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

This quarter, we measured particle densities, pore volumes and porosities for fresh, spent and regenerated catalysts by using a pycnometer method. The results are consistent with the values obtained from known literature. A coke burnoff procedure for regenerating spent catalysts was designed. By using this regeneration procedure, the physical properties of spent catalysts can be restored. For the equilibrium adsorption isotherm, we improved the experimental technique by using finer particles as adsorbent. To study configurational diffusion with larger molecules, we studied the adsorption and penetration behavior of TPP into catalyst particles. It is clearly shown that the adsorption distribution is a shell type in which the shell shrinks for longer times and finally reaches a uniform concentration distribution.

Planned Work

Next quarter we will continue the experiment for adsorption equilibrium and diffusion run for TPP with fresh catalysts. The effective diffusivity for TPP in cyclohexane with fresh catalysts will be obtained by fitting experimental data with the mathematical model. Experiments will also be done by using fresh as well as spent and regenerated catalysts. Experimental work will include both diffusional uptake and equilibrium adsorption experiments.

1. DETERMINATION OF CATALYST PHYSICAL PARAMETERS BY PYCNOMETER

METHOD

As shown in last quarterly reports, to fit the diffusion data with the mathematical model, certain catalyst physical parameters must be known. The following method was used to determine catalyst particle density, pore volume and porosity by employing a pycnometer:

The sample was vacuum dried in an oven at 100 °C for about 24 hours. The dried sample was collected and put into a calibrated pycnometer. The pycnometer was then filled with water, capped loosely with a stopper. In order for water to enter the pores of the catalyst particles effectively, this pycnometer was then placed in a vacuum oven at room temperature for about 5 hours. Then particle density, pore volume and porosity can be calculated from the following equations:

$$\rho_p = \frac{W_s}{V_s} \quad (1)$$

$$V_p = \frac{(W_{bsw} - (W_b + W_s + (V_b - V_s) \rho_w)) / \rho_w}{W_s} \quad (2)$$

$$e = \frac{V_p}{V_s} \quad (3)$$

where, ρ_p ----density of sample particle, g/cc(particle)

V_p ----pore volume, cc(pore)/g

e ----porosity, cc(pore volume)/cc(particle volume)

W_{baw} ---apparent weights of bottle plus sample and water after saturation, g

W_b ---weight of bottle, g

W_s ---weight of sample, g

V_b ---volume of bottle, cc

V_s ---bulk volume of sample(including pores), cc, obtained by measuring the lengths and the diameters of a number of cylindrical catalyst particles

ρ_w ---density of water, g/cc

The results for Criterion 324 and EXP-AO-60 fresh catalysts are listed in Table 1. The catalyst pore volumes reported by Wilsonville⁽¹⁾ are also shown in the Table. From these results it can be seen that the values obtained from pycnometer method are consistent with the reported values.

Table 1. Parameters for Criterion 324 and
EXP-AO-60 Fresh Catalysts

	Fresh Criterion 324		Fresh EXP-AO-60
ρ_p , g/cc	1.4		1.0
V_p , cc/g	0.47		0.76
ϵ , cc/cc	0.66		0.76
V_p^a , cc/g	0.48		0.78

a: Collected from (1)

Similar measurements for spent catalysts were also performed. Results are listed in Table 2. These results showed that due to the deposition of coke and metals in the pores of the catalyst, the particle density increased by about 30-40%, the pore volume decreased by about 50-70%, and the porosity decreased by about 35-60%.

Table 2. Parameters for Spent Criterion 324
and EXP-AO-60 Catalysts^a

	Spent Criterion 324		Spent EXP-AO-60
ρ_p , g/cc	1.96		1.33
V_p , cc/g	0.14		0.38
ϵ , cc/cc	0.27		0.50

a: The spent catalysts were first extracted in a Soxhlet extraction apparatus with THF for 9 days.

2. REGENERATION OF SPENT CATALYSTS

Two kinds of spent catalysts, Criterion 324 and EXP-AO-60, were used for regeneration. The spent catalysts were first extracted in Soxhlet extraction apparatus with THF for about 9 days.

It is known that the regeneration procedure for a spent catalyst is important for the restoration of both activity and mass transfer. Furimsky's results⁽²⁾ showed that for the coke burnoff of spent molybdate catalyst in air, the maximum formation of CO₂

occurred at about 450°C. The formation of SO₂ occurred at two temperatures, 250°C and 450°C. Hertan⁽³⁾ showed that for spent hydrotreating catalysts, the surface area can be fully recovered by treating the spent catalyst at 450°C for about 4.5 hours, and the chemical activity can be restored by treating at 450°C for about 20 hours. Based on the above references, the following regeneration procedures were chosen for the coke burnoff for the spent catalysts in our experiment.

