Supercritical Devolatilization of Polymers

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An increasing number of studies have been reported on the use of supercritical fluids to process polymers. The presence of impurities such as residual solvents, unreacted monomers, catalysts, and side reaction products can adversely affect the end-use properties of polymeric materials. Therefore, these impurities must be reduced to a level below the maximum permissible limit. Conventional devolatilization techniques for the purification of polymers have limited effectiveness. Devolatilization with supercritical fluids, however, can enhance impurity removal by increasing the thermodynamic driving force and molecular diffusivity. A model for supercritical devolatilization developed incorporates swelling of the polymer film and convection induced by the diffusion that arises because of the nonideal volumetric behavior. The perturbed soft-chain theory is used to predict the nonideal thermodynamic behavior. Free volume theory is utilized to predict the influence of plasticization and relaxation on impurity mass transfer. The removal of benzene from polystyrene film with supercritical carbon dioxide was simulated. This analysis, which is consistent with experimental results in the literature, indicates that, contrary to conventional wisdom, impurity extraction can be dominated by mass transfer during the quick depressurization step at the end of a supercritical-fluid extraction process.

Introduction

Recently, the use of supercritical fluids in the processing of polymers has received much attention. Applications include fractionation of polymers (Yilgor and McGrath, 1984; Kumar et al., 1986b; Scholsky et al., 1987; Elsbernd et al., 1990; Meilchen et al., 1990; Pratt et al., 1993; Saltzman et al., 1993) with respect to molecular weight, chemical composition and backbone structure, modification of synthetic polymers by using supercritical fluids as a solvent medium (Trivedi et al., 1994; Watkins and McCarthy, 1996), dissolution and precipitation of polymers using a supercritical solvent (Kumar et al., 1986a), separating polymer solutions with supercritical fluids by inducing a phase split (McHugh and Guckes, 1985), generation of microcellular polymeric foams using supercritical carbon dioxide (Goel and Beckman, 1992), impregnation of polymers (Sand, 1986; Berens et al., 1992), and the utilization of supercritical fluids to extract impurities from polymers (Copelin, 1981; Yilgor and McGrath, 1984; Krukonis, 1985; Scholosky, 1987; Jarzebski et al., 1990; Venema et al., 1993). The removal of volatile impurities such as monomers, solvents, condensation by products, catalysts, and side-reaction products from polymers represent an important step in polymer processing. These impurities can adversely affect the final use of polymeric products, since they can change the taste, color, toxicity, or thermophysical properties of polymers through plasticization or depolymerization. Excess levels of these impurities constitute both environmental and health hazards. Therefore, strict regulations have been enacted to establish maximum permissible levels of various impurities. Conventionally, polymers are purified by either vacuum or steam stripping or solvent extraction. In some cases these methods are not sufficient to reduce the residual contents to the required permissible levels. Supercritical devolatilization has the potential to produce high-purity, high-quality products with lower energy costs (Copelin, 1981). Successful commercial technologies for processing polymers by using the supercritical fluids are very limited, but this alternative is being considered more today to meet the stringent requirements in an economical way. The extension of the process from a laboratory scale to the pilot-plant scale requires the appropriate modeling to optimize the operating

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conditions for existing devolatilizers and to optimize the design parameters for new devolatilization units.

Mathematical models have been developed to analyze the devolatilization process in different configurations (Lee and Biesenberger, 1989; Maffettone et al., 1991). The role of stripping agents in devolatilization in a thin stagnant film has been analyzed (Vrentas et al., 1985; Ravindranath and Mashelkar, 1988).

A devolatilization process with supercritical fluids is significantly different from conventional devolatilization processes. In a typical supercritical devolatilization process the first step is the compression of the fluid to elevated pressures above its critical pressure. The second stage is the extraction stage, in which polymer is exposed to the supercritical fluid, it is swollen, and the free volume in the polymer is increased so that diffusion of the impurities out of the polymer is enhanced. Supercritical-fluid polymer systems are highly thermodynamically nonideal, and therefore they can show significant volume change on mixing. During the extraction stage, in addition to the plasticization effect, this nonideal volumetric behavior can cause convection induced by diffusion that can influence the transport of the impurities out of the polymer. The final stage in supercritical devolatilization is the depressurization stage where pressure is reduced and supercritical fluid diffuses out of the polymer. During that stage, the rate of removal of supercritical fluid from the polymer can be fast compared to relaxation of polymer to its original unswollen state. As a result, this can lead to a coupling between the polymer relaxation and the mass transfer.

In this work, a model for supercritical devolatilization is developed that incorporates both swelling and thermodynamic effect. An analysis of the process is presented including all the phenomena just mentioned. Vrentas–Duda free-volume theory for diffusion in polymer–solvent systems is used to predict the influence of plasticization and relaxation on impurity mass transfer (Duda et al., 1982; Vrentas et al., 1984). The perturbed soft chain theory is utilized to predict nonideal thermodynamic behavior to determine the influence of diffusion-induced convection (Pretel and Danner, 1996). The advantage of using a different coordinate system and volume average velocity in the formulation of a species continuity equation is illustrated. Supercritical fluid extraction of polymers is a very complex process, and for the sake of clarity, the following model development focuses on some important aspects of this process that have previously not been considered. Specifically, the process is assumed to be isothermal, mass-transfer resistances in the supercritical phase above the polymer phase are neglected, and it is assumed that the concentration of impurity that is being extracted is zero during all stages of the process in the supercritical phase.

