DOE/PC/91311--T17

QUARTERLY PROGRESS REPORT
ON
CONFIGURATIONAL DIFFUSION OF
ASPHALTENES IN FRESH AND
AGED CATALYST EXTRUDATES

Grant No. DE-FG22-91PC91311

9-20-95 to 12-20-95

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Statement of Work

Configurational Diffusion of Asphaltenes in Fresh and Aged Porous Catalyst Extrudates

Objective: The objective of this research is to determine the relationship between the size and shape of coal and petroleum macromolecules and their diffusion rates i.e., effective diffusivities, in catalyst pore structures. That is, how do the effective intrapore diffusivities depend on molecule configuration and pore geometry.

Task 1. Relationship Between Effective Intrapore Diffusion Coefficients, Molecular Size and Pore Geometry.

Finite bath-type diffusion experiments will be performed using both coal and petroleum-derived macromolecular species, e.g. asphaltenes, as well as model compounds, e.g. porphyrins, polymers, of known molecular size. By monitoring the concentration of solute macromolecules in the bath, the effective intrapore diffusion coefficients will be determined through application of the appropriate diffusion equations. Macromolecular species concentrations will be monitored by size exclusion chromatography (SEC). Relationships will be sought between the size, and shape, e.g. planar, coil, of the diffusing solutes and the pore geometry (pore size distribution) of the catalyst support. The effects of molecule configuration and catalyst pore size distribution on the effective intrapore diffusivity will be examined. Specially prepared laboratory catalysts with very narrow pore size distributions and other model porous media, e.g. porous Vycor glass, will be utilized in the experiments. Pore structures of all catalysts and other porous media will be characterized by mercury porosimetry and surface area (BET) analysis.

Task 2. Effects of Solvent Composition, Solute Concentration, and Temperature on the Molecular Configuration and Diffusion Rate of Coal and Petroleum Asphaltenes in Catalyst Pores.

Diffusion experiments such as in Task 1 will be performed with varying solvent compositions,

i.e., paraffinic-aromatic mixtures, to examine the effects of the state of molecular aggregation (self-assemblies) on the rates of diffusion of coal and petroleum asphaltenes in the catalyst pores. Similar experiments will be performed to study the effect of *temperature* and solute (macromolecule) *concentration* on the state of molecular configuration and aggregation on the resulting pore diffusivity.

Task 3. Assessment of Diffusional Limitations in Aged Catalysts

Diffusivity measurements such as conducted in Task 1 will be performed with both model compound and coal-derived macromolecular species using extrudate-type aged catalysts from laboratory experiments as well as aged catalysts obtained from actual coal liquefaction pilot plants such as the Wilsonville, AL Advanced Coal Liquefaction R & D Facility. From the experimental diffusivities so obtained, an evaluation of effects of changes in catalyst pore structure, e.g. tortuosity, pore plugging, shall be made. The changes in pore diffusivities associated with the pore structural changes caused by coke and metals deposition will be investigated, as compared with the fresh catalysts. An assessment of the relationship of increased diffusional limitations to coke and metals deposition in the catalyst pores will be made based on the results of the diffusivity measurements. The degree to which pore diffusivities can be restored to their original values by carefully controlled oxidation and/or extractive catalyst regeneration techniques also will be explored. The practical importance of these findings to coal liquefaction technology will be evaluated.

Summary

This quarter, the GPC column efficiency was rechecked by using acetone injection. The calibration curve for the GPC was rechecked through polystyrene standards with narrow molecular weight distributions. Some experiments on adsorption and diffusion of coal asphaltenes through porous catalysts were performed. The asphaltenes were grouped into nine fractions with the concentration being determined via GPC. It was found that the uptake rate for one asphaltene fraction is different from those for other fractions. Comparison of experimental uptake data shows a difference in hindered diffusion behavior between petroleum asphaltenes and coal asphaltenes.

Planned Work

Next quarter, more detailed experiments on adsorptive diffusion with both the petroleum and the coal asphaltenes into porous catalysts will be performed. The adsorption-diffusion behavior of asphaltenes will be ascertained by simulating experimental data with a simplified mathematical model.

Experiments for Hindered Diffusion of Coal Asphaltenes

Introduction

Hindered diffusion studies of asphaltenes through porous media are recent and few in number. Thrash and Pildes(1981) studied the transport of petroleum asphaltenes through mica membranes. They treated the asphaltenes as a single solute and obtained an average diffusivity, being around $4 \times 10^{-6} \text{ cm}^2/\text{s}$ at 22°C , for hexane insoluble, chloroform soluble asphaltenes from Middle East vacuum residua in toluene solvent. Baltus and Anderson(1983) also studied hindered diffusion of petroleum asphaltenes through porous membranes. They grouped the asphaltenes into five fractions, with the equivalent molecular weights of the fractions being defined as those of polystyrenes with same elution volumes on GPC. By fitting experimental data with a mathematical model, some diffusion properties of the asphaltene fractions were obtained, as shown in Table 1, and the relationship between the effective diffusivity D_e and molecular diffusivity D_m of the asphaltene fractions was found as

$$D_e = D_m \exp(-3.89\lambda) \quad (1)$$

As shown in Table 1, the molecular diffusivities of asphaltene fractions are roughly half those of polystyrenes, indicating different diffusion behavior of petroleum asphaltenes and polystyrenes.

