Hindered Diffusion of Asphaltenes at Elevated Temperature and Pressure

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Abstract

During this time period work proceeded in two main areas, the performance and analysis of petroleum asphaltene diffusional uptake experiments at 325 °C and the preparation and testing of some new carbon based catalysts. In the first area, we performed studies of the diffusion controlled uptake of petroleum asphaltenes into a porous carbon catalyst at 325 °C. The experiments were performed under an inert He atmosphere using 1-methylnaphthalene as a solvent. The purpose of these experiments was to extend our previous data which was taken and reported in the prior semi-annual report. These previous experiments were performed only up to a temperature of 250 °C. A comparison between the experimental data and model simulated data showed that the mathematical model satisfactorily fitted the adsorptive diffusion of the petroleum asphaltenes onto the porous carbon at 325 °C. Comparing with previous results, the adsorption constant continued to decrease with an increase in temperature for the petroleum asphaltene/1-methylnaphthalene system.

Also during this time period, some carbon catalyst supports were prepared in our laboratory and several sets of data were obtained in adsorption-diffusion uptake experiments using a petroleum asphaltene with toluene as solvent. These data are presented in this report, although, complete fitting of the data with the mathematical model has not yet been performed. These calculations will be performed during the next time period.

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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 coal and petroleum asphaltenes in porous catalysts.
2. To examine the effects of temperature on the intraparticle diffusivity of asphaltenes.

EXECUTIVE SUMMARY

The general aim of this project is to obtain a better understanding of the diffusion controlled uptake of model compounds and asphaltenes in porous catalysts at various elevated temperatures. During this particular time period we have performed experiments on the diffusion of petroleum asphaltenes in porous carbons. The porous carbons utilized were a commercial activated carbon sample, and two laboratory prepared porous carbon supports, termed Support A and Support B, and described in more detail later. Experiments were performed at 325 °C for the petroleum asphaltene with 1-methylnaphthalene as solvent and a commercial carbon support. In addition, experiments were run at 25, 50, and 75 °C using a petroleum asphaltene with toluene as the solvent and some laboratory prepared carbon supports. A previously developed C++ program was used to simulate the experimental data at 325 °C using a mathematical model. A comparison between the experimental data and model simulation data showed that the mathematical model satisfactorily fitted the diffusion controlled adsorption of the petroleum asphaltenes onto porous carbon. In keeping with theories of exothermic adsorption, the adsorption constant continued to decrease with an increase in temperature for the petroleum asphaltene/1-methylnaphthalene system.

Personnel: During this time period, Mr. Ganesh Ramakrishnan, the M. S. student who had been working on the project for the past year received his M.S. degree and has obtained employment. The work on the project has been continued by two B. S. undergraduate students in chemical engineering, Mr. Keiji Asada, and Mr. Brian Mosley. Due to the limited amount of project funds remaining for the final year (no-cost extension) of the project, it is expected that

the work will be continued by part-time undergraduate students rather than a new full time graduate student for the balance of the project.

INTRODUCTION

In this project we are attempting to add to the understanding of how coal and petroleum macromolecules, operationally defined as asphaltenes, diffuse into the pores of a porous catalyst. Since the diffusion process is directly coupled to the chemical reactions and upgrading of asphaltenes to smaller molecules, such an increased understanding would be of benefit to reactor modeling and would also aid in the design of improved catalysts. In the previous report we described our work in asphaltene diffusion, as well as the modeling of the results by a computer simulation at temperatures of up to 250 °C. In the current work we have extended these experiments and computer modeling to the higher temperature of 325 °C where we have investigated the effect of temperature on the adsorptive uptake of the asphaltenes in the 1-methylnaphthalene solvent system.

In a second phase of the work during this period, we have prepared some carbon based catalysts in our laboratory, termed Supports A and B, using a resin binder material in conjunction with a carbon black particulate material, followed by extrusion and then carbonization in an inert atmosphere at high temperature (Schmitt, Jr., 1976, Vissers, 1987). This carbonization process converts the binder to carbon. The resulting porous carbon particles have potential for use as catalysts and catalyst supports. Carbon supported catalysts are of interest in many areas, including hydrotreating, based on their tendency to form less coke, and hence undergo less catalyst deactivation than the corresponding metal oxide supports. The diffusion of asphaltenes in these porous carbon supports is being studied at this time.

