1 of 1

QUARTERLY PROGRESS REPORT

ON

**CONFIGURATIONAL DIFFUSION OF
ASPHALTENES IN FRESH AND
AGED CATALYST EXTRUDATES**

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**James A. Guin
A. Ray Tarrer**

**Chemical Engineering Department
Auburn University
Auburn, AL 36849**

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Table of Contents

Objective and Work Statement-----	1
Summary of Progress-----	3
Planned Work-----	3
Detailed Progress---Hindered Diffusion Studies Using Polystyrene/Cyclohexane/Alumina System	
Introduction-----	4
Materials-----	4
Polystyrene/Cyclohexane Solutions-----	4
Alumina Extrudates-----	7
Procedures-----	9
Results and Discussion-----	9
Adsorption Isotherms-----	9
Conclusions-----	12
References-----	13

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 past quarter experiments utilizing narrow molecular weight polystyrenes and alumina extrudates made in the lab were carried out. The Freundlich and Langmuir constants for the adsorption equilibrium isotherms were determined for these materials. Typically, a Langmuir isotherm was a slightly better fit for the data. The results follow the expected trend and may be used to predict the adsorption isotherm for any polystyrene and alumina combination.

Planned Work

Diffusional uptake experiments will be conducted next quarter using the polystyrene/alumina system to determine effective diffusivities for specific ratios of molecule radius to pore radius. Experiments using binary or multiple solute systems will be used as well. In addition, a diffusional model in which the pore size is a function of radial position and time will be developed.

HINDERED DIFFUSION STUDIES USING POLYSTYRENE/CYCLOHEXANE/ALUMINA SYSTEM

INTRODUCTION

In order to more fully understand the relationship between diffusing molecule size, pore size, and diffusion, experiments utilizing polystyrene were undertaken in the past quarter. Polystyrene is useful for the study because it is available in a large range of molecular weights (sizes) and molecular weight distributions. Often polystyrene is used as a standard in gel permeation and size exclusion chromatography. Hence, it is readily obtained with narrow molecular weight distributions (polydispersity index = $M_w/M_n \approx 1$). Polystyrene has been used by Bishop et al. (89,86), Colton et al. (75), Guo et al. (90), and Satterfield et al. (73) to analyze restricted diffusion in porous glass. To this author's knowledge, the diffusion of polystyrene in alumina extrudates has not yet been studied. The primary focus of these studies is to further the understanding of the connection of the effective diffusivity in relation to a wide range of molecule and catalyst pore sizes found in the hydroprocessing of coal. This is made possible by the recent use of narrow molecular weight polystyrenes in diffusion studies and the ability to produce catalyst structures of desired qualities in the laboratory.

MATERIALS

Polystyrene/Cyclohexane Solutions

Cyclohexane was chosen as the solvent for several reasons. The primary reason is that cyclohexane is the theta solvent for the polymer at 34.5 °C and, thus, many of the parameters necessary for calculations would be readily available in the literature. In addition, the polymer must adsorb onto the

pore surface to use the diffusion model given in past quarterly reports (Guin and Tarrer 92a). Preliminary experiments in the lab showed that polystyrene adsorbed onto the surface of alumina from cyclohexane. Cyclohexane is also transparent in the UV spectra; hence, the concentration of the solution may be determined by UV spectroscopy. Smakula (34) and Meehan (46) have found that polystyrene will have the same absorption per unit weight at 262 nm, regardless of molecular weight (McGovern et al. 48). Thus, a general calibration curve was constructed using a wavelength of 262 nm.

The radius of the polystyrene in solution may be correlated to the molecular weight. From the Einstein viscosity relationship for a dilute suspension of hard spheres, the following expression may be derived (Rudin and Johnston 71; Sperling 92):

$$r_e = \left(\frac{3}{10} \frac{M_v [\eta]}{N_0 \pi} \right)^{\frac{1}{3}} \quad (1)$$

where r_e = equivalent sphere radius (cm)

M_v = the viscosity average molecular weight of the solute (g/mole)

$[\eta]$ = intrinsic viscosity (cc/g)

N_0 = Avogadro's number = 6.02×10^{23}

The well known Mark-Houwink relation for the viscosity average molecular weight of a polymer and intrinsic viscosity is

$$[\eta] = K \sqrt{M_v} a^3 \quad (2)$$

Thus, combining equations 1 and 2, the following relation for the equivalent sphere radius is

$$r_e = \left(\frac{3}{10} \frac{K}{N_0 \pi} \right)^{\frac{1}{3}} \sqrt{M_v} \quad (3)$$

For a cyclohexane/polystyrene solution at 34.5 °C, α is equal to 1 (mole/g)^{1/6} and K equal to 84.6x10⁻³ cc/g (Sperling 92; Altares et al. 64). Applying these values to equation 3, the relationship for r_e and M_v for polystyrene in cyclohexane at 34.5 °C is

$$r_e = 0.2376 \sqrt{M_v} \quad (\text{\AA}) \quad (4)$$

Equivalent sphere radii calculated with the above equation are comparable to those reported by Roovers and Toporowski (80).

