Hindered Diffusion of Asphaltenes At Elevated Temperature and Pressure

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Abstract

The mathematical model which we have developed previously for diffusion controlled adsorption was extended to allow for the inclusion of the effects of extraparticle film mass transfer resistance as embodied in a finite Sherwood number. A Mathcad based program was used to simulate the experimental data using summation of a large number of terms in the infinite series solution. Parametric studies and accompanying plots revealed that the effects of film resistance on the uptake process were found to increase in significance as the adsorption capacity parameter in the model decreased. In addition, the two carbon catalyst supports prepared in our own laboratory were tested for their diffusional characteristics in uptake experiments using petroleum asphaltenes dissolved in toluene at three temperatures. The resulting experimental data were simulated with the mathematical model developed in the report.

Table of Contents

Disclaimer	1
Abstract	2
Objectives	4
Executive Summary	5
Introduction	6
Results and Discussion	7
Hindered Diffusion Model for Finite Sherwood Numbers	7
Uptake Experiments for Laboratory Prepared Carbon Supports	14
Conclusions	15
Planned Work	16
Nomenclature	34
References	35

Objectives

The overall goal of this project is to obtain a better understanding of the diffusion controlled uptake of model compounds and asphaltenes in porous catalysts at elevated temperatures. Generally past investigations have been restricted to uptake experiments at ambient temperatures and pressures. Thus we are seeking:

1. To investigate the hindered diffusion of both coal and petroleum asphaltenes in porous catalysts at elevated temperatures.
2. To examine the effects of temperature on the intraparticle diffusivity of asphaltenes.

Executive Summary

Our research project centers around obtaining a better understanding of the diffusion of model compounds and asphaltenes in porous catalysts at elevated temperatures. These matters are of interest in the design and tailoring of catalysts for reactions under elevated temperature and pressures such as may occur in coal liquefaction and petroleum resid upgrading, where diffusional influences often present themselves. Our efforts during the current reporting period have concentrated on both theoretical and experimental areas. The theoretical studies involved extending the previously developed mathematical diffusion model, to allow for the presence of an external film resistance for mass transfer. Incorporation of this boundary condition as represented by a dimensionless Sherwood number parameter has allowed us to assess the importance of external mass transfer in the diffusional uptake process, in comparison to intraparticle diffusional resistance. As a result of parametric studies and plots made by solving the model equations with a Mathcad program, we have found that the external mass transfer resistance is most significant for small values of the adsorption capacity parameter, B . We have used the extended model to examine some of the experimental data obtained earlier in the project, as well as newly obtained data using some of our own laboratory prepared porous carbon supports. The new experiments were conducted at 25, 50, and 75°C using a petroleum asphaltene with toluene as the solvent. The modified mathematical model, which accounts for the presence of external mass transfer resistances, was solved via a Mathcad program, and model parameters were estimated from literature correlations and by fitting of the experimental uptake data.

Introduction

In our project we are seeking a better understanding of the diffusion of model compounds and asphaltenes in porous catalysts at elevated temperatures. The relevance of this study is that many catalytic reactions, especially those occurring in coal liquefaction and petroleum resid upgrading, are carried out at relatively high temperatures and pressures using supported catalysts where diffusional influences may intrude. For this reason it is advantageous to seek to understand diffusion and adsorption behavior at elevated temperatures and pressures in order to provide reasonable judgment in catalyst design and process development. The literature review performed earlier in our project revealed that, due to the experimental difficulties involved, very few investigators have studied pore diffusion and surface adsorption at higher temperatures and pressures. In our project, we have taken data for a number of both coal and petroleum asphaltenes, as well as a number of model compounds diffusing in both alumina and carbon porous catalysts. Then, these experimental data were modeled by fitting a diffusional uptake model using parameters estimated from the theories of hindered diffusion, as applied to the systems under study. In the work reported for this time period, we mainly discuss the extensions made to the hindered diffusion model, relating to the introduction of film mass transfer resistance factors. Also, during this particular time period we have performed some new experiments on the diffusion of petroleum asphaltenes in porous carbons which were prepared in our own laboratory. The porous carbons utilized were termed Support A and Support B, and are described in more detail later. The new experiments were performed at 25, 50, and 75° C for a petroleum asphaltene with toluene as solvent.

