FISCHER TROPSCH SYNTHESIS IN SUPERCRITICAL FLUIDS

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QUARTERLY TECHNICAL PROGRESS REPORT

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I. Objectives for the First Quarter, Year 2:

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

Our objectives for this quarter were to measure diffusion coefficients of 1-tetradecene in subcritical propane and the diffusion coefficients of 1-octene and 1-tetradecene in subcritical and supercritical ethane. We planned to use ethane as a solvent because its lower critical temperature enabled measurements without modification of the existing unit. Our objective was to investigate the behavior of the diffusion coefficients in crossing from subcritical to supercritical conditions

B. Fischer Tropsch Reaction Related Studies

Our objectives for this quarter were: (1) to install and test the temperature probe and the flammable gas detector: (2) to conduct Fischer-Tropsch experiments at baseline conditions and at a high pressure in order to test the newly constructed fixed bed reactor assembly.

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

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

We have measured the diffusion coefficients for 1-tetradecene in propane (Figure 1). The data appear to be linear (plot of $D/\sqrt{T}$ vs density) throughout the region studied, confirming the theoretical expectation and our reported data on 1-octene diffusion in the previous quarterly. A linear extrapolation of the data zero diffusion coefficient theoretically should yield the triple volume of propane and results in a volume of 66.3 cc/mol, which is off by 9% compared to the triple point value of 60.13 cc/mol (NBS, Monograph 170). In order to obtain data using 1-tetradecene, samples injected into the Taylor Dispersion apparatus had to be diluted with sufficient solvent so that infinite dilution was achieved. Because of the more viscous nature of this solute, infinite dilution became a more critical parameter. We believe this is because the velocity profile of the solvent is more affected by the increased viscosity of the injected sample. Dilution of samples using 1-octene was not as critical and data could be reproduced using larger concentrations of injected sample. The problems occurred in the subcritical region so we do not believe that the problems were caused by a change in the critical point of the mixture. We are currently working on a correlation to predict the data by using this and earlier data.

We have also measured the diffusion coefficients for 1-octene and 1-tetradecene in ethane. Although this fluid will not be used in our studies, we wanted to study the change in the behavior of the diffusion coefficient going from sub-critical to the supercritical region at the same temperature. The data are presented in Figures 2 and 3. The supercritical transition is noted by an arrow in each figure. As can be seen from the figures, the linear relationship predicted by theory holds throughout the subcritical and supercritical region. The triple point volumes obtained by the extrapolation to zero diffusivity are 49.15 cc/mol and 45.84 cc/mol for tetradecene and octene, which are off by 7% and 6% respectively, from the reported triple point volume of 46.125 cc/mol (NBS Technical Notes 684).

B. Fischer Tropsch Reaction Related Studies

1) Temperature probe and flammable gas detector

We have installed and used the temperature probe during the shake down run for monitoring the axial temperature profile of the fixed bed reactor. One of the six thermocouples was found malfunctioning. We are planning to contact the manufacturer and correct the problem before the next test.

We have also installed and tested the flammable gas detector unit, which consists of a Sensidyne combustible gas transmitter and a Sensidyne Model 1000 single channel controller (Sensidyne Inc., Clearwater, FL), for monitoring propane vapors/gases at concentrations below its lower explosive limit (LEL). The detector was calibrated using a calibration gas containing 1.5 vol % (30 % LEL) methane obtained from Sensidyne, and was adjusted to read directly the equivalent % LEL concentration of propane (55 % LEL of propane) using a conversion factor provided by the manufacturer. The low level alarm on the controller was set at 20 % LEL of propane while the high alarm at 40 % LEL. The high alarm relay contacts were also wired to a solenoid valve installed immediately downstream of the propane tank regulator. In the case of a propane leak when its vapor concentration exceeds the 20 % LEL (0.4 vol % propane) the audible alarm on the detector will sound, and when the propane concentration exceeds the 40 % LEL (0.8 vol % propane), the relay will further activate the solenoid valve to stop the propane flow. The detector reading can be easily converted to % LEL of other gases by respective conversion factors if other supercritical solvents besides propane will be used in the future.

(2) Shake-down run

We have completed a Fischer-Tropsch reaction test during this quarter. The purpose of the experiment was mainly two fold: first, as a shake-down run to test the newly constructed fixed bed reactor assembly; and second, to study the effect of total reaction pressure on catalyst activity and selectivity.

A Ruhrchemie catalyst designated LP 33/81 (Ruhrchemie AG, Oberhausen - Holten, Germany) was used in this test. Catalyst pellets were crushed to 30-60 mesh size and diluted with glass beads of same size prior to loading into the reactor. Details of our fixed bed experimental procedures can be found in Bukur et al. (*Ind. Eng. Chem. Res.*, 1989, 28, 1130-1140). The catalyst was reduced with hydrogen at 220°C, ambient pressure and a flowrate of 5100 cc/min (which corresponds to linear superficial velocity of 150 cm/s) for 1 h. Then it was tested at baseline reaction conditions of 250°C, 200 psig, 2.0 NL/g-cat/h and H₂/CO ratio of 0.67 for the first 140 h on stream. After that, the total reaction pressure was increased to 1000 psig using nitrogen as a balance gas while keeping the syngas partial pressure and space velocity the same as at the baseline conditions (i.e., P(H₂+CO) = 200 psig, P(N₂) = 800 psig). Testing at high pressure lasted for another 145 h, followed by establishment of the baseline conditions at 288 h on stream. This test (FA-3143) was terminated voluntarily after 320 h on stream, and results from four mass balances, two each at the baseline conditions and at high reaction pressure conditions, are reported in Table 1.

