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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 Second Quarter, Year 2:

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

Our objectives for this quarter were to start working on theoretical developments for prediction of diffusion coefficients in supercritical fluids so that we have a correlation for data prediction. We were also planning to modify the apparatus so that propane and similar solvents can be studied in the supercritical and subcritical regions. In order to that we have to be able to heat the diffusion tube to temperatures in excess of 250°C. This will necessitate re-evaluation of the Taylor dispersion equipment design criteria. However, while the equipment was set to operate at lower temperatures, we decided to develop the methodology for measuring effective diffusivities of octene in subcritical propane and subcritical and supercritical ethane.

B. Fischer Tropsch Reaction Related Studies

Our objectives for this quarter were: (1). to make modifications on the reactor assembly; (2). to carry-out Fischer-Tropsch reaction experiment using propane as the supercritical solvent.

II. Accomplishments and Problems, Second Quarter, Year 2:

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

We modified the experimental apparatus to measure the effective diffusivities in the catalyst pores. Initially we were faced with many experimental problems. The UV detector is very sensitive to large pressure drops across the system and is prone to breakage if this occurs. Due to the small size of the catalyst particles, a pressure drop in the system will occur periodically. This pressure drop causes "cold flow" which breaks the view mirrors in the detector. We added an extra valve before the detector in order to isolate the detector from the system so that it does not see a large pressure drop during maintenance work, saving possible breakage and added expense. It took us some time to find a zero volume valve so that we do not add additional volume on line which will cause dispersion of the peak masking the dispersion due to diffusion. We wanted to make few measurements at conditions where we already have molecular diffusion data. The effective diffusivity is given by:

$$D_{eff} = \frac{\epsilon_p}{\tau} D_m$$

where ϵ_p is the particle porosity and τ is the tortuosity. The porosity can be determined by

independent experiments and is also specified by the catalyst manufacturer. By measuring the molecular diffusivity D_m and the effective diffusivity D_{eff} we can determine the tortuosity from the experimental data and it should be a constant independent of temperature and pressure. Thus by making experiments at varying conditions we can determine its value which is needed in any scale-up calculation. In fact, once the porosity and the tortuosity are determined accurately, since they are temperature and pressure independent parameters of the system, the only property that needs to be determined at the reaction conditions is the molecular diffusivity.

The second problem we had was adsorption on the catalyst. In measuring effective diffusivities with tracer response the dispersion (or the variance) of the eluting peak is due to adsorption, pore diffusion, film mass transfer, and axial dispersion. The second moment of the peak or the variance is given by:

$$\sigma^2 = 2 \frac{L}{u} \left[\delta_1 + \frac{D_{ax}(1 + \delta_0)^2}{u^2} \right]$$

where δ_0 and δ_1 are given by equations:

$$\delta_0 = \frac{1 - \epsilon_B}{\epsilon_B} [\epsilon_p + \rho_p K_A]$$

$$\delta_1 = \frac{1 - \epsilon_B}{\epsilon_B} \left[\frac{\rho_p K_A^2}{k_a} + (\epsilon_p + \rho_p K_A)^2 \left(\frac{1}{5 D_{eff}} + \frac{1}{k_f R} \right) \frac{R^2}{3} \right]$$

In these equations L is the bed length, u is the velocity, D_{ax} is the axial dispersion coefficient, ϵ_B and ϵ_p are the bed and particle porosities respectively, K_A is the adsorption equilibrium constant, k_a is the adsorption rate constant, R is the particle radius, and k_f is the film mass transfer coefficient. Normally the film mass transfer is not important at high enough a flow rate and in absence of adsorption the variance becomes a function of axial dispersion and effective diffusivity only. The equation reduces to:

$$\sigma^2 = 2 \frac{L}{u} \left(\frac{1 - \epsilon_B}{\epsilon_B} \frac{(\epsilon_p R)^2}{15 D_{eff}} + \frac{D_{ax}}{u^2} \left(1 + \frac{(1 - \epsilon_B) \epsilon_p}{\epsilon_B} \right)^2 \right)$$

The effective diffusivity is a pore space phenomenon and hence should be independent of the velocity. Thus by making measurements at different flow rates, from the variance data we can obtain the effective diffusivity and the velocity functional dependence of the axial dispersion coefficient.