Results and Discussion

Extension of Hindered Diffusion Model for Finite Sherwood Numbers. The diffusional uptake model developed so far in our project is based on a model in which solute molecules diffuse into porous particles where they are adsorbed onto the solid surface. As a result of the diffusion – adsorption (uptake) process, the solute concentration in the liquid bath is depleted. The porous solid particles are modeled as spheres, the equivalent radius of the sphere being based on the ratio of particle volume to external surface area, as shown in our previously reported work. Generally the uptake process is controlled by fluid particle mass transfer (film resistance) or by intraparticle diffusion (pore diffusion) resistances. Up until now, we have assumed that the controlling resistance is the latter factor, and have neglected the effect of film resistance. However, in many cases the rate controlling processes are a combination of the above two resistances. Therefore, during the current time period we have extended our previously developed diffusion model to include the fluid-solid (film) mass transfer resistance, as well as the previously included pore diffusion resistance. The film mass transfer process is governed by the fluid-solid mass transfer coefficient k_L as shown in the following development. The basic change in the previous model is the inclusion of the film mass transfer boundary condition as shown by equation (4) in the following development. The mass transfer coefficient can be estimated from experiments or from previously developed literature correlations. When put into a dimensionless form, the mass transfer coefficient appears in a new model parameter, the Sherwood number.

The pertinent equations as modified for the inclusion of the film mass transfer resistance are given in the following development. The mass balance for the solute in the porous particles is :

$$\frac{\partial(K_p e C_s)}{\partial t} + \frac{\partial(r_p q)}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 D_e \frac{\partial C_s}{\partial r} \right) \quad (1)$$

with the following initial and boundary conditions:

$$C_{t=0} = C_0 \text{ for all } r \quad (2)$$

$$\frac{\partial C_s}{\partial r} = 0 \text{ at } r = 0 \quad (3)$$

The new film mass transfer boundary condition at the particle surface is given by equation (4) where k_L is the fluid-particle mass transfer coefficient.

$$\left(D_e \frac{\partial C_s}{\partial r} \right)_{r=R} = k_L \{ C_b(t) - (C_s)_{r=R} \} \quad (4)$$

A material balance for the solute in the bath yields :

$$\frac{d(V C_b)}{dt} = -4\pi R^2 n \left(D_e \frac{\partial C_s}{\partial r} \right)_{r=R} \quad (5)$$

with an initial condition:

$$C_b = C_i \text{ at } t = 0 \quad (6)$$

In the pore diffusion equation (1), q is the adsorption term. Here a linear adsorption isotherm is assumed as indicated by equation (7).

$$q = K C_s \quad (7)$$

The following dimensionless variables are defined:

$$\mathbf{x} = \frac{r}{R}$$

$$t^* = \frac{D_e}{(K_p \mathbf{e} + \mathbf{r}_p K)} \frac{t}{R^2}$$

$$\mathbf{q}_s = \frac{C_0 - C_s}{C_0 - C_i}$$

$$\mathbf{q}_f = \frac{C_0 - C_b}{C_0 - C_i}$$

With the above dimensionless variables the system of governing equations reduce to :

For the catalyst pellet :

$$\frac{\mathcal{I} \mathbf{q}_s}{\mathcal{I} t} = \frac{1}{\mathbf{x}^2} \frac{\mathcal{I}}{\mathcal{I} \mathbf{x}} \left(\mathbf{x}^2 \frac{\mathcal{I} \mathbf{q}_s}{\mathcal{I} \mathbf{x}} \right) \quad (8)$$

with the initial and boundary conditions:

$$\text{at } t^* = 0 \quad \mathbf{q}_s = 0 \quad (9)$$

$$\text{at } t^* = 0 \quad \left. \frac{\mathcal{I} \mathbf{q}_s}{\mathcal{I} \mathbf{x}} \right|_{\mathbf{x}=1} = Sh \left\{ \mathbf{q}_f - (\mathbf{q}_s)_{\mathbf{x}=1} \right\} \quad (10)$$

In equation (10) we see the appearance of the Sherwood number, $k_L R / D_e$, which is the dimensionless group characterizing the extent of film mass transfer resistance. We also have the additional boundary condition at the particle center given by equation (11)

$$\text{at } \mathbf{x} = 0 \quad \mathbf{q}_s = \text{finite} \quad (11)$$

For the surrounding solution in the microautoclave:

$$\frac{d\mathbf{q}_f}{dt^*} = -\frac{3}{B} \frac{\mathbf{q}_s}{\mathbf{x}} \quad \text{at } \mathbf{x} = 1 \quad (12)$$

with the initial condition:

$$\text{at } t^* = 0 \quad \mathbf{q}_f = 1 \quad (13)$$

where B is a dimensionless adsorption capacity parameter

$$B = \frac{V \mathbf{r}_p}{W} \frac{1}{(K_p \mathbf{e} + \mathbf{r}_p K)} \quad (14)$$

