due to environmental concerns over stratospheric ozone-depleting substances [e.g., 1-6]. In addition to environmental benefits, adsorption heat pumps have several advantages compared to conventional vapor compression systems. These advantages include simplicity, no moving parts, low maintenance requirements, low potential for corrosion, and the use of stable, non-toxic reactants as adsorbents or adsorbates.

Various adsorption pairs (adsorbent/adsorbate) have been used, such as zeolite/water and activated carbon/methanol. Very few studies have been reported regarding the adsorption capacities and heats of adsorption of adsorbents used in heat pumps. The objectives of this study are to experimentally determine heats of adsorption and adsorption capacities, and to correlate these results to the physical structure of selected adsorbents.

Experimental

Two activated carbon adsorbents, a coconut shell-based activated carbon (AC) and an activated carbon fiber (ACF), were characterized using nitrogen adsorption isotherm measurements at 77 K with a Micromeritics ASAP 2010 instrument. Samples were obtained from the School of Power and Energy Engineering in Shanghai Jiao Tong University. Pore size distribution results were calculated using the modified DR model [7]. Micro-calorimetric heats of adsorption at 25°C were measured with an isothermal flow micro-calorimeter (CSC, model 4400) to evaluate the heat generated as methanol adsorbs onto the activated carbon materials. The unit is based on a double-cell differential heat flow design and can measure heat flows as low as 25 nano-calories/sec (0.1 μ W). The samples were purged with dry helium after being degassed in a vacuum oven overnight. Methanol was then added to the helium stream by means of a fritted bubbler. The concentration of methanol at room temperature, as determined by its vapor pressure of 121 torr was roughly 16%. The methanol flow rate was 5 mL/min.

Results and Discussion

Table 1 summarizes BET surface areas, total pore volumes, methanol adsorption capacities, heats of adsorption per mole of adsorbed methanol, and adsorption heats per gram of adsorbent, for the two activated carbon samples. In comparison with AC powder, ACF has ~80% higher BET surface area, ~50% higher pore volume, ~55% higher methanol adsorption capacity, and ~70% higher adsorption heat per gram of carbon adsorbent.

In general, activated carbon fibers have higher BET surface areas and pore volumes compared to activated carbons made from coal or coconut shell. This is because carbon fibers consist of a uniformly sized graphite planar structure. Its smaller geometric size (i.e., the fiber diameter) also allows greater microporosity to develop during steam activation. The pore size distribution results (Figure 1) show that both samples are microporous (< 20 Å) with negligible mesopore (20 - 500 Å) and macropore (> 500 Å) volumes. The corresponding experimental and calculated nitrogen adsorption isotherms for both samples are plotted in Figure 2. A larger fraction of micropores in adsorbents is desirable to maximize the heat output per pore volume because the enhanced adsorption energy boosts the heats of adsorption.

The methanol adsorption capacities of both samples appear to consistently dependent on their pore volumes. However, some of the micropores in the AC powder, namely ultra-micropores (< 7 Å), may not be accessible to methanol due to the molecular dimensions of the adsorbate. Consistent with this interpretation, we find a lower adsorption capacity and heat of adsorption (per gram of adsorbent) for the AC powder as compared to ACF.

Figure 3 shows the heat released due to methanol adsorption as a function of time, indicating that both materials have similar adsorption kinetics with a similar sample mass (~0.25 g). On the other hand, the kinetics of methanol desorption is quite different for both samples (Figure 4). The entire desorption period for the AC powder is longer than that for ACF. This is reasonable because the AC powder has a higher fraction of ultra-micropore

volume (Figure 1). Although the overlapped adsorption potential in ultra-micropores increases the heat output per unit pore volume, the slow kinetics of desorption may reduce the overall system efficiency. In addition, ultra-micropores tend to trap some of the methanol and reduce the desorption capacity. For example, 12% and 5% of adsorbed methanol are not desorbed for the AC powder and ACF, respectively. Incomplete desorption and a heat of adsorption higher than the heat of condensation for methanol, are indicative of an enhanced adsorption potential in micropores.