Theory

Model description

The model equations for supercritical devolatilization were developed based on the geometry shown in Figure 1 where unsteady-state diffusion takes place in a thin film sitting on a flat plate. Initially, the polymer film has a thickness, L, and it contains a small amount of impurity, solvent 1, such as benzene, with initial mass density $\rho_1 = \rho_{1_o}$. At time $t = 0$, the polymer film is exposed to a supercritical fluid, solvent 2, that reaches its equilibrium concentration ρ_{2E} at the surface instantaneously. Also, this supercritical fluid stream sweeps away the impurity from the surface, diffusion is fast in the supercritical phase, and it is assumed that the concentration of solvent 1 at the supercritical fluid polymer interface is maintained at $\rho_{1E} = 0$. Mass transfer is assumed to be one-dimensional since the width of the sample is much greater than the thickness. Also, the process is assumed to be effectively isothermal. It is further assumed that the Fickian diffusion takes place in this stage of the process and that there is no reaction in the sample. Finally, for lack of sufficient information, it is assumed that the cross-diffusion coefficients, D_{ij}, are smaller than the principal diffusion coefficients, D_{ii}, that is, they are assumed to be zero. The main diffusion coefficients are approximated by self-diffusion coefficients, D_i of each component in the polymer.

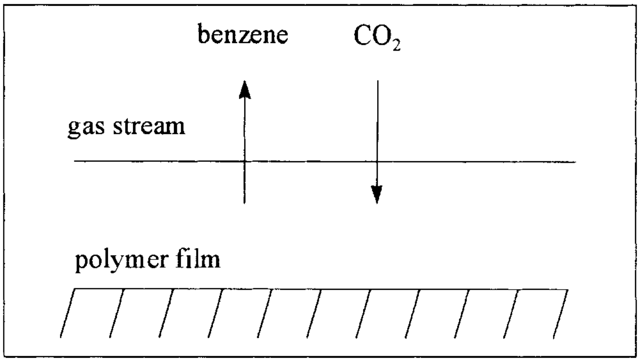

Figure 1. Geometry of devolatization process.

Extraction stage

In the extraction stage of the process, the polymer containing the impurities is exposed to the supercritical fluid. The supercritical fluid diffuses into the polymer phase, swells it, and the impurity diffuses out. In the development of the equations, a coordinate transformation (Duda and Vrentas, 1971) is used to eliminate the boundary movement and volume change on mixing effects. Species continuity equations for solvent 1 (impurity), solvent 2 (supercritical fluid), and the polymer denoted by component 3 can be written as

$$\frac{\partial \rho_1}{\partial t} + \frac{\partial (\rho_1 v_1)}{\partial x} = 0 \tag{1}$$

$$\frac{\partial \rho_2}{\partial t} + \frac{\partial (\rho_2 v_2)}{\partial x} = 0 \tag{2}$$

$$\frac{\partial \rho_3}{\partial t} + \frac{\partial (\rho_3 v_3)}{\partial x} = 0. \tag{3}$$

The total flux of component i can be defined as follows:

$$\rho_i v_i = \rho_i v_N + J_i^{O\neq}. \tag{4}$$

Utilization of the new concentration variables

$$q_1 = \frac{\rho_1}{\rho_3 \hat{V}_3^O} \qquad q_2 = \frac{\rho_2}{\rho_3 \hat{V}_3^O} \tag{5}$$

and a new length variable

$$\xi(x,t) = \int_0^x \rho_3 \hat{V}_3^O \, dx \tag{6}$$

in connection with Eqs. 3 and 4 yields the following form of the species continuity equations defined by Eqs. 1 and 2:

$$\left(\frac{\partial q_1}{\partial t}\right)_\xi + \left(\frac{\partial J_1^{O\neq}}{\partial \xi}\right)_t = 0 \tag{7}$$

$$\left(\frac{\partial q_2}{\partial t}\right)_\xi + \left(\frac{\partial J_2^{O\neq}}{\partial \xi}\right)_t = 0 \tag{8}$$

The diffusive flux, $J_i^{O\neq}$ is defined as follows:

$$J_i^{O\neq} = \frac{J_i^{\neq}\rho_N \bar{V}_N + \rho_i \Sigma_{i=1}^{N-1} J_i^{\neq} \bar{V}_i}{\rho_N \bar{V}_N}. \tag{9}$$

The mass diffusive fluxes of solvent 1 and solvent 2 in terms of volume average velocity are defined by the following equations:

$$J_1^{\neq} = -D_1 \frac{\partial \rho_1}{\partial x} \tag{10}$$

$$J_2^{\neq} = -D_2 \frac{\partial \rho_2}{\partial x}. \tag{11}$$

In terms of new length and concentration variables, Eq. 9 can be rewritten as follows for solvent 1 and solvent 2:

$$-J_1^{O\neq} = D_{11\text{eff}} \frac{\partial q_1}{\partial \xi} + D_{12\text{eff}} \frac{\partial q_2}{\partial \xi} \tag{12}$$

$$-J_2^{O\neq} = D_{21\text{eff}} \frac{\partial q_1}{\partial \xi} + D_{22\text{eff}} \frac{\partial q_2}{\partial \xi}. \tag{13}$$

