SUPERCRITICAL FLUID ADSORPTION AT THE GAS-SOLID INTERFACE

Jerry W. King

CPC International, Moffett Technical Center, Argo, Illinois 60501

INTRODUCTION

Supercritical fluids (SCF) in tandem with adsorbent media are currently being used in a number of chemical processes. Such applications as the regeneration of adsorbents, catalysis under supercritical conditions, analytical and preparative chromatography, and the proposed storage of radioactive gases in their supercritical state (1-4) require an understanding of the role of SCF at the sorbent/gas interface. Adsorbate equilibrium between a dense gas and adsorbent is not totally controlled by the "volatility enhancement" of the sorbate by the supercritical fluid, but can include such additional mechanisms as displacement of the sorbate from the interface by the SCF as well as thermally-induced desorption (5). Unfortunately, many investigators do not appreciate the competitive adsorption effect of the SCF at the gas-solid interface and employ extraction conditions which are solely based on the solubility of the adsorbate in the supercritical fluid. In this presentation, we shall discuss the adsorption of supercritical fluids on active adsorbents and show the relevance of this information for the design of adsorbent regeneration processes.

The physical conditions for regenerating adsorbents vary widely as shown by the reduced state correlation in Figure 1. The choice of these regeneration conditions is partially empirical or based on solute solubilities in the SCF. Whereas, high reduced temperatures (T_r) and pressures (p_r) maybe required to displace polar species or higher molecular weight components from the carbon surface, these conditions can have an adverse effect on the cycle lifetime of the adsorbent. The displacement capability of supercritical fluids on previously adsorbed solutes can be maximized by studying the adsorption isotherm of the SCF on the adsorbent of interest. The results presented in this paper are relevant to the latter phenomena and can be of significant importance in regenerating weak to moderately adsorbed species from the solid surface using minimal gas compression.

EXPERIMENTAL AND DATA SOURCES

Data for the adsorption of supercritical gases on activated carbon were taken from the studies of Ozawa and Ogino (6-8). Correlation of the adsorption maxima for supercritical fluids on various adsorbents as a function of pressure were derived from the work of Menon (9). Tracer pulse chromatographic experiments were performed by the author at the University of Utah. The basic apparatus required for performing these experiments has been previously described (10). Desorption breakthrough volumes were determined at 40°C using supercritical CO_2 and He as carrier gases. Two sorbent columns packed with alumina and crosslinked styrene/divinylbenzene resin were utilized in these studies. Retention volume data were determined for a a homologous series of n-alkanes (n-propane through n-heptane) as well as benzene and naphthalene on the above adsorbents.

RESULTS AND DISCUSSION

A typical adsorption isotherm for a supercritical gas adsorbing on activated carbon is shown in Figure 2. Such isotherms show a linear increase in the amount of gas adsorbed with increasing pressure and eventually exhibit a maxima in the pressure range corresponding to p_r = 0.5-1.0. The shape of such isotherms is partially influenced by the adsorption and pressure scales that are utilized (11), the maxima being more pronounced when the surface excess is used as a measure of the quantity

of gas adsorbed. Further compression of the SCF results results in a decrease of the surface excess as the density of the bulk fluid becomes equal to or exceeds the density of the adsorbed gas. The occurence of a pressure maximium in the adsorption isotherm for the supercritical gas on a given adsorbent is important, since it represents a condition favorable for the displacement of the adsorbed specie from the adsorbent surface. Typical conditions associated with the occurence of the pressure maximium (p_{max}) are presented in Figure 3 for microporous carbons. Note that the pressure requirements for attaining p_{max} are lower when the adsorption is conducted close to the critical temperature of the gas. This is consistent with the larger uptake of supercritical fluid by the porous medium.

Menon (11) has correlated p_{max} for various gases in terms of their respective critical properties and has proposed the following equation which is applicable for adsorption on macroporous adsorbents:

$$p_{max} = p_c T_r^2 \qquad 1)$$

The predicted p_{max} from this relationship have been plotted in Figure 4 from 20 to 100°C for carbon dioxide, ethylene, and chlorotrifluoromethane. The values for p_{max} obtained from Equation 1 occur at reduced temperatures which are greater then unity, a result which is quite different from the cases cited in Figure 3 for the microporous sorbents.

