Modeling of Desorption at Supercritical Conditions

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In recent papers, Tan and Liou (1988a, b) studied the desorption of activated carbon loaded with either ethyl acetate or toluene, by supercritical carbon dioxide. In their study, an optimal desorption temperature of around 313 K was observed when the operating pressure was over 10.13 MPa. A single-parameter model assuming linear desorption kinetics was proposed by these authors, and was found to match the experimental data quite well. The apparent desorption activation energies at fixed pressures could then be obtained through the plot of the desorption rate constants vs. the reciprocal of temperature, i.e., the Arrenhuis expression. However, the question may arise as to whether the calculated desorption activation energy is incorrect, because of the existence of an optimal temperature.

In the past years it has been realized that density plays an important role at supercritical conditions (Paulaitis et al., 1983; Funazukuri et al., 1985; McHugh and Krukonis, 1986; Deshpande et al., 1986). It may therefore be more suitable to calculate the apparent desorption activation energies at fixed densities, than at fixed pressures. The objective of the present note is to see if this suitability exists, and to propose a proper relation between desorption rate constant, and density.

Experimental Section

The experimental apparatus and procedures used for adsorption and desorption experiments have been described in detail, elsewhere (Tan and Liou, 1988a, b). The adsorbate employed in this study was toluene, adsorbed by activated carbon from a gas stream. In order to operate at the same density in the supercritical desorption stage, the operation temperatures and pressures were selected, shown in Table 1. Since the concentration of toluene in carbon dioxide was not high, the density of the supercritical mixture was regarded as that of pure carbon dioxide. But it should be noted here that this assumption may not be correct for strong solute at near critical densities, since a significant volume contraction may occur (Eckert et al., 1983 and 1986). Three densities: 0.32, 0.45, and 0.62 g/cm^3, were chosen in the present study. All the desorption experiments were executed at the same superficial velocity of carbon dioxide, 1.27 cm/min.

Model Description

The single-parameter model used to describe desorption, may be written for the bulk fluid phase (Tan and Liou, 1988a, b):

$$\epsilon \frac{\partial C}{\partial t} + u \frac{\partial C}{\partial z} = -(1-\epsilon) \frac{\partial S}{\partial t} \tag{1}$$

$$t = 0, \quad C = 0 \tag{2}$$

$$z = 0, \quad C = 0 \tag{3}$$

and for the solid phase:

$$\frac{\partial S}{\partial t} = -kS \tag{4}$$

$$t = 0, \quad S = S_0 \tag{5}$$

The concentration at the exit of the packed bed can then be expressed by:

$$C_e = \frac{1-\epsilon}{\epsilon} S_0 \left\{ \exp\left[-k\left(t - \frac{\epsilon L}{u}\right)\right] - \exp(-kt) \right\} \tag{6}$$

Table 1. Desorption Temperatures and Pressures with Constant Densities

$\rho = 0.32$ g/cm^3		$\rho = 0.45$ g/cm^3		$\rho = 0.62$ g/cm^3	
T,K	*P*,Mpa	*T*,K	*p*,Mpa	*T*,K	*P*,Mpa
308	6.20	308	8.13	308	8.82
318	8.51	318	9.64	318	12.47
328	9.79	328	11.78	328	14.40
338	10.82	338	13.16	338	17.23

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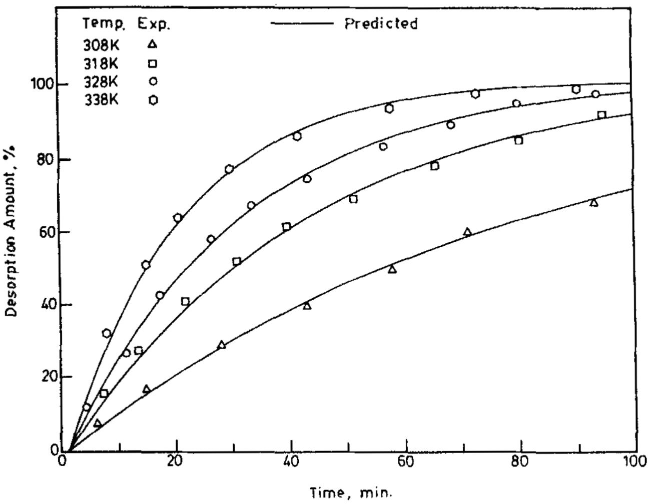

Figure 1. Experimental and predicted desorption rates under supercritical operations, $\rho = 0.32$ g/cm^3.