It is interesting that even though the cross-diffusion coefficients are assumed negligible ($D_{12} = D_{21} = 0$) in the new coordinate system, effective cross-diffusion coefficients arise because of diffusion-induced convection and swelling. Effective diffusivities $D_{ii\text{eff}}$, and $D_{ij\text{eff}}$, are defined as follows:

$$D_{11\text{eff}} = \left(\rho_3 \hat{V}_3^O\right)^2 \Big\{ \left[A D_1 - \rho_3 \hat{V}_3^O (A q_1 D_1 + B q_2 D_2) \bar{V}_1 \right] - \rho_3 (A q_1 D_1 + B q_2 D_2) \left[\frac{\partial \bar{V}_3}{\partial q_1} + \hat{V}_3^O \left(q_1 \frac{\partial \bar{V}_1}{\partial q_1} + q_2 \frac{\partial \bar{V}_2}{\partial q_1} \right) \right] \Big\} \tag{14}$$

$$D_{12\text{eff}} = \left(\rho_3 \hat{V}_3^O\right)^2 \Big\{ \left[B D_2 - \rho_3 \hat{V}_3^O (A q_1 D_1 + B q_2 D_2) \bar{V}_2 \right] - \rho_3 (A q_1 D_1 + B q_2 D_2) \left[\frac{\partial \bar{V}_3}{\partial q_2} + \hat{V}_3^O \left(q_1 \frac{\partial \bar{V}_1}{\partial q_2} + q_2 \frac{\partial \bar{V}_2}{\partial q_2} \right) \right] \Big\} \tag{15}$$

$$D_{21\text{eff}} = \left(\rho_3 \hat{V}_3^O\right)^2 \Big\{ \left[C D_1 - \rho_3 \hat{V}_3^O (C q_1 D_1 + D q_2 D_2) \bar{V}_1 \right] - \rho_3 (C q_1 D_1 + D q_2 D_2) \left[\frac{\partial \bar{V}_3}{\partial q_1} + \hat{V}_3^O \left(q_1 \frac{\partial \bar{V}_1}{\partial q_1} + q_2 \frac{\partial \bar{V}_2}{\partial q_1} \right) \right] \Big\} \tag{16}$$

$$D_{22\text{eff}} = \left(\rho_3 \hat{V}_3^O\right)^2 \Big\{ \left[D D_2 - \rho_3 \hat{V}_3^O (C q_1 D_1 + D q_2 D_2) \bar{V}_2 \right] - \rho_3 (C q_1 D_1 + D q_2 D_2) \left[\frac{\partial \bar{V}_3}{\partial q_2} + \hat{V}_3^O \left(q_1 \frac{\partial \bar{V}_1}{\partial q_2} + q_2 \frac{\partial \bar{V}_2}{\partial q_2} \right) \right] \Big\}. \tag{17}$$

The dimensionless groups A, B, C, and D are defined as follows:

$$A = \frac{(1 - \rho_2 \bar{V}_2)}{\rho_3 \bar{V}_3} \qquad B = \frac{\rho_1 \bar{V}_2}{\rho_3 \bar{V}_3} \tag{18}$$

$$C = \frac{\rho_2 \bar{V}_1}{\rho_3 \bar{V}_3} \qquad D = \frac{(1 - \rho_1 \bar{V}_1)}{\rho_3 \bar{V}_3}. \tag{19}$$

If there is no volume change on mixing, that is, $\bar{V}_1$, $\bar{V}_2$, and $\bar{V}_3$ are not functions of composition, the last term in Eqs. 14 through 17 becomes zero. Finally, Eqs. 7 and 8 can be written as follows:

$$\left(\frac{\partial q_1}{\partial t}\right)_\xi = \frac{\partial}{\partial \xi}\left[D_{11\text{eff}} \frac{\partial q_1}{\partial \xi} + D_{12\text{eff}} \frac{\partial q_2}{\partial \xi} \right] \tag{20}$$

$$\left(\frac{\partial q_2}{\partial t}\right)_\xi = \frac{\partial}{\partial \xi}\left[D_{21\text{eff}} \frac{\partial q_1}{\partial \xi} + D_{22\text{eff}} \frac{\partial q_2}{\partial \xi} \right], \tag{21}$$

which are subject to the following initial and boundary conditions:

$$q_1(\xi,0) = q_{1O} \qquad q_2(\xi,0) = q_{2O} \tag{22}$$

$$\left(\frac{\partial q_1}{\partial \xi}\right)_{\xi=0} = 0. \qquad \left(\frac{\partial q_2}{\partial \xi}\right)_{\xi=0} = 0 \tag{23}$$

$$q_1(\xi_L,t) = q_{1E} \qquad q_2(\xi_L,t) = q_{2E} \tag{24}$$

$$\xi_L = \rho_{3O} \hat{V}_3^O L. \tag{25}$$

Finally, introducing the following dimensionless variables

$$q_1^* = \frac{q_1 - q_{1O}}{q_{1E} - q_{1O}} \qquad q_2^* = \frac{q_2 - q_{2O}}{q_{2E} - q_{2O}} \tag{26}$$

$$\xi^* = \frac{\xi}{\xi_L} \qquad t^* = \frac{t D_1}{\xi_L^2} \tag{27}$$

in Eqs. 7 and 8 yields the following equations:

$$\frac{\partial q_1^*}{\partial t^*} = -\frac{\partial}{\partial \xi^*}(J_1^{O\neq *}) \tag{28}$$

$$\frac{\partial q_2^*}{\partial t^*} = -\frac{\partial}{\partial \xi^*}(J_2^{O\neq *}). \tag{29}$$

Normalized fluxes of solvent 1 and 2 can be defined by the following equations:

$$-J_1^{O\neq *} = D_{11\text{eff}}^* \frac{\partial q_1^*}{\partial \xi^*} + D_{12\text{eff}}^* \frac{\partial q_2^*}{\partial \xi^*} \tag{30}$$

$$-J_2^{O\neq *} = D_{21\text{eff}}^* \frac{\partial q_1^*}{\partial \xi^*} + D_{22\text{eff}}^* \frac{\partial q_2^*}{\partial \xi^*}. \tag{31}$$

Normalized diffusion coefficients in Eqs. 30 and 31 are defined as follows:

$$D_{11\text{eff}}^* = \frac{D_{11\text{eff}}}{D_1} \qquad D_{12\text{eff}}^* = \frac{D_{12\text{eff}}\beta}{D_1} \tag{32}$$

$$D_{21\text{eff}}^* = \frac{D_{21\text{eff}}}{D_1\beta} \qquad D_{22\text{eff}}^* = \frac{D_{22\text{eff}}}{D_1}. \tag{33}$$