Studies by several investigators (6-8) utilizing different adsorbent/gas combinations indicate that the pore structure of the adsorbent has a pronounced effect on the value for p_{max}. As shown in Figure 5, a decrease in the mean pore diameter of the activated carbon decreases the pressure to attain maximium adsorption of the gas. This suggests that there maybe some advantage to utilizing a microporous adsorbent in a supercritical fluid regeneration process, provided there is no inhibition to desorption due to restricted diffusion of the displaced adsorbate from the sorbent bed. For activated carbons, the p_{max} occurs between 25-72 atmospheres depending on the pore size distribution of the adsorbent. Prediction of the adsorption isotherm for the supercritical gas on activated carbons of varying pore size distribution can be accomplished by application of the Pickett equation (6).

The temperature dependence for p_{max} on carbons exhibiting microporosity is similar to that predicted by Equation 1, however the absolute values for p_{max} are correspondingly lower due to the pore size dependence. Figure 6 suggests that lower values for p_{max} can be obtained by reducing both the temperature and pore size of the adsorbent. However, a corresponding reduction in adsorbent surface area occurs upon decreasing the pore size and this is usually undesirable in terms of providing a large adsorbent capacity.

A knowledge of the dependence of adsorbate breakthrough volume on pressure can greatly aid in the design of a supercritical fluid regeneration process. There is a paucity of information in the literature concerning this phenomena, hence, we have measured the desorption breakthrough volumes for reversibly adsorbed species on beds of alumina and crosslinked styrene/divinylbenzene resin using the elution pulse analog of frontal analysis. The desorption breakthrough volume, V_r, can be readily obtained from the capacity factor, k', for the various injected sorbates and is given by Equation 2 as:

$$V_r = V_o(k' + 1) \qquad 2)$$

where V_o is the void volume of the column.

Figure 7 illustrates the dependence of the desorption breakthrough volume on gas pressure for benzene desorbing from crosslinked resin matrix. Close examination of the plot reveals that there is a linear decrease in the breakthrough volume for benzene up to a pressure of approximately 70 atmospheres. Beyond this pressure, there is a rather dramatic decrease in breakthrough volume which continues up to a pressure of 100 atmospheres. Benzene breakthrough volumes at pressures beyond 100

atmospheres tend to asymptotically appraoch a constant volume largely determined by the dimensions associated with the bed voidage. This general trend in desorption breakthrough behavior has been confirmed by running additional solutes on both alumina as well as the crosslinked resin. Interestingly, the transition to a constant breakthrough volume occurs in approximately the same pressure range for all of the adsorbates we have studied suggesting the maximium adsorption of the carrier fluid occurs in this pressure interval. This result suggests that carbon dioxide is displacing the adsorbate from the surface of the adsorbent. It should be noted, that selective fractionation of the adsorbed solutes can be achieved by operating in the lower pressure regime, but this segregation capability is rapidly lost when pressures exceed 80 atmospheres

The above behavior has been verified with similar adsorbates on alumina columns. Figure 8 shows the dependence of the capacity factor for n-butane adsorbing on alumina as a function of gas pressure. The recorded decrease in the capacity factor parallels the reduction in adsorbate breakthrough volume as a function of pressure and it becomes constant as the breakthrough volume approaches the void volume of the adsorbent bed. Additional experiments performed using helium as a carrier gas also showed a decrease in the k' for n-butane as a function of increasing gas pressure. As shown in Figure 8, the magnitude of this change was not as dramatic as that exhibited for the alumina-CO_2-n-butane system, however the recorded reduction in k' suggest that a displacement mechanism is responsible for the capacity factor changes when using this relative inert gas.

The above results strongly support the hypothesis that displacement of bound adsorbates by a supercritical fluid can be a major factor in regenerating adsorbent beds. Additional support for this concept can be found from the regeneration studies of Eppig and coworkers (3) who recovered ethanol, methyl ethyl ketone, and toluene from activated carbon beds using modest CO_2 pressures (100 atm.). Competitive adsorption studies of CO_2/light hydrocarbon mixtures desorbing from molecular sieves (12) also indicate that CO_2 is preferentially adsorbed over the alkane moieties. Clearly, this mode of adsorbent regeneration can be used for desorbing selected solutes without the need for excessive gas compression.

REFERENCES

1. M. Modell, R. deFilippi, and V. Krukonis in "Activated Carbon Adsorption of Organics from the Aqueous Phase-Vol. 1", I.H. Suffet and M.J. McQuire, eds., Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, (1983), pgs. 447-461.

2. R. deFilippi, V. Krukonis, R. Robey, and M. Modell, "Supercritical Fluid Regeneration of Activated Carbon for Adsorption of Pesticides", EPA Report 600/2-80-054, USEPA, (1980).

