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FISCHER TROPSCH SYNTHESIS IN SUPERCRITICAL FLUIDS

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FINAL REPORT

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ABSTRACT

The objective of this study was to investigate Fischer-Tropsch Synthesis (FTS) in the supercritical phase employing a commercial precipitated iron catalyst. As the supercritical fluid we used propane and n-hexane. The catalyst was Ruhrchemie LP 33/81 with nominal composition of 100 Fe / 5 Cu / 4.2 K / 25 SiO_2 on mass basis and was used in a fixed bed reactor under both normal (conventional) and supercritical conditions. Experimental data were obtained at different temperatures (235°C, 250°C, and 260°C) and synthesis gas feed compositions (H_2/CO molar feed ratio of 0.67, 1.0 and 2.0) in both modes of operation under steady state conditions. We compared the performance of the precipitated iron catalyst in the supercritical phase, with the data obtained in our laboratories on the performance in gas phase (fixed bed reactor) and slurry phase (STS reactor). Comparisons were made in terms of bulk catalyst activity and various aspects of product selectivity (e.g. lumped hydrocarbon distribution and olefin content as a function of carbon number). In order to gain better understanding of the role of intraparticle mass transfer during FTS under conventional or supercritical conditions, we have measured diffusivities of representative hydrocarbon products in supercritical fluids, as well as their effective diffusion rates into the pores of catalyst at the reaction conditions. We constructed a Taylor dispersion apparatus to measure diffusion coefficients of hydrocarbon products of FTS in sub and supercritical ethane, propane, and hexane. The data were taken at a temperature range from room temperature to 260°C, and pressures of 6.0-17.0 MPa. In addition, we developed a tracer response technique to measure the effective diffusivities in the catalyst pores at the same conditions. Based on these results we have developed an equation for prediction of diffusion in supercritical fluids, which is based on the rough hard sphere theory.

Our results indicate that α-olefins and, to a smaller extent n-paraffins are the primary products of FTS. Comparison of olefin selectivities in the two modes of operation reveals that total olefin selectivity is greater while the 2-olefin selectivity is smaller during supercritical FTS, i.e 1-olefins are the primary products of FTS. Decrease in total olefin selectivity and increase in 2-olefin selectivity with increase in carbon number was significantly less pronounced for supercritical FTS. This is attributed to higher diffusivities of high molecular weight α-olefins in supercritical propane (or n-hexane), and higher desorption rates of these products relative to conventional FTS. Also, reaction rates are slightly higher in supercritical fluids, and the activity maintenance is good due to removal of hydrocarbon waxes and carbonaceous deposits from the catalyst pores by the supercritical fluid. Secondary reactions (isomerization, hydrogenation, and readsorption) of high molecular weight 1-olefins occur to a lower extent during supercritical FTS, again due to higher diffusivities and more rapid removal (desorption) of high molecular products relative to conventional FTS where the catalyst pores are filled with hydrocarbon wax. The measured diffusion coefficients and effective diffusivities are consistent giving constant porosity/tortuosity ratio for a wide range of operating conditions. Hence if the molecular diffusivity is known, one can calculate the effective diffusivity at any condition. The predictive equation developed, based on the rough hard sphere theory, gives excellent predictions for diffusion in supercritical fluids for a wide range of temperatures and pressures.

INTRODUCTION

Several technologies are currently available or are under development for conversion of coal- or natural gas-derived synthesis gas to liquid transportation fuels. Technologies that have been commercially proven or that are close to commercialization include Fischer-Tropsch synthesis (FTS), methanol synthesis and the Mobil methanol to gasoline (MTG) process. Of these technologies, Fischer-Tropsch (FT) hydrocarbon synthesis produces the widest slate of products and has been in operation for the longest period. FTS was first developed and practiced in Germany during the 1930's and 1940's in fixed bed reactors on cobalt based catalysts. Subsequently, the process was commercialized on a large scale by SASOL in South Africa. The SASOL process includes both tubular fixed bed (TFB) and circulating fluidized bed (CFB) operation and uses promoted iron catalysts (Dry, 1981).

TFB are used for production of high molecular weight hydrocarbons (waxes) and diesel fuel, whereas CFB are used for production of gasoline. Each of these two types of reactors has a rather narrow range of operating conditions with respect to fresh feed composition and the reaction temperature. Both reactors are not suitable for direct processing of synthesis gas produced in modern coal gasifiers, where hydrogen to carbon monoxide molar ratio is 0.5 - 0.7. Heat transfer removal is a major problem with TFB reactors, and thus they operate at low temperatures, low single pass conversions and high recycle ratios. Also, waxy products formed during synthesis accumulate in the catalyst pores decreasing catalyst effectiveness. CFB reactors operate at high temperatures (high reaction rates) in order to avoid formation of high molecular weight products, which would wet catalyst particles and have adverse effect on their fluidization properties. Therefore, yields of methane and light gases are high in CFB reactors, and this has a negative impact on the process economics. In order to avoid some of these limitations SASOL has been working on development of more efficient reactors for Fischer-Tropsch synthesis (Geertsema, 1990). A new commercial scale conventional fluidized bed reactor and a slurry bubble column (SBC) reactor have been constructed and placed on stream in 1989 and 1993, respectively. These reactors are less expensive to construct, maintain and operate than the conventional fixed bed or circulating fluidized-bed reactors.

Slurry processing provides the ability to more readily remove the heat of reaction, minimizing temperature rise across the reactor and eliminating localized hot spots. As a result of the improved temperature control, yield losses to methane are reduced and catalyst deactivation due to coking is decreased. This, in turn, allows much higher conversions per pass, minimizing synthesis gas recycle, and offers the potential to operate with CO-rich synthesis gas feeds without the need for prior water-gas shift (Kölbel and Ralek, 1980). The SBC reactor can operate in either gasoline or wax mode of operation (Kuo, 1985). However, both modes require further upgrading of light and heavy ends of production spectrum to maximize yields of transportation fuels (gasoline and diesel). Reaction rates are lower in slurry phase reactors, relative to those in gas phase reactors, due to low reactant concentrations (solubility limitation) and low diffusivities of reactants and products in a liquid medium (mass transfer limitations).

Supercritical fluids (SCFs) have been increasingly used as solvents for separations and chemical reactions in the chemical, food, pharmaceutical and biochemical industries. They offer many advantages over traditional solvents such as: (1) the solvent power of SCFs for dissolving nonvolatile substances approach that of conventional solvents due to liquid like densities; (2) the low viscosity and high diffusivity of SCFs result in superior mass transfer characteristics; (3) surface tension of the SCFs is low enabling easy penetration into the pores of a solid matrix (catalyst) for extraction of nonvolatile materials in the pores; (4) gases are completely miscible with SCFs resulting in high concentrations compared to liquid solvents, and (5) the high compressibility of SCFs near the critical point induces large changes in density with very small changes in pressure and/or temperature enabling separation of the dissolved material from the SCF very easily and completely (Johnston and Penninger, 1989; Bruno and Ely, 1991). The properties (1) - (4) above, would be useful in overcoming some of the disadvantages of the fixed bed and slurry phase Fischer-Tropsch synthesis (FTS), where the catalyst pores are filled with high molecular weight hydrocarbons.

Recently, Fujimoto and co-workers studied FTS in a supercritical n-hexane (Yokota and Fujimoto, 1989; 1991; Fan et al., 1992). They compared performance of silica supported cobalt-lanthanum and/or alumina supported ruthenium catalysts in a gas phase, liquid phase (trickle bed operation with n-hexadecane and nitrogen) and supercritical phase FTS conducted in a fixed bed reactor. Supercritical Fischer-Tropsch synthesis (SFTS) was found to result in: (1) higher heat transfer rate compared to the gas phase, but lower than in the liquid phase; (2) more efficient mass transfer compared to the liquid phase, but lower than the gas phase; (3) in situ extraction of high molecular weight products from the pores; (4) higher CO conversion compared to the liquid phase, but lower than that in the gas phase; (5) higher apparent activation energy compared to the liquid phase, but lower than that in the gas phase, and (5) higher olefin selectivities compared to both the gas phase and the liquid phase synthesis. Results were explained in terms of differences in diffusion rates of reactants and products, desorption rates of high molecular weight olefins, and general properties of supercritical fluids listed above. Duration of all experiments was six hours, and it is not clear whether this was sufficient to reach a steady state.