We attempted measuring the effective diffusivities of 1-octene in sub-critical propane and observed that octene adsorbs on the catalyst. The octene peak comes out very late almost as a flat peak with a very long tail, indicating strong adsorption. Packing the reactor with glass beads gives a proper sharp peak proving that the delay in elution and the long tail we observed with the catalyst are in fact due to adsorption. The adsorption is due to the experimental conditions (308 K), low temperature which would enhance adsorption. When we heated the system to 333 K, the peak got sharper but the adsorption is still significant. We can still measure effective diffusivities by accounting for the adsorption effect by using a step input. The adsorption equilibrium constant can then be determined from the mean or the residence time of the breakthrough curve given by:

$$t_R = \frac{L}{u} (1 + \delta_0)$$

where δ_0 is defined above. However, in case of an adsorbing tracer, the variance equation has to be fitted for 4 parameters, D_{ax} , D_{eff} , k_a , and k_r . The adsorption rate constant is normally very large and the term $(\rho_p K_A^2 / k_a)$ in the variance equation can be neglected provided that K_A is not also very large. Similarly, by making experiments at high enough flow rates the effect of the film mass transfer coefficient on the dispersion can be neglected. Thus the variance can still be fitted for the remaining two parameters as explained above. But, the variance of a step input is harder to determine experimentally in comparison to that of a pulse input. Currently we are modifying the equipment both to operate at higher temperatures and to be able to use a step input.

B. Fischer Tropsch Reaction Related Studies

(1) Reactor assembly modifications

We have fabricated a new glass trap to replace the existing ambient pressure (low temperature, 0°C) trap. The new trap has fins on the inside wall to increase the heat exchange area, and it was found effective in condensing liquid products during the supercritical Fischer-Tropsch experiment conducted during this reporting period. A small trap filled with

glass-wool was also installed before the on-line gas chromatograph (GC) in order to prevent liquid condensation in the GC sampling loop. A propane bypass line was added, to enable the calibration of the liquid pump prior to the experiment.

We have received one pound of Carusorb 200 purification sorbent from the Carus Chemical Company (Ottawa, IL). Carusorb 200 is designed for removal of trace hydrogen sulfide and other sulfur compounds. About 200 g of Carusorb 200 sorbent (in 5 x 8 mesh spheres) was loaded into a purification trap for the purpose of removing sulfur contaminants in the propane stream, since sulfur compounds are known poisons for iron FT catalysts.

(2) Reaction experiment with supercritical propane

We have completed our first Fischer-Tropsch synthesis test under supercritical conditions to study the effect of supercritical fluid (propane) on catalyst activity and selectivity.

We used the Ruhrchemie LP 33/81 catalyst in this test (i.e. the same catalyst which was used in the test FA-3143 described in the previous quarterly report). The catalyst was reduced with hydrogen at 220°C, ambient pressure and a flowrate of 5,100 cc/min (which corresponds to a linear superficial velocity of 150 cm/s) for 1 h. During the middle of the reduction, the hydrogen feed flowrate decreased to about 4,000 cc/min for 20 min, due to an increase in downstream reactor pressure during the reduction. Following the reduction, the catalyst was first tested at our baseline reaction conditions of 250°C, 1.48 MPa (200 psig), 2.0 NL/g-cat/h and H₂/CO ratio of 0.67 for 92 h on stream. The catalyst activity was stable and the (H₂+CO) conversion was about 52 % (Figure 1) during this period. The H₂/CO usage ratio was about 0.66. The (H₂+CO) conversion was lower than that obtained in several of earlier tests of this catalyst. In the previous tests the (H₂+CO) conversion was about 60 % at these process conditions. Also, the catalyst produced less methane (4.0 wt %) and more C₁₂+ hydrocarbons (65 %, see Table V), in comparison to 6-8 % methane selectivity, and 50% C₁₂+ selectivity obtained in our previous tests. The subtle differences during the catalyst reduction may be responsible for the observed differences in the catalyst performance. The decrease in hydrogen flowrate during the reduction period results in lower degree of iron catalyst reduction, which in turn favors lower catalyst activity and higher selectivity of high molecular weight products.