Changes in catalyst activity, measured in terms of (H₂+CO) conversion, and stability with time on stream (TOS) and total reaction pressure are illustrated in Figure 4. The catalyst was fairly stable with time at the baseline conditions. The steady state values of (H₂+CO) and CO conversion were about 59 %. The H₂/CO usage ratio was similar to the feed ratio, about 0.67.

After increasing reaction pressure to 1000 psig using nitrogen (N₂) as balance gas, we had experienced some experimental problems. Due to high gas flow rate, a low pressure cold trap was unable to condense all liquid products. During the two mass balances at 1000 psig, only a small amount of organic phase products and hardly any aqueous phase products were collected in the cold trap. Consequently, the total mass balance closures for these two balances were relatively low (96.5 and 98.7%), and hydrocarbon selectivity could not be determined accurately. ncondensed liquids were carried by the tail gas stream to an on-line gas

chromatograph (Carle 400 Series) causing problems with gas analysis (introduction of additional peaks, baseline drift). The presence of large amount of nitrogen resulted in dilution of product concentrations, which also had some effect on the accuracy of gas analysis. The syngas flow rate drifted slightly from the expected value, based on a mass flowafter calibration before the test, during operation at high pressure. Problems in gas analysis and flow rate caused some fluctuations in the (H_2+CO) conversion measurements, as shown in Figure 4. Nevertheless, the average (H_2+CO) conversion was about 58 %, which is nearly the same as that at the baseline conditions. Therefore, the catalyst activity was not affected by increase in total pressure. The (H_2+CO) conversion increased to about 65 % after returning to the baseline conditions during the last part of the experiment, and the usage ratio was about 0.64 (A smaller usage ratio is indicative of higher water-gas-shift activity). We have observed similar increases of activity with TOS in our previous tests with the Ruhrchemie catalyst.

Hydrocarbon product distribution shifted gradually towards low molecular weight products with TOS. The average values from the two mass balances at the baseline conditions (TOS = 67 and 116 h) were: C_1 = 7.4 wt%, $\text{C}_2\text{-C}_4$ = 18.7, $\text{C}_5\text{-C}_{11}$ = 26.0 and $\text{C}_{12}+$ = 47.9 %. During testing at 1000 psig, with N_2 as balance gas, the selectivity of methane increased to 8.6 wt %, $\text{C}_2\text{-C}_4$ to 21.0 %, $\text{C}_5\text{-C}_{11}$ 34.9 %, whereas $\text{C}_{12}+$ selectivity decreased to 35.5 %. It should be noted that selectivity results reported here as well as in Table 1 for high pressure conditions represent values after adjustments, compensating for the loss of liquid products. Olefin selectivity and 2-olefin selectivity as a function of carbon number up to C_{15} are plotted in Figures 5 and 6, respectively. The olefin and 2-olefin selectivities were not affected by changes in total reaction pressure and remained stable with time on stream. This indicates that the increase in reaction pressure and the presence of diluent gas, while maintaining the syngas partial pressure and space velocity constant, do not have effect on the adsorption of H_2 and olefins on the catalyst surface, and diffusion rates of reactants and products inside the catalyst pores.

Methane selectivity was about 8.1 wt% after returning to the baseline conditions. The gas chromatograph used for organic products analysis was out of order at this time, therefore, hydrocarbon selectivity data for this period were not determined (TOS = 290-360 h).

In summary, the reactor assembly performed basically well according to the design. Introduction of nitrogen as a balance gas did not have effect on the catalyst activity and

selectivity under the conditions studied. To alleviate problems related to products collection encountered during operation at high pressure (i.e., at high gas flow rates) we will make a new low pressure (glass) trap with a larger heat exchange area and longer gas residence time. Also we will add another trap before the on-line GC to collect any uncondensed liquid products, in order to reduce problems with gas analysis in the presence of C_6+ liquid hydrocarbons.

III. Plans for the Second Quarter, Year 2.

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

We will start working on theoretical developments for prediction of diffusion coefficients in supercritical fluids so that we have a correlation for data prediction. We plan 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.

B. Fischer Tropsch Reactor Assembly

Our work plans for the next quarter are: (1) complete the safety report for the experimental apparatus and submit it for approval; (2) make modifications of the reactor assembly (product collection traps); (3) make the Fischer-Tropsch test with propane as a supercritical solvent.

Table 1. Summary of results for fixed bed run FA-3143 .