OBJECTIVES AND SIGNIFICANCE

Objectives

The objective of this project is to investigate FTS in the supercritical phase employing a commercial precipitated iron catalyst (Ruhrchemie LP 33/81). This catalyst was used initially in TFB reactors at SASOL, and it has been tested at Texas A&M University in both fixed bed and stirred tank slurry reactors (Bukur et al., 1990; Zimmerman and Bukur, 1990). Thus, we will be able to compare performance of the same catalyst in the supercritical phase, gas phase (fixed bed reactor), and slurry phase (stirred tank slurry reactor). Comparisons will be made in terms of bulk catalyst activity, space-time-yields per unit mass of catalyst and various aspects of product selectivity (i.e. hydrocarbon product distribution and olefin content as a function of carbon number). Also, we plan to measure diffusivities of representative hydrocarbon products in supercritical fluids, as well as their effective diffusion rates into the pores of catalyst at the reaction conditions. These measurements will allow us to determine kinetics of the rate of disappearance of reactants (rate constants, activation energies, and functionality of reaction rate expression), which is not affected by physical transport processes. Specifically we will:

(a) procure all necessary parts and instrumentation to modify the existing apparatuses for Fischer-Tropsch catalyst evaluation and diffusion measurements to operate at supercritical conditions;

(b) perform FTS experiments in the supercritical phase in a fixed bed reactor with Ruhrchemie LP 33/81 catalyst using propane and/or n-hexane as the supercritical fluid;

(c) compare performance of this catalyst in supercritical mode of operation to that of the same catalyst in gas phase (conventional operation in a fixed bed reactor) and liquid phase (slurry reactor) mode of operation;

(d) measure diffusion coefficients of selected Fischer-Tropsch products in the supercritical fluid;

(e) measure effective diffusivities of some reaction products into the pores of the Ruhrchemie catalyst in supercritical fluids.

Significance

This research is intended to provide information needed to assess feasibility of Fischer-Tropsch synthesis in supercritical fluids by securing reliable data on steady state catalyst activity and selectivity in supercritical mode of operation and by comparison with more conventional types of operation (fixed bed reactor and stirred tank slurry reactor). Also, this study will provide methodology for measurement of molecular and effective diffusivities and kinetic parameters, which are needed for preliminary design and process simulation studies. Data obtained from this research will be useful for techno-economic studies by industrial organizations and DOE contractors interested in Fischer-Tropsch technology.

EXPERIMENTAL

Detailed descriptions of the equipment used, operating and data analysis procedures for reaction studies and diffusivity measurements can be found in Appendices I and IV, respectively.

RESULTS AND DISCUSSION

Fischer - Tropsch Reaction Studies

Six fixed bed reactor tests were conducted with a precipitated iron catalyst (Ruhrchemie LP 33/81). Test designations, process conditions and brief description of the purpose of each test are listed in Table 1. Baseline process conditions for conventional FTS were: 1.48 MPa, 250°C, 2 L (STP)/g-cat/h, $H_2/CO = 0.67$.

Table 1. Summary of Fischer-Tropsch synthesis tests in a fixed bed reactor

Run No.	P (MPa)	T (°C)	SV (Nl/g·h)	Fluid	TOS (h)	Comment
FA-3143	1.48, 7	250	2	N_2	320	Effect of inert gas
FA-0844	1.48, 7	250	2	Propane	270	Supercritical FTS in propane
FB-1644	1.48	235 250 265	0.5-9	SG	600	Conventional FTS Effect of process conditions
FA-1724	1.48 5.5	235 250 265	0.4-7	Propane	780	Supercritical FTS Effect of process conditions
FA-2984	1.48 3, 4.1	250	2	Hexane	370	SFTS and subcritical FTS in hexane
FA-1075	1.48 5.5	250	2	Propane	330	SFTS, Effect of co-feeding of 1-dodecene

SG - synthesis gas.

Major findings from these tests are briefly described below, whereas detailed description and discussion are provided in Appendices.

Effect of Inert Gas and Supercritical Propane

The purpose of run FA-3143 was to determine the effect of total pressure on catalyst activity and selectivity in the presence of an inert gas (nitrogen), while maintaining the constant partial pressure of the reactants (synthesis gas with H_2 : CO molar feed ratio of 2 : 3). Baseline process conditions (conventional mode of operation) were: 250°C, 1.48 MPa, 2 L(STP)/g-cat·h and $H_2/CO = 0.67$ (with no nitrogen), whereas in the presence of nitrogen the total pressure was 7 MPa (syngas flow rate and partial pressure were the same as at the baseline conditions). Catalyst activity (Figure 2 of Appendix I) and selectivity (Figure 3 of Appendix I) were not affected during high pressure operation, and the catalyst was stable during 320 h of continuous testing.

Process conditions in run FA-0844 were the same as in Run FA-3143, except that propane was used instead of nitrogen during operation at a total pressure of 7 MPa. Since the reaction temperature (250°C) and pressure (7 MPa) were above the corresponding critical values for propane (96.7°C and 4.19 MPa), this is referred to as supercritical mode of operation. Catalyst activity (Figure 4 of Appendix I) and lumped hydrocarbon product distribution (Figure 5 of Appendix I) during operation at supercritical conditions were similar to those obtained during conventional FTS at the baseline conditions, however, a significant enhancement of 1-olefin selectivity (particularly with increase in molecular weight) was observed during the supercritical FTS (Figure 6 of Appendix I). This suggests that the rate of FTS is not diffusion limited under the reaction conditions used in this study, whereas the secondary hydrogenation, isomerization and readsorption reactions of 1-olefins are diffusion limited. Diffusivities of high molecular weight 1-olefins are higher and their removal (desorption) from the catalyst surface is faster during SFTS, which results in inhibition of secondary reactions. The observed increase in olefin selectivity during SFTS is in agreement with results obtained by Fujimoto and co-workers in tests of short duration with cobalt and ruthenium based FT catalysts in supercritical n-hexane (Yokota and Fujimoto, 1989; 1991; Fan et al., 1992).

Effect of Process Conditions on Olefin Selectivity

In runs FB-1644 (conventional FTS) and FA-1724 (supercritical FTS) experimental data were obtained at different temperatures (T = 235°C, 250°C and 265°C) and synthesis gas feed compositions (H_2/CO molar feed ratio of 0.67, 1 and 2). At a given reaction temperature and feed composition, the gas space velocity was varied to achieve different levels of syngas conversion. Variations in gas residence time allow us to distinguish primary and secondary reaction steps that control olefin selectivity. Reaction pressure during conventional FTS was ~1.5 MPa, whereas during supercritical Fischer-Tropsch synthesis (SFTS) with propane the total pressure was 5.5 MPa while maintaining the synthesis gas partial pressure at ~1.5 MPa.

It was found that total olefin content decreased and 2-olefin selectivity increased with either decrease in gas space velocity (Figures 2 and 3 in Appendix II) or increase in H_2/CO molar feed ratio (Figures 7 and 8 in Appendix II), whereas olefin selectivities were essentially independent of reaction temperature (Figure 6 in Appendix II).

Results from bed residence time effect studies in both modes of operation indicate that α-olefins are the dominant primary products of FTS. Normal paraffins and 2-olefins are primary products also, and their primary selectivities on the Ruhrchemie catalyst were approximately 20% and 3%, respectively. Selectivity of n-paraffins and 2-olefins increases, whereas α-olefin selectivity decreases with increase in carbon number, due to secondary reactions of α-olefins.

Bed residence time and carbon number (molecular weight) effects were more pronounced during conventional FTS than during supercritical FTS. During conventional FTS high molecular weight products (C_8+ hydrocarbons) leave the reactor preferentially in the liquid state, and their residence time is much longer than that of either the gas phase products, or the products formed during supercritical FTS. Also, diffusivities of high molecular weight α-olefins in the liquid hydrocarbon wax are much lower than the corresponding diffusivities in the supercritical propane, and hence the pore residence time of these products is longer during the conventional FTS. Longer residence time in the reactor and/or catalyst pores increases probability for secondary readsorption of α-olefins, and results in secondary formation of n-paraffins and 2-olefins. At high syngas conversions (~80%), selectivities of high molecular weight α-olefins during SFTS were significantly higher than those obtained during conventional operation (Figure 5 in Appendix II). These results indicate that SFTS is a potentially attractive route for synthesis of high molecular weight alpha olefins from the synthesis gas.

Kinetic Parameters for Rate of Disappearance of the Synthesis Gas

Apparent rate constant for disappearance of synthesis gas was determined by assuming that the FTS is first order with respect to hydrogen, i.e.

$$r_{H_2+CO} = kp_{H_2} \tag{1}$$

where: k - apparent rate constant (mol/gFe·h·MPa); p_{H_2} - partial pressure of hydrogen (MPa); r_{H_2+CO} - rate of disappearance of the synthesis gas (mol/g-Fe·h)

The rate constant was estimated from experimental data assuming that: (1) the reactor is at steady state; (2) isothermal and isobaric conditions in the reactor; (3) plug flow of gas; and (4) negligible interphase mass transfer resistance. If one assumes that the usage ratio (H_2/CO consumption ratio) is constant along the reactor length, the apparent rate constant can be expressed in terms of measurable quantities as:

$$\frac{RT_s}{P_s}\frac{P}{s}k = -\frac{1+U}{U}\left\{\left[\frac{F(1+U)}{U(1+F)}y_{SG}^0\alpha + 1\right]\ln\left[1 - \frac{U(1+F)}{F(1+U)}X_{H_2+CO}\right] + \alpha y_{SG}^0 X_{H_2+CO}\right\} \tag{2}$$

where: F - H_2/CO molar feed ratio; P - total pressure (bar) ; P_s and T_s - standard pressure (1 bar) and temperature (273 K); R - universal gas constant (8.314 (cm^3·MPa)/(mol·K)); s - gas hourly space velocity (cm^3 (STP)/(g-Fe·h)); U - usage ratio at the exit from the reactor; X_{H_2+CO} - syngas conversion; y_{SG}^0 - mole fraction of syngas in the feed (y_{SG}^0 = 1 for conventional FTS); $\alpha = -\frac{1+m/2n-1/n}{2+m/2n}$ gas contraction factor (m - average number of hydrogen atoms in hydrocarbon product; n - average number of carbon atoms in hydrocarbon product).