Between 95 and 215 h on stream, the Fischer-Tropsch synthesis was carried out at 250°C, total pressure of 7 MPa (1,000 psig) with supercritical propane as the balance gas (The critical temperature and pressure of propane are 96.7°C and 4.19 MPa, respectively). Propane was pumped from a liquid propane dip tube tank using a Milton Roy miniPump (model VS).

In order to prime the pump, the pressure of the liquid propane tank was increased to about 1.15 MPa (156 psig) by heating the tank with a heating tape, and maintained at this pressure during the entire test. The syngas partial pressure and space velocity were kept at the baseline (standard) conditions, i.e., $P(\text{H}_2+\text{CO}) = 1.48 \text{ MPa}$ (200 psig). During the testing under supercritical conditions the catalyst activity was stable with time on stream (100 - 215 h) as shown in Figure 1. The (H_2+CO) and CO conversion were both about 54 %, whereas the usage ratio varied between 0.63 and 0.61.

During the supercritical Fischer-Tropsch (SFT) synthesis period, wax and liquid products were collected daily (total of five times) for better estimation of the wax/liquid production rates. Sufficient amounts of liquid products were collected in the new glass trap (at ambient pressure, and 0°C) and the problem of uncondensed liquid products carried to the on-line GC was alleviated. Three mass balances were completed during this period with satisfactory closures, and the results are summarized in Table I. Because of the presence of large quantity of propane in the feed, the amount of propane produced by FT synthesis could not be determined directly by gas chromatography. The propane production rate was estimated by assuming that the propene/propane ratio during the SFT is the same as that at the baseline conditions, and it was calculated from the measured amount of propene formed by FT reaction under the supercritical conditions. This estimated propane production rate was used in the calculation of overall hydrocarbon product distribution. During the SFT synthesis period, the methane selectivity gradually increased with time from 4.4 to 5.8 wt %, whereas the $\text{C}_{12}+$ fraction decreased from 59 to 51 wt %. The drift in hydrocarbon distribution towards lighter products could be due either to effects of supercritical fluid, or catalyst aging.

The most profound effect of the SFT operation was on the olefin selectivity and 2-olefin selectivities. Figure 2 illustrates gas chromatography traces of organic phase products, collected at the baseline conditions (top part) and the SFT synthesis conditions (bottom part). At a given carbon number, it can be seen that the relative amount of 1-olefins to normal paraffins is much higher in the bottom trace than in the top one, indicating that more 1-olefins are formed under SFT conditions. Olefin selectivity and 2-olefin selectivity as a function of carbon number are plotted in Figures 3 and 4, respectively, up to carbon number C_{15} . The three sets of data obtained under SFT conditions show excellent reproducibility of results. The results for C_3 hydrocarbons were omitted from Figure 3 when using supercritical propane, because the propane selectivity could not be determined directly as explained before. Also, the 2-olefin

selectivity data points for C_4 - C_8 hydrocarbon under SFT conditions were not included in Figure 4, because of large errors in their analysis. Clearly, under the SFT conditions, the olefin selectivity, especially those of the liquid phase hydrocarbons (C_7+) was higher and the 2-olefin selectivity was lower, in comparison with the FT synthesis at the baseline conditions (i.e., without the supercritical fluid). This observation of enhanced selectivity of the primary FT reaction products (1-olefins) under SFT conditions is in agreement with the findings of Yokota and Fujimoto (Ind. Eng. Chem. Res. 30, 95-100, 1991), who used normal hexane as the supercritical fluid. It should be noted that the increase in selectivity of 1-olefins is not the result of higher total reaction pressure, as shown in our previous test of the same catalyst (Run FA-3143). In this test nitrogen was used as the balance gas (instead of propane), and the total olefin and 2-olefin selectivities were the same as at the baseline conditions. However, the ethene selectivity did not increase during the SFT operation, instead, it decreased from 60% to about 35 % (Figure 3). A decrease in ethene selectivity, from 41% to 35 %, was also observed during the test FA-3143 when the reaction pressure was increased from 1.48 MPa (baseline conditions) to 7 MPa using nitrogen as the diluent. The reasons for lower ethene selectivity under the SFT conditions are not understood at the present time.