The diffusion model represented above can be solved analytically (1,2). The solution for the dimensionless bath concentration is given by equation (15):

$$\mathbf{q}_f = \frac{B}{1+B} + 6B Sh^2 \sum_{k=1}^{k=\infty} \frac{e^{-b_k^2 t^*}}{B^2 b_k^4 + B Sh b_k^2 (B Sh - B - 6) + 9 Sh^2 (1+B)} \quad (15)$$

where b_k are the non zero roots of the following equation ;

$$\frac{\tan(b_k)}{b_k} = \frac{3Sh - B b_k^2}{3Sh + B b_k^2 (Sh - 1)} \quad (16)$$

In the case where the Sh number is sufficiently large, equation (15) reduces to the solution used in our previous work, viz.,

$$\mathbf{q}_f = \frac{B}{1+B} + 6B \sum_{k=1}^{k=\infty} \frac{e^{-b_k^2 t^*}}{B^2 b_k^2 + 9(1+B)} \quad (17)$$

where the b_k are roots of

$$\tan(b_k) = \frac{3b_k}{3 + B b_k^2} \quad (18)$$

The fractional approach to equilibrium M_t / M_∞ is given by

$$\frac{M_t}{M_\infty} = (1 + B)(1 - q_f) \quad (19)$$

In some cases information can be extracted from concentration vs. time behavior by average properties of the temporal concentration curve obtained as moments. Thus, if we define moments μ_n of the dimensionless concentration decay according to eq (20)

$$m_n = (B + 1) \int_0^\infty (q_f - (q_f)_\infty) t^n dt \quad (20)$$

then the following expressions can be derived for the first two moments (3).

$$m_0 = \frac{T_d}{15} \left(1 + \frac{5}{Sh} \left(\frac{B}{B+1} \right) \right) \quad (21)$$

$$m_1 = m_0^2 + \frac{1}{525} \left(T_d^2 \left(\frac{B}{B+1} \right) \right) \quad (22)$$

where the time constant T_d is given by

$$T_d = \left(\frac{D_e}{(K_p \mathbf{e} + \mathbf{r}_p K) R^2} \right)^{-1} \quad (23)$$

Termwise integration of eq (15), or (17) as the case may be, also can be used to find the moments μ_0 and μ_1 as given by the expressions in (24) and (25), viz.

$$m_0 = T_d 6B(B+1) Sh^2 \sum_{k=1}^{k=\infty} \frac{\frac{1}{b_k^2}}{B^2 b_k^4 + B Sh b_k^2 (B Sh - B - 6) + 9 Sh^2 (1+B)} \quad (24)$$

$$m_1 = T_d^2 6B(B+1) Sh^2 \sum_{k=1}^{k=\infty} \frac{\frac{1}{b_k^4}}{B^2 b_k^4 + B Sh b_k^2 (B Sh - B - 6) + 9 Sh^2 (1+B)} \quad (25)$$

Equation (15) gives the solution for the dimensionless fluid concentration θ_f as a function of dimensionless time, t^* , for any value of the Sherwood number, Sh , and adsorption capacity parameter, B . We have written a computer program using Mathcad to study the effects of Sh and B on the adsorption of solute from a finite bath according to equation (15). Using equations (15) and (19), we have computed the dimensionless fluid concentration and approach to equilibrium for various values of Sh and B . The results of these calculations are plotted in Figures 1 to 8 for values of adsorption capacity parameter B of 10, 0.1, 0.01, and 0.001. It is worth noting that some of these plots required more than 10,000 terms in the series solution in order to converge, especially for small values of the adsorption parameter B . From Figures 1-8 we note that the uptake of adsorbate is greater at the higher Sherwood numbers, increasing to a limiting value as the Sherwood number approaches infinity. From the plots it is apparent that the effect of film mass transfer is more significant at lower values of B . For example, film mass transfer is negligible at a Sherwood number of around 50 if $B = 10$ as shown in Figures 1 and 2, whereas a Sherwood number of around 10000 is required to achieve the same result if B

= 0.01 as shown in Figures 5 and 6. Thus, for smaller values of B it may be useful to include the film mass transfer resistance in the model simulation for the uptake process.

