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# Modeling the Biological Solubilization of Coal in a Liquid Fluidized-Bed Reactor

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## ABSTRACT

A fully predictive mathematical model has been developed to describe the behavior of liquid fluidized beds in which the biological solubilization of coal particles is occurring. This model is based on the particle mass-transport mechanisms of dispersion and convection, and accounts for the changes in the size of the particles as they are solubilized. Two different cases are compared: one in which the bed is replenished with large coal particles and one in which small particles are fed to the bed. The simulation results indicate that replenishment with small coal particles enhances the overall solubilization rate without significantly increasing the mass elutriated.

**Index Entries:** Coal; biosolubilization; dynamic model.

## INTRODUCTION

Biotransformation of coal into useful organic chemicals by bacteria and fungi has recently attracted a great deal of interest (*1*). Before systems that depend on biological transformations of coal for either solubilization or liquefaction can be commercialized, new reactors must be developed. These reactors must provide efficient mass transport in a relatively low shear environment. Liquid fluidized-bed reactors have great promise for providing such capabilities because of their unique transport behavior and their ability to operate in a continuous fashion. In order to design and

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operate such a reactor effectively, however, detailed knowledge about the behavior of the reactor bed is required. Unlike a conventional fluidization process, the biosolubilization of coal in a fluidized bed has a unique characteristic, i.e., particles having a wide size range will be present in the bed as the coal is gradually solubilized. This phenomena is the result of the fact that as the particles are solubilized, small particles will be produced. These particles will eventually elute from the bed. Hence, in order to have a continuous operation, the coal particles have to be replenished in a continuous fashion.

In our previous work (2–5), a fully predictive model of a liquid fluidized bed containing nonreactive coal particles was developed. Those models were based on the particle mass-transport mechanisms of dispersion and convection. Through direct comparisons with experimental observations, the previous model was demonstrated to be able to describe bed expansion and segregation tendencies (4,5). In addition, that previous work demonstrated that both transient and steady-state behavior for both mono- and bimodal component coal particles could be predicted. In this article, this mathematical model is extended such that it is able to be used to predict the transient profiles that will develop during the solubilization processes.

## MODEL DESCRIPTION

In order to model the solubilization process, an expression that describes the reaction kinetics must first be assumed. The biological solubilization of coal particles is a fairly slow process. In addition, we have assumed that the solubilization process will be driven by the rate at which the microbes can reach and attack the surface of the particle. Thus, as a first approximation, we assumed that the solubilization rate was dependent on the surface area of coal particles available. Additionally, since most surface-catalyzed reactions usually follow zero-order kinetics (6), we can reasonably assume that the solubilization process will also be of zero order. Thus, we can write:

$$-(1\ /\ \text{surface area})\,(dm\ /\ dt) = k_o \tag{1}$$

where $m$ is the mass of coal particles within the bed and $k_o$ is the rate constant. The first piece of information that is required is an estimate of the rate at which the coal solubilizes. Based on data from Crawford (7), a typical value $k_o$ is $0.38 \times 10^{-6}$ g/h·mm$^2$ for a coal sample containing particles having a mean size of 250 $\mu$m. In addition, if we further modify Eq. (1), it can be simplified to:

$$-(d\mu\ /\ dt) = (2k_o\ /\ \rho_s) = S \tag{2}$$

where $\mu$ is the particle size, $S$ is the solubilization constant, and $\rho_s$ is the density of coal particles. If we take $\rho_s$ as a constant equal to 1.3 g/cm$^3$, and using the data of Crawford, $S$ is calculated to be $0.585 \times 10^{-3}$ mm/h. Since solubilization is a slow process, as indicated by this value of $S$, we can discretize the solubilization time into small time intervals $\Delta t$ (i.e., $\Delta t \approx 400$ s). Then we can assume that there is no solubilization during each time interval $\Delta t$. Instead, solubilization of coal particles only occurs at discrete times. A method can then be devised to solve the set of equations. In essence, we are assuming that the particles migrate for a time period equal to $\Delta t$, and then all the reaction time that would have occurred during that time interval occurs instantaneously. The particles are then moved to appropriate size bins, and the process is repeated. The detailed procedure is described as follows.