The apparent activation energy and Arrhenius constant were estimated from values of the apparent rate constant at different reaction temperatures, by plotting ln k vs. 1/T. From data in run FA-1724, the apparent rate constant as a function of temperature is given by:

$$k = 6.4 \times 10^9 \exp(-12630/T) \qquad (3)$$

where: T - reaction temperature in K.

Estimated value of the apparent activation energy, 105 (kJ/mol), is consistent with previously reported literature values on iron FTS catalysts, and is about 20% higher than the value obtained from experiments with the same catalyst (after CO reduction) in a stirred tank slurry reactor (Zimmerman and Bukur, 1990).

Supercritical FTS in n-hexane

Run FA-2984 was conducted to investigate the effect of n-hexane as a supercritical fluid, for comparison with runs FA-0844 and FA-1724, in which propane was used as a supercritical fluid. In some portions of the test the total pressure was 4.1 MPa, which is above the critical pressure of n-hexane (3 MPa), but the partial pressure of n-hexane was either 2.6 MPa or 1.3 MPa. Reduction of partial pressure of n-hexane is economically beneficial, but the operating conditions will shift below the supercritical properties of reaction mixture (subcritical FTS), and some of the benefits of supercritical operation (higher activity and 1-olefin selectivity) may be lost.

Process conditions for Run FA-2984 are summarized in Table 2. Reaction temperature and H_2/CO molar feed ratio were maintained at 250°C and 0.67, respectively, whereas the total gas flow rate and pressure varied throughout the test. In periods 2 - 4 (Table 2) n-hexane at different partial pressures was fed concurrently with the synthesis gas, which resulted in supercritical (period 2), subcritical (period 4), and liquid phase operation (period 3).

Table 2. Experimental Conditions for Run FA-2984

Period	Time on Stream (h)	P_{total} MPa	P_{H2+CO} MPa	P_{hexane} MPa	(H_2+CO) Feed Rate at STP	
					Nl/g-cat·h	cm^3/min
1	24 to 68	1.48	1.48	0	2.0	100
2	69 to 192	4.1	1.48	2.62	2.0	100
3	193 to 237	3.0	1.48	1.52	2.0	100
4	238 to 300	4.1	2.8	1.3	4.0	200
5	322 to 358	1.48	1.48	0	2.0	100

Reaction temperature and H_2 to CO feed ratio were maintained at 250°C and 0.67, respectively.

Catalyst Activity

Figure 1 shows changes of (H_2+CO) conversion with process conditions and time on stream (TOS). In period 1 (24 to 68 h on stream), FTS was conducted at the baseline conditions. The (H_2+CO) conversion and apparent reaction constant were about 60% and 207 mmol/g-Fe·h·MPa, respectively, and are very similar to the values obtained in Run FB-1644 at the same process conditions (59% and 208 mmol/g-Fe·h·MPa).

In period 2, FTS was conducted at total pressure of 4.1 MPa with n-hexane as a supercritical fluid, while maintaining the synthesis gas partial pressure and gas space velocity at 1.48 MPa and 2.0 Nl/g-cat·h, respectively. The (H_2+CO) conversion and apparent reaction rate increased to 65.6% and 279 mmol/g-Fe·h·MPa, respectively. In run FA-1724, the (H_2+CO) conversion also increased after the supercritical propane was introduced.

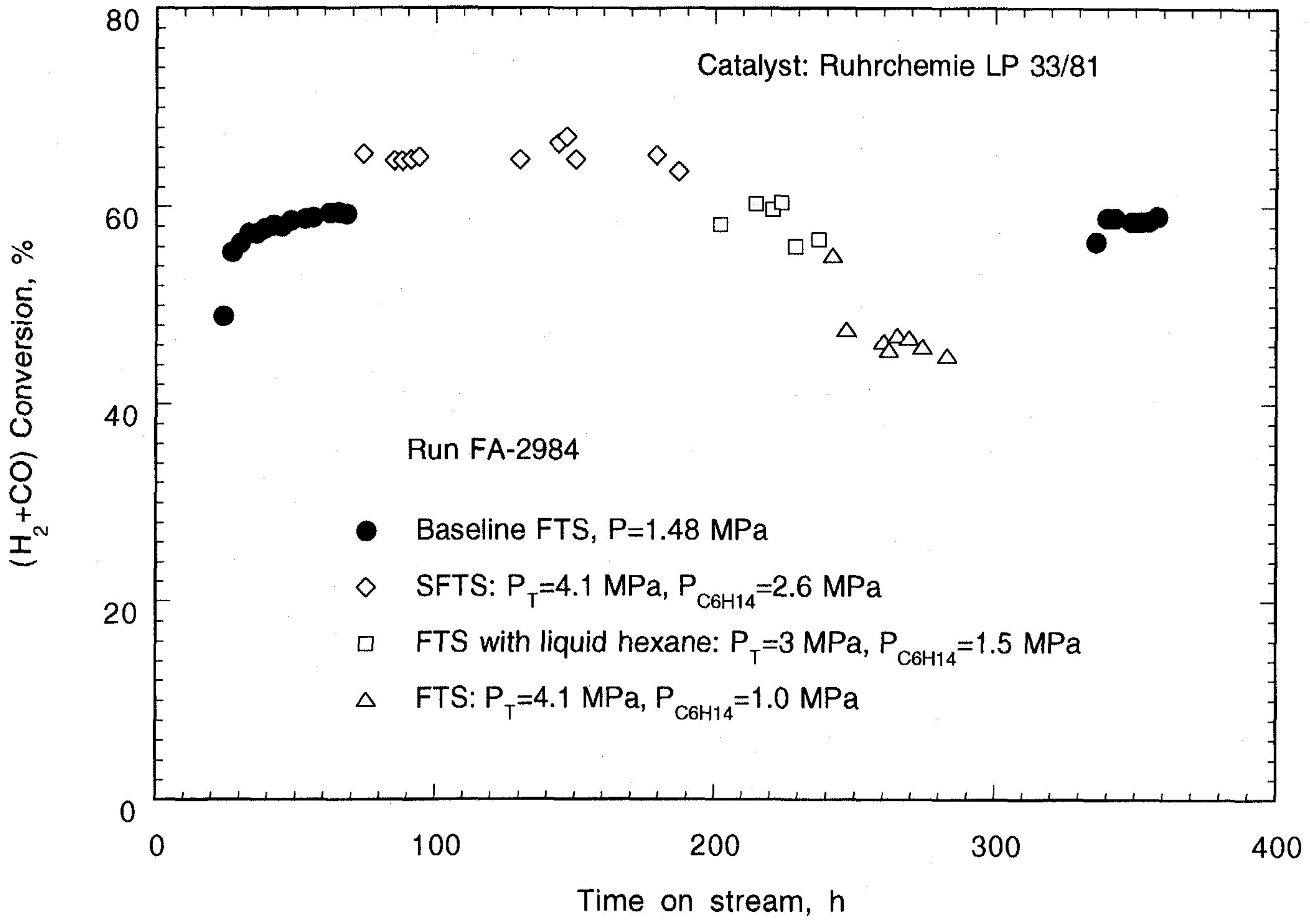

Figure 1. Variation in synthesis gas conversion with process conditions and time on stream during Run FA-2984.

In period 3 (193 to 237 h on stream), FTS was conducted at a total pressure of 3 MPa, and n-hexane behaved as a regular liquid. The (H_2+CO) conversion and the apparent rate constant were 58% and 238 mmol/g-Fe·h·MPa, respectively. The value of reaction rate constant was between values observed during conventional FTS and SFTS.

In period 4 (238 to 300 h on stream), the total operating pressure was 4.1 MPa, whereas the synthesis gas partial pressure and gas space velocity were 2.8 MPa and 4.0 Nl/g-cat·h. (FTS under subcritical conditions, due to low value of the partial pressure of n-hexane). The (H_2+CO) conversion (47.7%) and the apparent reaction rate constant (173 mmol/g-Fe·h·MPa) were markedly lower than the corresponding values in periods 1-3.

During period 5 (322 to 358 h on stream), FTS was conducted at the baseline process conditions (normal or conventional operation). The (H_2+CO) conversion (58.6%) and the apparent reaction rate constant (206 mmol/g-Fe·h·MPa) were only slightly lower than those in period 1, i.e. the catalyst did not deactivate after 360 h on stream.

Hydrocarbon product distribution

Selectivities of CH_4, C_2-C_4 hydrocarbons and C_5^+ hydrocarbons (as mol % carbon selectivity to hydrocarbons) are shown in Table 3. Selectivities during testing at baseline conditions (period 1) were: 5.9% CH_4 and 18.8% C_2-C_4 hydrocarbons. Gas phase selectivities in run FB-1644 at the same conditions were similar: 6.3% CH_4 and 17.4% C_2-C_4 hydrocarbons. Selectivities during SFTS (period 2) were: 6.6% CH_4 and 10.4% C_2-C_4. Significant decrease in C_2-C_4 gas phase selectivity, relative to conventional FTS, is attributed to high solubility of hydrocarbons in n-hexane. During period 3, FTS in liquid n-hexane at 3 MPa, hydrocarbon selectivities were similar to those obtained in period 2. In period 4, the FTS at total pressure of 4.1 MPa and the synthesis gas partial pressure of 2.8 MPa, C_2-C_4 selectivity increased significantly. Finally, in period 5, during FTS at the baseline conditions, the selectivities of CH_4 and C_2-C_4 were slightly higher than those in period 1.