Nortz et al.(1990) studied the relationship between the molecular diffusivity, effective solute diffusion radius and molecular weight of fractionated samples from heavy oils. The heavy oils were first fractionated into nine fractions on preparative GPC. The number average molecular weight of each fraction was determined in toluene at 40°C by using a vapor pressure osmometer, and the molecular diffusivity was ascertained by Taylor dispersion measurements. It was found that

$$\text{at } 50^{\circ}\text{C}, D_e = 3.63 \times 10^{-5} MW^{0.50} \text{ cm}^2/\text{s} \quad (2)$$

$$\text{at } 70^{\circ}\text{C}, D_e = 5.82 \times 10^{-5} MW^{0.51} \text{ cm}^2/\text{s} \quad (3)$$

and there was no significant difference in the effective size of each fraction at 50 and 70 °C. The difference in diffusivity values at the two temperatures was attributed to the difference in temperature and solvent viscosity. By using the Stokes-Einstein equation, they obtained a relationship between the molecular size and molecular weight of each fraction, viz.,

$$r = 0.36 MW^{0.50} \text{ \AA} \quad (4)$$

Mieville et al. (1989) were the first who studied the adsorptive diffusion of petroleum asphaltenes in toluene through porous catalysts by uptake experiments. First, they treated the asphaltenes as a single solute and used a UV detector at 510 nm wavelength to monitor the concentration change in the bath solution. A linear adsorption isotherm was found for the Jobo asphaltene/toluene/alumina system. In their study of several asphaltenes with molecular weights and cluster sizes (diameters) ranging from 2862 to 4465 and 17 to 25 Å respectively, the effective diffusivities were found to be in the range of from 2.0 to 5.1x10⁻⁶cm²/s. The asphaltenes were also fractionated into several cuts on GPC. The effective diffusivities for the cuts were measured and a relationship between effective diffusivity and molecular weight was obtained, viz.,

$$D_e = (-0.223 \cdot \frac{310}{\sqrt{MW}}) \times 10^7 \text{ cm}^2/\text{s} \quad (5)$$

In this quarterly report, we show our recent results on adsorptive diffusion of coal asphaltenes

through porous catalysts. More detailed studies will be performed in the coming quarter.

Experimental

1. Materials

Chemicals. Coal asphaltenes obtained from a Wilsonville Run 258 D coal liquid were used in the adsorption-diffusion experiments this quarter. HPLC grade tetrahydrofuran (THF) was employed as solvent. Polystyrenes with narrow molecular weight distributions were used as GPC calibration standards.

Catalyst. A commercial unimodal catalyst, Criterion 324, with an average pore diameter of 125 °Å, was used in this study. Catalyst samples were calcined at 673 K for 12 hours prior to use in adsorption and diffusion experiments.

2. Apparatus and Procedures

GPC Equipment. A GPC (gel permeation chromatograph) device with a UV detector was used to analyze the concentration of asphaltenes in THF. HPLC grade THF was used as a mobile phase with a flow rate of 1 cc/min. Each asphaltene sample for GPC analysis was filtered before injection through a 0.1 µm syringe filter.

Equilibrium Adsorption Experiments. Equilibrium adsorption experiments were performed to measure coal asphaltene uptakes on catalyst samples at different concentrations. Solutions of 50 cc of coal asphaltenes in THF with 0.05 mg/ml initial concentration were placed in bottles containing -45 µm(-325 mesh) weighed catalyst particles. The bottles were placed in an environmental shaker at 298 K for 15 hours, assuming equilibrium was reached. The concentration of coal asphaltenes was

determined by GPC.

Diffusion Experiments. Diffusion experiments were performed using the adsorptive uptake of asphaltenes in THF from a finite bath surrounding the catalyst particles. Experiments were conducted in glass bottles placed in a shaker at a constant temperature of 298 K. The diffusion process was monitored periodically by analyzing the concentration of asphaltenes in the bath solution using GPC.