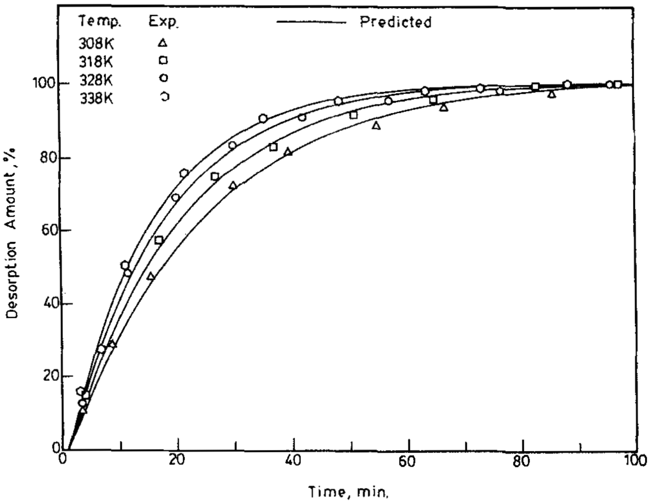

Figure 3. Experimental and predicted desorption rates under supercritical operations, $\rho = 0.62$ g/cm^3.

Results and Discussion

The desorption rate constant, k, can be estimated by fitting Eq. 6 with the experimental data. Figures 1 to 3 illustrate that this fit, at fixed densities, was in good agreement with an average deviation of less than 3.5%. As shown in these figures, the desorption efficiency increased with temperature. This trend is different from those mentioned by Tan and Liou (1988a, b), where the desorption efficiency decreased with temperature when the pressure was fixed at 8.81 MPa, and an optimal temperature of around 313 K existed when the pressures were fixed and larger than 10.13 MPa. With the present observation, the Arrhenius expression,

$$k = k_0 \exp\left(-\frac{E}{RT}\right) \tag{7}$$

can be more practically used to calculate the apparent desorption activation energy. Figure 4 shows these Arrhenius plots, and the calculated k_0 and E at different densities are given in Table 2. It can be seen in Table 2 that less desorption activation energy is required at a higher density. This means that desorption is easier at higher pressures when the temperature is fixed. This is consistent with observations DeFilippi et al. (1980), and Tan and Liou (1988a, b).

Since k_0 and E are functions of density, the following two relations are proposed in this study:

$$K_0 = k_r \rho^n \tag{8}$$

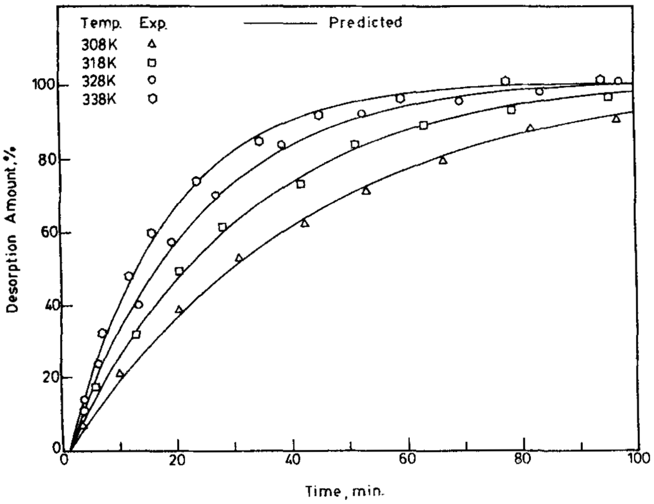

Figure 2. Experimental and predicted desorption rates under supercritical operations, $\rho = 0.45$ g/cm^3.

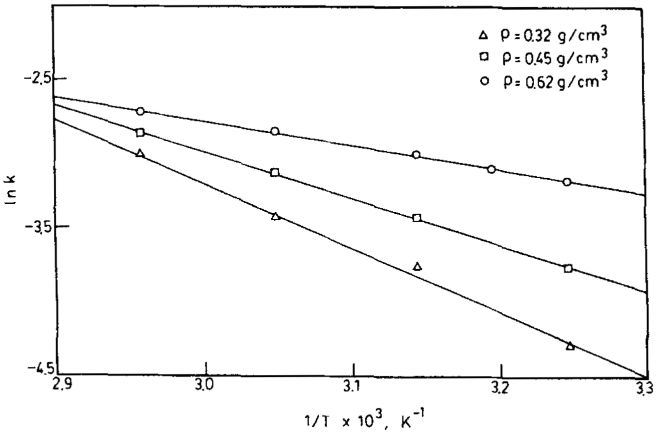

Figure 4. Plot of ln k vs. 1/T.