The dimensionless quantity β is defined as follows:

$$\beta = \frac{q_{2E} - q_{2O}}{q_{1E} - q_{1O}}. \tag{34}$$

Initial and boundary conditions defined by Eqs. 22 through 24 can be rewritten as follows:

$$q_1^*(\xi^*, 0) = 0 \qquad q_2^*(\xi^*, 0) = 0 \tag{35}$$

$$\left(\frac{\partial q_1^*}{\partial \xi^*}\right)_{\xi^*=0} = 0 \qquad \left(\frac{\partial q_2^*}{\partial \xi^*}\right)_{\xi^*=0} = 0 \tag{36}$$

$$q_1^*(1, t^*) = 1 \qquad q_2^*(1, t^*) = 1. \tag{37}$$

Results and Discussion

The effective diffusivities in the model equations combine the effect of the ratio of diffusivity of carbon dioxide to that of benzene, the effect of swelling, and the effect of volume change on mixing. These diffusivities are analogous to multicomponent Fickian diffusion coefficients. The main effective diffusion coefficients $D_{11\text{eff}}^*$ and $D_{22\text{eff}}^*$ are positive, but cross terms $D_{12\text{eff}}^*$ and $D_{21\text{eff}}^*$ may take negative or positive signs. Also, main effective diffusion coefficients are larger in magnitude than the cross terms. It can also be shown that as $\omega_{\text{benzene}} \to 0$ and $\omega_{CO_2} \to 0$,

$$D_{11\text{eff}}^* \to D_1, \quad D_{22\text{eff}}^* \to D_2, \quad D_{12\text{eff}}^* \to 0 \quad \text{and} \quad D_{21\text{eff}}^* \to 0.$$

Ignoring convective transport can result in large differences in the predicted values of effective diffusivities. During the extraction stage of supercritical devolatilization, in addition to the convection induced by diffusion, plasticization of the polymer by supercritical fluid also enhances the diffusional rate process. The high solubility of supercritical fluids in polymers swell the polymer and increase the free volume in the polymer so that diffusion of the impurities out of the polymer is enhanced. This plasticization effect can be predicted by using the Vrentas–Duda free-volume theory (Duda et al., 1982; Vrentas et al., 1984). The basic equations for free-volume theory for a ternary system are as follows:

$$D_1 = D_{o1}\exp\left(-\frac{\omega_1\hat{V}_1^* + \omega_2\hat{V}_2\frac{\zeta_{13}}{\zeta_{23}} + \omega_3\hat{V}_3\zeta_{13}}{\omega_1\hat{V}_{\text{FH}_1} + \omega_2\hat{V}_{\text{FH}_2} + \omega_3\hat{V}_{\text{FH}_3}}\right) \tag{38}$$

$$D_2 = D_{o2}\exp\left(-\frac{\omega_1\hat{V}_1^*\frac{\zeta_{23}}{\zeta_{13}} + \omega_2\hat{V}_2 + \omega_3\hat{V}_3^*\zeta_{23}}{\omega_1\hat{V}_{\text{FH}_1} + \omega_2\hat{V}_{\text{FH}_2} + \omega_3\hat{V}_{\text{FH}_3}}\right). \tag{39}$$

To illustrate this plasticization effect, the diffusivities of benzene and carbon dioxide were predicted from Vrentas–Duda free-volume theory. Free-volume parameters used in the predictions are given in Table 1. Figure 2 shows that diffusivity of benzene is increased by three orders of magnitude as the weight fraction of carbon dioxide increases from 0 to 10% in the mixture. The increase in the diffusivity of benzene is more pronounced than that of CO_2, which is shown in Figure 3. These results show that all the diffusivities will be strong functions of concentration, and free volume can be used to predict this concentration dependency. However, to simplify the analysis of the extraction stage of the process and to clearly demonstrate the influence of volume change on mixing, constant values of D_1 and D_2 were employed. Also, any possible complication associated with the coupling of the diffusion process with the relaxation of the polymer chains was neglected.

Equations 28 and 29 are parabolic nonlinear equations for which analytical solutions cannot be obtained by using the standard functions. An implicit finite difference approxima-

Table 1. Free Volume Parameters Used in the Predictions

		PS/Benzene/CO_2
D_{o1}^*	(cm^2/s)	4.47×10^{-4}
D_{o2}^{**}	(cm^2/s)	7.49×10^{-5}
$\hat{V}_1^*$	(cm^3/g)	0.901
$\hat{V}_2^{*\dagger}$	(cm^3/g)	0.589
$\hat{V}_3^*$	(cm^3/g)	0.85
$\zeta_{13}^{\dagger\dagger}$		0.558
$\zeta_{23}^{\ddagger}$		0.187
$(\hat{V}_{\text{FH}}/\gamma)_{CO_2}^{\dagger\dagger}$	(cm^3/g)	0.231
$(\hat{V}_{\text{FH}}/\gamma)_{\text{PS}}^{\dagger\dagger}$	(cm^3/g)	0.0225
$(\hat{V}_{\text{FH}}/\gamma)_{\text{Benzene}}^{*}$	(cm^3/g)	0.33

[*] Hong (1994).

[**] Vrentas and Duda (1977).

[†] Ganesh et al. (1992).

[††] The values were regressed from the diffusivity data for PS/Benzene/CO_2 (Sasaki et al., 1990); PVAC/Benzene/CO_2 (Sasaki et al., 1990), and PS/Benzene (Kosfeld and Zumkley, 1979) systems at 40°C.

[‡] ζ_{23} was estimated by using the correlation suggested by Zielinski (1992).