## During Each Time Interval Δt

Since we assume that no solubilization occurs during each time interval $\Delta t$, the liquid fluidized bed can be treated in a manner similar to those described by our previous model, e.g., one containing nonreactive coal particles having a wide size distribution. Asif et al. (*4*) followed Kennedy and Bretton's approach (*8*) and developed a mathematical model based on a mass balance, which accounts for mass transport by both dispersion and convection. In our previous work (2–5), it has been demonstrated that this model is able to predict both the transient and the steady-state behavior of such a fluidized bed. The governing mass-balance equation for the particle species $i$ present in the fluidized bed can be written as:

$$\frac{\partial C_i}{\partial t} = \frac{\partial}{\partial Z}\left[D_i\left(\frac{\partial C_i}{\partial Z} - \frac{C_i}{\rho}\frac{\partial \rho}{\partial Z}\right) - U_i C_i\right] \quad (3)$$

where the coal charge is divided into $n$ subfractions, each denoted by subscript "$i$", based on size, $\rho$ is the bulk density, and $C_i$ is the fractional volumetric concentration of particle species $i$, $D_i$ its dispersion coefficient, and $U_i$ its velocity.

The solution of Eq. (3) requires the evaluation of the particle velocity, $U_i$, and the particle dispersion coefficients, $D_i$, for each individual particle species. The particle classification velocity, $U_i$, can be evaluated using the following expression:

$$U_i = Q_0 + \sum_{i=1}^{n_t} U_{t_i}\epsilon^{n_i-1}C_i - U_{t_i}\epsilon^{n_i-1} \quad (4)$$

where $\epsilon$ is the bed void fraction, $n_i$, is the index of Richardson and Zaki correlation, which has been experimentally evaluated in the previous work by Asif et al. (*4*), $U_{ti}$ is the particle terminal velocity, and $Q_0$ is the liquid flow rate.

Based on several different sets of experimental data, Asif and Petersen (*3*) proposed a correlation that would allow the evaluation of the particle dispersion coefficient, $D_i$. Since for some of the particle species examined here, this correlation is out of the applicable range, a single particle dispersion coefficient based on the harmonic mean particle diameter of the sample mixture was evaluated and applied to all particle species in order to minimize the error in the estimation of the particle dispersion coefficient. The details of the estimation of this average particle dispersion coefficient have been described previously by Wang et al. (5).

Two boundary conditions are respectively employed at the top and bottom of the fluidized bed. At the bottom of the fluidized bed, coal particles are replenished at a fixed rate. Thus, at $z = 0$, the boundary condition is:

$$D_i \left( \frac{\partial C_i}{\partial Z} - \frac{1}{\rho} \frac{\partial \rho}{\partial Z} C_i \right) - U_i C_i = U_o C_{io} \tag{5}$$

where $U_o$ is the liquid superficial velocity and $C_{io}$ is the fractional volumetric concentration of particle species $i$ at $z = 0$. At the top of the bed, when the bed height exceeds the total column height, i.e., the maximum allowable height of the fluidized bed, some mass will be lost owing to elutriation of small coal particles:

$$D_i \left( \frac{\partial C_i}{\partial Z} - \frac{1}{\rho} \frac{\partial \rho}{\partial Z} C_i \right) - U_i C_i = U_i(L_t,t) C_i(L_t,t) \tag{6}$$

where $L_t$ is the total column height or the maximum allowable height of the fluidized bed. This model is then solved for a time period equal to $\Delta t$.

## Discrete Time Processes

In an actual reactor, the particles will be solubilized continuously. However, in this approach, we assume that solubilization occurs instantaneously at regular, discrete time intervals. Thus, after each time interval $\Delta t$, the particle size of species $i$ decreases from $\mu_{i,o}$ to $\mu_i$ owing to the solubilization that occurred during $\Delta t$. Then, using Eq. (2), $\mu_i$ can be determined as:

$$\mu_i = \mu_{i,o} - S \, \Delta t \tag{7}$$

Since the mass of coal particles is proportional to $\mu^3$, the mass of species $i$ after time interval $\Delta t$ can also be estimated:

$$m_i = m_{i,o} \left[ (\mu_i \, / \, \mu_{i,o}) \right]^3 \tag{8}$$

where $m_i$ and $m_{i,o}$ are, respectively, the mass after $\Delta t$ and before $\Delta t$ for particle species $i$. Now, using the interpolation method based on surface area of coal particles, we can regroup the coal particles into the same subfractions that were used to classify the initial coal charge. The new mass of species $i$ with size $\mu_{i,o}$ can thus be calculated:

$$m_i' = \frac{\mu_2 - \mu_{i+1,o}{}^2}{\mu_{i,o}{}^2 - \mu_{i-1,o}^2} m_i + \frac{\mu_{i-1,o}{}^2 - \mu_{i-1}{}^2}{\mu_{i-1,o}{}^2 - \mu_{i,o}{}^2} m_{i-1} \tag{9}$$

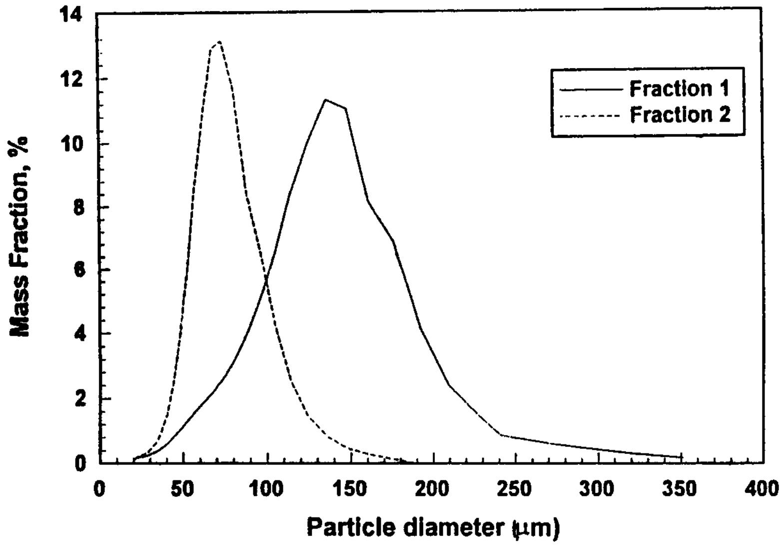


Fig. 1. Particle size distribution assumed for the two fractions used in this study.

From the above description, we can see that this method for describing the solubilization process has two appealing features. First, the introduction of the additional dimension needed to describe the solubilization process, e.g., the change of particle size with time, will not significantly increase the computation time required to solve the problem. Second, our previous work demonstrates that the model based on the mass balance is able to predict the hydrodynamic behavior of liquid fluidized beds containing nonreactive coal particles. Thus, it should be able to predict the similar bed behavior during each of these time intervals.

## RESULTS AND DISCUSSION

The above model was used to simulate the solubilization of coal in a fluidized-bed column using conditions similar to those employed previously for nonreacting particles. In particular, the fluidized bed was assumed to have an internal diameter of 25.4 mm and a length of 1.22 m. Based on previous studies (*5*), the liquid superficial velocity was set at 0.016 cm/s. Two fractions of coal particles with different particle size distribution were used. In Fig. 1, the volume fraction of particles in a given size range is provided as a function of particle size for both of the fractions.

The governing time-dependent, partial different equations (PDEs), Eq. (3), were solved using a FORTRAN 77 software package, PDECHEB, developed by Berzin and Dew (*9*) on a DEC 3000/400 computer using DEC FORTRAN 77 and double-precision arithmetic. The PDECHEB software implements a family of spatial discretization formulas based on piecewise Chebyshev polynomial expansions with $C^0$ continuity. This