Table 2. Estimated k_0 and E from Experimental Data at Fixed Densities

	Density		
	0.32 g/cm^3	0.45 g/cm^3	0.62 g/cm^3
lnk_0	11.06	6.41	2.45
E,J/kmol	3.95×10^7	2.61×10^7	1.45×10^7

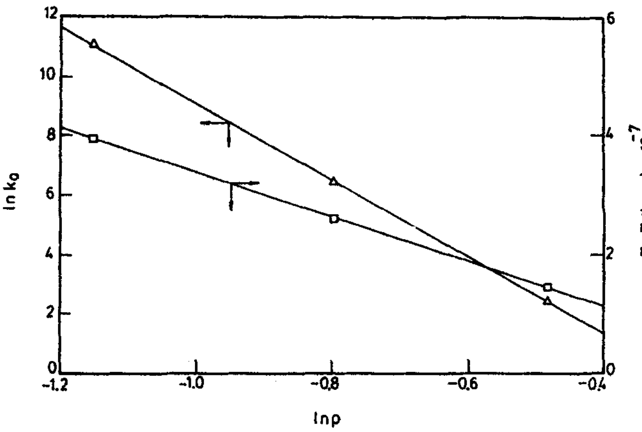

Figure 5. Plot of ln k_0 and E vs. ln ρ.

and

$$E = a + b \ln \rho \tag{9}$$

Using these relations, fairly straight lines could be obtained, shown in Figure 5. From the slopes and intersects in this figure, the constants in Eqs. 8 and 9 can be determined, giving the complete expression of k as:

$$k = 0.0224\, \rho^{-12.87} \exp\left[\frac{3.59 \times 10^6 + 3.73 \times 10^7 \ln \rho}{RT}\right] \tag{10}$$

When the predicted exit concentrations, using Eq. 10, were then compared with the experimental data, it was found that the agreement was still satisfactory, with an average deviation less than 5.0%.

Notation

C = concentration of toluene in CO_2, mol/cm^3
C_e = exit concentration of toluene, mol/cm^3
E = apparent desorption activation energy, J/kmol
k = desorption rate constant, 1/min
k_0 = preexponential factor, 1/min
k_r = constant, Eq. 8
L = column length, cm
P = pressure, MPa
R = universal gas constant, 8314.3 J/kmol · K
S = loaded toluene on activated carbon, mol/cm^3
S_0 = initially loaded toluene on activated carbon, mol/cm^3
T = temperature, K
t = time, min
u = superficial velocity, cm/min
z = axial position in column, cm
ϵ = void fraction in column
ρ = density of CO_2, g/cm^3

Literature Cited

DeFilippi, R. P., V. J. Krukonis, R. J. Robey, and M. Modell, *Supercritical Fluid Regeneration of Activated Carbon for Adsorption of Pesticides*, EPA-600/2-80-054, Washington D.C. (1980).

Deshpande, G. V., G. D. Holder, and Y. T. Shah, "Kinetics of Coal Liquefaction under Supercritical Conditions," *Ind. Eng. Chem. Proc. Des. Dev.*, **25**, 705 (1986).

Eckert, C. A., D. H. Ziger, K. P. Johnston, and T. K. Ellison, "The Use of Partial Molal Volume Data to Evaluate Equations of State for Supercritical Fluid Mixtures," *Fluid Phase Equil.*, **14**, 167 (1983).

Eckert, C. A., D. H. Ziger, K. P. Johnston, and S. Kim, "Solute Partial Molal Volumes in Supercritical Fluids," *J. Phys. Chem.*, **90**, 2738 (1986).

Funazukuri, T., S. Ogasawara, N. Wakao, and J. M. Smith, "Subcritical and Supercritical Extraction of Oil from Used Automotive Tire Samples," *J. Chem. Eng. Jap.*, **18**, 455 (1985).

McHugh, M. A., and V. J. Krukonis, *Supercritical Fluid Extraction, Principles and Practice*, Butterworth, Stoneham, MA (1986).

Paulaitis, M. E., J. M. L. Penninger, R. D. Gray, and P. Davidson, *Chemical Engineering and Supercritical Fluid Conditions*, Ann Arbor Science, Ann Arbor, MI (1983).

Tan, C. S., and D. C. Loiu, "Desorption of Ethyl Acetate from Activated Carbon by Supercritical Carbon Dioxide," *Ind. Eng. Chem. Res.*, **27**, 988 (1988a).

———, "Regeneration of Activated Carbon Loaded with Toluene by Supercritical Carbon Dioxide," *Sep. Sci. Technol.*, **24**, 111 (1988b).

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