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FISCHER TROPSCH SYNTHESIS IN SUPERCRITICAL FLUIDS

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QUARTERLY TECHNICAL PROGRESS REPORT

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I. Objectives for the Fourth Quarter, Year 1:

A. Diffusion Coefficients of F-T Products in Supercritical Fluids

Our objectives for the fourth quarter on diffusion coefficient measurements were (1) to determine the optimal wavelength for olefins in the UV range; (2) make the necessary modifications to the Taylor dispersion apparatus; and (3) start measuring the diffusion coefficients of various olefins in supercritical propane.

B. Fischer Tropsch Reactor Assembly

Our objectives for the fourth quarter on Fischer-Tropsch reaction related studies were (1) to complete the safety report for the experimental apparatus and submit it for approval; (2) to select the solvent and the catalyst for sulfur removal from the supercritical fluid of choice; (3) to install and test the temperature probe and the flammable gas detector; (4) to run Fischer-Tropsch experiments at standard conditions (250°C, 200 psig, H₂/CO ratio of 0.7) in order to test the newly designed fixed bed reactor assembly.

II. Accomplishments and Problems, Fourth Quarter, Year 1:

A. Diffusion Coefficients of F-T Products in Supercritical Fluids

We have determined a wavelength for the detection of 1-octene in the UV spectrum. This wavelength is 215 nm and gives a reliable signal for detecting 1-octene. We ran different concentrations of a 1-octene/hexane mixture through the apparatus and integrated the area under the output signal. Hexane is not visible in the UV range we are interested in. As seen in Figs. 1 and 2, it was found that our response was linear over the entire range of concentrations, from 0-100%, corresponding to Beer's law

$$A = abc$$

where A = absorbance

a = absorptivity constant

b = path length

c = concentration

Deviations from Beer's law did not occur at high concentrations, as shown in Fig.2. The reason is believed to be the lack of a significant π electron system in 1-octene and the molecular homology of propane and octene. Thus, deviations in the π -electron system are insignificant at high concentrations.

We determined the reason for problems with the UV detector reported in the last quarterly report. Initially, we suspected sulphur compounds in the propane were causing problems with the auto-zero feature on the UV detector. After working with the manufacturer of the detector, however, we found that a part specific to the cell we are using was not installed. This part was not significant in earlier studies using different solvents but caused problems when we began propane studies.

Next, we set out to determine the optimal flow conditions in the diffusion tube in order to determine the diffusion coefficient, D_{12} . The objective was to determine flow rates at which secondary flow due to the coiling of the diffusion tube is negligible. This was done by plotting D_{12} calculated from the data at each flow rate vs. the retention time and finding the region in which D_{12} was not affected. As shown in Fig. 3, this occurred at a retention time of about 2000 s, or a flow rate of 20 ml/hr.

Fig. 4 compares the voltage output from the detector (the data points) to the fitted equation to extract the diffusion coefficient. It should be noted that the output is Gaussian as expected. For purposes of clarity, only 15 data points (readings of voltage) are given in the figure, however, we typically record a reading every second, so the output is over 400 readings. This regression is the basis for determining D_{12} . As the figure shows, the data fit well to the equation giving us better than 2% accuracy.

We have measured the diffusion coefficients of octene in propane at two pressures, 800 psig and 1300 psig, reduced pressures in the range 1.29-2.1. Fig. 5 is a plot of $D_{12} / \sqrt{T(K)}$ vs. ρ , the mass-density, for 1-octene in propane. Although strictly speaking the temperatures corresponding to this density range are subcritical, the reduced temperatures are in the range 0.80 to 0.91. $D_{12} / \sqrt{T}$ varies linearly with density and does not vary appreciably with pressure. This type density dependency is observed by us

V and a linear regression extrapolated to zero. It is interesting to note that the diffusion coefficient goes to zero at a molar volume of 60 cc/mole which corresponds to the close-packed hard spheres volume of propane and is within 5% of the volume calculated from the literature. This indicates that the data are theoretically sound as well.

B. Fischer Tropsch Reactor Assembly

The progress in this area had been hampered by the fact that the graduate student working on this project was on an extended leave of absence without pay during the past quarter, except for a two week period, for personal reasons and withdrew from the University in September.

During this quarter we have tested and calibrated six thermocouples of the temperature probe assembly. We obtained additional information on potential supercritical fluids from several vendors. we found out that all three potential supercritical solvents (propane, butane, and hexane) have less than 1 ppm sulfur impurities, whereas the maximum amount of sulfur in the feed should be less than 0.05 ppm. This remains to be a potential problem, since high levels of sulfur in the feed will result in catalyst poisoning. However, this would be the case with all three potential solvents, and thus we have decided to use propane as the supercritical fluid in our reaction studies based on its cost and favorable supercritical properties. In our shake down tests we will not use a catalyst guard bed for sulfur removal. If we experience problems with catalyst deactivation due to sulfur in feed, the guard bed will be installed in the propane feed line.

III. Plans for the First Quarter, Year 2.

A. Diffusion Coefficients of F-T Products in Supercritical Fluids

We have ordered 1-tetradecene and will begin measuring diffusion coefficients of this compound in subcritical propane. We have not measured coefficients in the supercritical region because of limitations in the apparatus. The water bath in which the diffusion coil is placed will necessitate changes. The critical temperature of propane is 96.8°C and we can not

use the water bath for heating to such temperatures since water will boil off. Therefore, we need to use other heat transfer fluids which will require installation of a vent hood over the bath to allow use of fluids with higher boiling points. Before proceeding with that, we are planning to use ethane as a solvent because of its lower critical temperature. Table 1 shows the various properties of the solvents we are interested in. We will study the diffusion coefficients on either side of the critical temperature in ethane and if significant changes in the coefficients are not observed, extrapolate this data to propane for initial feasibility evaluations.

Table 1: Critical Properties of Various Solvents

	Ethane	Propane	Butane
T _c (C)	32.2	96.8	152.0
P _c (psia)	708.3	617.2	551.1
T _r (our range)	0.98 - 1.1	0.80 - 0.91	0.70 - 0.80
P _r (our range)	1.1 - 1.8	1.29 - 2.1	1.5 - 2.4

B. Fischer Tropsch Reactor Assembly

Since Mr. Joshi, the graduate student working on the project, left the University, for the short term we will use a post-doctoral fellow to install and test the flammable detector and perform the shakedown run with syngas at baseline conditions and also at high pressures. Dr. Lang is a post-doctoral associate working with Dr. Bukur on development of Fischer Tropsch catalysts for about 3.5 years and he will devote a portion of his time to perform these studies.

Area vs. Concentration

Figure 1 : Area vs. Concentration curve of 1-octene in hexane at low concentrations corresponding to Beer's Law.

Area vs. Concentration

Figure 2 : Area vs. Concentration curve of 1-octene in hexane, 0-100 mole percent concentration, corresponding to Beer's Law.

Secondary Flow Effects at high flow rates

Figure 3 : The secondary effects of high flow rates on the diffusion coefficient.

Figure 4 : Fit of the data to a non-linear regression.

Diffusion Coefficient of 1-Octene in Propane

Figure 5 : Plot of $D_{12} / T(K)$ vs. ρ , the mass-density, for 1-octene in propane.

Diffusion Coefficients of 1-Octene in Propane

Figure 6 : Plot of $D_{12} / T(K)$ vs. V , the molar-volume, for 1-octene in propane. The data are extrapolated to zero.

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