Table 3. Summary of Results for Run FA-2984

Period	1	2	3	4	5
TOS, h	50	187	230	280	350
SV, Nl (H_2+CO)/g-cat·h	2.0	2.0	2.0	4.0	2.0
Total pressure, MPa	1.48	4.1	3.0	4.1	1.48
Type of operation	Conventional FTS	SFTS with hexane	FTS with hexane	FTS with hexane	Conventional FTS
H_2 conv, %	63.0	65.0	57.7	55.2	59.5
CO conv, %	57.9	66.0	58.1	42.9	58.0
(H_2+CO) conv, %	59.9	65.6	57.9	47.7	58.6
H_2/CO usage ratio	.70	.64	.64	.83	.66
Mol%[a] CH_4	5.9	6.6	6.8	7.0	6.3
Mol%[a] C_2-C_4	18.8	10.4	10.7	23.1	21.0
Mol%[a] C_5^+	75.4	83.0	82.5	69.9	72.7
k, mmol/g-Fe·h·MPa	207	279	238	173	206

a. from gas phase composition

Olefin selectivity

Figure 2a shows total olefin selectivity during different periods of Run FA-2984. At a given carbon number, the olefin selectivity during SFTS operation was generally higher than that during conventional FTS. The olefin selectivities during FTS with liquid n-hexane (period 3) and subcritical FTS (period 4) were between those obtained during SFTS and conventional FTS.

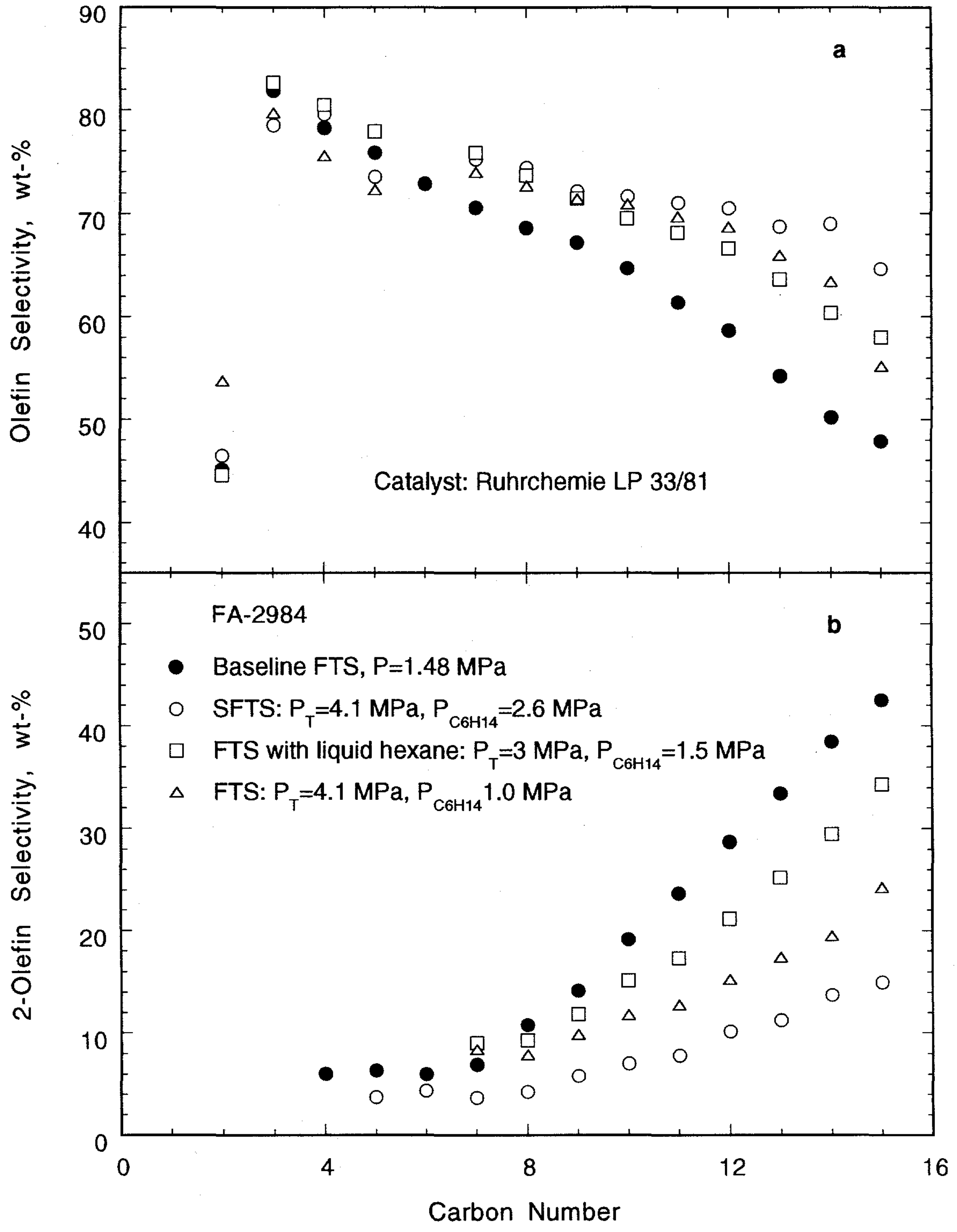

Figure 2. Olefin and 2-olefin selectivities during different periods of Run FA-2984.

At a given carbon number, the 2-olefin selectivity during SFTS operation was generally lower than that during conventional FTS (Figure 2b). The 2-olefin selectivities during FTS with liquid n-hexane and subcritical FTS were between those obtained during SFTS and conventional FTS.

The above observation that selectivity of primary FTS reaction products (1-olefins) is greater under SFTS conditions is consistent with results obtained in tests with supercritical propane (Runs FA-0844 and FA-1724). The selectivity of 1-olefins was also enhanced during FTS at subcritical conditions (periods 3 and 4), but the effect was less pronounced than during operation at higher partial pressure of n-hexane (period 2). Olefin selectivities obtained during period 2, were similar to those obtained during SFTS with supercritical propane (Figures 3 and 4 in Appendix III).

Effect of co-feeding of 1-dodecene during Conventional and Supercritical FTS

The objective of run FA-1705 was to study the effect of co-feeding a 1-olefin on the Ruhrchemie catalyst activity and selectivity, during both conventional FTS and during FTS under supercritical conditions. We used propane as the supercritical fluid and 1-dodecene (1-$C_{12}H_{24}$) in this test. Motivation for this study was the work of Fujimoto et al. (1995), who reported that suppression of methane and enhancement of high molecular weight hydrocarbons selectivities occurs during SFTS with co-feeding of 1-olefins (1-heptene, 1-tetradecene, or 1-hexadecene), but not during the conventional FTS (Co-La catalyst supported on silica in supercritical n-pentane).

Table 4 summarizes process conditions for run FA-1075. In period 1, the reaction was conducted at the baseline conditions. In period 2, 1-dodecene was introduced at a feed rate of 1.67 cm^3/h, which corresponds to 4 mol% of CO feed rate, while maintaining the synthesis gas flow rate, reaction temperature and pressure at baseline values (conventional FTS with co-feeding of 1-dodecene). In period 3, the feed rates of synthesis gas and 1-dodecene were maintained at the same values as in period 2, while propane was introduced at total system pressure of 5.5 MPa (SFTS with co-feeding of 1-dodecene). In period 4, the flow of 1-dodecene

Table 4. Experimental Conditions for Run FA-1075[a].

Period	Time on Stream (h)	Total Pressure (MPa)	Type of Operation
1	22 to 70	1.48	Conventional FTS
2	71 to 127	1.48	Conventional FTS co-feeding of 1-dodecene
3	128 to 218	5.5	SFTS with propane co-feeding of 1-dodecene
4	219 to 296	5.5	SFTS with propane
5	297 to 331	1.48	Conventional FTS

a. Reaction temperature, synthesis gas partial pressure, gas space velocity and H_2 to CO feed ratio were maintained at 250°C, 1.48 MPa, 2 Nl/g-cat· h, and 0.67, respectively. Flow rates (at STP): syngas - 117 cm^3/min; propane - 350 cm^3/min; 1-dodecene - 1.7 cm^3/h.

was terminated, while other conditions were the same as in period 3 (SFTS in propane at 5.5 MPa). In period 5, FTS was carried out at the baseline conditions to investigate deactivation of the catalyst.

