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REMOVAL OF POLLUTANTS FROM SOLID MATRICES USING SUPERCRITICAL FLUIDS

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ABSTRACT

Several supercritical fluid extraction (SCFE) processes have been proposed for removing toxic and intractable organic compounds from a range of contaminated solids. These include soil remediation and the regeneration of adsorbents used to treat wastewater streams such as granular activated carbon (GAC). As a separation technique for environmental control, SCFE has several distinct advantages over conventional liquid extraction methods and incineration. Most notably, the contaminant is removed from the solvent in a concentrated form via a change in pressure or temperature and can be completely separated upon expansion to atmospheric pressure.

The viability of SCFE hinges on process conditions such as solvent-feed ratio and solvent recycle ratio. The necessity of recycling solvent complicates the contaminant separation step since a complete reduction to atmospheric pressure would create large recompression costs. Because of this, the pressure and temperature dependence of contaminant solubility must be understood so that operating conditions for the separation step can be defined. Fortunately, this is the most developed aspect of SCF technology. However, the mass transfer limitations to removing contaminants from solids change with solvent flow rate.

This paper discusses the use of SCFE for environmental control and presents results for the removal of DDT and 2-chlorophenol from GAC. 2-chlorophenol is almost completely removed with pure CO_2 at 40°C and 101 bar while only 55% of the DDT is removed at 40°C and 200 bar. These differences in regeneration efficiency cannot be understood solely in terms of solubility but point to a need for detailed studies of adsorption equilibrium and mass transfer resistances in supercritical fluid systems.

INTRODUCTION

Supercritical fluids (SCF's) have attracted much interest as extraction solvents for well over a decade. When a compound (usually a gas) is heated and compressed above its critical temperature (T_c) and pressure (P_c), respectively, it becomes essentially a tunable solvent capable of dissolving high molecular weight organics. In this state, the solvent power is extremely sensitive to small changes in pressure and temperature such that a solute may be extracted from a matrix at one set of conditions and completely separated from the solvent in a downstream operation at slightly different conditions. Applications have been commercialized in the food industry (decaffeination of coffee) and are beginning to appear in other industries as well such as spray application of varnishes and paints, and the cleaning of electronic parts.

Supercritical fluid processing has some distinct advantages over liquid-liquid extraction and distillation for separations. Unlike liquid-liquid extraction, the solute is easily and completely removed from the solvent via a drop in pressure to atmospheric. Also, since the SCF is usually a gas at ambient conditions it will leave any substrate completely free of solvent residues. In the separation of thermally labile compounds, supercritical fluid extraction (SCFE) can often be carried out near ambient temperatures as opposed to distillation which even under vacuum requires elevated temperatures. There are however some disadvantages.

For example, not every compound will dissolve to an appreciable extent in a SCF and because of the sensitivity to pressure, the control of a SCFE process must be very good to avoid solute precipitation in process lines. Also, because the thermodynamics of phase equilibria near the critical point is extremely complicated, the models for predicting solubility are not well developed which requires extensive experimentation for each new application. Finally, and most importantly for new applications is the capital cost. High pressure operation incurs substantial capital costs which must be recovered over an extended lifetime of the process.

One area in which SCFE may have application is in the area of environmental cleanup. Spent adsorbents are currently incinerated, landfilled, or subjected to a harsh thermal regeneration which destroys most of the capacity in a few cycles. As costs for incineration and landfills increase there will be more emphasis on increasing the efficiency of the regeneration process and SCFE has proven to be a promising technique for this application on the bench scale (1-4). In addition, the remediation of contaminated soil is of growing concern. Accidental spills, underground tank leakage, and unrestrained dumping of waste streams have led to a massive array of various hazardous compounds adsorbed onto and trapped in the soil. Very few technologies currently exist for this application and again SCFE has much potential.

BACKGROUND

It is useful to define those issues which must be addressed in any experimental study of SCFE. These are outlined broadly and then the studies involving regeneration of granular activated carbon (GAC) and soil remediation are reviewed.

The basic principle of SCFE that has been used in developing the environmental applications for this technology is that when the feed material is contacted with a supercritical fluid an equilibrium is established in which the contaminant will preferentially partition into the supercritical phase. Once this equilibrium has been achieved the supercritical fluid containing the dissolved contaminant is removed from the feed material. The extracted component is then completely separated from the SCF by means of a temperature and/or pressure change. The SCF is then recompressed to the extraction conditions and recycled. A simplified flow sheet of such an extraction process is shown in Figure 1.