3. C. Eppig, R. deFilippi, and R. Murphy, "Supercritical Fluid Regeneration of Activated Carbon Used for Volatile-Organic-Compound Vapor Adsorption", EPA Report 600/2-82-067, USEPA, (1982).

4. G.H. Findenegg, B. Korner, J. Fischer, and M. Bohn, Ger. Chem. Eng., 6, 80 (1983).

5. R. Kander and M. Paulaitus in "Chemical Engineering at Supercritical Fluid Conditions", M. Paulaitus, J. Penninger, R. Gray, Jr., and P. Davidson, eds., Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, (1983), pgs. 461-476

6. S. Ozawa, S. Kusumi, and Y. Ogino in "Proceedings of the 4th International Conference on High Pressure-Kyoto-1974", The Physico-Chemical Society of Japan, Kyoto, Japan (1975), pgs. 580-587.

7.)S. Ozawa and Y. Ogino, Nippon Kagaku Kaishi, (1972), 1.

8. S Ozawa and Y. Ogino, Nippon Kagaku Kaishi, (1972), 8.

9. P.G. Menon, J. Phys. Chem., 72, 2695 (1968).

10. J.C. Giddings, M. Myers, and J.W. King, J. Chrom. Sci., 7, 276 (1969).

11. P.G. Menon, Chem. Rev., 68, 277 (1968).

12. D. Basmadian and D. Wright, Chem. Eng. Sci., 36, 937 (1981).

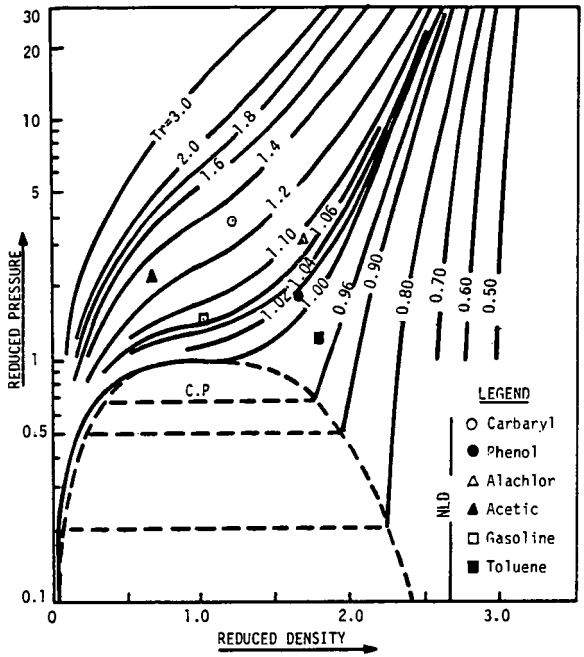

FIGURE 1. Reported Conditions for SCF Desorption of Selected Adsorbates from Activated Carbon