Activity

Figure 3 shows changes of (H_2+CO) conversion with time and process conditions. During conventional FTS at baseline conditions the (H_2+CO) conversion and apparent reaction constant were about 59% and 202 mmol/g-Fe·h·MPa, respectively. Upon introduction of 1-dodecene (period 2) the (H_2+CO) conversion and the apparent reaction rate constant decreased to

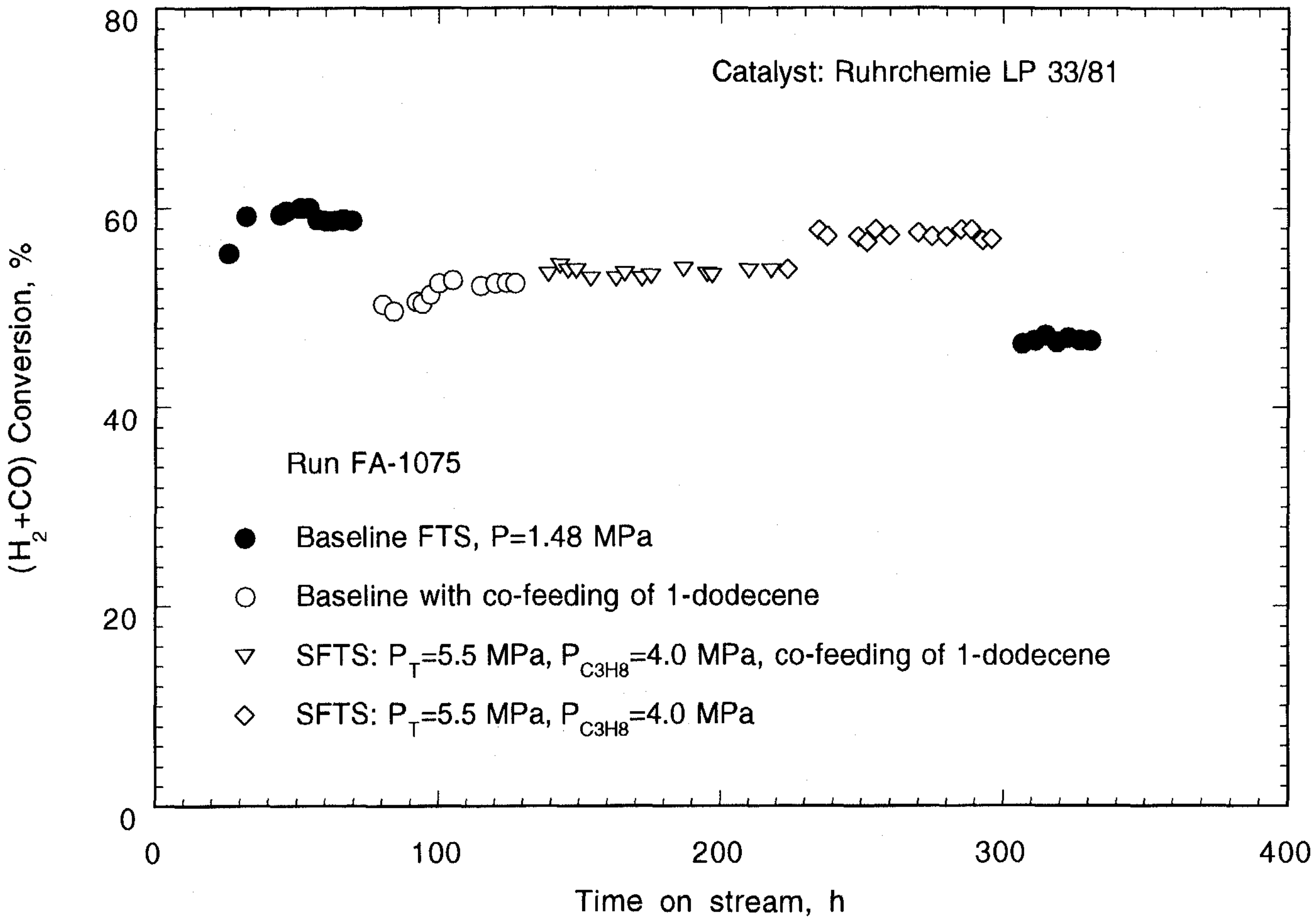

Figure 3. Variation in synthesis gas conversion with process conditions and time on straem during Run FA-1075.

During SFTS with propane and 1-dodecene at 5.5 MPa and 250°C (period 3), the (H_2+CO) conversion and apparent reaction rate constant were 54% and 215 mmol/g-Fe·h·MPa, respectively. When the 1-dodecene feed was discontinued (period 4) the (H_2+CO) conversion and the apparent reaction rate increased to 57% and 231 mmol/g-Fe·h·MPa, respectively. In period 5 (297 to 331 h on stream), corresponding to conventional FTS at the baseline conditions the (H_2+CO) conversion (46%) and the apparent reaction rate constant (160 mmol/g-Fe·h·MPa) were lower than those in period 1 indicating catalyst deactivation.

Hydrocarbon product distribution

Selectivities of CH_4, C_2-C_4 and C_5^+ hydrocarbons (as %C selectivity to hydrocarbons) are shown in Table 5. Gas phase hydrocarbon selectivities did not vary significantly from period 1 to period 4 (i.e. they were independent of the mode of operation). In period 5, selectivities of CH_4 and C_2-C_4 were slightly higher than those in period 1, due to deactivation of the catalyst.

Olefin selectivity

Total olefin and 2-olefin selectivities during different periods of run FA-1075 are shown in Figure 4. At a given carbon number, the total olefin selectivity decreased in the following order: SFTS > SFTS with co-feeding of 1-dodecene > conventional FTS with co-feeding of 1-dodecene > conventional FTS, whereas 2-olefin selectivity decreased in the following order: conventional FTS > conventional FTS with co-feeding of 1-dodecene > SFTS with co-feeding of 1-dodecene > SFTS with propane.

Selectivity of the primary FTS reaction products (1-olefins) was greater during SFTS, which is in agreement with results obtained in previous tests (runs FA-0844, FA-1724, and FA-2984). The presence of 1-dodecene during the conventional FTS (Period 2) also enhanced the selectivity of 1-olefins, but the effect was not as profound as that during operation with supercritical propane. This effect may be attributed to lower surface concentrations of high molecular weight olefins in the presence of a large amount of 1-dodecene which adsorbs on the surface (competitive chemisorption).

Table 5. Summary of Results for Run FA-1075

TOS, h	60	110	200	270	325
Total pressure, MPa	1.48	1.48	5.5	5.5	1.48
Type of operation	conventional FTS	conventional FTS with 1-dodecene	SFTS with 1-dodecene	SFTS with propane	conventional FTS
H_2 conv, %	57.8	54.0	54.7	55.7	49.8
CO conv, %	59.4	51.3	53.1	58.1	44.2
(H_2+CO) conv, %	58.8	52.4	53.7	57.2	46.4
H_2/CO usage ratio	0.65	0.70	0.69	0.65	0.75
Mol % ^{a} CH_4	5.8	5.7	6.0	5.7	6.6
Mol % ^{a} C_2-C_4	19.1	20.0	17.2	18.9	24.7
Mol % ^{a} C_5^+	75.1	74.3	76.8	75.4	68.7
k, mmol/g-Fe·h·MPa	202	178	215	231	160