The key to the process is the equilibrium that exists between the SCF and the organic pollutants. The equilibrium is partially described by the solubility of the pure organic species in the SCF. The solubility of a solute in a SCF represents the equilibrium that exists when no other species are present but when the solute is present in a solid matrix then the composition of the matrix, as well as the presence of any co-contaminants, will alter the solubility. In effect, a new equilibrium exists in which the solute may be more soluble or less soluble than in the binary case. Moreover, during the course of the extraction this equilibrium may change as the concentration of contaminant in the matrix changes. This equilibrium must be described by some adsorption model such as the Langmuir, Toth, or Freundlich isotherms (6) but the *rate* of change in concentration must be described with mass transfer principles.

SCFE from solid matrices therefore also requires consideration of the effect that the properties of each system will have on the extraction process. Some of the properties that will affect a particular SCFE process include the physical and chemical properties of the solid matrix (e.g. porosity, particle size, and pore size), the presence or absence of water and how the material has been adsorbed. In addition to temperature and pressure affecting the equilibrium the solvent flow rate must also be considered as it affects the mass transfer. In order to fully describe the extraction from a porous matrix, one must in general consider three aspects of the solid-contaminant-fluid system. First, what happens at the solid fluid interface (it is usually assumed that equilibrium is reached); second, how quickly does the contaminant diffuse through the pores; and finally how quickly

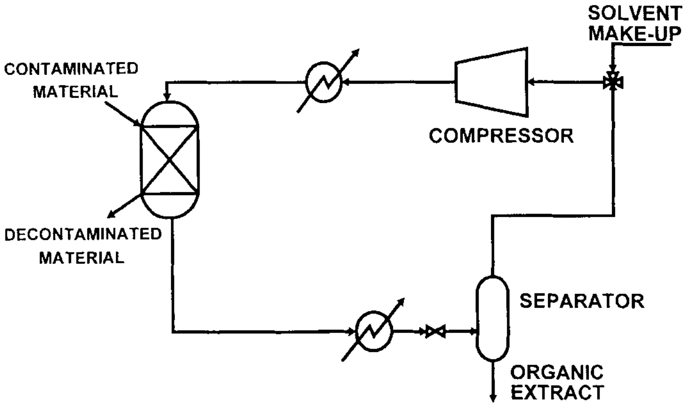

FIGURE 1. Schematic of a Supercritical Fluid Extraction Process (5).

does the contaminant diffuse from the external surface of the particle to the bulk fluid. Three mass conservation equations are required with associated boundary conditions. In the notation of Recasens, et al. (7):

$$\varepsilon \frac{\partial C}{\partial t} + u\frac{\partial C}{\partial x} = -\frac{3(1-\varepsilon)k_m}{r_0}\left[C-(C_i)_{r=r_0}\right] \qquad \text{(Bulk)}$$

$$\beta\frac{\partial C_i}{\partial t} = D_e \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_i}{\partial r}\right) - \rho k_a C_i + \rho k_d C_a \qquad \text{(Pore)}$$

$$\frac{\partial C_a}{\partial t} = k_a C_i - k_d C_a \qquad \text{(Surface)}$$

with initial and boundary conditions as follows:

$$D_e\left(\frac{\partial C_i}{\partial r}\right)_{r=r_0} = k_m\left[C-(C_i)_{r=r_0}\right] \qquad \text{(Particle-Fluid Interface)}$$

$$\left(\frac{\partial C_i}{\partial r}\right)_{r=0} = 0 \qquad \text{(Parabolic Profile in Particle)}$$

$$C(r,x,t=0)=C_i(r,x,t=0)=0 \qquad \text{(Pure Solvent in Pores Initially)}$$

$$C_a(r,x,t=0)=C_{a0} \qquad \text{(Initial Adsorbed Concentration)}$$

$$C(r,x=0,t)=0 \qquad \text{(Pure Solvent Entering Bed)}$$

One can see the parameters influencing each aspect of the extraction in these equations: for the bulk fluid k_m is an external (to the particle) mass transfer coefficient; in the pore D_e is an effective diffusivity of the contaminant; and at the surface k_a and k_d are the adsorption and desorption rate constants respectively. Assuming equilibrium at the surface makes use of $K_{eq} = k_a/k_d$ which is obtained from an adsorption model. The above equations are highly coupled and cannot be solved analytically without simplifying assumptions (7).