In order to include the effects of film mass transfer in the model fits, it is necessary to estimate the value of the Sherwood number. This can be accomplished by using equation (26) given below from Bird et al.(4) which gives the Sherwood number N_{Sh} as a function of the Reynolds number N_{Re} and Schmidt number N_{Sc} for flow around a spherical particle.

$$N_{Sh} = 2.0 + 0.60 [N_{Re}]^{0.5} [N_{Sc}]^{0.33} \quad (26)$$

In equation (26) the Sherwood number N_{Sh} is based on the molecular diffusivity in the fluid and particle diameter, rather than the intrapore diffusivity and particle radius as in equation (10) and the associated mathematical model. Consideration of this fact shows that the two Sherwood numbers are related by the expression: $Sh = N_{Sh} [D_m / (2 D_e)]$. The Sherwood numbers for the adsorptive uptake runs made in this project can be approximated from the estimated fluid velocity surrounding the catalyst particles and the fluid properties in conjunction with the intraparticle diffusivity. Following this procedure results in the curves shown in Figure 9 showing data from our previous report for the uptake of coal asphaltene from 1-methylnaphthalene on a BPL porous carbon catalyst. The solution incorporating the effects of film mass transfer is plotted as shown with a Sherwood number of 13,280 estimated using equation (26) above. This solution as computed from equation (15) required 10^5 terms in the series to obtain convergence. The results in the plot indicate that in this case, the effects of film mass transfer are not particularly significant, as the two curves lie quite close together, with the curve for finite Sherwood number agreeing closely with the curve based on equation (17) for infinite

Sherwood number. Figure 10 is a companion plot of the same data plotted as approach to equilibrium computed from equation (19).

Uptake experiments for laboratory prepared carbon catalyst supports. As noted in the previous project report, two carbon based laboratory prepared supports were also utilized in diffusion experiments. These supports, termed Supports A and B, were examined in absorptive uptake experiments with the P-AAK petroleum asphaltenes and a toluene solvent. The preparation of these laboratory prepared supports was described in detail in the prior reporting period. In essence, the carbon based catalyst supports were prepared by mixing appropriate amounts of carbon black particles with a binder composed of a polymeric resin material in the presence of a catalyst for hardening, followed by drying and calcination under an inert atmosphere (5,6). Two different carbon based supports, denoted as A and B, were prepared depending on the source of carbon black and binder and the ratio of carbon black : binder utilized:

Support A: Prepared using Strem acetylene black : resorcinol resin at a 1:4 weight ratio.

Support B: Prepared using Cabot Black Pearls carbon black : Penn furfuryl alcohol resin at a 2 : 1 weight ratio.

Characterization of the pore structures of the two carbon supports was performed by mercury intrusion porosimetry (Micromeritics, Inc.) up to a pressure of 60000 psia. Pertinent properties from the mercury porosimetry characterizations are presented in Table 1. The corresponding pore size distributions are shown in Figure 11. From this figure, one can observe that the carbon supports have a fairly broad range of pore sizes, consisting of both macro and mesopores. Support B has a larger pore volume accessible to mercury than support A. In addition to the mercury porosimetry analyses, BET surface

area analyses revealed the presence of micropores at diameters too small to be penetrated by the mercury intrusion (less than 3 nm). The two carbon catalyst supports as prepared in the laboratory were tested for their diffusional characteristics in asphaltene diffusional adsorptive uptake experiments using petroleum asphaltenes and toluene as a solvent at three temperatures. The results of several of these diffusive uptake experiments performed with the laboratory catalysts are shown in Figures 12-17. The curves in the figures were generated from the mathematical model presented in this report and include the effects of a finite Sherwood number as well as the limiting curve for Sherwood number equal to infinity. In general, the extended mathematical model developed in this time period provides a reasonable representation of the experimental uptake data.

Conclusions

The effects of extraparticle film mass transfer resistances were added to our previously developed mathematical model and were examined by calculations in parametric plots with various Sherwood numbers. A Mathcad based program was used to prepare plots using summation of a sufficient number of terms in the analytical infinite series solution. As a result of these studies we found that the effects of film resistance on the uptake process increased in significance as the adsorption capacity parameter B in the model decreased. In addition, the two carbon catalyst supports prepared in our laboratory were tested for their diffusional characteristics in asphaltene diffusion experiments using petroleum asphaltenes and toluene solvent at three temperatures and the resulting experimental data were simulated with the extended mathematical model developed

herein. In most cases, the model simulations represented the adsorptive uptake data fairly well.