Overview

In our prior work, we have been conducting finite bath diffusional uptake experiments using asphaltenes from both coal and petroleum. Following obtaining of the experimental uptake data, we have applied a computer mathematical model to simulate the uptake process and have compared the model behavior with the experimental data. To perform the simulation calculations, a key parameter required for the mathematical model is the effective pore diffusivity for the asphaltene molecules. To obtain an estimate of this parameter, we have calculated the molecular diffusivity by the Stokes Einstein equation,

$$D_{\infty} = kT/6\pi\eta r_m \quad (1)$$

where D_{∞} is the molecular diffusivity, k is the Boltzmann constant, T is the temperature, η is the viscosity and r_m is the solute molecular size. In the catalyst pores, this diffusivity is reduced by several factors to give an effective pore diffusivity as,

$$D_e = K_p K_r \epsilon D_{\infty} / \tau \quad (2)$$

where K_p is the steric factor, K_r is the drag factor, ϵ is the porosity and τ is the tortuosity. The steric factor accounts for the fact that a localized region near the wall of a pore is not available for diffusion to the solute molecules. Ferry (1936) studied the steric factor and postulated that

$$K_p = (1-\lambda)^2 \quad (3)$$

where λ is the ratio of molecule size to pore size. The drag factor accounts for the enhanced hydrodynamic drag experienced by a solute molecule due to the finite confines of the fluid within a pore. The drag factor can be estimated using the relation given by Pappenheimer et al. (1951),

$$K_r = 1 - 2.104\lambda + 2.089\lambda^3 - 0.948\lambda^5 \quad (4)$$

In our mathematical simulation of the diffusion process, we use equations (1) to (4) to provide estimates of the effective diffusivity of asphaltenes in catalyst pores. A complete explanation of the mathematical model together with a more detailed derivation of the pertinent equations has been presented in the previous semi-annual technical reports on this project.

EXPERIMENTAL SECTION

Materials for asphaltene diffusion experiments.

In the work performed here, the petroleum asphaltenes used were labeled as P-AAD and P-AAK. The properties of these two petroleum asphaltenes are given in the dissertation by Yang (1997), a previous PhD candidate supported on the project, and have been summarized in our previous reports. A porous commercial carbon catalyst, with an irregular shape, an equivalent particle radius of 0.2cm, and a surface area of 1100 m²/g was used as the adsorption-diffusion medium for the diffusion experiments with the P-AAD asphaltenes at 325 °C. As noted in our previous report, several important properties of this porous carbon catalyst are given in Table 1. Also, the pore size distribution for the catalyst is given in Figure 1. In addition to the commercial carbon catalyst support, two new laboratory prepared supports were also utilized in diffusion experiments. These supports were termed Supports A and B, and were used with the P-AAK petroleum asphaltenes and a toluene solvent. The preparation of these laboratory prepared supports is described in greater detail below.

Materials for preparation of carbon catalysts.

In this phase of the work, two carbon blacks and two different binder materials were utilized to prepare carbon-based catalyst supports. The carbon blacks used were (1) acetylene carbon black obtained from Strem Chemical Co. and (2) Black Pearl 1100 carbon black obtained from Cabot Co. Binder materials used for preparing of the composite supports were (1) resorcinol resin / catalyst system, Weldwood Co., and (2) Quacorr 1001 furfuryl alcohol resin / 2001 catalyst system, Penn Specialty Chemicals, Inc., Memphis, TN.

Preparation of carbon based supports.

The carbon based catalysts 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 (Vissers, et al., 1987, Schmitt, Jr. et al., 1976). This mixture was well stirred and then extruded into cylindrical pellet form. In some cases acetone was used as a solvent to allow easier dispersal of the carbon black. Following drying in a hood overnight, the pellets were calcined at 650 °C in a tube furnace under an inert nitrogen atmosphere flowing at 250 sccm. In these experiments two different carbon based supports were prepared depending on the source of carbon black and binder and the ratio of carbon black : binder utilized. These two supports were:

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 is currently in progress.

Asphaltene diffusion experiments.

1. Petroleum asphaltene / 1-methylnaphthalene system

A microautoclave batch reactor was used to study the adsorptive uptake of petroleum asphaltene P-AAD in 1-methylnaphthalene on porous activated carbon at 325°C. The porous carbon particles, presoaked in 1-methylnaphthalene, were supported in a wire mesh compartment in the microautoclave to avoid direct contact with the solution until the experiment was begun. Air was removed from the system by purging the microautoclave with helium 5 times. Then, the microautoclave was left pressurized to 250 psig with helium for the duration of the experiment. The microautoclave was attached to a horizontal agitator and lowered into a fluidized sand bath whose temperature was maintained by a temperature controller. The runs were made for various time periods. On completion of a run, the liquid phase was collected and filtered. The initial concentration of asphaltene P-AAD was 0.07g/L of solution. The P-AAD concentration in the liquid phase after the diffusional uptake experiments was obtained using a UV-VIS spectrophotometer at 400nm.

