QUARTERLY PROGRESS REPORT

ON

CONFIGURATIONAL DIFFUSION OF ASPHALTENES IN FRESH AND AGED CATALYST EXTRUDATES

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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

Work this quarter consisted of preparation of a literature review in the configurational diffusion area. In addition we also ordered some materials and obtained some catalyst samples from the coal liquefaction facility at Wilsonville, AL. At this time one M.S. student is working on the project and it is planned to add 1 Ph.D. student in March. A more detailed account of the work performed during this first quarter is in the following pages.

Configurational Diffusion - A Literature Review

The diffusion of a spherical solute in an *unbounded* system with much smaller solvent molecules as compared to the solute can be described the Stokes-Einstein equation.

$$D_{\infty} = \frac{kT}{6\pi\eta r_s} \quad (1)$$

Here D_{∞} is the diffusivity in dilute bulk solution, k is the Boltzmann constant, T is temperature, η is the solvent viscosity, and r_s is the Stokes-Einstein radius of the solute, defined as the radius of a sphere of equal diffusivity. A frequent observation in the transport of the solute in a restrictive environment such as in a solution in pores is that if the molecular size of the diffusing species becomes comparable to the sizes of the pores which it diffuses through, the diffusivity of the diffusing species is reduced significantly from its value for an unbounded solution. This phenomenon is termed hindered, restricted, or configurational diffusion. One effect of hindered diffusion on reactive systems is the retardation of the reaction rate or/and a decrease in the overall conversion rate. The phenomenon of hindered diffusion can be explained in terms of the hydrodynamic drag exerted by the constrained space of a pore as well as factors that affect the equilibrium partitioning of solutes between pores and bulk solution, including steric exclusion, steric restriction and long-range intermolecular forces, which in turn influence the hydrodynamic interactions between the solutes and pore walls. During the past decade a large number of studies have led to a great deal of progress concerning the hydrodynamic motions of molecules, the effects of electrostatic interactions, the influences of molecular configuration on transport rates, and the effects of solution concentration on partitioning and diffusion coefficients. The effective diffusivity of solutes in liquids within microporous materials has been found to be less

than would be measured in unrestricted liquid media. The reduction is aggravated with increasing ratio of the molecular solute size to the average pore size. In previous studies, it was found that the effective diffusivity was strongly influenced by the ratio of molecular solute diameter to the pore diameter and adsorption coefficient. The reduction of effective diffusivity in hindered diffusion results from two factors: (1) a steric exclusion for molecules from a portion of the pore volume near the pore wall. This factor causes a reduction of the concentration from its value in the bulk phase due to an excluded volume near the pore wall. (2) a frictional drag caused by the short distance (compared with the diameter of diffusing species or pore size) between the pore wall and the diffusing molecules. More detailed reviews of these factors are presented in the following subsections.

Steric Exclusion. The concept of an equilibrium partition coefficient was first introduced by Ferry (1936, (2)) in term of a geometric exclusion effect. In a diffusion process, the molecules can not diffuse into the pore, if the distance between the pore wall and the center of the molecule is less than its radius. Therefore, an annular region near the pore wall becomes unavailable for diffusion within the pores, thus decreasing the concentration of the diffusing species within the pores. This explanation is based on the assumption of a system of rigid spherical molecules and cylindrical pores. Based on these assumptions , an equation can be derived relating the bulk phase concentration to the concentration within the pores with no pore wall-molecule interactions, viz.

$$k_p = (1 - \lambda)^2 = \frac{C}{C_b} \quad (2)$$

Here λ is the ratio of molecular to pore diameter, C is the concentration of solute inside the pores, C_b is the solution concentration in the bulk phase, and K_p is called the steric partition factor. Another equation was proposed by Satterfield et al. (1973, (3)) based on similar reasoning, when the molecular size of the solvent also is comparable to the pore diameter:

$$k_p = \frac{[1 - \lambda_{solute}]^2}{[1 - \lambda_{solvent}]^2} \quad (3)$$

In the prediction or interpretation of the partition coefficient, it is essential that consideration of particle-particle interaction is taken into account. At very low concentrations, the particles are so well isolated that only the interaction between particles and pore walls is relevant. In this case, the partition coefficient remains a constant. The range of the concentration will be extremely narrow in the presence of long-range electrostatic interaction, or particle adsorption onto the solid surface. When the concentration is increased, the partition coefficient is no longer concentration-independent and is affected by the particle-particle interaction. A variety of characteristic length scales have been proposed to describe the molecule and pore size. In the estimation of the molecule and pore size, Giddings et al. (1968, (4)) introduced two parameters to characterize molecules and pores. The sizes of the molecules can be depicted by an orientation-averaged projected length, R_m , and pores can be described by their hydraulic radius, R_h , which is equal to the ratio of pore volume to surface area, $(V/S)_p$. The ratio of R_m to $(V/S)_p$ was defined as λ . In the work of Satterfield et al. (1973, (3)), diffusivities were related to λ_c , the ratio of the radius of the smallest circular cylinder through which the molecule can pass to the mean pore radius. In the work of Baltus and Anderson (1983, (5)), diffusivities were related to λ_R , the ratio of the molecule Stokes-Einstein radius r ,

to the radius of an equal area circular pore. In the work of Chantong and Massoth (1983, (6)), diffusivities were related to λ , the ratio of the disc-like molecule radius to pore radius. The molecular radius was calculated from the bond angles and bond lengths.

If the solutes are flexible polymers, the dimensions assigned to such molecules can only be evaluated based on the statistical averages of many configurations achieved by random motion of chain segments. When the concentrations of the polymers are high enough to cause chain interaction among molecules, entanglements begin to occur, thus changing the average dimensions of the polymers.

Theoretically, the partition factor can be evaluated from equilibrium experiments with a non-adsorbing solute. Colton and Satterfield (1975, (7)) studied the diffusion and partitioning of macromolecules within finely porous glass and observed the equilibrium partition coefficients to decrease monotonically from unity for polystyrene having molecular weights from 600 to 670,000, as well as for two proteins.

The partition factors have been studied in pores of different shapes including spherical cavities (Glandt, 1981a, (8)), rectangular and elliptical cross sections (Anderson, 1981, (9)), and various regular polygons (Glandt, 1981b, (10)).

Enhanced Frictional Drag. For diffusion of a solute in porous materials, where the size of the solute is insignificant compared to the pore size, the effective diffusivity can be expressed by the following equation:

$$D_e = \frac{D_b e}{\tau} \quad (4)$$

Here D_e is the effective coefficient, D_b is the bulk diffusivity, ϵ is the porosity, and the tortuosity, τ , is a function of the pore size distribution, pore connectivity, pore shape, and degree of pore constrictions of the porous material. When the sizes of the solutes become comparable to the pore diameters, the effective diffusivity becomes less than would be expected in the unbounded fluid, and can be expressed by multiplying the effective diffusivity a restriction factor K_r ,

$$D_e = \frac{D_b \epsilon k_r}{\tau} \quad (5)$$

The restriction factor K_r is a complex function of solute and pore geometry, flow regime, etc. In order to model this complex restrictive effect, several assumptions of an idealized model are required; first, the shape of the diffusing molecule has to be considered as a rigid sphere; secondly, the pores are assumed to be cylindrical and the ratio of pore length to pore diameter is assumed to be extremely large. Even though the restriction factor is a complex function of the solute, pore geometry, and flow regime, based on the assumptions described above, several theoretical expressions have been derived to depict the enhanced frictional drag.

Pappenheimer (1953, (11)) and Renkin (1954, (12)) suggested a combination of the above two effects to account for the reduction of effective diffusion in micropores; thus the overall effect of steric exclusion and enhanced frictional drag on effective diffusivity can be expressed as follows,

$$\frac{D_e}{D_b} = k_r k_p = F(\lambda) \quad (6)$$

The equation describing the restrictive effect given by Pappenheimer and Renkin is,

$$F(\lambda) = (1-\lambda)^2 (1 - 2.1044\lambda + 2.089\lambda^2 - 0.948\lambda^5) \quad (7)$$

Here λ is the ratio of the molecular to pore diameter.