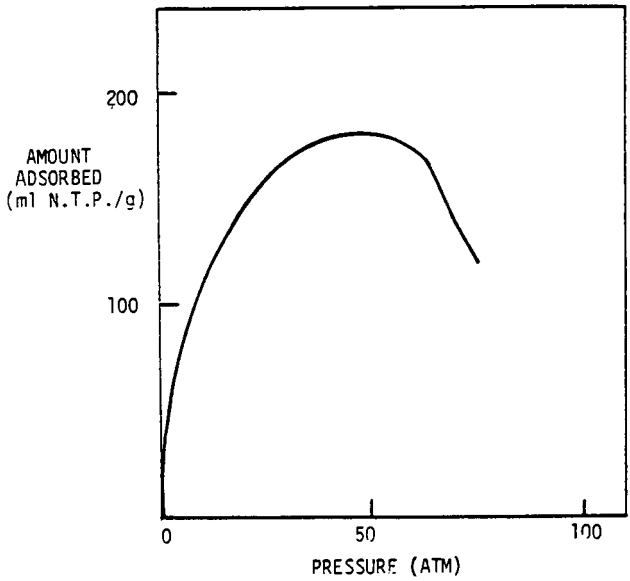

FIGURE 2. Adsorption Isotherm for the CO_2/ Activated Carbon System

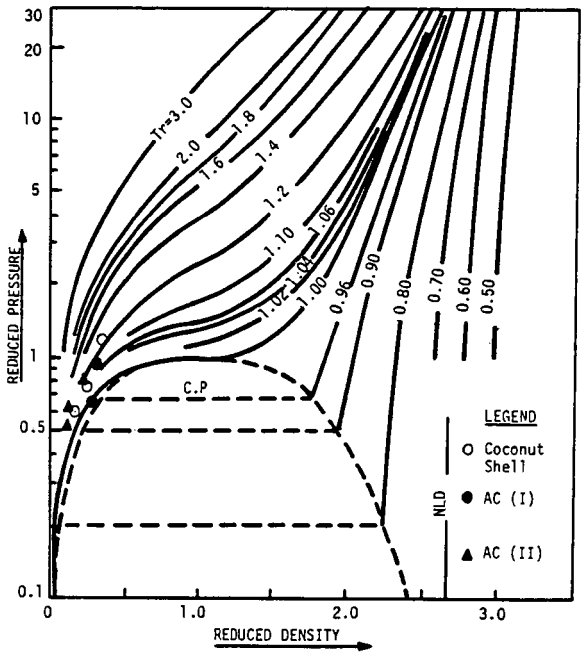

FIGURE 3. Conditions for Occurence of Adsorption Maximium (P_{max}) in CO_2/Activated Carbon Systems

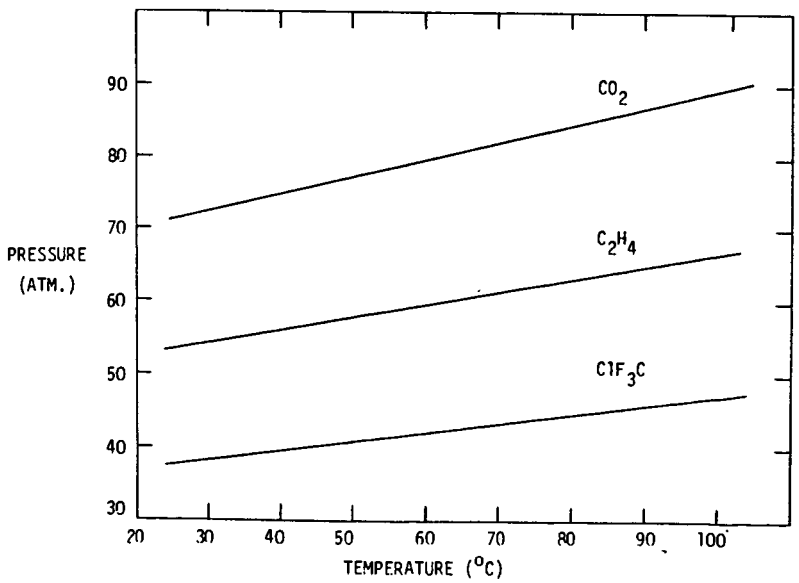

FIGURE 4. Dependence of P_{max} on Temperature According to Menon for Various Gases

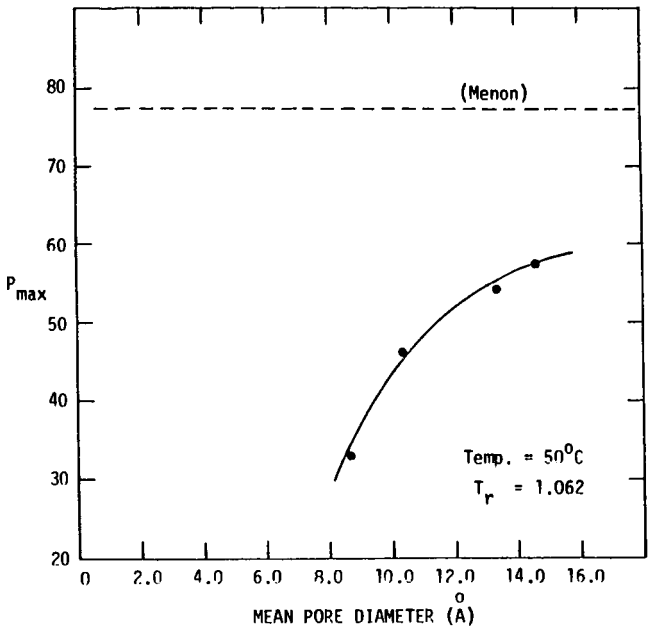

FIGURE 5. Pressure For Maximium Gas Adsorption vs. Mean Pore Diameter of Activated Carbons