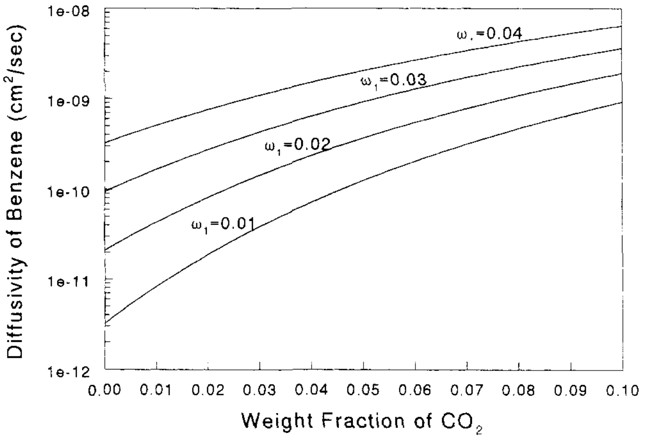

Figure 2. Self-diffusion coefficient of benzene as a function of carbon dioxide composition in PS/benzene/CO_2 ternary mixture.

tion was used to solve these equations. A variable grid was applied to generate a finer mesh near the interface since the concentration gradients are steeper there (Alsoy, 1997). Supercritical devolatilization characteristics predicted by the model depend on the diffusivities of each solvent, equilibrium composition of the supercritical fluid, and composition dependence of partial specific volume of each component. Polystyrene/CO_2/benzene was chosen as a model system for simulation since the experimental data were collected for this system at 40°C and 7.95 MPa pressure by Sasaki et al. (1990). The parameters used in the calculations are given in Table 2. Diffusion coefficients of benzene and CO_2 and equilibrium weight fraction of CO_2 were obtained from different sources (Duda and Vrentas, 1970; Sasaki et al., 1990; Wissinger and Paulaitis, 1987). The value of the diffusion coefficient of the benzene in the polymer swollen by the CO_2 and the associated parameters is a point of contention. The results of Sasaki et al. (1990) indicate that the plasticization of the polymer associated with the CO_2 raises the benzene diffusivity approximately from 10^{-13} cm²/s in the pure glassy polystyrene to the range of 10^{-9} cm²/s. However, the studies of Dooley et al. (1995) in a similar supercritical extraction experiment indicate that the presence of CO_2 increases the diffusivity of ethylbenzene in swollen polystyrene to 10^{-6} cm²/s. This apparent discrepancy may be due to the inadequacy of the simple models used to analyze the extraction results as indicated by Dooley et al. (1995). In both cases, the data for the amount of impurity extracted as a function of time are correlated with a simple mass-transfer model that does not include the swelling of the polymer sample, diffusion-induced convection, resistance in the supercritical phase, or the finite solubility of the impurity in the supercritical phase. Also, coupling between the CO_2 sorption process and the impurity desorption is neglected in determining the impurity diffusion coefficient. The Sasaki et al. (1990) results were chosen to determine the free-volume parameters, since these results are more consistent with the plasticization effects observed in nonsupercritical fluid systems (Zielinski and Duda, 1992), provide a conservative estimate of the influence of the carbon dioxide, and in contrast to other studies, the Sasaki et al. study includes measurements of the material extracted both during the conventional extraction phase of the experiment and the depressurization step.

Table 2. Parameters Used in the Simulation

Polymer: Polystyrene
Solvent 1: Benzene
Solvent 2: Carbon dioxide
Initial conditions
Initial composition of benzene: 4.5 wt. %
Initial composition of carbon dioxide: 0
Initial length of the polymer film: 0.5 mm
Operating conditions
Temperature: 313 K
Pressure: 7.95 MPa
Other parameters:
D_1: 6.05×10^{-9} cm²/s
D_2: 58×10^{-9} cm²/s
ω_{1E}: 0
ω_{2E}: 0.101

Supercritical fluid polymer systems are thermodynamically nonideal and therefore they can show significant volume change on mixing. This situation can be clearly seen in Figure 4, where the absolute deviation in volume from the ideal mixing assumption can be as large as 20% as the weight fraction

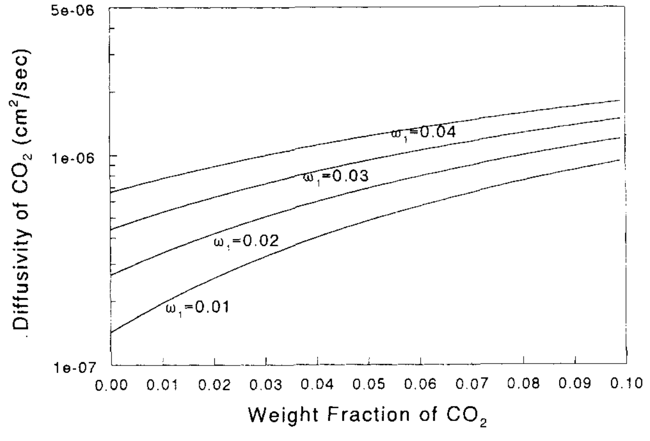

Figure 3. Self-diffusion coefficient of carbon dioxide as a function of weight fraction of carbon dioxide in PS/benzene/CO_2 ternary mixture.