The first term on the right hand side in equation (7) represents the steric exclusion effect, and the second term represents the enhanced friction drag resulting from the confinement of the solute by the proximity of the pore walls. Some subsequent studies showed reasonable agreement with the equation, but other studies did not. For example, Beck and Schultz (1970, (12)) studied the diffusion of several solutes with diameters ranging from 0.5 to 4.3 nm in mica membranes. Their results were in close agreement with Eq.7. Satterfield et al. (1973, (3)). studied restricted diffusion in liquids within fine pores with a variety of binary systems consisting of paraffins and aromatic hydrocarbons and silica-alumina bead catalysts (pore diameter = 3.2 nm). Their results with non-adsorbing solutes did not conform to Eq.7. They proposed empirical equation to correlate the data as a function of the critical molecule diameter to pore diameter,

$$F(\lambda) = \frac{D_e \tau}{D_b e} = e^{-4.6\lambda} \quad (8)$$

Chantong and Massoth (1983, (13)) investigated restrictive diffusion in four aluminas with different pore sizes, and concluded that the effective diffusivity decreased in the order of decreasing pore size. An empirical equation was derived using a least-squares analysis according to their data,

$$\ln\left[\frac{F(\lambda)}{\tau}\right] = \ln\left(\frac{D_e}{D_b e}\right) = -4.5\lambda - 0.23 \quad (9)$$

If the tortuosity is considered a function of λ , then the equation can be rearranged to a general form,

$$F(\lambda) = \frac{D_e \tau_o}{D_b e} = 1.03 e^{-4.5\lambda} \quad (10)$$

Here τ_o is the value of tortuosity when the ratio of molecular size to pore size approaches zero.

Prasher et al. (1978, (14)) studied restrictive diffusion using two types of catalyst pellets and a variety of solute-solvent systems including aromatic, aliphatic, and olefin compounds, and their results contradicted the hydrodynamic theories. Using their data, a semiempirical relationship was derived,

$$\ln \frac{D_e K_p \tau}{D_o} = b\lambda^3 - a \quad (11)$$

The values for the constants a and b within 95% confidence were found to be

$$a = 0.0575 \pm 0.147$$

$$b = 1241.8 \pm 242.4$$

The equilibrium partition coefficient, K_p , and the hydrodynamic drag coefficient, K_r , are both functions of λ , the ratio of molecule size to pore size, while the tortuosity, τ , was taken to be independent of λ . Smith (1986, (15)) studied the relationship between the ratio of molecule size to pore size and tortuosity pointing out that the tortuosity for restricted diffusion will be changed significantly as the ratio of molecule size to pore size changes, and stated that the assumption of a constant tortuosity factor may serve to account for the frequently observed

discrepancies between experiments and the steric exclusion-hydrodynamic drag theory for restricted diffusion. When the actual tortuosity was not known, Satterfield (1980, (16)) suggested a tortuosity factor of four.

Hindered Diffusion in Reactive Systems. In the previous studies, research was conducted in non-reactive systems to avoid the complexities of the possible reaction mechanisms. In a reactive system, the effective diffusivity of the reactants is related to feedstock properties, processing conditions, and catalyst age. A problem often encountered in a reactive petroleum or coal system is the characterization of the reactants, especially the class of materials called asphaltenes. The characteristics of asphaltenes include their high molecular weight, aromaticity, polarity and heteroatoms (sulfur, nitrogen, and oxygen) and metals content. Furthermore, the constituents of asphaltenes from different sources may be different even though the solubility/extraction procedures are the same. These properties make the catalytic processing of the asphaltene difficult. Of particular interest to our research is the correlation between the effective diffusivity and catalyst support pore structure, as well as the factors that can cause changes to pore structure.

Studies concerning the upgrading of heavy crude, residues, and coal derived liquids have indicated that diffusion in catalyst pores plays an important role in a reactive system. In order to utilize the catalysts more effectively, the large, multiringed aromatic compounds must diffuse into the catalyst supports and reach the active sites at sufficiently rapid rates. Spry and Sawyer (1975, (17)) discussed the problem of steric limitation of large molecules in pores, and suggested that the molecular sizes of petroleum derived asphaltene molecules were in the range of 25 to 150 Å. In general, the micropore sizes in catalyst supports are between 20-200 Å (Froment and