To calculate the bulk molecular diffusivity D_M of a polymer in solution the Stokes-Einstein equation may be used

$$D_M = \frac{kT}{6 \pi \eta_0 r_e} \quad (\text{cm}^2/\text{s}) \quad (5)$$

where k - the Boltzman constant = 1.38x10⁻¹⁶ g cm²/molecule K s²

T - the temperature of the solution, K

η_0 - the viscosity of the solution
 = 7.5E-3 g/cm s for cyclohexane at 34.5 °C

The value r_e in cm is determined using equation 4. Rudin and Johnston (71) have shown that the Stokes-Einstein equation is accurate in predicting molecular diffusivities of polystyrene in cyclohexane.

Table I gives the physical properties of the polystyrenes used in this study. The samples were purchased from Aldrich Chemical.

Table I. Physical Properties of Polystyrenes Used in
this Study in Cyclohexane at 34.5 °C

M_w (1)	M_n (2)	M_v (3)	M_w/M_n	r_o (4) (Å)	D_H (5) (cm ² /s)
794	700	687	1.13	6.23	4.82E-6
2514	2300	2727	1.09	12.41	2.42E-6
4136	3967	4075	1.04	15.17	1.98E-6
13502	12910	12860	1.05	26.94	1.11E-6
24670	23750	24150	1.04	36.92	8.13E-7
47950	45550	45730	1.05	50.81	5.91E-7
207750	198250	184200	1.05	101.91	2.94E-7
649400	617600	641340	1.05	190.28	1.58E-7

- Notes: 1. Weight average molecular weight. Determined by Aldrich Chemical using size exclusion chromatography
2. Number average molecular weight. Determined by Aldrich Chemical using size exclusion chromatography
3. Viscosity average molecular weight. Determined by Aldrich Chemical using intrinsic viscosity testing
4. Estimated using equation 4
5. Estimated using equation 5

Alumina Extrudates

Rhee (89, 93) and Tischer (81) have developed methods for making Al₂O₃ catalyst supports in the laboratory. They found that the calcination temperature of the extrudates determined the pore diameters. Using their procedures, aluminas with desired pore characteristics were prepared. Basically the procedure involves fully peptizing boehmite with 5 vol% acetic acid. The mixture is then extruded and dried at room temperature. After the

extrudates have dried, they are cut into smaller lengths and calcined. Since the diffusion experiments are non-reactive, other metals were not added to the pellets. The physical characteristics of these aluminas are given in Tables II and III.

Table II. Physical Characteristics of the Prepared Alumina Extrudates Used in this Study

Alumina Name	Pore Volume	Surface Area	Density		ϵ	Avg Pore Radius
	(1) (cc/g)	(2) (m ² /g)	ρ_p (3) (g/cc)	ρ_t (1)		(4) (Å)
580A	0.52	211	1.27	3.77	0.66	49
1000B	0.47	103	1.40	4.04	0.65	90
1083X	0.33	44	1.69	3.88	0.56	149
1083-10H	0.32	15	1.77	4.09	0.56	423

- Notes: 1. Determined by water displacement
2. Determined by single point BET/nitrogen adsorption
3. Determined using a micrometer caliper and weight measurement
4. Estimated assuming cylindrical pores

Table III. Dimensions of Prepared Alumina Extrudates Used in this Study

Alumina Name	Average Pellet Length (1) (mm)	Average Pellet Diameter (1) (mm)	Average L/D (1)	Equiv. Sphere Radius (mm)
580A	3.46±0.31	2.29±0.04	1.51±0.14	1.29
1000B	3.24±0.39	2.14±0.12	1.51±0.24	1.21
1083X	3.13±0.59	2.03±0.08	1.54±0.34	1.15
1083-10H	2.99±0.51	1.97±0.04	1.52±0.27	1.11

Notes: 1. Average of ten samples $\pm$ the population standard deviation

EXPERIMENTAL

As explained in past quarterly reports (Guin and Tarrer 92b, 93), to determined the effective diffusivity of a system two types of experiments need to be conducted: adsorption equilibrium and diffusional runs. In this quarter, adsorption equilibrium experiments using polystyrene and the prepared aluminas were conducted. The experiments were performed in the identical manner as in earlier reports except that they were run at 34.5 °C and the UV absorbance was measured at 262 nm. Next quarter diffusional uptake experiments will be carried out.