The spent catalysts were put in a tubular reactor. Air was used as coke burnoff gas for the regeneration process. The regeneration temperature was used as follows: 230 °C 4 hours, 300 °C 4 hours, 400 °C 14 hours, 500 °C 30 hours. Then the temperature was decreased to room temperature. During all the regeneration procedures, the ratio of air flow rate to catalyst volume was 1000 cc(air)/cc(catalyst)/min. After these procedures, the regenerated catalysts were kept in bottle under nitrogen atmosphere in a desiccator for later use.

Table 3 lists the values of particle density, pore volume and porosity obtained from pycnometer method. Compared with the results shown in Table 1, it can be seen that by using above regeneration process, the catalyst physical properties are restored almost completely.

Table 3. Parameters for Regenerated Criterion 324
and EXP-AO-60 Catalysts

	Regenerated Criterion 324	Regenerated EXP-AO-60
ρ_p , g/cc	1.42	1.08
V_p , cc/g	0.43	0.67
ϵ , cc/cc	0.61	0.72

3. IMPROVEMENT OF ADSORPTION ISOTHERM EXPERIMENT

As shown in last quarterly reports, the equilibrium isotherms for solute/solvent/catalyst systems were obtained with 1.6 mm particle sizes. For an equilibrium experiment, it is better to use as small a particle size as possible, particularly for the bigger solute molecules due to the increased intrapore diffusional control. According to the mathematical model described before, the time for reaching equilibrium is proportional to the square of catalyst particle size, or:

$$t = \frac{\tau K_p \epsilon}{D_e} R^2 \quad (4)$$

To compare the difference between using large and fine particle sizes for the equilibrium experiments, we also did the equilibrium isotherm by using a fine particle size (-45 μm or -325 mesh). Fig. 1 shows the concentration vs. time during equilibrium experiment for fine particles. It is shown that for quinoline/

cyclohexane/fresh criterion 324 system, the equilibrium can be reached in about 20 hours. To make sure that the equilibrium is reached, we used 11 days in our equilibrium experiment. Fig. 2 compared the equilibrium isotherms obtained from large(1.6 mm) and fine(-45 μ m) particle sizes. Freundlich isotherms for these two particle sizes are shown in the following equations:

$$1.6 \text{ mm size, } q_e = 44.2 * C_e^{(1/7.94)} \quad (5)$$

$$-45 \text{ um size, } q_e = 48.8 * C_e^{(1/7.90)} \quad (6)$$

From Figure 2 we can see that the equilibrium adsorption for fine particles was slightly higher than that for large particles. This implies that the larger particles were not at equilibrium totally.

4. PENETRATION OF TPP INTO CATALYST PARTICLES

TPP is a macromolecule with black-blue color, the critical molecular size of which is 19°A. Due to the comparable size of TPP to the pore size of catalyst, say 100°A for fresh Criterion 324, the diffusion or the penetration of TPP into particle pores is more difficult compared to smaller solute molecules.

To start the diffusion experiment for TPP in cyclohexane with catalyst, we first studied the penetration behavior of TPP in particle pores. When TPP is dissolved in cyclohexane, the color of the solution is dark-red. When TPP adsorbs on the surface of catalyst, the color of the catalyst approaches black. Thus, from the color change of the catalyst particle we can see an apparent

adsorption distribution of TPP on the surface of catalyst. The result for the apparent adsorption distribution of TPP in catalyst particles is shown in Table 4. It is found that at the first stage of adsorption, TPP adsorbs with a "shell" distribution. As time goes on, this "shell" distribution shrinks to the particle center. After some time of adsorption, TPP penetrates evenly through the catalyst particle.

Table 4. Penetration of TPP in Cyclohexane into Fresh
Criterion 324 Catalyst Particles^(a), $D_p=100^\circ\text{A}$

Days of Adsorption	Color of Catalyst outer/inner
0	white/white
1	black/white
2	black/white, shrinking
5	black/white, more shrinking
6	black/pink, more shrinking
7	black/pink, more shrinking
8	black/brown, more shrinking
9	black/black

a: Conditions: initial concentration 110 ppm,
0.07 g cylindrical catalyst particles
with 2 mm length and 1.6 mm diameter,
150 cc solution in diffusion cell

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1. Technical Progress Report, Prepared for the Department of Energy under Contract No. DE-AC22-90PC90033 and Electric Power Research Institute under Contract No. RP1234-1-2 by Southern Electric International, Inc., Wilsonville, Alabama, 1991
2. E. Furimsky and Y. Yoshimura, IEC Res., 26, 657(1987)
3. P. A. Hertan, et al., Fuel Pro. Tech., 10, 121(1985)

Fig. 1 Concentration of Adsorption Solution vs. Adsorption Time for Quinoline in Cyclohexane with 35 μ m Fresh Criterion 324 Particles

Fig.2 Freundlich Adsorption Isotherm for
 Quinoline/Cyclohexane with Crit 324
 Fresh Catalyst of Different Particle
 Sizes at 30 °C

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