[a] : from gas phase composition

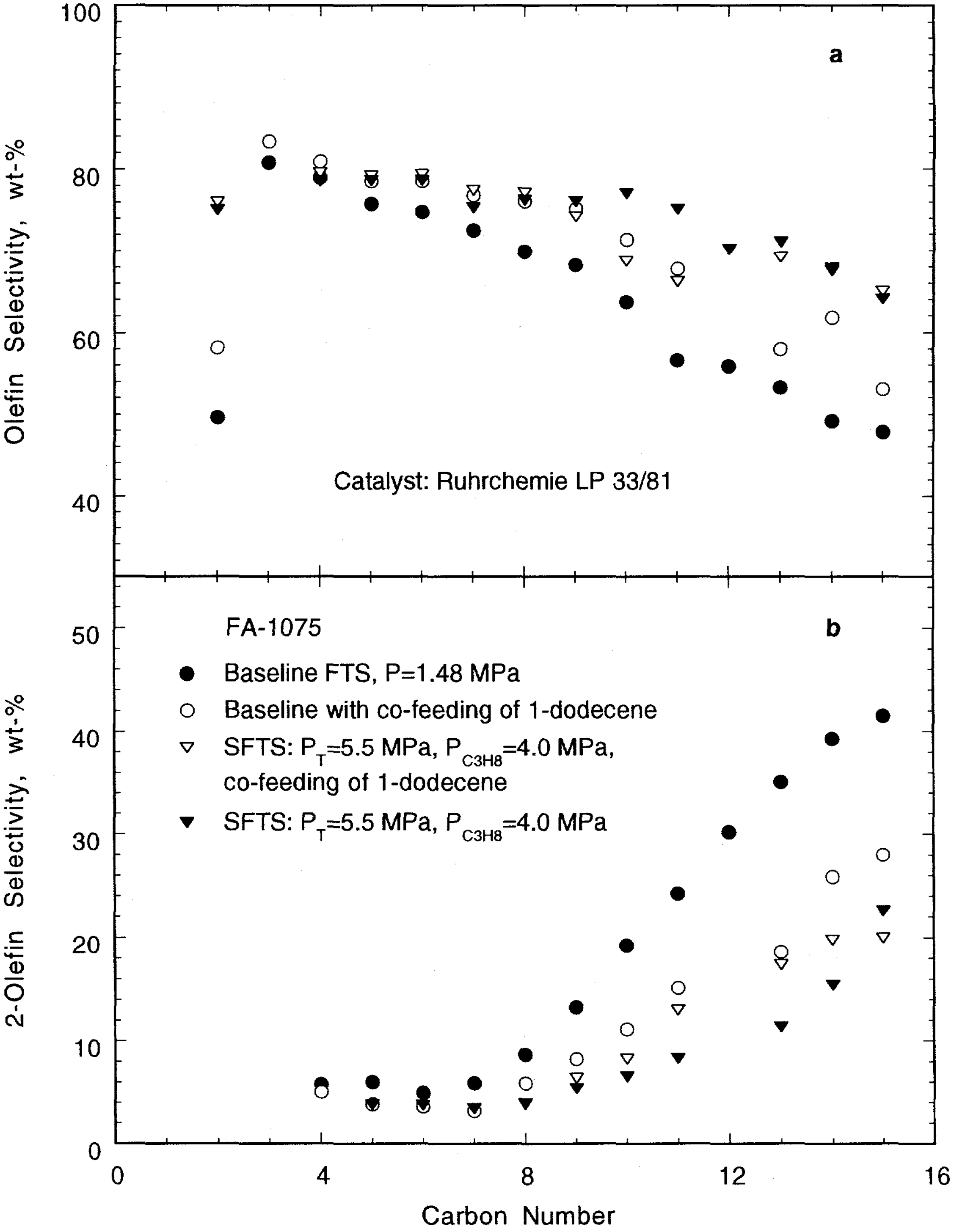

Figure 4. Olefin and 2-olefin selectivities during different periods of Run FA-1075.

Summary - Effect of co-feeding of 1-dodecene

Catalyst activity decreased during both conventional FTS and SFTS upon introduction of 1-dodecene. Gas phase hydrocarbon selectivities did not vary significantly during different periods of operation (with or without co-feeding of 1-dodecene, and/or with or without supercritical propane). In contrast to Fujimoto et al. (1995) we did not observe suppression of methane selectivity and enhancement of selectivity of high weight molecular hydrocarbons, during SFTS with co-feeding of 1-dodecene. Perhaps this is due to the fact that 1-olefin readsorption is much smaller on iron than on cobalt. Selectivity of primary products (1-olefins) was enhanced during synthesis under supercritical conditions. The presence of 1-dodecene had a mixed effect on selectivity of 1-olefins: during the conventional FTS, the selectivity of 1-olefins increased in the presence of 1-dodecene; whereas during supercritical operation the selectivity of 1-olefins decreased in the presence of 1-dodecene.

Comparison of Catalyst Performance in Stirred Tank Slurry and Fixed Bed Reactors

During the course of this project the Ruhrchemie LP 33/81 catalyst (100 Fe/5 Cu/4.2 K/25 SiO_2 on mass basis) was tested in a fixed bed reactor in both conventional and supercritical modes of operation. Also, this catalyst was tested previously in our laboratory in fixed bed and stirred tank slurry reactors (conventional mode of operation) during the DOE Contract No. DE-AC22-89PC89868 (Development of Improved Iron Fischer-Tropsch Catalysts). In all tests the catalyst was reduced in situ with H_2 at 220°C, 7500 cc/min for 1 h, and ambient pressure (fixed bed reactor test) or 0.8 MPa (slurry reactor test). Major conclusions from these tests at baseline set of process conditions: 250°C, 2 Nl/g-cat/h, syngas partial pressure of 1.48 MPa, and synthesis feed gas with H_2/CO molar ratio of about 0.67, are summarized below, whereas details are presented in Appendix III.

In fixed bed tests activity of the catalyst was slightly higher (~5%) in the supercritical mode of operation with propane as supercritical fluid, and about 33% higher in supercritical n-hexane. This is attributed to higher diffusivities of reactants in supercritical fluids relative to conventional mode of operation (pores filled with liquid hydrocarbon wax).

Catalyst activity in a stirred tank slurry reactor (STSR) was lower than in a fixed bed reactor. The apparent rate constant in STSR test SB-1370 was 143 mmol/g-Fe·h·MPa, whereas average values of the apparent rate constant during conventional FTS and SFTS (with propane) in fixed bed reactors were 209 mmol/g-Fe·h·MPa and 220 mmol/g-Fe·h·MPa, respectively. It is believed that low catalyst activity in run SB-1370 is due to low degree of iron reduction in the STSR. For example, the CO pretreated Ruhrchemie catalyst (run SA-0888) had the apparent rate constant of 193 mmol/g-Fe·h·MPa (Bukur et al., 1990; 1996), which is only about 10 % less than that obtained in fixed bed reactors (H_2 reductions).

Hydrocarbon selectivities in the fixed bed reactor were similar in both modes of operation (Table 4 of Appendix III). Methane selectivity in the STSR was lower than in fixed bed reactor tests (4.8 % vs. 6.2%), due to better temperature control in the former. Gasoline yield (C_5-C_{11} hydrocarbons) was higher in the STSR than in fixed bed reactors (29 % vs. 23.6 %), whereas the yield of high molecular weight hydrocarbons (C_{12}^+) was higher in the fixed bed reactor (53.5% vs. 50%).

Total olefin content was the highest (Figure 7 of Appendix III) and the 2-olefin selectivity was the lowest (Figure 8 of Appendix III) in the supercritical mode of operation. This is attributed to higher diffusivities of high molecular weight 1-olefins in supercritical fluids than in the liquid filled pores during the conventional FTS in either the fixed bed or the stirred tank slurry reactor. The olefin content was lower and the olefin isomerization activity was higher during conventional FTS in the fixed bed reactor than in the slurry reactor. These differences in olefin selectivities are partly caused by differences in conversion levels, since higher conversions favor secondary reactions (~61% syngas conversion in the fixed bed reactor, and 38% in the STSR).

Diffusion Studies

Our diffusion studies had the following objectives: (1) to design and construct an apparatus to measure molecular diffusivities of Fischer-Tropsch reaction products in supercritical propane and hexane at the Fischer-Tropsch reaction conditions; (2) to develop a technique to measure the effective diffusivities of the same products at the same conditions in the pores of the iron based Ruhrchemie LP 33/81 catalyst; (3) to develop a predictive equations for *a-priori* determination of the molecular diffusivities and the effective diffusivities of solutes in supercritical fluids.

In order to model the supercritical phase Fischer-Tropsch reaction data, effective diffusivities (D_{eff}) in the catalyst pores are needed. The effective diffusivities are related to the molecular diffusion coefficients. Using the relationship

$$D_{eff} = \frac{\epsilon_p}{\tau} D_{12} \qquad \textbf{(1)}$$

if the tortuosity τ and particle porosity ϵ_p were known, only the molecular diffusion coefficient D_{12} at the reaction conditions would be needed. Although the tortuosity and porosity of each catalyst particle must be determined independently, if ϵ_p/τ is determined at one set of conditions D_{eff} can then be calculated at any other set of conditions provided that D_{12} is known or can be estimated. Hence the focus of this objective of the project was on *a-priori* prediction of D_{12}.

We have used the Taylor dispersion technique (Taylor, 1953; Aris, 1956; Erkey and Akgerman, 1990, 1991; Alizadeh et al., 1980) to measure the molecular diffusion coefficients in supercritical fluids and a tracer response technique (Levenspiel and Smith, 1957; Wakao and Kugei, 1982; Erkey and Akgerman, 1990) to measure effective diffusivities. The predictive equation was developed using the extension of rough hard sphere theory to supercritical fluids.

The details of the experimental technique used are explained in our publications (Noel et al., 1994; Eaton et al., 1995) given in Appendix IV. In the experimental technique, the supercritical fluid was allowed to flow through stainless steel tubing to a preheater in the furnace which is temperature was controlled to ±1°C. The supercritical fluid then passes through an injection valve to a stainless steel column with an approximate diameter of 0.635 cm packed with Ruhrchemie LP 33/81 catalyst (100 Fe/5 Cu/4.2 K/25 SiO_2 on mass basis), or through a 15.84 m long Taylor dispersion coil, or through a bypass line. This switching between the apparatus was completed by two zero dead volume connections that could be unconnected and reconnected without added dispersion. The bypass was employed to measure the amount of dispersion incurred in the system (minus the packed column or the dispersion coil) due to flow and most important due to the cooling length necessary, since the detector could not handle the high temperature fluid. After the column or the dispersion coil, the supercritical fluid passed to a high pressure UV detector (ISCO V^4) with a dead volume of 0.25 μl. The system pressure was set by a back pressure regulator placed after the UV detector. A second back pressure regulator at 54.4 atm reduced pulsations in the system by utilizing the double expansion technique developed in our laboratories (Erkey and Akgerman, 1990). The system pressure was measured by an internal pressure transducer in the syringe pump calibrated to a precision of ±1 bar.

The Taylor dispersion tubing was coiled to a diameter of 0.28 m to allow it to fit into the furnace. The maximum flow rate that can be used in the diffusion coil depends on many criteria which are summarized by Erkey and Akgerman (1991), and flow rates less than 9 ml/h were used.