Even if one completely ignores mass transfer effects and assumes that equilibrium is reached between all the contaminated surface and the bulk fluid, there are still complications regarding the subsequent separation step. Hess, et al. (8) examined the response of six soil samples contaminated with phenol to extraction with supercritical CO_2. The six soil samples had a range of physical properties including surface area (0.67 to 256 m^3/g), organic content (0.0 to 2.7 wt %) and moisture content. The partitioning coefficient of phenol between the soil phase and the supercritical CO_2 phase was measured for each sample and was found to vary over two orders of magnitude. The significance of this is that the actual solubility of a solute in a SCF in the presence of a solid matrix can vary significantly from the binary solute/SCF system solubility and this partitioning cannot be predicted. Whilst experimental data are scarce in this area, evidence suggests that both solubility enhancements and depressions can occur. Solubility enhancements are usually caused by a cosolvent effect resulting from other organic solutes present in the sample which also dissolve into the SCF. Reductions in solubility are often the result of the solid matrix having a strong affinity for the solute being extracted, but may also be due to mass transfer limitations.

This behavior is very significant in terms of the design and scale up of a SCFE processes. When solubility enhancement occurs the impact on the overall process design is positive as the solvent to feed ratio is reduced without seriously altering the behavior of the rest of the process. However a serious complication can arise when the solute solubility is reduced in the presence of a solid matrix. In this case, if the solute-solvent separation step was designed based on the binary system equilibrium solubility, then it is possible that it would fail to separate any solute from the supercritical solvent. This is because once the fluid stream leaves the soil extraction vessel the system equilibrium returns to the simple binary system equilibrium. If the solubility of a solute in the presence of a solid matrix is only 10% of its binary system solubility and the separation step employs an 80% solubility reduction based on its binary system behavior then no separation will occur.

Carbon Studies

Several authors have looked at desorption from GAC using supercritical carbon dioxide. Tan and Liou (3,9,10) have studied model compounds ethyl acetate, benzene, and toluene varying flow rate, temperature, pressure, and density. They were the first to show the "cross-over" behavior in a supercritical desorption system where the fraction desorbed increases with temperature at low pressure and decreases with temperature at high pressure. McCoy and coworkers (4,7) have developed the most complete models to date incorporating mass transfer and linear adsorption kinetics. They used data from Tan and Liou (10) as well as their own ethyl acetate data to test the various assumptions in their models. Their results show a noticeable external mass transfer resistance at low flow rates. DeFilippi et al (1,2) performed some of the first studies of supercritical regeneration of carbon. The adsorbates were all pesticides or herbicides and they showed the efficacy of using SCF's to significantly extend the lifetime of the carbon. All but one pesticide exhibited a stable adsorption level on carbon that had been regenerated multiple times (up to 31). Although the early literature contains one study of adsorption of phenol from a supercritical fluid (11), others have begun to recognize the importance of adsorption equilibrium data for describing desorption data and have reported adsorption data for toluene, and several polyaromatic hydrocarbons (12-13). These results demonstrate a similar loading on activated carbon which seems to be relatively (but not completely) independent of the solubility of the compound in supercritical CO_2.

Soil Studies

Several investigators have used supercritical fluids to remove organics from soil samples. As mentioned above, Hess et al. (8) demonstrated the effects of organic content, moisture, and surface area of six different soils on the distribution of phenol between the adsorbed and fluid phases. Their results point to the conclusion that surface area is a primary factor determining distributions as the distribution coefficient steadily decreased with increasing surface area. The results were mixed for the cosolvent effect of methanol in that the cosolvent enhanced the extraction of phenol from dry soil but decreased the extraction of phenol from wet soil. There are clearly competing effects in such a complex system. The effect of water in other soil work is similar. Brady et al. (14) showed that the removal of PCB and DDT was much slower from soil containing 20 wt % water than from dry soil although the final concentrations on the soil were approximately the same (60-70% removed). In subsequent work from the same group, Dooley et al. (15) showed that toluene has little effect as a cosolvent on the removal of DDT from an actual spill-site topsoil while methanol has a large effect and results in approximately 95% removal of the organic. While these results demonstrate the feasibility of SCFE for soil remediation, there is still a need for supporting data for design. One study of adsorption on soil from supercritical CO_2 has been reported (16) but unfortunately it does not include any of the compounds for which remediation data exist.

