

FISCHER-TROPSCH SYNTHESIS IN SUPERCRITICAL FLUIDS

QUARTERLY TECHNICAL PROGRESS REPORT

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I. Objectives for the First Quarter, Year 3:

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

Our objectives for this quarter were to measure molecular diffusion coefficients and effective diffusivities at the same conditions. This will give us the porosity over tortuosity ratio that relates molecular diffusivities to effective diffusivities. From equation (1) (Wakao and Kaguei, "Heat and Mass Transfer in Packed Beds", Gordon and Breach, New York, 1982) this value is independent of temperature and pressure, thus effective diffusivities can easily be determined from molecular diffusion coefficients without further experimentation.

$$D_{eff} = \frac{\epsilon_p}{\tau} D_m \quad (1)$$

The porosity has been determined from independent experiments. Thus the tortuosity can be determined from the previous ratio.

B. Fischer-Tropsch Reaction Related Studies

Our objectives for this quarter were to conduct two additional tests with the Ruhrchemie catalyst and a catalyst synthesized in our laboratory under supercritical conditions.

II. Accomplishments and Problems, First Quarter, Year 3

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

We previously had reported on the methodology to extract molecular diffusion coefficients from experimental data in Taylor dispersion. However, since we are now analyzing data in the

temperature range of 500 - 600 K, we needed to determine whether or not the method was viable. Once again the apparatus was modified so that molecular diffusion coefficients could be measured. A 15.75 m coil was installed and various valves and fittings were removed in order to eliminate any dead volume in the system which may affect the accuracy of Taylor dispersion experiments. Data were obtained at the same conditions as the effective diffusivity experiments. However, when working at high temperatures, the effluent from the Taylor dispersion column has to be cooled for UV analysis (must be cooled to 333 K from 523-543 K). Thus in data analysis, we have used the method of moments. Basically, as the stream from the Taylor dispersion tube is cooled to ambient conditions, even in a very short tubing, the density of ethane increases by about 4-7 fold, introducing a significant error. In method of moments the first and the second moment are determined from the data and new experiments are performed at the same condition with the diffusion tube removed from the system, hence determining the response of the system (minus the diffusion tube) to the pulse input. The moments are determined for system response and subtracted from the diffusion measurement moments. This would eliminate any added dispersion due to the length of tubing added for cooling purposes. Once this method was employed we completed experiments at temperatures of 523 - 543 K and pressures of 900 - 1500 psi. Results from these experiments seemed to follow the Enskog relationship as expected.

Methodology for Analysis of Experimental Data

The molecular diffusion coefficient was obtained using the method of moments as described in Alizadeh *et al.* (1980) using results of Aris (1956), Levenspiel and Smith (1957), and Pratt and Wakeham (1975). In this methodology the first and second moments of the peak (or the residence time and variance) are used to calculate the diffusion coefficient. The equations for the mean residence time and variance are (Alizadeh *et al.*, 1980):

$$t_{id} = \bar{t}_{obs} - \bar{t}_i \quad (2)$$

where:

t_{id} = corrected residence time

t_{obs} = first moment of response signal with diffusion tube

t_i = first moment of input signal without diffusion tube

Similarly,

$$\sigma_{id}^2 = \sigma_{obs}^2 - \sigma_i^2 \quad (3)$$

where:

σ_{id} = corrected variance

σ_{obs} = second moment of response signal with diffusion tube

σ_i = second moment of input signal without diffusion tube

Knowing the corrected moments allows us to calculate the molecular diffusion coefficient from the equation (Alizadeh *et al.*, 1980):

$$D_{12} = \frac{1}{2} \left(\frac{L^2}{t_{id}} (1 + 2\zeta_0) \zeta_0 - \left[\frac{L^4}{t_{id}^2} \zeta_0^2 (1 + \zeta_0^2) - \frac{4L^2 R^2}{48 t_{id}^2 (1 + 2\zeta_0)^2} \right]^{\frac{1}{2}} \right) \quad (4)$$

where:

$$\zeta_0 = \frac{2 \sigma_{id}^2 - t_{id}^2 + [t_{id}^4 + 4 t_{id}^2 \sigma_{id}^2]^{\frac{1}{2}}}{[8 t_{id}^2 - 4 \sigma_{id}^2]} \quad (5)$$

Thus by inserting equations (2), (3), and (5) into equation (4) the molecular diffusion coefficient can be determined. According to Alizadeh these results are accurate to about one percent providing that the design criterion is met. Results of the molecular diffusion experiments are included in Table 2.

B. Fischer-Tropsch Reaction Studies

Two tests were completed during the reporting period as planned. In the first test, designated as Run FA-2984, n-hexane ($T_C = 507.4$ K, $P_C = 2.97$ MPa) was employed both as a supercritical fluid (total reaction pressure of 3.89 MPa) and subcritical fluid (total reaction pressure of 2.93 MPa), to determine the effects of solvent type (propane vs. hexane) and pressure on the Ruhrchemie catalyst FT activity and selectivity. In the second test (FA-3194) we used one of the catalyst developed in our laboratory, with nominal composition 100 Fe/5 Cu/6 K/24 SiO₂. This catalyst had high activity and low selectivity to methane and gaseous hydrocarbons under normal FT synthesis conditions in a stirred tank slurry reactor test conducted during our DOE Contract DE-AC22-89PC89868. The catalyst was subjected to supercritical propane immediately after the reduction, which differs from the procedure used in previous tests where the catalyst was tested first under the normal FT baseline conditions for 2-3 days before switching to supercritical conditions. After FT testing in supercritical propane, the catalyst was also tested in supercritical hexane at a total reaction pressure of 3.41 MPa. The analysis of data from these two tests is underway, and the results will be described in the next quarterly report.

III. Plans for the Second Quarter, Year 3:

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

We will develop the algorithm for curve fitting in the real time domain to extract effective diffusivities from the data. We will also verify the results we reported on the molecular diffusion coefficients at the same conditions. This will allow us to verify the accuracy of the results and continue on with the tortuosity calculation. We will determine the tortuosity for this catalyst and thus be able to calculate effective diffusivities from molecular diffusion coefficients without dual experimentation.

B. Fischer-Tropsch Reaction Related Studies

The plan for the next quarter is to complete analysis of data from the two tests FA-3194 and FA-3434.

Table 1.

Properties of the Taylor Dispersion Apparatus

«private » Tube Inner Radius	3.81×10^{-04} m
Tube Coil Radius	0.055 m
Tube Length	15.74 m
Volume of Detector Cell	5 μ l
Cooling Tube Length	1.09 m
Connector Tube Radius	3.81×10^{-04} m
Connector Tube Length	0.781 m

Table 2.

Experimental Results

T (K)	P (psia)	Density (g/cc)	$D_{ab} * 10^{+08}$ (m ² /s)
523	900	0.04569	7.03 ± 0.246
533	900	0.04460	6.91 ± 0.24
543	900	0.04357	6.70 ± 0.278
523	1500	0.07839	4.99 ± 0.606
533	1500	0.07626	5.71 ± 0.668
543	1500	0.07428	6.29 ± 0.734