RESULTS AND DISCUSSION

Adsorption Isotherms

The adsorption may be described by a Langmuir or Freundlich equilibrium isotherm. The equilibrium adsorption isotherm equations respectively are

$$q_e = \frac{q_m m_L C_e}{1 + m_L C_e} \quad (6)$$

and

$$q_e = m_F C_e^{\frac{1}{n}} \quad (7)$$

where q_e - the mass of solute A adsorbed per mass of alumina (mg A/g)

C_e - the equilibrium concentration of solute A (mg A/cc)

The parameters q_m , m_L , m_F , and n are constants dependent on the adsorption system.

Adsorption equilibrium experiments were carried out as described in earlier reports (Guin and Tarrer 92b, 93) using selected polystyrenes and prepared aluminas. The adsorption isotherms were determined at 34.5 °C. Figures 1 through 4 and illustrate the experimental data and the Langmuir and Freundlich fits. Constants for the fits are given in Table IV.

Table IV. Experimentally Determined Langmuir and Freundlich Adsorption Isotherm Constants

Polystyrene M_w	Alumina Name	λ	Langmuir		Freundlich	
			q_m	m_L	m_F	n
649400	1083-10H	0.45	37	1049	41	19
207750	1083-10H	0.24	30	2697	32	50
47950	1083X	0.34	56	918	56	203
24670	1083X	0.25	49	800	53	22
13502	1083X	0.18	38	206	40	19
13502	1000B	0.30	86	100	91	13
13502	580A	0.55	170	60	184	8
4135	580A	0.31	102	168	156	5
2514	1000B	0.14	51	34	55	7
794	1000B	0.07	9	369	12	4
794	580A	0.13	23	396	28	3

Since chemically the polystyrenes and aluminas used in the adsorption experiments were identical, it was expected that the adsorbance for a specific molecular weight polystyrene should be equal for any sample. Obviously, though, an alumina with a high surface area will adsorb more polymer than one with a low surface area. Thus, if the adsorbance is expressed in mg polystyrene per m^2 alumina rather than mg polystyrene per g alumina, the adsorbance for a given polystyrene should be the same for any alumina. Figure 5 illustrates this. There was no observable difference in the adsorbance (mg/m^2) amounts of polystyrene with M_w of 794 for aluminas 580A and 1000B. There was only slight difference in the adsorbance amounts (mg/m^2) of

polystyrene with M_w of 13502 for aluminas 580A, 1000B, and 1083X. It is believed the difference is related to λ (ratio of molecule radius to pore radius). The adsorbance decreased as λ increased. Since the difference between the results is small, it can be assumed that the adsorbance in mg/m^2 for a given molecular weight polystyrene will be the same for all aluminas. Hence, the Langmuir and Freundlich constants for a given polystyrene may be estimated for any alumina from one adsorption fit.

The amount of adsorbance of a polymer is greatly dependent on its size (Sperling 91; Takahashi et al. 80). The entire length of low molecular weight polymers will adsorb to the surface. Whereas, only parts of the chain will adsorb onto the surface for a high molecular weight polymer due to coiling of the chain in solution. Thus, a larger mass of polymer will adsorb to a surface for a larger molecular weight polymer. Figures 6 and 7, plotting adsorbance in mg/m^2 , show that this is true. If the adsorbance in mg/m^2 is plotted versus the natural log of M_w , a straight line will form. This is shown in Figure 8.

CONCLUSIONS

Based upon the above work, the following conclusions can be drawn:

1. The equilibrium adsorption isotherm of polystyrene in cyclohexane with alumina may be described well by a Langmuir or Freundlich isotherm. A Langmuir isotherm fit the data slightly better.
2. The adsorbance of a polystyrene with a given molecular weight will adsorb the same amount in mg/m^2 for any alumina sample.

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Figure 1. Adsorption Isotherms for Various Polystyrenes in Cyclohexane with Alumina 1083-10H (34.5 °C)

Figure 2. Adsorption Isotherms for Various Polystyrenes in Cyclohexane with Alumina 1083X (34.5 °C)

Figure 3. Adsorption Isotherms for Various Polystyrenes in Cyclohexane with Alumina 1000B (34.5 °C)

Figure 4. Adsorption Isotherms for Various Polystyrenes in Cyclohexane with Alumina 580A (34.5 °C)

Figure 5. Effect of Lambda on the Adsorption Isotherm of Polystyrenes with M_v of 794 and 13502 in Cyclohexane with Alumina (34.5 °C)

Figure 6. Adsorption Isotherms for Polystyrenes of M_v between 24670 and 649400 in Cyclohexane with Alumina using Surface Area Basis (34.5 °C)

Figure 7. Adsorption Isotherms for Polystyrenes of M_w between 794 and 13502 in Cyclohexane with Alumina using Surface Area Basis (34.5 °C)

Figure 8. Adsorbance at an Equilibrium Polystyrene Concentration of 0.3 mg/cc versus M_w (34.5°C)

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