If the flow rate is above the criteria's maximum, then results will scatter mostly because of secondary flow effects (Erkey and Akgerman, 1991). A set of six experiments were completed at each temperature and pressure condition for both the Taylor dispersion coil and the bypass in order to obtain an accurate measurement of the molecular diffusion coefficients and to confirm the reproducibility of the experiments.

Flow rates of the solvent varied from 25 to 100 ml/h with an accuracy of ±4% for effective diffusivity measurements. The injection valve contained a 10 μl sample of solute dissolved in supercritical fluid. This sample was produced by injection of 3 ml of solute into a saturation system, with a volume of 9 ml, placed before the injection valve. Supercritical fluid was then put into the saturator and left for sufficient time to dissolve the solute injected. A column frit was placed before the saturator to prevent entrainment of the solute fluid. The 10 μl sample was injected into the column, which was filled with catalyst, and the response was measured on-line with the UV detector and recorded in one second intervals by means of an Intel 486 SX computer. This procedure was completed three times at each flow rate, pressure, and temperature condition to obtain an accurate result. The catalyst was prepared by crushing and sieving particles to a size of approximately 250-295 μm. The catalyst was then calcined at a temperature of 673.15 K for a period of four hours and re-sieved to eliminate any particles which were reduced in size during the calcining process. The particle porosity as well as the mean pore size and the specific surface area were determined by standard nitrogen adsorption techniques, completed independently. The particle density was determined by pycnometer analysis. Bed porosity was determined from the mass of a known volume of particles.

Our results are given in our publication (Eaton et al., 1995) in Appendix IV. For all measurements D_{12}/D_{eff} was 9.72±1.22, indicating that ϵ_p/τ was ~ 0.103 and was independent of temperature, pressure, and diffusing species as expected. Thus, if D_{12} can be predicted, one can easily determine D_{eff} at any condition.

The predictive equation was based on the rough hard sphere theory. The theory and the development of the predictive equation are given in our publication (Eaton and Akgerman, 1997) presented in Appendix V. The final equation developed does not have any adjustable parameters, although it includes two fitted parameters. The final form of the equation is given by

$$D_{12} = \beta\sqrt{T}\left(\frac{\sigma_1}{\sigma_2}\right)^{\gamma}\left[\frac{m_1+m_2}{m_1 m_2}\right]^{1/2}\left(\frac{V_0}{\sigma_{12}^2}\right)\left[\left(\frac{V}{V_0}\right)^{\alpha}-b\right] \tag{2}$$

where

$$\alpha = \frac{\sigma_2}{\sigma_1}-\frac{1}{3} \qquad b = \left[-0.2440\left(\frac{\sigma_2}{\sigma_1}\right)^2+0.8491\left(\frac{\sigma_2}{\sigma_1}\right)+0.6001\right]\left(\frac{m_1}{m_2}\right)^{-0.03587} \tag{3}$$

in this equation σ_1 and σ_2 are the effective hard sphere diameters of the solute and the solvent, respectively, calculated from Purkait and Majumdar (1981) equation, σ_{12} is the arithmetic average of the two hard sphere diameters, m_1 and m_2 are the molecular masses, V is the molar volume, V_0 is the close packed hard sphere volume, and T is the absolute temperature. The two paramerters β and γ were postulated to be universal constants and were fitted from our data on diffusion coefficients of 1-octene in supercritical ethane, propane, and hexane in the temperature range 314 - 563 K and pressure range 44 - 124 bar yielding a solvent density range of 70 - 500 kg/m^3. They were determined as

$$\beta = 4.486599 x 10^{-29}\left[\frac{m}{s}\sqrt{\frac{g\,gmol}{K}}\right] \qquad \gamma = 1.7538 \tag{4}$$

Tables 6 - 8 give our measured data on 1-octene diffusion in supercritical ethane, propane and hexane as well as the absolute error of prediction using the above equation. The parity plot for the predictions is given in Figure 5.

Table 6. Diffusion Coefficients of 1-Octene in Ethane

T, K	P, bar	density kg/m^3	molar vol. $m^3/kmol$	10^9 x D_{12} m^2/s	prediction abs. error
322	124.1054	349.9	85.8703	16.26 ± 0.625	0.704
340	124.1054	299.9	100.1867	18.52 ± 0.940	5.84
357	124.1054	249.2	120.5698	22.67 ± 0.612	5.67
378	124.1054	199.9	50.3052	31.12 ± 0.346	4.63
414	124.1054	150.5	199.6412	37.61 ± 2.515	1.98
503	124.1054	100.9	297.7800	55.49 ± 4.476	1.60

Table 7. Diffusion Coefficients of 1-Octene in Propane

T, K	P, bar	density kg/m^3	molar vol. $m^3/kmol$	10^9 x D_{12} m^2/s	prediction abs. error
314	124.1054	500.7	88.0647	11.81 ± 0.288	10.70
354	124.1054	450.7	97.8345	14.31 ± 0.393	4.62
384	124.1054	401.1	109.9327	16.29 ± 0.746	4.67
408	124.1054	350.2	125.9109	22.70 ± 0.547	7.20
429	124.1054	300.6	146.6866	26.88 ± 0.843	3.98
453	124.1054	249.6	176.6587	24.59 ± 0.664	7.12
485	124.1054	200.6	219.8106	44.88 ± 0.640	9.33
544	124.1054	150.4	293.1782	54.65 ± 0.395	0.455
523	62.0527	73.64	598.7778	86.89 ± 1.610	0.560
533	62.0527	71.31	618.3425	88.77 ± 3.551	0.227
543	62.0527	69.18	637.3808	90.61 ± 0.451	0.960

Table 8. Diffusion Coefficients of 1-Octene in Hexane

T, K	P, bar	density kg/m^3	molar vol. m^3/kmol	10^9 x D_{12} m^2/s	prediction abs. error
483	124.1054	500.2	172.2711	18.50 ± 0.325	4.79
523	103.4212	437.7	196.8700	22.50 ± 0.110	2.54
523	82.7369	416.5	206.8908	26.22 ± 0.715	1.74
523	62.0527	381.6	225.8124	29.70 ± 1.521	1.82
523	44.8158	312.1	276.0974	38.97 ± 2.336	5.52
563	62.0527	257.2	335.0311	53.00 ± 2.755	5.08
563	44.8158	149.8	575.2336	82.10 ± 3.145	4.53

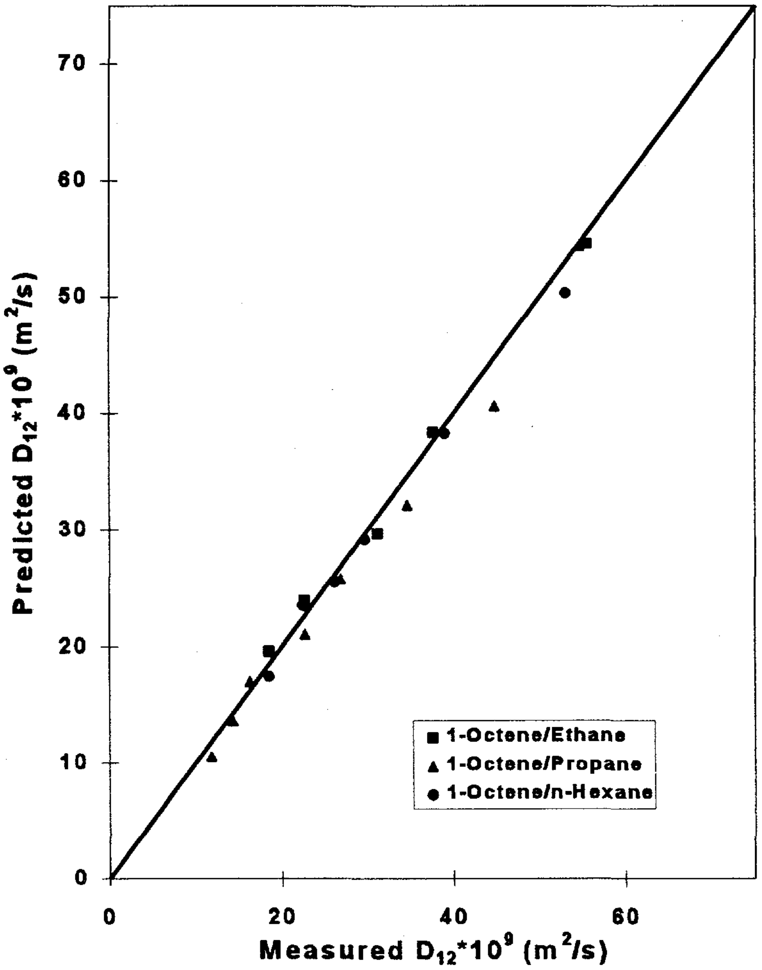

Figure 5. Comparison of experimental and predicted diffusivities for data presented in Tables 6-8.

Using the above values of β and γ we attempted to predict all the available data on diffusion in supercritical fluids in the literature. The self diffusion data ($\sigma_1=\sigma_2$ and $m_1=m_2$) can be predicted with an average absolute deviation of 3.64% as shown in Figure 6.

