HINDERED DIFFUSION OF ASPHALTENES AT EVALUATED TEMPERATURE AND PRESSURE

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Table of Contents

<u>Disclaimer</u>	2
<u>Abstract</u>	3
<u>Objectives</u>	3
<u>Executive Summary</u>	4
<u>Introduction</u>	5
<u>Experimental Section</u>	6
1. Materials	6
2. Apparatus and Procedures	6
<u>Results and Discussion</u>	7
1. Development of Autoclave Operation Procedures	7
2. System Reproducibility and Mass Transfer Effects	13
<u>Conclusion</u>	17
<u>Planned Work</u>	17

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Abstract

During this time period, the high temperature/high pressure autoclave, received from Parr Instrument Company, has been set up and checked out. A detailed autoclave operation procedure was developed and implemented. The system reproducibility was verified by performing several runs for the uptake of quinoline in mineral oil onto Al_2O_3 , indicating that the system is reproducible, with an error of less than 10%. The effect of external mass transfer was studied by the uptake of quinoline in mineral oil onto Al_2O_3 at different stirring speeds, varying from 100 rpm to 800 rpm. The results showed that when the stirring speed was greater than 100 rpm, the effect of external mass transfer was negligible.

Objectives

1. To investigate the hindered diffusion of coal and petroleum asphaltenes in the pores of catalyst particles at elevated temperature and pressures.
2. To examine the effects of concentration, temperature, solvent type, and pressure on the intraparticle diffusivity of asphaltenes.

Executive Summary

During this time period the high pressure/temperature autoclave from the Parr Instrument Company was received and set up. The autoclave is equipped with a sampling tube for time-concentration data collection, and a rotating basket for catalyst containment. To assure safety and reproducibility of the experiments, a detailed procedure was developed for the operation and data collection. During the setup procedures, the magnetic drive motor failed and necessitated replacement. All autoclave functions are now operational.

To test the reproducibility and mass transfer characteristics of the autoclave diffusion system, a series of runs was made in which the adsorptive uptake of the model compound quinoline from a mineral oil solvent onto an alumina catalyst was studied. The data were satisfactory and showed little influence of external mass transfer effects. During the next time period, it is planned to examine the diffusional uptake of model compounds and asphaltenes at elevated temperatures.

Introduction

The extensive coal reserves of the United States offer excellent future potential for the production of transportation fuels (jet, diesel, and gasoline), as well as chemical feedstocks through various technologies, including the direct liquefaction of coal by high pressure hydrogenation. Primary liquids from such direct coal liquefaction processes are high boiling mixtures containing a class of high molecular weight macromolecules, operationally referred to as asphaltenes. Closely related macromolecular asphaltene moieties also occur in the petroleum industry, where, as a result of a dwindling supply of lighter boiling crude oils, it has become necessary to facilitate the conversion of heavier residua to obtain products in the transportation fuels range. The residua typically contain up to 30 wt% of a benzene soluble, pentane insoluble fraction generically termed asphaltenes. The exact chemical nature of both coal and petroleum derived asphaltenes is still an open question; however, they are believed to consist of relatively large micellar structures held together loosely by weak forces such as van der Waals and hydrogen bonds.

In order to obtain high value end-use products, such as the aforementioned transportation fuels, it is necessary to catalytically upgrade the primary products to remove heteroatoms (O, S, N), and reduce the molecular weight prior to downstream processing operations such as reforming. The catalytic hydroprocessing operations typically are effected over metal sulfide catalysts supported on a porous support, e. g., NiMo, CoMo, or NiW on Al₂O₃. Because of the large sizes of the macromolecular asphaltene moieties as compared to the catalyst pore sizes, these reactions are significantly limited by intraparticle pore diffusion. In an attempt to minimize

the limitations due to diffusional processes, various catalyst pellet shapes, e. g. trilobe vs. cylindrical, etc. and various pore size modifications, e. g., bimodal vs. unimodal, have been utilized. However, because of a lack of fundamental understanding of the over all asphaltene diffusion mechanism, the relative merits of these various catalyst modifications are often unclear and contradictory results are sometimes obtained. With this in mind, the objective of the research proposed herein is to obtain a better fundamental understanding of asphaltene intrapore diffusion as it applies to catalytic hydroprocessing, with the long range goal of aiding in the design of improved catalysts for the processing of macromolecular feedstocks.