Propane feed was stopped after 215 h on stream and the catalyst was tested again at the baseline conditions for additional 50 h before the run was terminated at 260 h on stream. The (H_2 +CO) conversion was about 50 %, which is similar to the values obtained between 45 and 95 h on stream. The hydrocarbon product distribution was: C_1 = 5.5, C_2 - C_4 = 15.8, C_5 - C_{11} = 23.8 and $C_{12}+$ = 54.8 wt%. In comparison to the results obtained at 72 h on stream, there is a shift toward lower molecular weight hydrocarbons. This distribution is similar to that obtained at 194 h on stream, under the SFT conditions (see Table I). The olefin and 2-olefin selectivities were the same as those obtained during the initial baseline testing period (Figures 3 and 4). This again demonstrates the effect of supercritical fluid on increasing olefin and decreasing 2-olefin selectivity.

In summary, we have successfully completed our first Fischer-Tropsch synthesis test with propane as the supercritical fluid. The catalyst activity and hydrocarbon product distribution under the SFT conditions were similar to those obtained during the normal Fischer-Tropsch synthesis, however, the use of supercritical fluid resulted in higher selectivity of the primary products.

The use of a new trap with larger inside surface area, improved the collection of liquid

products and thus enabling us to achieve better atomic and overall mass balance closures. This has also improved results from on-line GC analysis. However, further improvement are needed to achieve more stable and reproducible gas phase analysis, including the capability of the on-line analysis of the feed gas (mixture of hydrogen, carbon monoxide and propane).

III. Plans for the Third Quarter, Year 2.

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

We will continue with our effective diffusivity measurements so that we can determine the particle porosity and tortuosity in order to calculate effective diffusivities from the molecular diffusivity data.

B. Fischer Tropsch Reactor Assembly

(1) to purchase a new liquid pump for future supercritical experiments. A pump temporarily available in our laboratory was used in this first run (2) to make further improvements in the on-line GC analysis procedure and reactor assembly; (3) to continue Fischer-Tropsch reaction tests using propane as the supercritical solvent with different reaction conditions and/or operating procedures; and (4) to perform a more detailed analysis of the data collected in run FA-0844.

Table I. Summary of results for fixed bed run FA-0844.

Catalyst: 3.50 g^a, Ruhrchemie LP 33/81
Catalyst volume: 5.40 cc

Diluent: 53.60 g, Glass beads
Diluent Volume: 34.60 cc

Period	1	2	3	4	5
Time on Stream (h)	72.5	120.0	171.0	194.0	238.0
Balance Duration (h)	19.5	21.0	19.0	21.5	21.0
Average Temperature (°C)	250.	250.	250.	250.	250.
Maximum Δ Temperature (°C) ^b	1.00	1.00	1.00	1.00	1.00
Pressure (MPa)	1.48	7.00	7.00	7.00	1.48
H ₂ /CO Feed Ratio	.667	.667	.667	.667	.667
Space Velocity (NI/g-cat·h) ^a	2.0	2.0	2.0	2.0	2.0
Space Velocity (NI/g-Fe·h)	3.81	3.81	3.81	3.81	3.81
GHSV (h ⁻¹) ^c	175.	175.	175.	175.	175.
CO Conversion (%)	51.6	55.8	55.3	54.1	50.1
H ₂ +CO Conversion (%)	51.5	54.7	53.4	52.3	50.5
H ₂ /CO Usage	.66	.63	.61	.61	.68
STY (mols H ₂ +CO/g-cat·h) ^a	.046	.049	.048	.047	.045
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	3.64	67.9	58.1	85.3	5.17
Weight % of Outlet					
H ₂	2.19	2.14	2.26	2.32	2.21
H ₂ O	2.71	.174	.212	.142	1.85
CO	45.5	41.9	42.5	43.9	47.0
CO ₂	35.9	40.7	40.8	40.2	35.8
Hydrocarbons	5.00	7.09	7.14	7.65	6.25
Oxygenates	.813	.200	.249	.256	.666
Wax ^d	7.90	7.75	6.77	5.45	6.28
Yield (g/Nm ³ H ₂ + CO Converted)					
CH ₄	7.94	9.43	10.8	11.6	10.9
C ₂ -C ₄ Hydrocarbons	24.7	37.3	34.8	34.1	31.4
C ₅ -C ₁₁ Hydrocarbons	37.0	41.2	43.7	49.5	47.2
C ₁₂ + Hydrocarbons	130.	126.	116.	101.	108.
Wax ^d	122.	112.	99.9	81.6	99.2
Oxygenates	12.6	2.88	3.67	3.83	10.5
Total	213.	217.	209.	200.	208.
1+2 Olefins/n-Paraffin Ratio					
C ₂	1.53	.606	.436	.477	1.26
C ₃	5.50	4.66	5.14	5.17	5.36
C ₄	4.08	3.21	2.98	3.83	3.86
C ₈	3.27	3.88	3.27	3.16	2.70
C ₁₀	2.17	2.78	3.07	2.78	2.21