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References

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Table 1. Summary of physical properties of select activated carbon samples.

Sample	BET area [m ² /g]	Pore vol. [cm ³ /g]	Methanol capacity [wt.%]	ΔH [kJ/mol]	ΔH [kJ/g]
AC powder	695	0.42	24.70	52.4	0.400
ACF	1234	0.64	38.45	55.2	0.684

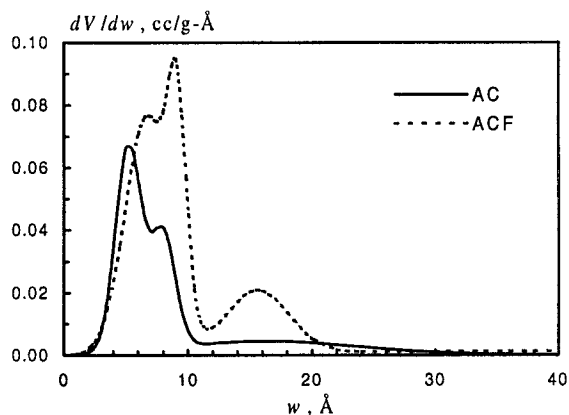


Figure 1. Pore size distribution of AC powder and ACF.

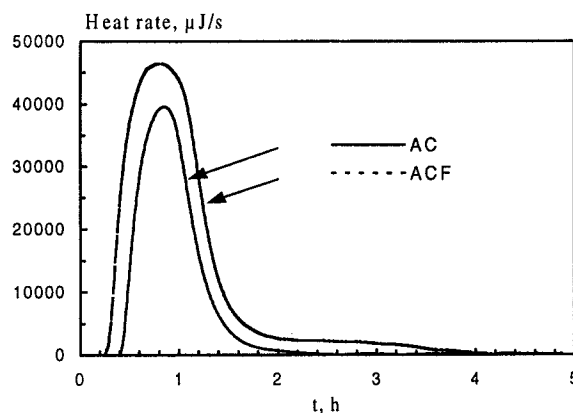


Figure 3. Heat rate of methanol adsorption.

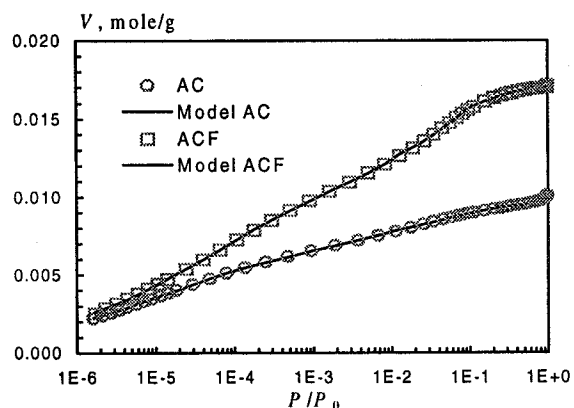


Figure 2. Exp and calculated nitrogen isotherms.

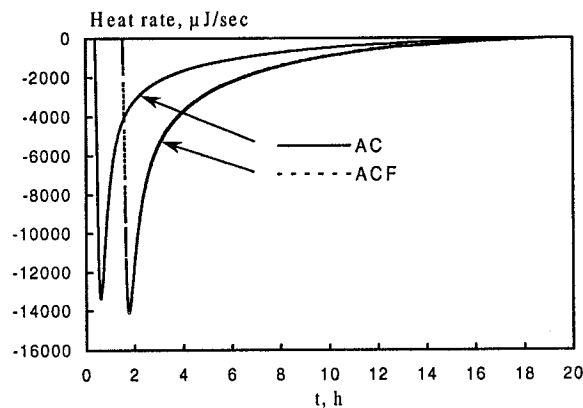


Figure 4. Heat rate of methanol desorption.