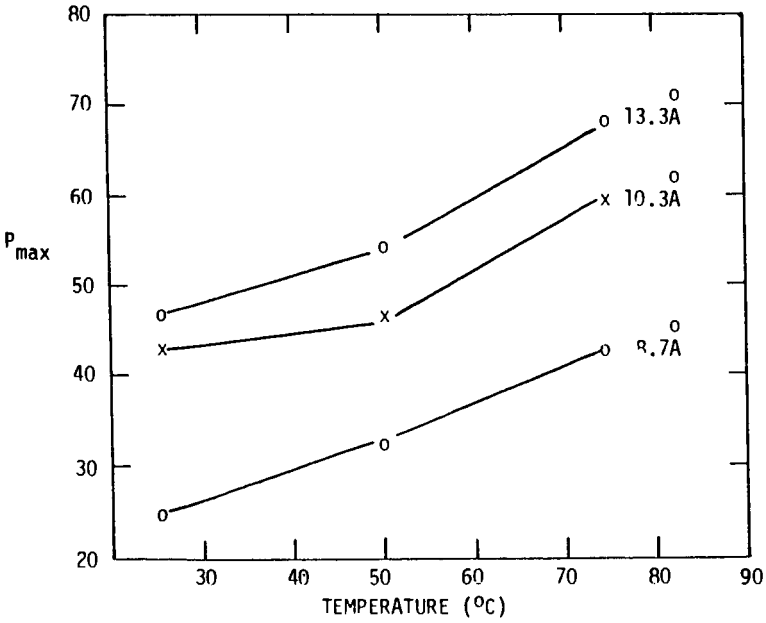

FIGURE 6. P_{max} vs. Temperature for CO_2 Adsorption on Activated Carbons of Various Pore Sizes

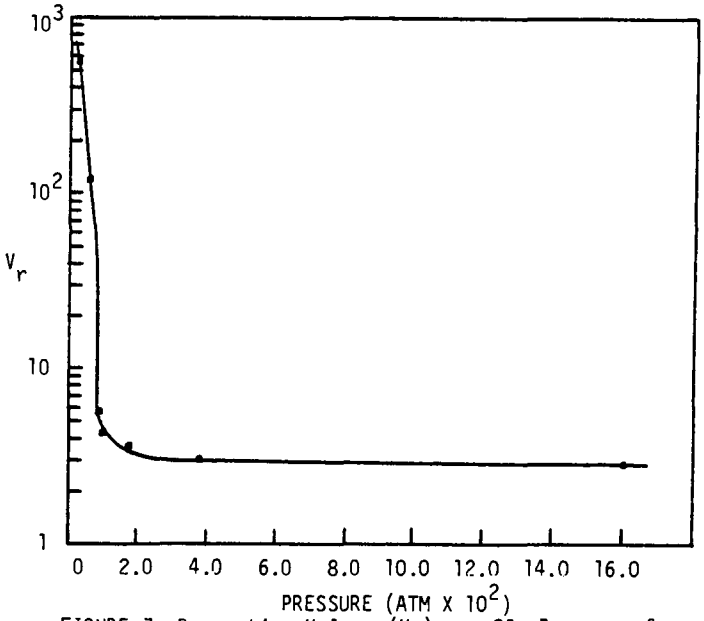

FIGURE 7. Desorption Volume (V_r) vs. CO_2 Pressure for Benzene/Styrene-Divinylbenzene Resin System

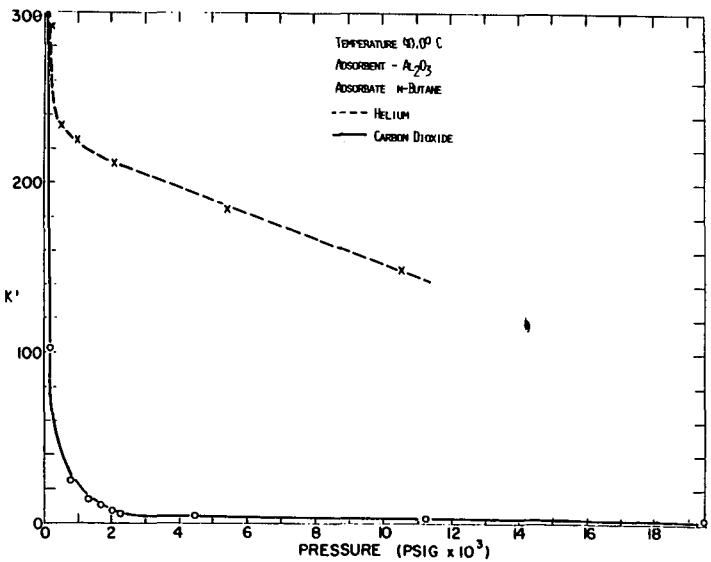

FIGURE 8. Capacity Factor (k') for n-Butane on Al_2O_3 vs. Carbon Dioxide or Helium Pressure