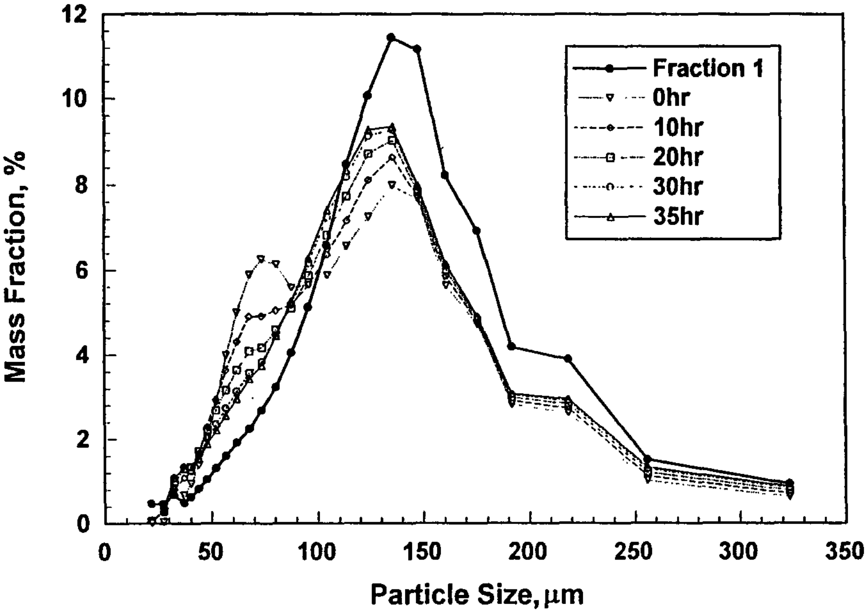


Fig. 2. Mass distribution at various times at a constant feeding rate of 2.24 g/h of particles from the larger size fraction.

package has been designed to be used in conjunction with a general integrator for initial value problems to provide a powerful software tool for the solution of parabolic-elliptic PDEs with coupled differential algebraic equations. To achieve these solutions, each of the coal samples was divided into 26 subfractions, and each of these subfractions was defined with a PDE. Note that the number of subfractions was chosen arbitrarily; a larger or smaller number would have yielded similar results. The resulting set of nonlinear PDEs was solved simultaneously.

In all the studies, the simulated column would be initially charged with a mixture of 80 g of coal from fraction 1 and 40 g of coal from fraction 2 (refer to Fig. 1 for size distribution of these coal samples). After the coal was charged to the column, the bed was allowed to reach a steady state with the superficial velocity at 0.016 cm/d. Then, simulated biosolubilization and replenishment of coal particles would be assumed to take place. In the following context, the effects of replenishing with fraction 1 and fraction 2 coal particles at a fixed feeding rate of 2.24 g/h on the simulated transient behavior of the fluidized-bed reactor are presented and discussed.

## Change of Mass Distribution

In the operation of a continuous fluidized bed for coal solubilization, as the coal is solubilized, additional coal will need to be continuously fed to the reactor. To examine the impact of the size of the particles that are fed to the bed on the solubilization rate and on the particle size distribution that will develop in the bed, two different cases were simulated. In

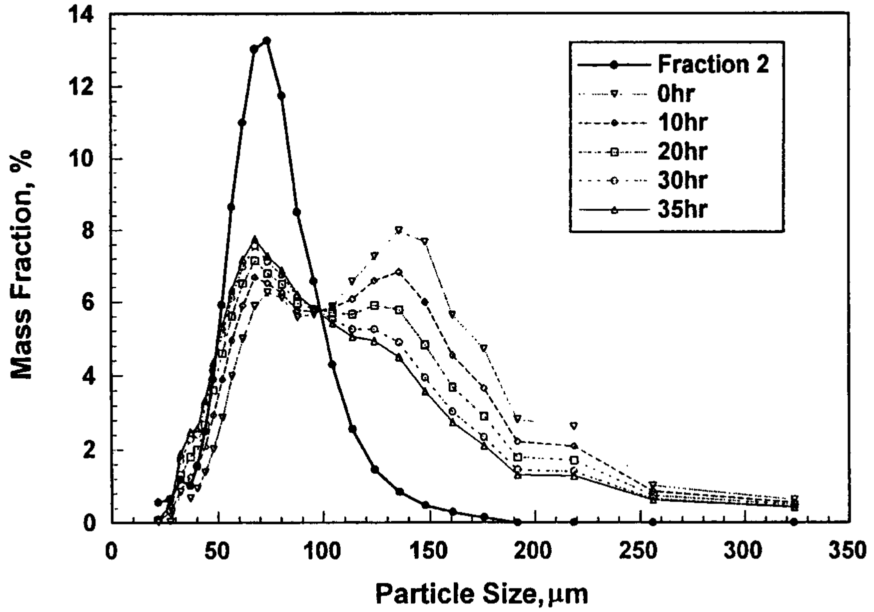


Fig. 3. Mass distribution at various times at a constant feeding rate of 2.24 g/h of particles from the smaller size fraction.

