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QUARTERLY PROGRESS REPORT

ON

CONFIGURATIONAL DIFFUSION OF ASPHALTENES IN FRESH AND AGED CATALYST EXTRUDATES

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James A. Guin

Chemical Engineering Department
Auburn University
Auburn, AL 36849

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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. As 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, three petroleum and two coal asphaltene samples were prepared from petroleum asphalts and coal derived solids separated by the ROSE Critical Solvent Deashing process, respectively, using solvent extraction method. The solvents used in the extraction process were THF and n-pentane. The asphaltene samples were defined as THF-soluble and pentane-insoluble. It was found that the asphaltene content in petroleum asphalt is less than that in coal derived solids. The asphaltene samples were characterized by SEC (Size Exclusion Chromatography) analysis. The molecular weight distribution of the asphaltene samples was ascertained by polystyrene standards in SEC. It was found that the molecular weight of petroleum asphaltene sample is larger than that of coal asphaltene sample.

Planned Work

Next quarter, adsorptive diffusion experiments with both the petroleum and the coal asphaltene samples into porous catalysts will be performed. The adsorption-diffusion parameters of asphaltene samples will be ascertained by simulating experimental data with a simplified mathematical model. The adsorption-diffusion behavior of petroleum and coal asphaltene samples will be compared. The stability of asphaltene samples in solvent at different conditions will also be investigated next quarter.

Preparation and Characterization of Asphaltenes

1. Preparation of Asphaltenes

This quarter, two coal asphaltenes and three petroleum asphaltenes were prepared from coal solid residues and petroleum asphalts, respectively, using solvent extraction method. The coal residues were from the Wilsonville Advanced Coal Liquefaction Research and Development Facility, Alabama. These two coal residues were Solvent Refined Coal(SRC) from runs 257 K and 258 D respectively, of Illinois No. 6 Coal from the Burning Star Mine #2. The three petroleum asphalt samples were used as received. Table 1 shows some properties of the petroleum asphalts.

The asphaltenes in our work are defined as THF solubles and pentane insolubles. The following solvent extraction procedures were used to prepare coal and petroleum asphaltenes.

- (1). A coal solid or petroleum asphalt was first dissolved in THF solvent in a beaker, with an asphalt/THF ratio of 1g/ml, and filtered through a 1 μ m filter paper.
- (2). An excess amount of solvent n-pentane was added to the asphalt/THF solution with a pentane/THF ratio of 10. The pentane-insoluble and THF-soluble solid was precipitated during this solvent extraction process;
- (3). The above mixture was centrifuged in a centrifuge bottle for 10 minutes;
- (4). After decanting the supernatant, the precipitate was transferred to the beaker;
- (5). Steps (2) to (4) were repeated for two more times;
- (6). The precipitate was transferred to a bottle, washed with pentane for several times

until the upper pentane solution in the bottle was clear;

- (7). The precipitate was dried in a hood at room temperature overnight to remove all solvent and then dried again in an oven at 110 °C for 10 hours;
- (8). The dried precipitate (solid powder) was weighed and the mass yield of the precipitate from the original asphalt was calculated;
- (9). The precipitate (the asphaltenes) was crushed and sealed in a bottle for later use.

Table 2 shows the mass yields of the asphaltenes prepared by the solvent extraction method. It can be seen that the mass yield for the petroleum asphaltenes are small, particularly for AAG-1 asphaltenes (2.2 wt%). On the other hand, the mass yield for the two coal asphaltenes, 38 wt% and 54 wt% respectively, are relatively larger. These results indicated that asphaltene contents in petroleum asphalts are less than those in coal liquefaction residues. It should be noted in Table 2 that the three petroleum asphaltenes are black, whereas the coal asphaltenes are brown. These maybe due to the higher metal contents, e.g., Fe, in coal asphaltenes than in petroleum asphaltenes.