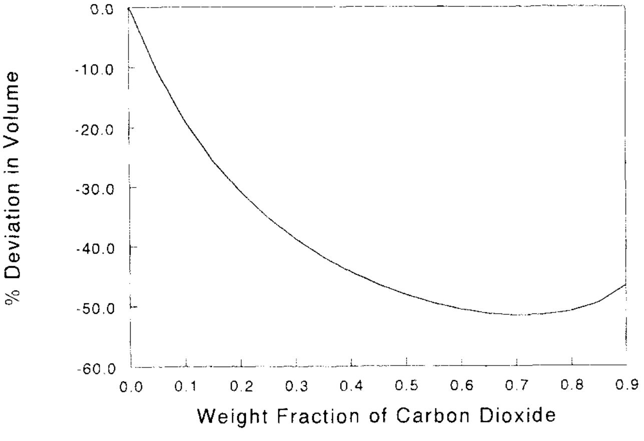

Figure 4. Deviation of the volume of the CO_2-polystyrene phase from ideal behavior of no volume change on mixing at 7.95 MPa and 40°C.

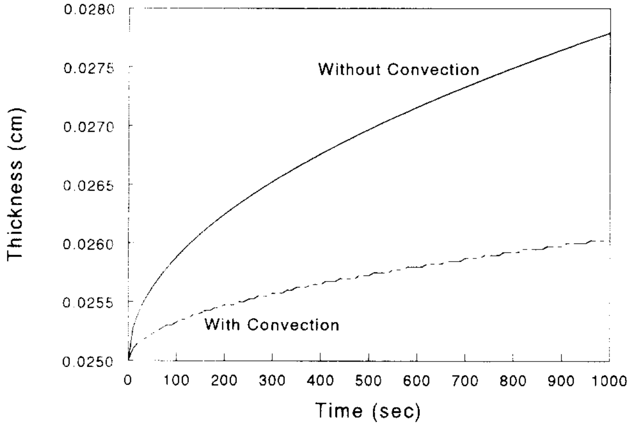

Figure 5. Thickness of the polymer film as a function of the time exposed to the absorbing supercritical CO_2 fluid.

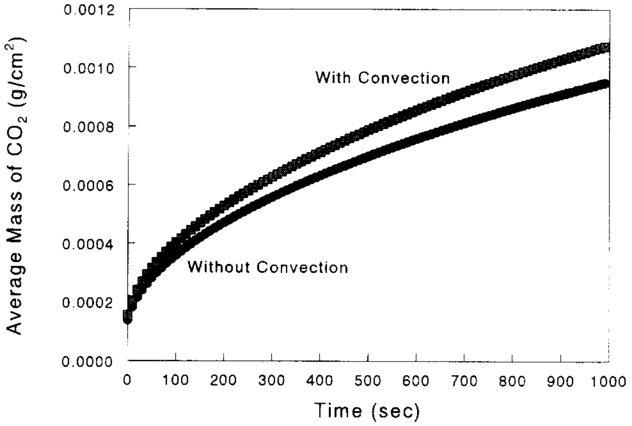

Figure 7. Mass of CO_2 per unit surface area of a polymer film as a function of time during the absorption of the CO_2.

of CO_2 increases from 0 to 0.1. The partial specific volume of the components was predicted by using perturbed soft-chain theory (Pretel and Danner, 1996). The diffusive flux of the carbon dioxide causes a convective term in the same direction of the carbon dioxide diffusive flux. Consequently, as one would expect, the convective term enhances the rate at which carbon dioxide enters the polymer. One would naturally infer that since this convection is in the opposite direction to the benzene diffusive flux that the volume change on mixing would inhibit the removal of the impurity. However, this is specious reasoning since the volume change on mixing, which causes the convective term, actually leads to less swelling of the polymer film, as shown in Figure 5 and, consequently, the benzene molecules have a shorter diffusion path to escape from the polymer phase. Figures 6 and 7 show that both the uptake of the carbon dioxide and loss of the benzene are enhanced by the inclusion of volume change on mixing. As indicated by Figures 5 and 7, the incorporation of volume change on mixing with a fixed value of ρ_{1E} leads to less total mass of carbon dioxide in the polymer phase and less volume swelling of that phase at equilibrium conditions. Figures 8 through 11 show how the normalized effective diffusion coefficients defined by Eqs. 32 through 33 change as a function of time. The coordinate transformation used in deriving the equations has eliminated the moving-boundary problem and the convective term by concentrating these nonlinearities in the definition of effective diffusivities.

In the final stage of the extraction process, the swollen polymer phase is depressurized. During the swelling and deswelling of the polymers, significant changes occur in the polymer morphology, especially in glassy polymers. Hong and coworkers (1997) applied a novel technique, positron annihilation spectroscopy, to measure the free-volume properties of a polycarbonate exposed to carbon dioxide. They have found that free-volume fraction is always higher during depressurization than it is under pressurization, and the total free-volume hole fraction is increased about 1.2% at zero pressure. Similar hysteresis behavior after depressurization has been observed in macroscopic volume measurements by Fleming and Koros (1989). When the pressure is reduced, rate of removal of supercritical fluid can be fast compared to the relaxation of the polymer to its unswollen state. As a first approximation, the diffusivity of the impurity in the unre-

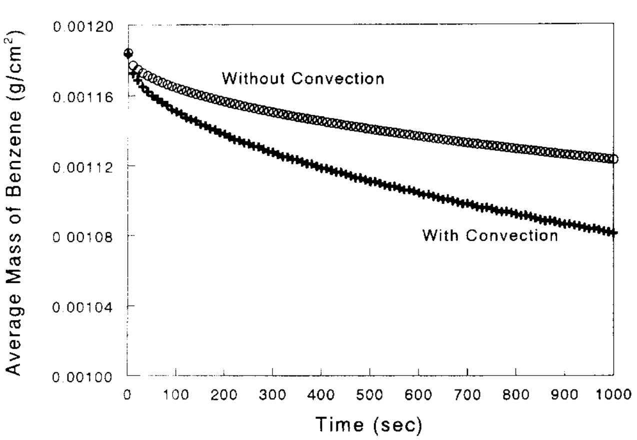

Figure 6. Mass of benzene per unit area of the polymer film as a function of time during the absorption of the carbon dioxide.