^a Based on unreduced catalyst

^c Based on reactor volume

^b Maximum axial temperature difference

^d Unanalyzed products collected from hot trap

Table I (cont'd). Summary of results for fixed bed run FA-0844 .

Period	1	2	3	4	5
Weight % of Hydrocarbons					
CH ₄	3.97	4.40	5.25	5.90	5.52
Ethane	1.28	4.04	4.00	3.94	1.81
Ethylene	1.82	2.29	1.63	1.76	2.13
Propane	.814	1.16	1.09	1.16	1.04
Propylene	4.27	5.18	5.36	5.72	5.33
n-Butane	.792	1.15	1.27	1.02	1.17
1+2 Butenes	3.12	3.57	3.64	3.78	4.36
C ₄ Isomers	.260	.00102	.00109	.00121	.00859
n-Pentane	1.10	.978	1.23	1.50	1.60
1+2 Pentenes	3.01	3.20	3.62	4.82	4.77
C ₅ Isomers	.107	.00018	.00019	.00020	.136
n-Hexane	.721	.833	.824	.909	.953
1+2 Hexenes	2.45	3.08	2.97	3.15	3.37
C ₆ Isomers	.432	.467	.459	.503	.431
n-Heptane	.648	.778	.835	.820	.865
1+2 Heptenes	1.91	2.61	2.72	2.77	2.58
C ₇ Isomers	.249	.00350	.372	.422	.411
n-Octane	.493	.607	.702	.769	.695
1+2 Octenes	1.59	2.31	2.25	2.39	1.85
C ₈ Isomers	.107	.0194	.238	.313	.224
n-Nonane	.585	.593	.531	.707	.642
1+2 Nonenes	1.42	1.81	1.61	2.25	1.56
C ₉ Isomers	.161	.0489	.0513	.0686	.181
n-Decane	.551	.212	.398	.597	.579
1+2 Decenes	1.18	.582	1.20	1.64	1.26
C ₁₀ Isomers	.161	.0639	.0797	.0946	.163
n-Undecane	.536	.253	.293	.361	.498
1+2 Undecenes	.992	.680	.812	1.07	.929
C ₁₁ Isomers	.127	.0922	.105	.119	.149
C ₂ -C ₄	12.4	17.4	17.0	17.4	15.9
C ₅ -C ₁₁	18.5	19.2	21.3	25.3	23.9
C ₁₂ +	65.2	59.0	56.5	51.4	54.8
Wax ^d	61.2	52.2	48.7	41.6	50.1

^d Unanalyzed products collected from hot trap

Figure 1. Variation of (H₂+CO) conversion with time-on-stream during test FA-0844. P = 1.48 MPa at baseline condition, P (total) = 7.0 MPa (P(H₂+CO) = 1.48 MPa, P(C₃H₈) = 5.52 MPa) during FT synthesis with supercritical propane (SFT).

Figure 2. GC traces of organic phase products. (top) collected at the baseline operating conditions (TOS = 72-92 h); (bottom) at the supercritical operating conditions (TOS = 120-140 h).

Figure 3. Effect of supercritical fluid (propane) on olefin selectivity during FT synthesis.

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Figure 4. Effect of supercritical fluid on 2-olefin selectivity during FT synthesis

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