Bischoff, 1979, (18)). It is obvious that most asphaltene molecules will experience hindered diffusion due to the large ratio of molecule to pore size. One possible approach to circumvent this dilemma is the introduction of macroporous, e.g., bimodal catalyst supports (Guin et al., 1991, (19)). It is believed that macroporous catalysts offer the possibility of improved performance through two avenues: (1) the macropores minimize the effects of hindered diffusion experienced by the macromolecules as they negotiate the catalyst pore structure, and (2) the accumulation of coke and metals deposits will possibly be less detrimental to catalyst activity. Results of the study of Guin and Wang (1991, (19)) indicated that most macroporous catalysts showed higher initial activity and were able to retain their activity for a longer time period, when compared to the completely microporous catalysts. This advantage, however, was offset to some extent when the two kinds of catalysts were used on an equal volume basis. Eigenson et al. (1977, (20)) observed an increasing catalytic activity of $\text{MoO}_3/\text{Alumina}$ when the catalyst pore size was increased from 70 to 150 Å. Ho and Weller (1981, (21)) observed that the conversion of coal increased as catalyst pore diameter increased from 100 to 500 Å in hydroliquefaction of coal with $\text{Co-MoO}_3/\text{Alumina}$ catalysts. However, the catalytic surface area is usually smaller for a macroporous catalyst with lower density. This compromise between high surface area and macroporosity results in an optimal catalyst pore size. Inoguchi (1977, (22)) studied desulfurization of residua and found an optimum catalyst activity with a catalyst pore size of around 100 Å.

One major contributor to the reduction in effective diffusivity is the change of pore geometry caused by the deposition of coke and metals, occurring during the reaction process. A consequence of the deposition is an increase in tortuosity and a reduction in porosity with an

associated reduction of effective diffusivity. Guin et al. (1986, (23)) investigated intraparticle diffusivity reduction during hydrotreatment of coal-derived liquid with catalysts of different aging time periods in an octane/decane solution and demonstrated that a reduction in effective diffusivity, of up to 2 orders of magnitude was observed. The reduction implied an increase in tortuosity, or a decrease in k_p , possibly resulting from pore blockage during hydrotreatment of coal-derived liquids.

Surface Diffusion. When a diffusing species is adsorbed onto the solid phase in a porous matrix, the adsorbed phase may not be stationary and the contribution to diffusion made by the adsorbed molecules can be significant compared to the total flux within the porous medium. This type of diffusion is referred to as surface diffusion. In some cases, the contribution of surface diffusion to the total flux can be substantial, even exceeding that of the pore volume diffusion. When the diffusing species is non-adsorbing, the contribution of surface diffusion disappears.

Aromatic compounds tend to be more easily adsorbed onto the surface of alumina, a common material for catalyst supports, and the magnitude of this effect increases as the number of aromatic rings in the molecule increases (Satterfield, 1973, (3)).

Neretnieks (1976b, (24)), and Sudo et al. (1978, (25)) reported a significant contribution of surface diffusion to intraparticle transport of aromatic compounds in activated carbons. It was also found that adsorption of benzaldehyde on porous Amberlite and activated carbon particles gave unreasonably high effective diffusivities (Furusawa and Smith, 1973, (26)).

Komiyama and Smith (1974, (27)) studied surface diffusion of benzaldehyde by changing the adsorption capacity of benzaldehyde from high capacity in aqueous solutions to low capacity in

methanol solutions with two porous materials, XAD-4 and XAD-7 Amberlite. The adsorption capacity in aqueous solution was about three orders of magnitude larger than that in methanol solution. The result yielded a effective diffusivity in aqueous solution about one order greater than that in the methanol solution. These results showed that surface diffusion could dominate the intraparticle mass transport in liquid-filled pores.

Track-Etched Membrane Diffusion . The track-etched membrane was first developed in 1970. The development in recent years of track-etched membranes has provided an excellent model system to examine restricted diffusion. The membrane is generally made from thin films of polycarbonate, polyester, or mica. Tracks are created first by bombarding the thin films with heavy fission fragments or radioactive materials, and pores are then created by treatment with an etching agent. The pore size can be controlled by changing the etching time, or the concentration of etching agent. The resultant pores are highly regular and resemble those described in idealized diffusion models. The track-etched membranes provide uniform and well-defined pore geometry without ambiguities, such as occur in the complex structure of catalyst supports with the possibility of interaction between diffusing species and support. Much research has been carried out with track-etched membranes with solutes of different configurations to investigate hindered diffusion, diffusional partitioning, and diffusional resistance, but these studies can not be directly applied to actual catalyst pore diffusion because of the lack of additional factors, such as pore size distribution, tortuosity, and surface area, in the idealized membranes. Diffusion in membranes has been recently reviewed by Deen (1987, (28)).

Planned Work

Next quarter it is planned to continue with the literature review and to begin the experimental measurements of diffusion coefficients. Equipment will be assembled for making these measurements and supplies will be procured. A new Ph.D. student will be added to the project.

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