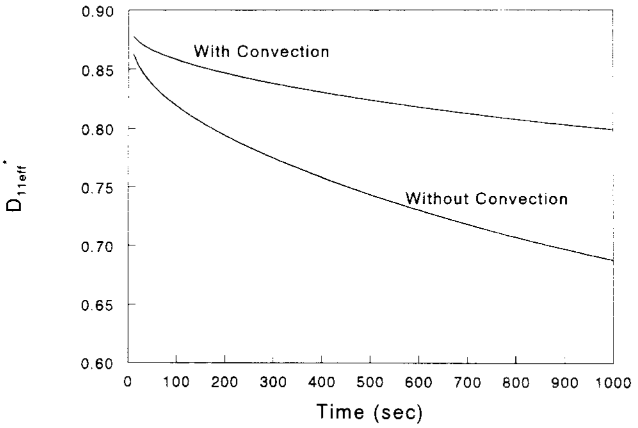

Figure 8. Influence of volume change on mixing on the normalized main diffusion coefficient, $D_{11\mathrm{eff}}^{*}$, as a function of time during the sorption of carbon dioxide.

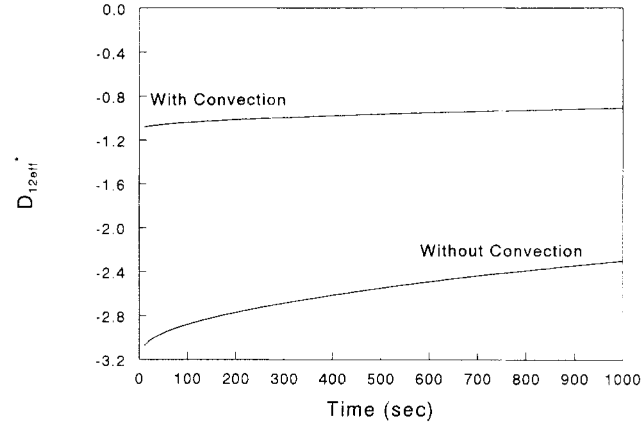

Figure 9. Influence of volume change on mixing on the normalized cross-diffusion coefficient, D^*_{12eff}, as a function of time during the sorption of carbon dioxide.

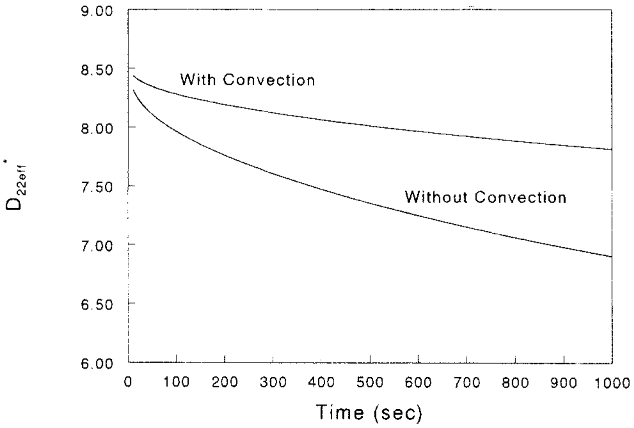

Figure 11. Influence of volume change on mixing on the normalized main diffusion coefficient, D^*_{22eff}, as a function of time during the sorption of carbon dioxide.

laxed polymer can be estimated using free-volume theory by assuming all the volume occupied by the supercritical fluid sorbed in the polymer will become free volume during depressurization and desorption. This would represent the maximum diffusivity for the impurity, which would decrease as the polymer consolidates and relaxes toward its equilibrium state. Following this approach, the free-volume theory indicates that the diffusivity of benzene in unrelaxed polystyrene at 40°C after 10 wt. % carbon dioxide has desorbed would be 3.7×10^{-4} cm^2/s. This is an enormous diffusivity compared to the estimated diffusivity of 3×10^{-13} cm^2/s for benzene in conventional glassy polystyrene at 40°C or even the 6×10^{-9} cm^2/s diffusivity for benzene in polystyrene plasticized with 10 wt. % carbon dioxide. This mechanism of rapid impurity extraction during the depressurization step is supported by the observations of Sasaki and coworkers (1990), which are illustrated in Figure 12. This figure shows that if polystyrene containing 4.5 wt. % benzene is exposed to the supercritical carbon dioxide at 40°C for 1.5 h, the concentration of benzene is reduced to approximately 3.5%. However, during the very short depressurization step, the concentration of benzene is reduced to 3%. The authors observed a similar trend for the polyvinylacetate benzene system at the same temperature. Unfortunately, Sasaki et al. (1990) do not give details concerning the depressurization step, since like all previous investigators, they implicitly assumed in the design of their experiment that the dominant mechanism for the removal of the impurity occurs when the polymer sample is exposed to the supercritical fluid and that impurity removal during the depressurization step is inconsequential. These results are also consistent with Koros (Fleming and Koros, 1989) experiments where carbon dioxide is reabsorbed into an unrelaxed polymer. These results suggest that we really do not need supercritical fluids, just high sorption of a material followed by a quick desorption step.

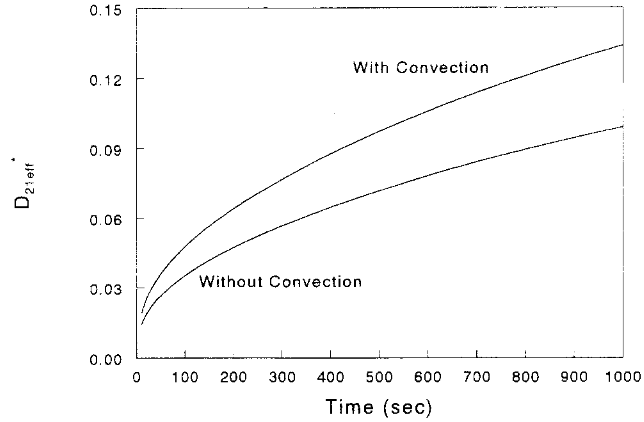

Figure 10. Influence of volume change on mixing on the normalized cross-diffusion coefficient, D^*_{21eff}, as a function of time during the sorption of carbon dioxide.