EXPERIMENTAL

The apparatus used for 2-chlorophenol studies has been described earlier (17). The DDT (2,2-bis(p-chlorophenyl)-1,1,1-trichloroethane) desorption studies were carried out in a bench scale apparatus also described elsewhere (18). The 2-chlorophenol was adsorbed onto activated carbon from a nitrogen stream using a technique similar to that of Tan and Liou (9) and DDT was adsorbed from supercritical CO_2 at 318.1K and 119.8 bar. The loadings were 0.53 g/g GAC for 2-chlorophenol and 0.551 g/g GAC for DDT.

DISCUSSION

We have measured the desorption profile for DDT at 40°C and 200 bar. Figure 2 shows the fraction DDT removed as a function of time and moles of CO_2. Only 55% of the DDT is removed and the data are clearly reaching an asymptotic value. A more clear indication of the diminishing return is in Figure 3 which shows the mole fraction of DDT in the CO_2 exiting the bed as a function of time. The mole fraction in the SCF is quickly approaching the limit of detection and further addition of solvent would only yield marginal improvement in the desorption. The final concentration on the carbon is approximately 0.23 g/g which may be acceptable for reuse (i.e. in a regeneration process) but is not satisfactory for disposal. This result is compared with the data for 2-chlorophenol which was extracted at 40°C and 101 bar in Figure 4. Obviously, there is a substantial difference between the two which cannot be explained solely by differences in solubility but must include a comparison of the adsorption equilibria. In the absence of mass transfer resistances (which are discussed below) the desorption would be limited by the equilibrium distribution between the adsorbent and the SCF (i.e. the adsorption equilibrium). In this case the limiting behavior has little effect on the removal of 2-chlorophenol but has dramatic consequences for the removal of DDT.

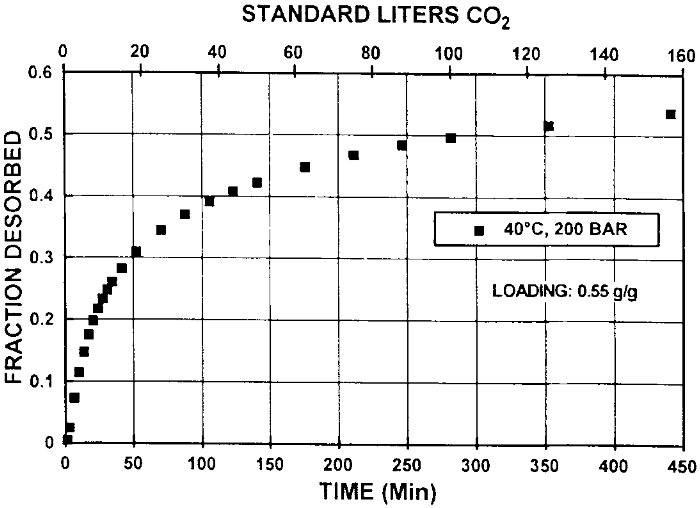

FIGURE 2. Fraction of DDT Desorbed at 40°C and 200 Bar as a Function of Time and Amount of Solvent.

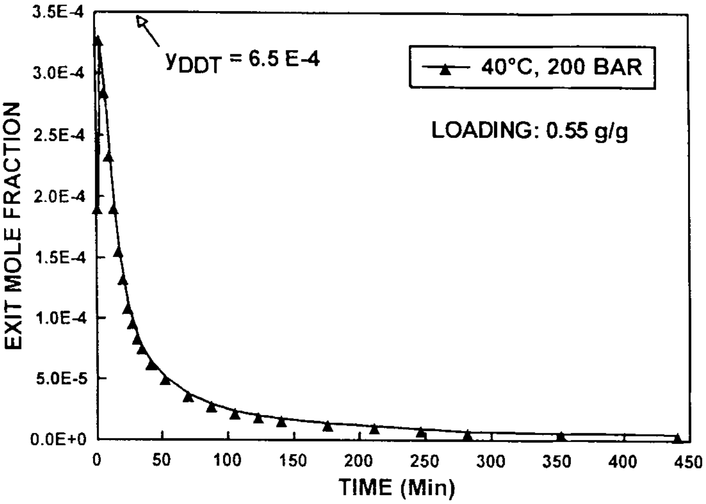

FIGURE 3. Exit Concentration of DDT in CO_2 as a Function of Time.