Experimental Section

1. Materials

In uptake experiments, mineral oil (Humco) and quinoline (Aldrich) were used as solvent and solute, respectively. A commercial alumina catalyst (Johnson Mathey), with a surface area of 100 m²/g and particle size of 3.40 nm in diameter, was used as the adsorption-diffusion medium. The original alumina was washed with water to remove fine particles and dust, and then dried in an oven at 120 °C overnight. The alumina was dried again in a muffle furnace at 200 °C for 4 hours and at 400 °C for 12 hours. The dried Al₂O₃ was kept in a sealed bottle under N₂ for later use.

2. Apparatus and Procedures

The uptake of quinoline in mineral oil onto alumina was carried out in the Parr autoclave.

Detailed autoclave operation procedures will be shown in the following section. In general terms, the solute uptake rate depends on the intrapore diffusivity and the equilibrium adsorption isotherm. Blank experiments without catalysts (alumina) showed that there was no adsorption and the compounds were stable.

During each adsorptive diffusion run, the quinoline uptake rate was monitored periodically by taking samples from the autoclave and analyzed via UV spectrophotometry at 272 nm. Before UV analysis, each sample was filtered through a 5 μm filter.

Results and Discussion

1. Development of Autoclave Operation Procedures

In this time period, the autoclave reactor, received from Parr Instrument Company, was set up and tested. Figure 1 shows the schematic diagram of the autoclave. In order to properly and safely operate the autoclave reactor and accurately perform experiments, a detailed operation procedure was developed, as is given:

- (1). Catalyst Loading. Charge 50 ml of 3 mm glass beads in the sample basket. Load catalyst sample (10.0g, 3.40 nm in diameter) into the basket, then tighten the basket cover. Place the loaded sample basket on the head of the autoclave, and screw the head bolts on using a torque wrench.

Figure 1. Autoclave Flow diagram

V: valve, TV: 3-way valve, QC: quick-connect, IC: injection cylinder, FF: feed funnel
M: motor, R&C: record and control, T: thermocouple, P: pressure transducer.

- (2). Leak Testing. Close valves V4, V5, open V3, switch 3-way valve (TV) to N₂. Open V2 and set the N₂ gas pressure to 100 psi by adjusting the N₂ output valve V1. Pressurize the system to 100 psi. Close V2 and watch for any pressure decrease (leak test) on the display for ~30 min.
- (3). Cooling Water. Connect cooling water to the cooling jackets of the magnetic stirring device and the pressure transducer. This will prevent the magnetic stirring device and the pressure transducer from overheating due to conduction from the autoclave.
- (4). In-Situ Catalyst Drying. Open V5 and V2, adjust V1 to set the N₂ flow rate to be ~1000 ml/min. Increase autoclave temperature to 150 °C, which takes several hours. Dry the catalyst sample *In-situ* at 150 °C for 3 hours. Cool down the system overnight to room temperature (still with N₂ purging).
- (5). Solvent Charging. Close V2, switch TV to FF (feed funnel). At room temperature, pour 650 ml of solvent into FF, and let the solvent flow into the autoclave through the injection cylinder (IC) by gravity.
- (6). System Purging. Switch TV to N₂. Close V5, open V2. Pressurize the system with N₂ to 100 psi. Open V5 and vent gas to hood to eliminate moisture and air. Repeat the purging process for 5 times. Then close V5 and adjust the pressure to 50 psi. Close V3.
- (7). Catalyst Pore Filling. Turn on stirring to 500 rpm. Wait at least 2 hours to let the solvent completely fill catalyst pores, during which time the temperature is increased to the value required for the experiment.
- (8). IC Charging/Purging. Close V2, and switch TV to FF to depressurize IC. Disconnect

quick connect QC1. Pour a precalculated concentrated solution of 50 ml into IC by using a small funnel, and then connect QC1. Switch TV to N₂, and pressurize IC to 100 psi. Purge IC to remove moisture and air by switching TV to FF. Repeat the purging process 5 times. Switch TV to N₂, and pressurize IC to 50 psi above the autoclave pressure, then close V2.

- (9). Solute Injection. Turn off stirring. Open V3. The concentrated solution (50ml) in IC is injected into the autoclave due to the pressure difference. Wait 30 seconds to let the concentrated solution in IC completely flow into the autoclave. Then close V3.
- (10). Solution Sampling. Start stirring at 500 rpm for 1 min. Open V4 and take a sample of solution at t=0. In taking the sample, purge the first 5 ml of solution, and collect the next 5 ml of solution for analysis, then close V4. Take additional samples at later different time intervals as needed for the experiment duration.
- (11). System Cooling. After finishing the experiment, turn off the main power to let the temperature cool down to room temperature, which takes several hours.