the first of these, only particles from fraction 1, i.e., larger particles, were fed; in the second case, the coal that was fed to the bed was from fraction 2, the smaller particles. Figure 2 and 3 show the predicted mass distribution of coal as a function of time when the bed is replenished with coal from fraction 1 and fraction 2, respectively. The mass distribution of the fractions fed to the reactors are also included on the figures for comparison.

In Fig. 2, the peak in the smaller particle size range is predicted to decrease gradually with time, since there is no replenishment of these smaller coal particles. The mass fraction of species with particle size $\leq \sim 50$ μm increases slightly with time because of the partial solubilization of the larger coal particles. On the other hand, the peak in the larger particle size range steadily increases with time owing to continuous replenishment of the coal from the larger-size fraction. Since the solubilization rate of the larger coal particles is slower than that for smaller particles, and since the larger coal particles are continuously replenished, there is an accumulation of the mass fraction of species with particle size $\geq \sim 130$ μm. In addition, the peak in the larger coal partaicle size range consecutively shifts to the smaller particle size range as time increases, since the average particle size of this mass fraction decreases as a result of continuous solubilization.

Similarly, when the bed is replenished with the smaller particles only, the peak in the smaller particle size range is predicted to increase gradually with time, as shown in Fig. 3. The continuous increase in the mass fraction of species with particle size $\leq \sim 70$ μm is caused by both the replenishment of the coal within the column and by the solubilization of larger

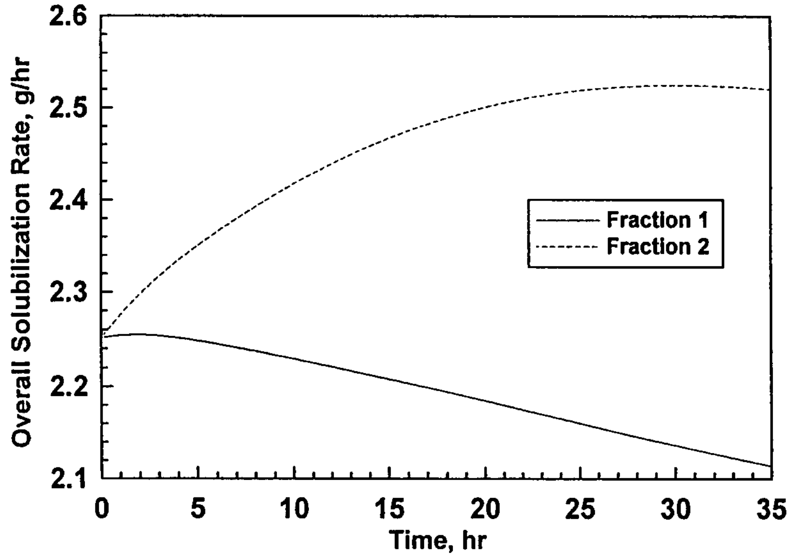


Fig. 4. Total solubilization rate as a function of time for the two cases examined.

coal particles. The shift of the peak at ~75 μm to a smaller size range is also the result of the fact that the average particle size of this mass fraction decreases as a result of continuous solubilization. Since there is no replenishment of larger coal particles and the larger particles are continuously solubilized, both the peak and mass fraction in the larger particle size range consecutively decrease with time.

## Overall Solubilization Rate

Figure 4 shows the simulated results about the total solubilization rate as a function of time when the bed is replenished with larger particles from fraction 1 or when it is replenished with the smaller coal particles. If it is replenished only with larger particles, the overall solubilization rate first increases slightly with time. Then, after reaching a maximum, the solubilization rate gradually decreases. Even after 35 h of simulation, the model predicts that this solubilization rate will continue decreasing.