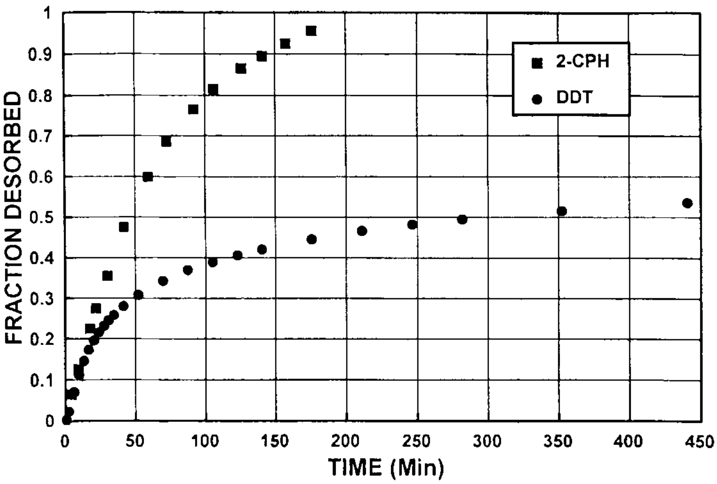

FIGURE 4. Effect of Contaminant on Fraction Desorbed.

The relative magnitudes of the interactions bewteen solvent and solute can be discerned from the solubility data. While the solubility of 2-chlorophenol has not specifically been determined in supercritical CO_2 it is reported to be miscible with liquid CO_2 at 25°C (1) and therefore would undoubtedly exhibit a high degree of miscibility with supercritical CO_2. On the other hand, the solubility of DDT is typically less than 1×10^{-3} mole fraction and is only 6.6×10^{-4} at the conditions of the desorption (18). We infer from this that the interactions between CO_2 and 2-chlorophenol are stronger than those between CO_2 and DDT which is consistent with the greater initial slope of the desorption curve for 2-chlorophenol.

Our results seem to indicate that a high percentage of the DDT is irreversibly adsorbed on GAC or it has a very steep adsorption isotherm (high degree of adsorption from dilute solution). A more significant comparison would use the adsorption data for each of these compounds on GAC.

A comparison with the soil data discussed earlier (14,15) demonstrates that DDT has a slightly higher affinity for GAC than soil. Therefore, the carbon data becomes a conservative estimate of the required conditions for soil remediation. Further improvements in the desorption will come from altering the density or composition in the SCF phase to increase the interactions between the solute and the adsorbate (i.e. altering the equilibrium).

For regeneration purposes, one would be interested in reaching the final concentration as quickly as possible. For equilibrium desorption the results should be independent of flow rate, however in experiments at different flow rates a distinct dependence on the solvent flow rate has been reported (3,4). The rate of desorption becomes very slow at low flow rates indicating a possible film resistance impeding the transfer of solute from the pore to the bulk fluid. Preliminary results from this work are consistent with these observations. However, if one compares results from different flow rates as a function of moles of CO_2 used, the low flow rates essentially collapse onto a single curve and the data at the highest flow shows a deviation indicating a lower desorption efficiency. There apparently is a limit at which diffusion and/or desorption kinetics begin to limit the overall rate of desorption. This is but one example of the complications exhibited by these types of systems.

To date, the experiments and models put forward to discern mass transfer effects in these systems make simplifying assumptions regarding the adsorption equilibrium. For example, Tan and Liou (10) developed a single parameter model assuming linear desorption kinetics which essentially lumps an equilibrium coefficient and a mass transfer coefficient into a single adjustable parameter. Recasens et al (7) showed that one must assume a linear driving force model for external and intraparticle mass transfer in combination with either local equilibrium or irreversible desorption to obtain analytical solutions for desorption from fixed beds. Unfortunately, neither of these has the capability to incorporate a more sophisticated model of the adsorption equilibrium which can have the dominant influence on desorption behavior (18).

CONCLUSIONS

Supercritical fluids have some distinct advantages as extraction solvents for environmental control such as the ability to remove contaminants from a solid matrix such as soil or an adsorbent without leaving any solvent residue. There is however, much more to consider in this application than the basic ability of a SCF to dissolve the component of interest. Adsorption equilibrium and mass transfer resistances must not only be considered but studied in detail in order for SCF technology to become economically competitive.