Conclusion

In conventional supercritical extraction, high solubility of impurities in the supercritical fluid can enhance the thermo-

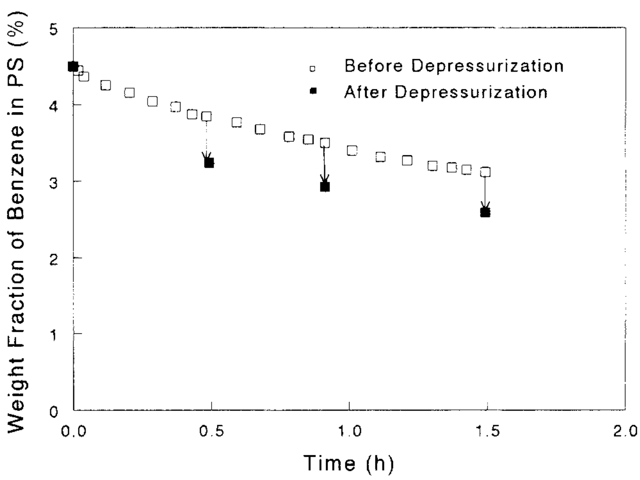

Figure 12. Weight fraction of benzene in the polystyrene phase as a function of time in the extractor.

Data taken from the study of Sasaki et al. (1990) at a pressure of 7.95 MPa and 40°C.

dynamic driving force for extraction. In addition, high solubility of the supercritical fluid in the polymer can swell the polymer and can increase the mobility of the volatile impurity. This study suggests that in addition to these two effects, there are two other phenomena that can be important in supercritical devolatilization of polymers. During the extraction stage, the nonideal volumetric behavior of carbon dioxide in polymer can cause convection induced by diffusion, which can influence the transport of impurities out of the polymer. Furthermore, during the depressurization step, the coupling between mass transfer and the polymer relaxation can be important. Free-volume theory indicates that diffusion of the impurity in the unrelaxed polymer can be several orders of magnitude higher than the diffusivity that occurs in the plasticized polymer during the extraction stage. The most significant conclusion resulting from this analysis is that the mass transferred during the very short depressurization step may be the dominant mechanism in supercritical fluid devolatilization of polymers. This conclusion is supported by the experimental studies of Sasaki and coworkers. This conclusion leads to important implications for the optimum design and operation of the devolatilization of polymers with supercritical fluids. This proposed mechanism suggests that impurity removal can be facilitated by shortening the time of the depressurization step and lowering the operating temperature of the process. Both of these modifications will enhance the mass transfer associated with diffusion in an unrelaxed glassy polymer phase. Furthermore, for efficient devolatilization, the time of exposure of the polymer phase to the supercritical fluid can be significantly reduced by designing processes to exploit volatility removal during the depressurization phase of the operation. In addition to the very high mass-transfer rate in the unrelaxed glassy polymer phase, it is possible that impurity removal is also facilitated by a network of cracks or fissures associated with the crazing of the polymer during its relaxation. Depressurization above the glass transition temperature of the polymer will lead to microcellular foams (Goel and Beckman, 1992).

It should be emphasized that this model does not include all the complexities needed to accurately predict the behavior of a supercritical fluid extraction process. The models utilized for describing the temperature and concentration dependency of the diffusivities and the thermodynamics of the system are at best approximate. Furthermore, the ternary system was treated as two pseudobinary systems in terms of mass transfer, and multicomponent diffusion effects were neglected as well as mass-transfer resistances in the supercritical phase. It is also possible that non-Fickian effects of coupling of diffusion and polymer relaxation can complicate the sorption process when carbon dioxide is entering the polymer phase. However, this analysis does bring into focus some important aspects of this extraction process that have been implicitly neglected in previous analyses. This study can be viewed as a precursor for future work.

The model presented here has some unique features that facilitate the numerical solution of the governing equations. Use of coordinate transformation significantly reduced the complexity of the problem. In addition, casting the problem in terms of volume-average velocity produced the effective diffusion coefficients that combine the effect of the ratio of the diffusivity of carbon dioxide to that of benzene, the effect of swelling, and the effect of volume change on mixing. It is a useful tool to investigate the effect of operating conditions such as temperature and pressure on the performance of existing devolatilization units.

Notation

$D^*_{ii\text{eff}}$ = dimensionless main effective diffusivities defined by Eqs. 32 and 33
$D^*_{ij\text{eff}}$ = dimensionless cross-effective diffusivities defined by Eqs. 32 and 33
D_{oi} = constant preexponential factor
E = energy required to overcome attractive forces from neighboring molecules
q_{io} = initial value of q_i
q_{iE} = value of q_i at the surface of the film
R = gas constant
T = temperature
t^* = dimensionless time defined by Eq. 27
v_i = velocity of component i
v_N = velocity of polymer
$\bar{V}_i$ = partial specific volume of component i
$\hat{V}_3^o$ = specific volume of pure polymer
$\hat{V}_i^*$ = specific critical hole free volume of component i required for jump
$\hat{V}_{FH_i}$ = specific hole free volume of component i
x = distance variable in the direction of diffusion
ζ_{i3} = ratio of critical molar volume of solvent i jumping unit to that of polymer jumping unit
γ = overlap factor
ω_i = weight fraction of component i

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