The laboratory prepared carbon supports were also tested in diffusional uptake experiments using a petroleum asphaltene in a toluene solvent solution. In performing the experiments, the same general methodology as described above was used. For these particular experiments, 10 mL of solution at a P-AAK petroleum asphaltene initial concentration of 0.04 g/L was used. Uptake experiments were conducted at 25, 50, and 75 °C using the prepared supports and solution compositions were determined as before.

RESULTS AND DISCUSSION

Petroleum asphaltene / 1-methylnaphthalene system.

Effective and molecular diffusivities.

a) Experiments at 325 °C

In our earlier work (Yang, 1997), the average molecular weight of petroleum asphaltene P-AAD was estimated using GPC to be 2200. From this average molecular weight, the radius of the P-AAD molecule was estimated to be 16.9×10^{-8} cm using equation (5) presented in the previous semiannual report as:

$$r_m = 0.36 M_s^{0.5} \quad (5)$$

where M_s is the molecular weight of the asphaltene. As noted therein, in this case, the solute molecule size is greater than the average pore radius previously computed for the commercial carbon catalyst. This situation arises because the carbon catalyst contains some pores which are actually smaller than the asphaltenes, and hence are not accessible for adsorption. Therefore a new approach was adopted in the previous report and used to determine a new average pore size, taking into account only the accessible pores. In this modified approach, the assumptions were:

- 1) We did not consider the pores which are smaller than 16.9×10^{-8} cm (the size of the asphaltene molecules).
- 2) For the remaining pores, we found an average pore radius which we termed the effective (i. e., accessible), average pore radius.

Using these procedures, the effective (accessible) porosity, effective pore volume and effective surface area of the porous carbon were determined to be 0.27, 0.35 cc/g and 8.57×10^5 cm²/g, respectively. Based on these values, the effective average pore radius was found to be 8.17×10^{-7}

cm. At the experimental temperature of 325 °C, the viscosity of the 1-methylnaphthalene solvent may be determined from literature data (Yaws, 1995). Then, using equation (1), the value of the molecular diffusivity D_{∞} may be calculated. From the molecule radius and effective pore radius, using equation (3), the steric factor K_p may be computed and from equation (4), the hydrodynamic factor K_r may likewise be determined. The estimated effective pore diffusivity may then be determined from equation (2).

Comparison of experimental data with model simulations.

Petroleum asphaltene P-AAD/1-methylnaphthalene system at 325 °C.

The experimental adsorptive uptake data for the petroleum asphaltene P-AAD/1-methylnaphthalene system at 325 °C is compared with the uptake curves as simulated by the mathematical model for the diffusion-controlled uptake in Figures 2-4. Figure 2 shows the comparison between the experimental data and model simulations for three different values of K at 325 °C. It is apparent that the adsorptive uptake at the elevated temperature is not very great, with C_b/C_i decreasing only to about 0.95, i. e. only about 5% adsorptive uptake, even after 24 hours. Based on the mathematical simulation, the value of K which best fits the experimental data at 325 °C was found to be 6.5 cc/g by least square analysis as shown in Figure 2. Additional comparisons between the experimental data and model simulation for this single best fit value of K are shown in Figures 3 and 4. In general, the comparisons between model simulations and experimental data are reasonable; although, the data do tend to lie above the model curve at early times and decline below the curve at later times. The exact reasons for this are not completely clear, but could involve multilayer adsorption, or the more complex pore structure of the porous carbons.

Diffusional uptake experiments with laboratory prepared carbon catalysts.

Tables 2-4 present the numerical adsorptive uptake data taken in experiments with the two laboratory prepared carbon supports A and B, using the petroleum asphaltene P-AAK in toluene at several temperatures. At this time, the tabular data have not been analyzed graphically using the diffusion simulation model, however, this is planned to be accomplished during the next time period, once the pore geometries of the prepared supports have been more completely characterized.