It should be pointed out here that for taking samples at step (10), in order to get the true solution composition inside the autoclave, the residual liquid holdup left in the sampling tube (i.e., the tube containing V4 in the diagram Figure 1) from the previous sampling must be purged away using the liquid inside the autoclave. To measure the minimum liquid volume required for purging the sampling tube, an experiment without catalyst was performed. In this experiment, solvent (mineral oil) was first loaded into the autoclave, and the system was pressurized. The sampling tube was flushed with the solvent by opening V4, and then closing V4. At this stage, the

sampling tube is filled with pure solvent. Then solute (quinoline) was injected into the autoclave through IC. After stirring for 3 min, 5 samples, each with 5 ml, were taken and analyzed via UV. Figure 2 shows the UV absorbance vs. the number of sample taken during this experiment. It can be seen that the UV absorbances, or the concentrations, of the 2nd, 3rd, 4th and 5th samples are the same, indicating that after flushing the sampling tube with 5 ml of liquid solution from the autoclave, the sample truly represents the solution inside the autoclave. This is reasonable because the holdup volume of the sampling tube was measured to be 3 ml.

After finishing an experiment, the system must be carefully cleansed. To do this, the following cleansing procedures were developed.

- (1). Liquid Discharging. Discharge the liquid inside the autoclave into a waste bottle by opening V4. It is anticipated that after the system is discharged, the liquid left in the autoclave will be less than 2 ml.
- (2). Alcohol Washing. Switch TV to FF and open V5. Pour 100 ml of alcohol into the autoclave. Close V5 and switch TV back to N₂. Purge the liquid (left after system discharging, about 2 ml) and the alcohol into the waste bottle.
- (3). Water Washing. Open V5 and switch TV to FF. Pour ~900 ml of hot soapy water into the autoclave through FF, then close V5. Start stirring at ~500 rpm for 3 min, then turn off stirring. Switch TV to N₂, open V4, and purge out the soapy water. Wash the system again with hot plain water for two times. Switch TV to FF.
- (4). Parts Cleansing. Disassemble the autoclave. Clean autoclave body, head, and sample basket with soapy/plain water and rinse them with alcohol. Let the disassembled parts dry at room temperature in the hood.

Figure 2. Effect of sampling tube purging on the UV absorbances of samples

2. *System Reproducibility and Mass Transfer Effects*

In order to analyze the concentration of quinoline in mineral oil using UV spectrophotometry, a calibration curve was first obtained, with the results being shown in Figure 3. It can be seen that this curve is a good straight line through origin, with Beer's Law being expressed as,

$$C = 0.0365 A$$

where, C is the sample concentration, and A is the UV absorbance at 272 nm.

The reproducibility of the autoclave experiments were studied by performing 5 runs at the same conditions, in which the uptake of quinoline in mineral oil onto an alumina catalyst was employed. The results are shown in Figure 4, indicating that the system is reproducible, with an error of less than 10%.

For a diffusion bath system, if external mass transfer resistance exists, then this effect should be included as an additional term in the mass transfer model. On the other hand, if the external mass transfer is not significant, then the mathematical model can be simplified. Generally, the external mass transfer effect can be minimized or eliminated by increasing the stirring speed. To locate the minimum stirring speed at which the external mass transfer was negligible, several experiments at different stirring speeds, varying from 100 to 800, were performed for the uptake of quinoline in mineral oil onto the alumina catalyst, with the results being shown in Figure 5. It can be seen that as stirring speed changes from 100 rpm to 800 rpm, the uptakes for this particular system are about the same, with an error of less than 10%. This indicates that as long as the stirring speed is greater than 100 rpm, the external mass transfer is negligible. To assure the mass transfer resistance is eliminated, we used 500 rpm speed in our uptake experiments.

Figure 3. UV Calibration Curves for Quinoline/Mineral Oil System

Figure 4. Reproducibility of uptake experiments in autoclave reactor.

Figure 5. Effect of stirring speed on uptake rates in autoclave reactor.

Conclusion

The high temperature/high pressure autoclave, received from Parr Instrument Company, has been set up and checked out, and a detailed autoclave operation procedure was developed and implemented. Uptake experiments of quinoline in mineral oil onto Al_2O_3 at the same conditions showed that the system is reproducible, with an error of less than 10%. Uptake experiments at different stirring speeds, varying from 100 rpm to 800 rpm, showed that at stirring speeds larger than 100 rpm, the effect of external mass transfer was negligible.

Planned Work

During the next period we plan to further investigate diffusion and adsorption of model compounds and asphaltenes at higher temperatures and pressures in the autoclave reactor. Some preliminary runs have already been conducted at temperatures up to 90 °C and these results will be confirmed and reported in the next period. 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.