Planned Work

The project is now in its final six-month time period with a no-cost extension and will terminate in September of 2001. During this final time period, we plan to work primarily on examining and bringing together the entire body of data taken throughout the project and developing a final comprehensive project report.

Figure 1. Dimensionless concentration vs. dimensionless time for various Sherwood numbers and absorption parameter $B = 10$.

Figure 2. Approach to equilibrium vs. dimensionless time for various Sherwood numbers and absorption parameter $B = 10$.

Figure 3. Dimensionless concentration vs. dimensionless time for various Sherwood numbers and absorption parameter $B = 0.10$.

Figure 4. Approach to equilibrium vs. dimensionless time for various Sherwood numbers and absorption parameter $B = 0.10$.

Figure 5. Dimensionless concentration vs. dimensionless time for various Sherwood numbers and absorption parameter $B = 0.010$.

Figure 6. Approach to equilibrium vs. dimensionless time for various Sherwood numbers and absorption parameter $B = .010$.

Figure 7. Dimensionless concentration vs. dimensionless time for various Sherwood numbers and absorption parameter $B = 0.0010$.

Figure 8. Approach to equilibrium vs. dimensionless time for various Sherwood numbers and absorption parameter $B = 0.0010$.

Figure 9. Dimensionless fluid concentration vs. time for diffusional uptake of coal asphaltenes C-257K in 1- methylnaphthalene at 100° C on BPL porous carbon catalyst. [K = 62000 cc/g, B = 1.61 x 10⁻³].

Figure 10. Approach to equilibrium vs. time for diffusional uptake of coal asphaltenes C-257K in 1- methylnaphthalene at 100° C on BPL porous carbon catalyst. [$K = 62000$ cc/g, $B = 1.61 \times 10^{-3}$].

Figure 11. Pore size distribution obtained by mercury intrusion porosimetry for two laboratory prepared carbon catalyst supports A and B.

Figure 12. Dimensionless fluid concentration vs. time for diffusional uptake of petroleum asphaltenes P-AAK in toluene at 25 ° C on carbon laboratory catalyst A . [K= 13000 cc/g, B=0.00769].

Figure 13. Approach to equilibrium vs. time for diffusional uptake of petroleum asphaltenes P-AAK in toluene at 25 °C on carbon laboratory catalyst A. [$K= 13000$, $B=.00769$].

Figure 14. Dimensionless fluid concentration vs. time for diffusional uptake of petroleum asphaltenes P-AAK in toluene at 75 ° C on carbon laboratory catalyst A [K= 1300, B=.077].

Figure 15. Approach to equilibrium vs. time for diffusional uptake of petroleum asphaltenes P-AAK in toluene at 75 ° C on carbon laboratory catalyst A. [K= 1300, B=.077].

Figure 16. Dimensionless fluid concentration vs. time for diffusional uptake of petroleum asphaltenes P-AAK in toluene at 25 ° C on carbon laboratory catalyst B. [K= 250000, B=.0004].

Table 1. Properties of Laboratory Prepared Carbon Catalyst Supports Determined by Mercury Intrusion Porosimetry

Property	Catalyst A	Catalyst B
Particle Radius, cm	0.2	0.3
Pore Volume, cc/g	0.3	0.4
Surface Area, m ² /g	80	50
Average pore radius, nm	7.5	16.2
Porosity	0.31	0.23
Tortuosity	4	4

Nomenclature

Letters

C_b	solute bath concentration, g/cm^3
C_i	initial solute bath concentration, g/cm^3
D_∞	solute molecular diffusivity, cm^2/s
D_e	solute effective diffusivity, cm^2/s
k	Boltzmann constant, $1.38 \times 10^{-16} \text{ erg/K}$
K	linear adsorption constant, cc/g
K_p	steric factor
K_r	drag factor
M_{eq}	total amount of solute in the catalyst particle at equilibrium, g/cm^3
M_s	molecular weight of solute
M_t	total amount of solute in the catalyst particle after time t , g/cm^3
r_m	solute molecular size, cm
T	temperature, $^\circ\text{C}$
V	bath volume, cc
W	catalyst weight, g

Greek

ε	catalyst porosity
η	solvent viscosity, g/cm-s
τ	tortuosity
λ	ratio of solute molecular size to pore size

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