It is worth noting that the solubilization rate depends not only on the particle size, but also on the available mass of a particular species. Thus, the fact that the solubilization rate first increases with time and then decreases is because the particles having a diameter of ~75 μm are disappearing owing to reaction. These smaller particles have a higher reaction rate than do the larger particles that are added to the bed to replace them. Then, as these particles have reacted away, the overall particle distribution shifts to correspond to the larger particles that are being fed. Since these larger particles have less surface area per unit mass than do the smaller particles, it is not surprising that the overall solubilization decreases with time, since these larger particles tend to dominate the bed as time progresses.

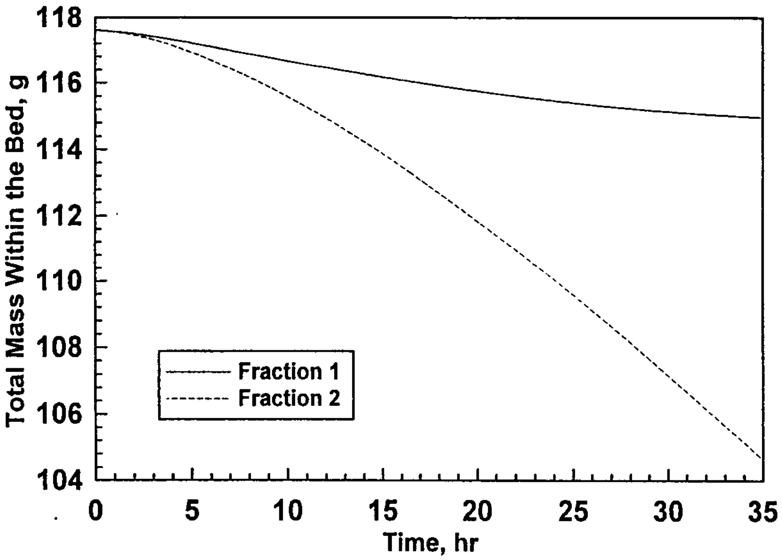


Fig. 5. Total mass in the bed as a function of time for the two cases studied.

However, when the smaller particles are fed, the overall particle distribution shifts to a smaller particle size range than the initial coal charge. In this case, the overall solubilization rate increases with time and reaches a maximum after 30 h. Then, the overall solubilization rate decreases slightly, since the total mass within the bed decreases at a faster rate when smaller particles are fed (Fig. 5). From this simulation, it is obvious that replenishing with larger coal particles results in slower overall solubilization rate within the bed than does replenishing with smaller particles. However, in a commerical system, the additional costs associated with generating the finer coal would have to be compared with the added benefit of the higher reaction rate associated with these smaller particles. Some particle size will, no doubt, exist at which the total cost is minimized. In addition, for a given physical column, this model could be used to determine the size of the particles that should be employed and the flow rate at which the system should be operated in order to maximize the productivity of the system.

## Elutriation Rate

One of the important features with biosolubilization of coal in a liquid fluidized-bed reactor is that the particle size of the coal will become smaller with time as the coal solubilizes. Thus, at some point, each particle will eventually react to such a size that it will elute from the bed. In our simulation studies, with the particular flow rate and bed characteristics employed, the coal particle species with diameter of 22 and 27.5 $\mu$m were found to elute. In Figs. 6 and 7, the individual and overall elutriation rates of these species are presented as functions of time when feeding with the larger fraction 1 and with the smaller fraction 2 coal, respectively.