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

Diluent: 52.30 g, Glass beads
Diluent Volume: 34.60 cc

Period	1	2	3	4
Date	11/13/93	11/15/93	11/19/93	11/21/93
Time on Stream (h)	69.0	116.0	220.0	261.0
Balance Duration (h)	28.0	24.0	18.0	10.5
Average Temperature (°C)	250.	250.	250.	250.
Maximum Δ Temperature (°C) ^b	2.00	2.00	2.00	2.00
Pressure (MPa)	1.48	1.48	7.00	7.00
H ₂ /CO Feed Ratio	.667	.667	.667	.667
Space Velocity (Nl/g-cat·h) ^a	2.01	2.02	2.04	2.04
Space Velocity (Nl/g-Fe·h)	3.81	3.85	3.88	3.88
GHSV (h ⁻¹) ^c	175.	177.	179.	179.
CO Conversion (%)	58.9	59.8	61.3	60.6
H ₂ +CO Conversion (%)	59.5	59.8	58.0	57.2
H ₂ /CO Usage	.685	.666	.576	.572
STY (mols H ₂ +CO/g-cat·h) ^a	.053	.054	.053	.052
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	4.52	4.40	133.	111.
Weight % of Outlet				
H ₂	1.81	1.84	2.15	2.20
H ₂ O	2.41	2.63	.115	.134
CO	39.2	38.2	36.9	37.6
CO ₂	41.5	42.2	46.0	45.0
Hydrocarbons	7.88	8.43	10.7	11.6
Oxygenates	.947	.988	.280	.457
Wax ^d	6.30	5.65	3.80	3.06
Yield (g/Nm ³ H ₂ + CO Converted)				
CH ₄	13.1	14.4	17.2	17.3
C ₂ -C ₄ Hydrocarbons	33.4	36.8	42.4	41.3
C ₅ -C ₁₁ Hydrocarbons	47.0	50.2	67.9	71.2
C ₁₂ + Hydrocarbons	94.3	84.6	69.2	71.7
Wax ^d	83.4	74.6	51.5	42.0
Oxygenates	12.5	13.0	3.79	6.28
Total	200.	199.	201.	208.
1+2 Olefins/ <i>n</i> -Paraffin Ratio				
C ₂	.748	.710	.572	.575
C ₃	4.37	4.06	3.88	4.61
C ₄	3.60	3.60	4.64	4.27
C ₈	2.18	2.20	2.13	2.08
C ₁₀	1.77	1.79	1.60	1.65

^a Based on unreduced catalyst

^c Based on reactor volume

^b Maximum axial temperature difference

^d Unanalyzed products collected from hot trap

Table 1 (cont'd). Summary of results for fixed bed run FA-3143 .

Period	1	2	3	4
Weight % of Hydrocarbons				
CH ₄	6.99	7.73	8.75	8.56
Ethane	2.71	2.99	3.43	3.45
Ethylene	1.89	1.98	1.83	1.85
Propane	1.36	1.61	1.88	1.55
Propylene	5.66	6.25	6.97	6.83
n-Butane	1.28	1.45	1.36	1.33
1+2 Butenes	4.46	5.05	6.07	5.50
C ₄ Isomers	.398	.454	.00042	.00530
n-Pentane	1.68	1.92	1.87	1.71
1+2 Pentenes	4.18	4.79	6.18	5.89
C ₅ Isomers	.130	.325	.00243	.0179
n-Hexane	1.03	1.17	1.43	1.41
1+2 Hexenes	2.96	3.40	4.40	4.30
C ₆ Isomers	.796	.540	.767	.755
n-Heptane	.937	1.04	1.44	1.40
1+2 Heptenes	2.33	2.61	3.43	3.34
C ₇ Isomers	.543	.556	.799	.475
n-Octane	.905	.963	1.40	1.39
1+2 Octenes	1.94	2.08	2.92	2.85
C ₈ Isomers	.339	.375	.543	.536
n-Nonane	.859	.865	1.33	1.37
1+2 Nonenes	1.66	1.72	2.42	2.41
C ₉ Isomers	.251	.262	.120	.167
n-Decane	.786	.767	1.13	1.38
1+2 Decenes	1.37	1.35	1.78	2.25
C ₁₀ Isomers	.219	.219	.161	.210
n-Undecane	.753	.720	.934	1.19
1+2 Undecenes	1.13	1.10	1.32	1.91
C ₁₁ Isomers	.226	.206	.154	.366
C ₂ -C ₄	17.8	19.8	21.5	20.5
C ₅ -C ₁₁	25.0	27.0	34.5	35.3
C ₁₂ +	50.2	45.5	35.2	35.6
Wax ^d	44.4	40.1	26.2	20.8

^d Unanalyzed products collected from hot trap

Figure 1:
Diffusion Coefficients
of 1-tetradecene in propane

Figure 2:
Diffusion Coefficients
of 1-octene in ethane

Figure 3:
Diffusion Coefficients
of 1-tetradecene in ethane

Figure 4. Change of catalyst activity with time-on-stream and with total reaction pressure

Figure 5. Change in olefin selectivity with time-on-stream and total reaction pressure

Figure 6. Change in 2-olefin selectivity with time-on-stream and total reaction pressure

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