

**TITLE:** HINDERED DIFFUSION OF ASPHALTENES  
AT ELEVATED TEMPERATURE AND PRESSURE

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### ABSTRACT

**OBJECTIVE:** Our overall project objective is to obtain fundamental information on the diffusion of coal and petroleum asphaltenes, as well as some model compounds, into catalyst pores at evaluated temperatures and pressures. To achieve this objective we are performing asphaltene diffusion experiments under nonreactive conditions, but at higher temperatures and pressures than normally used in diffusion experiments typically conducted near ambient conditions. In the study we are examining the effects of variables such as asphaltene concentrations, solvent type, and porous media properties on the intrapore diffusion rate. A mathematical model is used to simulate the results of the diffusion experiments by fitting parameters with experimental data.

**ACCOMPLISHMENTS TO DATE:** This past year, adsorptive uptake experiments were performed for the diffusion of quinoline in different solvents including cyclohexane and mineral oil onto alumina at different temperatures. Also uptake experiments were performed for the diffusion of quinoline in solvent mixtures of mineral oil and 1-methylnaphthalene in order to study the effect of solvent composition on the diffusion-adsorption process. The effect of aromaticity on the diffusion-adsorption process was also studied during this time period. A mathematical model with a linear adsorption isotherm incorporating the diffusion and adsorption mechanisms operating in the uptake process was developed and applied to simulate the experimental adsorptive uptake data. Some of the model parameters for the diffusion-adsorption uptake process were obtained from literature and others were obtained by comparing the experimental data with the model simulation. Experiments were performed in a wide range of temperatures, viz. 25 – 350°C. It was found that the effective diffusivity of quinoline increased and the adsorption constant decreased with increases in temperature. The logarithm of the adsorption constant was found to be linearly dependent on the temperature. This dependence was in agreement with the diffusion-adsorption results obtained by Yang (1997), a former PhD student supported on this project. Also equations were developed to estimate parameters including equilibrium concentrations and time taken to achieve a given percentage of the

equilibrium adsorption. Studies with mixed solvents involving the adsorptive uptake of quinoline in a mixture of mineral oil and 1-methylnaphthalene showed that the effective diffusivity of quinoline increased and the adsorption constant decreased with increases in the percentage of 1-methylnaphthalene. The logarithm of the adsorption constant was found to be linearly dependent on the mole fraction of 1-methylnaphthalene. The aromaticity factor which is defined to be the ratio of the number of aromatic carbons to the total number of carbons in the system was related to the adsorption constants in that the logarithm of the adsorption constant decreased linearly with increases in the aromaticity factor.

**SIGNIFICANCE TO FOSSIL ENERGY PROGRAMS:** Asphaltene diffusion into the pores of heterogeneous catalysts is an important facet of catalytic upgrading of heavy petroleum and coal liquids. Because of the comparable sizes of asphaltene molecules and catalyst pores, the effectiveness factors in the catalyst pellets can be significantly less than unity. Our project seeks to determine through estimation and mathematical modeling of experimental data how certain factors such as temperature, concentration, and solvent environment impact the diffusion rate of asphaltene molecules into catalyst pores. This information will be useful in the modeling of chemical reactions involving such species in heterogeneous, as well as catalyst and reactor design

**PLANS FOR THE COMING YEAR:** Our plans for the coming year are to utilize catalysts with varying pore sizes to explore the diffusion behavior of asphaltenes at higher temperatures. Recent work (C&E News, March 29, 1999, pp.25-27) at DOE's Argonne Labs has shown the importance of catalyst pore size as it relates to the diffusion of asphaltenes at various temperatures. Appropriate mathematical modeling will be applied to simulate the adsorptive uptake processes in order to model the effects of the adsorption and diffusion parameters on the overall process, especially as a function of temperature.

## **ARTICLES, PRESENTATIONS AND STUDENT SUPPORT**

### **Journal Articles (peer reviewed)**

- Yang, X. and Guin, J. A. "Diffusion-Controlled Adsorptive Uptake of Coal and Petroleum Asphaltenes into A NiMo/Alumina Hydrotreating Catalyst" *Chemical Engineering Communications*. 166 (1998), 57-79.

### **Theses and Dissertations**

- X. Yang, PhD Dissertation, Chemical Engineering, Auburn University, 1997.
- S. Vadlamani, M. S. Thesis, Chemical Engineering, Auburn University, 1999.

### **Students Supported under this Grant**

Xiaofeng Yang, Ph.D. Graduate Student in Chemical Engineering  
Rob Geelen, undergraduate in Chemical Engineering  
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Surya Vadlamani, M. S. Candidate in Chemical Engineering