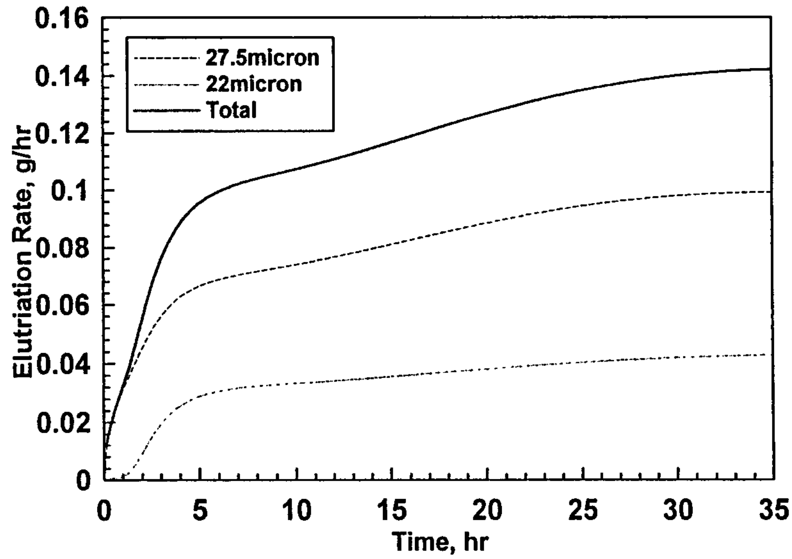


Fig. 6. Elutriation rate as a function of time at a constant feeding rate of 2.24 g/h of particles from the larger-size fraction.

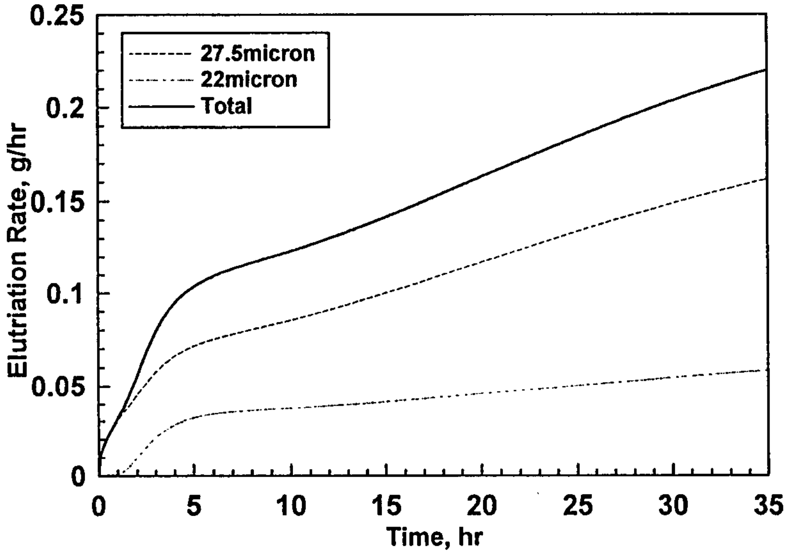


Fig. 7. Elutriation rate as a function of time at a constant feeding rate of 2.24 g/h of particles from the smaller-size fraction.

In both cases, the individual and overall elutriation rates increases with time. A greater fraction of the mass elutes as the larger particles, i.e., 27.5 μm, because the reacting particles first fall into this size range. In addition, the initial coal charge contains a high mass fraction of particle species with diameter of 32.5 μm. As these particles react, their size decreases, resulting in more particles in the 27.5- and 22-μm bins, which then elute from the bed. Therefore, the initial mass elutriation rates are higher owing to these phenomena. In addition, about 1.5 h are required for the mass in the 22-μm bin to reach the point in the bed such that elutriation occurs. Since the bed that is fed with large particles contains fewer particles that can elute, the overall elutriation rate from this system would be smaller than that from the system in which small particles are fed. However, in either case, the overall elutriation rate is $<10\%$ of the solubilization rate.

## CONCLUSIONS

A mathematical model has been developed to describe the transient behavior of a liquid fluidized bed reactor containing coal particles. Zero order biosolubilization kinetics have been assumed in the model derivation. This model is able to predict both the solubilization rate and elutriation rate of coal particles as a function of time. If the bed is simulated at a fixed superficial velocity of 0.016 cm/s and a fixed coal replenishment rate, it has been shown that replenishing with smaller coal particles can enhance the overall solubilization rate without significantly increasing the elutriation rate. However, the benefit of achieving this enhanced solubilization rate must be offset against the costs of preparing such small particles. This model could be used to determine the size of the particles in the feed stream and the flowrate of the fluidizing fluid which would, for a given column, maximize the productivity. In addition, with the help of this model, it would be possible to predict the optimum conditions (coal particle size, liquid superficial velocity, etc.) under which the solubilization process should be operated for a particular column. On the other hand, experiments must be performed which would allow the predictive capabilities of the model to be examined and verified.

## ACKNOWLEDGMENTS

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