Table 1. Properties of Original Asphalts

Asphalt	AAD-1	AAG-1	AAK-1
Crude	CA Coast	CA Valley	Boscan
Viscosity, 140°C, poise	1055	1862	3256
275°C, cSt	309	243	562
Penetration, 0.1 mm			
77°C, 100g, 5s	135	53	70
39.2°C, 100g, 5s	9	2	2
Ductility, cm (39.2°C, 1cm/min)	150+	0.0	27.8
Softening Point (R & B), °F	118	120	121
Component Analysis, %			
Asphaltenes (n-heptane)	23.0	5.8	21.1
Asphaltenes (iso-octane)	3.4	3.3	2.8
Polar Aromatics	41.3	51.2	41.8
Napthene Aromatics	25.1	32.5	30.0
Saturates	8.6	8.5	5.1
Elemental Analysis			
C, %	81.6	85.6	83.7
H, %	10.8	10.5	10.2
O, %	0.9	1.1	0.80
N, %	0.77	1.10	0.70
S, %	6.90	1.30	6.40
V, ppm	310	37	1480
Ni, ppm	145	95	142
Fe, ppm	13	48	24
Aromatic C, %	23.7	28.8	31.9
Aromatic H, %	6.81	7.27	6.83
Molecular Weight (Toluene)	700	710	860
IEC Separations (wt %)			
Strong Acid	11.0	18.1	3.7
Strong Base	7.8	12.0	8.0
Weak Acid	7.8	11.4	8.6
Weak Base	5.5	9.1	7.5
Neutral	51.7	50.4	52.5
SA Mol. Wt., VPO, Toluene	2500	1080	2780
Amphoterics	15	18.5	24.3

Table 2. Yields of Asphaltenes from Asphalts

asphalts	yield, wt%	color
petroleum, AAD-1	16.0	black
petroleum, AAG-1	2.2	black
petroleum, AAK-1	12.5	black
coal, 257 K	38.4	brown
coal, 258 D	53.7	brown

2. Characterization of Asphaltenes

An SEC (size exclusion chromatograph) device with a UV detector was used to characterize the asphaltenes in THF. HPLC grade THF was used as mobil phase with a flow rate of 1 cc/min. The UV wavelength was 235 nm. Before use in SEC analysis, THF was filtered through a filter paper with 0.1 μm nominal pore size and was degassed for 10 minutes by using a sonicator. The THF reservoir was purged with He gas to keep THF from forming peroxides. Each asphaltene sample for SEC analysis was filtered before injection through a 0.1 μm syringe filter.

Figure 1 shows SEC chromatography of the two coal asphaltenes and the three petroleum asphaltenes. It should be noted that there are two x-axes in Figure 1, one is the elution volume, and the other is the equivalent polystyrene molecular weight, which was calculated from a polystyrene calibration equation obtained last quarter, or

$$\log(M_w) = -0.152V_R + 8.015 \quad (1)$$

where M_w is the equivalent polystyrene molecular weight of an asphaltene fraction with the same elution volume V_R as a polystyrene standard. Table 3 shows the molecular weight

range of the asphaltenes. From Figure 1 and Table 3 it can be seen that in our work, the equivalent polystyrene molecular weights of the coal asphaltenes (50-2000) are much smaller than those of the petroleum asphaltenes (1000-30000).

Next quarter, diffusion experiments with both petroleum and coal asphaltenes prepared this quarter will be performed. The diffusion parameters will be ascertained by fitting experimental data with a simplified mathematical model.

Table 3. Molecular Weight Distribution of Asphaltenes from SEC Analysis

asphaltenes	asphalt source	molecular weight range
petroleum	AAD-1	200-30000
petroleum	AAG-1	100-10000
petroleum	AAK-1	200-20000
coal	257 K	50-2000
coal	258 D	50-1000

1. petroleum asphaltenes from AAD-1 asphalt
2. petroleum asphaltenes from AAG-1 asphalt
3. petroleum asphaltenes from AAK-1 asphalt
4. coal asphaltenes from Run No. 257 K
5. coal asphaltenes from Run No. 258 D

Figure 1. SEC Chromatograms of Coal and Petroleum Asphaltenes