Results and Discussion

1. Performance of GPC Columns

To insure the performance of GPC during asphaltene analysis, the columns should be tested and calibrated periodically. Therefore, at the beginning of this quarter, the column efficiency and calibration curve were obtained using acetone and polystyrene standards with narrow molecular weight distributions, respectively. It was found that the efficiencies obtained in February and November 1995 were 35,000 and 31,000 respectively, indicating only a little loss in the column efficiency.

Figure 1 shows the GPC chromatograms of polystyrene standards, and Figure 2 gives the calibration curve plotted as logarithms of polystyrene molecular weights (weight average) vs. elution time. For comparison, the calibration curve obtained in February 1995 was also shown in this figure. It can be seen that these two calibration curves are about the same. The calibration equation obtained this quarter is

$$\text{Log}(MW) = -0.1491V_e + 7.986 \quad (6)$$

After column calibration, a solution of coal asphaltenes in THF (0.05 mg/cc) was analyzed

via GPC, as shown in Figure 3. There are two x-axes in this figure, one is the elution volume, the other is the equivalent polystyrene molecular weight calculated from equation (6). No attempt was made to determine the actual molecular weights of the various asphaltene fractions. According to the calibration curve, the coal asphaltenes were grouped into nine fractions in terms of their equivalent polystyrene molecular weights. As can be seen from Figure 3, the equivalent molecular weights of coal asphaltenes are in the range of 50 to 2500.

2. Equilibrium Adsorption Experiments of Coal Asphaltenes

In order to simulate the adsorption-diffusion of coal asphaltenes through mathematical model, the equilibrium adsorption isotherms of asphaltenes are usually needed. Due to the complexity of asphaltenes, the asphaltenes were grouped into nine fractions according to their equivalent polystyrene molecular weights, as shown above. The adsorption isotherm for the asphaltene fraction was obtained by mass balance between the amount of the fraction at initial conditions and that at equilibrium. We assume that the concentration of each asphaltene fraction is linearly dependent on its UV absorbance.

Figure 4 shows GPC chromatograms of equilibrium asphaltene solutions with different amount of catalysts used. It can be seen that as the catalyst weight increased, the equilibrium concentrations of each asphaltene fractions are decreased. Figure 5 plots the amount of adsorption vs. the equilibrium concentration for each asphaltene fraction. It seems that the isotherms for all the asphaltene fractions do not pass through the origin. This behavior may be caused by a "nonadsorbable" component in each fraction. More detailed studies of the adsorption behavior of asphaltenes will be performed next quarter.

3. Hindered Diffusion Experiments of Coal Asphaltenes

Diffusion experiments for coal asphaltenes were performed this quarter. Figure 6 shows GPC chromatograms of asphaltenes concentration as a function of time. From this figure it can be seen that for each asphaltene fraction, the bath concentration decreases as the diffusion time increases, however, with different uptake rates for different asphaltene fractions, depending on their adsorption and diffusion properties.

It should be pointed out that in the case of petroleum asphaltenes, as shown in the last quarterly report, the bath concentrations for some fractions increased during the adsorption-diffusion process. This unusual behavior was explained partly due to phenomena such as the agglomeration of smaller molecules to larger ones, a process which needs further investigation. However, for coal asphaltenes, this unusual phenomena disappeared, as shown in Figure 6. More detailed studies on hindered diffusion of both coal and petroleum asphaltenes will be conducted next quarter.

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Table 1. Parameters for Kuwait petroleum asphaltenes in THF (Baltus and Anderson, 1983)

asphaltene fraction number	equivalent polystyrene molecular weight	asphaltene molecular diffusivity $\times 10^7 \text{ cm}^2/\text{s}^a$	molecular radius, Å		polystyrene molecular diffusivity $\times 10^7 \text{ cm}^2/\text{s}^c$
			from experimental ^b	from Stokes- Einstein equation	
A	3000	16.1	20	26	36.1
B	6000	13.1	32	32	24.7
C	12000	8.85	44	47	16.9
D	24000	5.24	69	79	11.6
E	48000	2.71	152	153	7.93

a. Calculated based on experiments from the interception of D_e vs. $1/r_p$ as $1/r_p \rightarrow 0$, where r_p is the pore radius.

b. Based on $D_e/D_\infty = \exp(-4.6 r_m/r_p)$, where r_m is the molecule radius.

c. Measured by light scattering technique.

Figure 1. GPC chromatograms for polystyrene standards made on November, 1995.

Figure 2 Comparison of GPC calibration curves from polystyrene standards made on February and November, 1995

Figure 3 Asphaltene fractions defined by their elution volumes on GPC

Figure 4 Equilibrium GPC Chromatograms of Coal Asphaltenes with Criterion 324 Catalyst in THF at 25 °C

Figure 5 Equilibrium isotherms for coal asphaltene fractions.

Figure 6 GPC Chromatograms of coal asphaltene solutions during adsorption-diffusion through Criterion 324 catalyst