Results were shown for the removal of DDT and 2-chlorophenol from GAC with SC CO_2. DDT is much more strongly bound by carbon than 2-chlorophenol and while pure CO_2 can completely remove the 2-chlorophenol, it is apparently not a strong enough solvent to completely remove all the DDT from the carbon. The use of a cosolvent should be considered for better extraction efficiencies with strongly bound adsorbates.

In order to understand the effects of molecular structure and solid characteristics on this process, careful studies of adsorption equilibrium are needed. Theoretical developments regarding the fugacity of an adsorbed phase and its dependence on solvent density are also needed. Finally, in order to uncouple the effects of equilibrium from mass transfer, complementary data from different experiments such as adsorption and desorption rates and equilibria and corresponding fluid phase equilibria are needed for the same adsorbent/adsorbate system.

NOMENCLATURE

C - Concentration in bulk SCF phase

C_a - Adsorbed concentration

C_{a0} - Initial adsorbed concentration

C_i - Concentration in pore

D_e - Effective diffusivity in pore

k_a - Adsorption rate constant
k_d - Desorption rate constant
k_m - Mass transfer coefficient in bulk SCF phase
K_{eq} - Adsorption equilibrium constant
r - Radial position from center of particle
r_0 - Particle radius
t - Time
u - Superficial velocity at conditions of bed
x - Axial position in bed

β - Particle porosity
ε - Void fraction of bed
ρ - Density of SCF

REFERENCES

1. R.P. DeFillipi, V.J. Krukonis, R.J. Robey, and M. Modell, Supercritical Fluid Regneration of Activated Carbon for Adsorption of Pesticides, Report EPA-600/2-80-054, U.S. Environmental Protection Agency, Washingon, DC, 1980.

2. R.P. DeFillip and R.J. Robey, Supercritical Fluid Regeneration of Adsorbents, Report EPA-600/2-83-038, U.S. Environmental Protection Agency, Washington, DC, 1983.

3. C-S. Tan and D-C. Liou, Ind. Eng. Chem. Res., 28, 1222 (1989).

4. M.P. Srinivasan, J.M. Smith, and B.J. McCoy, Chem. Eng. Sci., 45(7), 1885 (1990).

5. S.J. Macnaughton, D.L. Tomasko, N.R. Foster, and C.A. Eckert, Trans. IChemE, 71, Part B, 124 (1993).

6. Adamson, A.W., Physical Chemistry of Surfaces, 5th Ed., John Wiley & Sons, New York (1990).

7. F. Recasens, B.J. McCoy, and J.M. Smith, AIChE J., 35(6), 951 (1989).

8. R.K. Hess, C. Erkey, and A. Akgerman, J. Supercritical Fluids, 4, 47 (1991).

9. C-S. Tan and D-C. Liou, Sep. Sci. Tech., 24(1&2), 111 (1989).

10. C-S. Tan and D-C. Liou, Ind. Eng. Chem. Res., 27, 988 (1988).

11. R.G. Kander and M.E. Paulaitis, in Chemical Engineering at Supercritical Fluid Conditions, M.E. Paulaitis, J.M.L. Penninger, P. Davidson, and R.D. Gray, Eds., Ann Arbor Science: Ann Arbor, MI, 1983, p.461.

12. C-S. Tan and D-C. Liou, Ind. Eng. Chem. Res., 29, 1412 (1990).

13. G. Madras, C. Erkey, and A. Akgerman, Ind. Eng. Chem. Res., 32, 1163 (1993).

14. B.O. Brady, C-P. C. Kao, K.M. Dooley, F.C. Knopf, and R.P. Gambrell, Ind. Eng. Chem. Res., 26, 261 (1987).

15. K.M. Dooley, C-P. Kao, R.P. Gambrell, and F.C. Knopf, Ind. Eng. Chem. Res., 26, 2058 (1987).

16. C. Erkey, G. Madras, M. Orejuela, and A. Akgerman, Environ. Sci. Technol., 27, 1225 (1993).

17. D.L. Tomasko, K.J. Hay, G.W. Leman, C.A. Eckert, Environ. Prog., 12(3), 208 (1993).

18. S.J. Macnaughton and N.R. Foster, Ind. Eng. Chem. Res., to be submitted (1993).