Table 1. Properties of Activated Carbon (Calgon Carbon's BPL 4 x 6)

Shape	Irregular
Equivalent radius, cm	0.2
Surface area, m ² /g	1100
Particle density, g/cm ³	0.8
Pore volume, cm ³ /g	0.8
Porosity	0.62
Average pore diameter, nm	2.91

Table 2. Experimental diffusional uptake data for the P-AAK / toluene system with laboratory prepared support A at three temperatures.
(V=10ml, W=0.1g)

Time, hr	C_b/C_I 25 °C	C_b/C_I 50 °C	C_b/C_I 75 °C
0	1	1	1
2	0.81	0.84	0.85
4	0.72	0.75	0.80
8	0.60	0.65	0.76
12	0.55	0.64	0.74
16	0.54	0.62	0.72
24	0.53	-----	0.71

Table 3. Experimental diffusional uptake data for the P-AAK / toluene system with laboratory prepared support A at two temperatures.
(V=10ml, W=0.2g)

Time, hr	C_b/C_I 25 °C	C_b/C_I 50 °C
0	1	1
2	0.75	0.78
4	0.68	0.70
8	0.57	0.61
12	0.50	0.55
16	0.49	0.54
24	0.49	0.53

Table 4. Experimental diffusional uptake data for the P-AAK / toluene system with laboratory prepared support B using two weights of catalyst extrudates.
(V=10ml, T = 25 °C)

Time, hr	C_b/C_I W = 0.1g	C_b/C_I W=0.2g
0	1	1
2	0.60	0.52
4	0.56	0.45
8	0.40	0.35
12	0.22	0.15
16	0.12	0.01
24	0.01	0.00

Figure 1. Pore Size Distribution of Calgon Carbon's BPL 4 x 6 porous carbon (from Product Bulletin of Calgon Carbon, 1997)

Figure 2. Comparison between experimental data and model simulation for adsorptive uptake of petroleum asphaltene P-AAD in 1-methylnaphthalene on commercial carbon. ($V=10 \text{ mL}$, $W=0.1 \text{ g}$, $T = 325 \text{ }^\circ\text{C}$).

Figure 3. Comparison between experimental data and model simulation with the best fit value of K for the adsorptive uptake of P-AAD in 1-methylnaphthalene on porous carbon ($V=10\text{ml}$, $W=0.1\text{g}$, $T=325\text{ }^\circ\text{C}$, $K=6.5\text{cc/g}$)

Figure 4. Comparison between experimental data and model simulation with the best fit value of K for the adsorptive uptake of P-AAD in 1-methylnaphthalene on porous carbon ($V=10\text{ml}$, $W=0.1\text{g}$, $T=325\text{ }^{\circ}\text{C}$, $K=6.5\text{cc/g}$)

CONCLUSIONS

Experiments were performed in a microautoclave to study the diffusion controlled uptake of a petroleum asphaltene in 1-methylnaphthalene, onto a porous carbon catalyst substrate at 325 °C. As before, a C++ program was used to simulate the experimental data using the mathematical model which we have developed previously for diffusion controlled adsorption. A comparison between the data and model simulation showed that the mathematical model satisfactorily fitted the adsorptive diffusion data. The adsorption constant for the petroleum asphaltene P-AAD/1-methylnaphthalene system was found to continue to decrease with increases in temperature, in accordance with previous work. In addition, two new carbon catalyst supports were prepared in the laboratory and were tested for their diffusional characteristics in asphaltene diffusion experiments using petroleum asphaltenes and toluene solvent at three temperatures.

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

REFERENCES

- Anderson,J.L., and Quinn,J.A., Biophysical J., 14,130 (1974) as cited in Yang (1997).
- Deen,W.M., AIChE J., 33,1409,1987.
- Ferry,J.D., J.Gen.Physiol., 20,95,1936 as cited in Deen (1987).
- Pappenheimer,J.R., Renkin,E.M., and Borrero,L.M., Am.J.Physiol., 167,13,1951 as cited in Yang (1997).
- Schmitt, Jr., J. L., Walker, Jr., P. L. and Augustus, G. U. S. Patent No. 3,978,000, American Cyanamid Company, (1976).
- Visser, J. P. R. , Lensing, T. J. , DeBeer, V. H. J. and Prins, R., Applied Catalysis, 30, 21, (1987).
- Schmitt, Jr., Joseph Lawrence, Walker, Jr., Philip Leroy, Castellion, George Augustus., U. S. Patent No. 3,978,000. "Catalysts based on Carbon Supports", American Cyanamid Co. , Stamford, CT., August, 31, 1976.
- Yaws,C.L., Handbook of Viscosity, Vol. 3, Gulf Publishing Company, (1995).
- Yang,X., Ph.D. Dissertation, Auburn University, (1997).

PLANNED WORK

The project is now in its final year, with the granting of an additional year of no-cost extension time. During the next time period, we plan to further analyze the uptake data taken using the newly prepared carbon supports. Also we plan to perform some simulation calculations regarding the effects of external mass transfer on the diffusional uptake process.