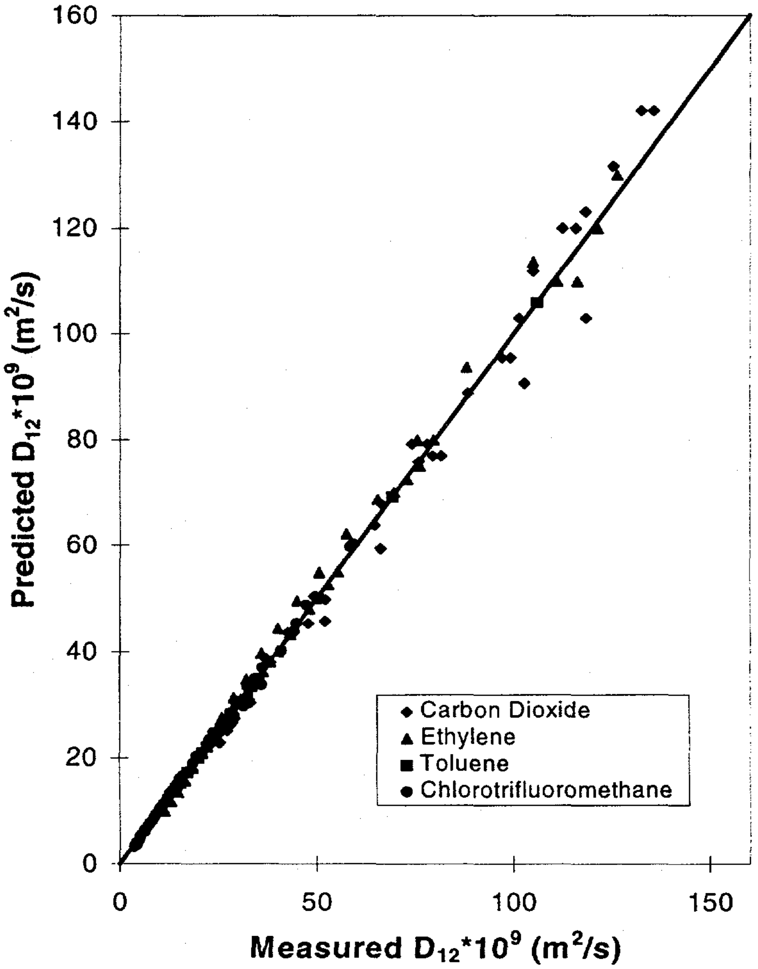

Figure 6. Prediction of self diffusion coefficients of supercritical carbon dioxide, ethylene, toluene and chlorotrifluoromethane.

The predictive equation uses the Purkait and Majumdar (1981) method for estimation of the hard sphere diameters which necessitates the critical temperature and critical volume of the species. These values are not available for some compounds and were estimated using available correlations (Eaton and Akgerman, 1997). Some estimates may have a large error resulting in large uncertainty in prediction of the diffusion coefficients. On the other hand, our predictions of all the data in the literature (101 systems and over 1500 data points), excluding our data, has an average absolute deviation of 15.08%. For systems where the critical properties (T_c and V_c) of the solute and the solvent are known, our average absolute deviation reduces to 9.62%. The data and predictions are presented in Appendix V.

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

A precipitated iron catalyst (100 Fe/5 Cu/4.2 K/25 SiO_2 on mass basis, prepared by Ruhrchemie AG) was tested in a fixed bed reactor under a variety of process conditions during conventional Fischer-Tropsch synthesis and supercritical Fischer-Tropsch synthesis. It was found that total olefin content decreased and 2-olefin content increased with either decrease in gas space velocity or increase in H_2/CO molar feed ratio, whereas olefin selectivities were essentially independent of reaction temperature (235-265°C).

Results from bed residence time effect studies in both modes of operation indicate that α-olefins are the dominant primary products of FTS. Normal paraffins are primary products also, and their fractional content on the Ruhrchemie catalyst was approximately 20%. Selectivity of n-paraffins and 2-olefins increases, whereas α-olefin selectivity decreases with increase in carbon number, due to secondary reactions of α-olefins.

Bed residence time and carbon number (molecular weight) effects were more pronounced during conventional FTS than during supercritical FTS. During conventional FTS high molecular weight products (C_8+ hydrocarbons) leave the reactor preferentially in the liquid state, and their residence time is longer than that of either the gas phase products, or the products formed during supercritical FTS. Diffusivities of high molecular weight α-olefins in the liquid hydrocarbon wax are significantly lower than the corresponding diffusivities in the supercritical propane, and hence the pore residence time of these products is longer during the conventional FTS. Longer residence time in the reactor and/or catalyst pores increases probability for secondary readsorption of α-olefins, and results in secondary formation of n-paraffins and 2-olefins. Also, desorption rates of heavy α-olefins are higher in supercritical propane than in liquid filled pores during conventional FTS, which results in higher selectivity of primary products. At high syngas conversions (~80%), selectivities of high molecular weight α-olefins during SFTS were significantly higher than those obtained during conventional operation. These results indicate that SFTS is a potentially attractive route for synthesis of high molecular weight alpha olefins from the synthesis gas.

Results with n-hexane as a supercritical fluid were qualitatively similar to those obtained with supercritical propane. Olefin selectivities obtained during were nearly the same as those obtained during SFTS with supercritical propane. α-olefin selectivity was higher during FTS at subcritical conditions than during conventional FTS, but the effect was less pronounced than during operation at higher partial pressure of n-hexane (SFTS).

Catalyst activity decreased during both conventional FTS and SFTS (propane as supercritical fluid) upon introduction of 1-dodecene. In contrast to the work of Fujimoto et al. (1995), on supported cobalt catalyst, we did not observe suppression of methane selectivity and enhancement of selectivity of high weight molecular hydrocarbons, during SFTS with co-feeding of 1-dodecene. Perhaps this is due to the fact that 1-olefin readsorption is significantly smaller on the iron than on the cobalt.

Major conclusions from tests in different modes of operation (conventional FTS in a fixed bed reactor, SFTS in a fixed bed reactor, and conventional FTS in a stirred tank slurry reactor - run SB-1370) at baseline process conditions: 250°C, 2 Nl/g-cat/h, syngas partial pressure of 1.48 MPa, and synthesis feed gas with H_2/CO molar ratio of about 0.67, are as follows.

In the fixed bed reactor tests activity of the Ruhrchemie catalyst was slightly higher (~5%) in the supercritical mode of operation with propane as supercritical fluid, and about 33% higher in supercritical n-hexane. This is attributed to higher diffusivities of reactants in supercritical fluids relative to conventional mode of operation (pores filled with liquid hydrocarbon wax). Catalyst activity in a stirred tank slurry reactor was lower than in a fixed bed reactor (conventional FTS). It is believed that low catalyst activity in run SB-1370 is due to low degree of iron reduction in the STSR.

Hydrocarbon selectivities in the fixed bed reactor were similar in both modes of operation. Methane selectivity in the STSR was lower than in fixed bed reactor tests (4.8 % vs. 6.2%), due to better temperature control in the former. Gasoline yield (C_5-C_{11} hydrocarbons) was higher in the

STSR than in fixed bed reactors (29 % vs. 23.6 %), whereas the yield of high molecular weight hydrocarbons (C_{12}^{+}) was higher in the fixed bed reactor (53.5% vs. 50%).

Total olefin content was the highest, and the 2-olefin selectivity was the lowest in the supercritical mode of operation. This is attributed to higher diffusivities of high molecular weight 1-olefins in supercritical fluids than in the liquid filled pores during the conventional FTS in either the fixed bed or the stirred tank slurry reactor. The total olefin content was lower and the olefin isomerization activity was higher during conventional FTS in the fixed bed reactor than in the slurry reactor. These differences in olefin selectivities are partly caused by differences in conversion levels, since higher conversions favor secondary reactions (~61% syngas conversion in the fixed bed reactor, and 38% in the STSR).

Our reaction studies indicate the importance of higher diffusion rates and pore cleaning effects of supercritical fluids when used as the reaction media. We have developed a sound equation for prediction of diffusion coefficients in supercritical fluids and have proven its validity at a wide range of conditions. We have also shown that the calculation of effective diffusivity from molecular diffusivity is through a constant conversion factor (ε_p/τ). This conversion factor can usually be approximated by ε_p^2 (Satterfield, 1970) which is a known parameter for a given catalyst or can easily be measured. Thus the ability to calculate the molecular diffusivity enables prediction of the effective diffusivity with reasonable accuracy. The prediction of effective diffusion rates in different solvents would give at least a qualitative comparison of product selectivity in FTS using different solvents at various conditions enabling optimization of the process conditions.

Recommendations for Future Work:

1. Studies with different supercritical fluids are recommended, since this may lead to improved catalyst performance.

2. Studies with cobalt based FTS catalysts are recommended. 1-olefin readsorption seems to be significantly more pronounced on cobalt than on iron, and this may lead to improved selectivities (higher yields of high molecular weight products and suppression of methane yield) as demonstrated in the study by Fujimoto et al. (1995).

3. Development of mathematical models for chemical reaction with diffusion in a porous catalyst pellet coupled with convective effects for fluid flow along the reactor is needed to quantify the effects of intraparticle diffusion. Kinetic parameters for multistep reaction network would need to be determined experimentally from experiments in fixed bed or stirred tank slurry reactors.

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APPENDIX I

Effects of Inert Gas and Supercritical Propane on Fischer - Tropsch Synthesis over an Iron Catalyst in a Fixed Bed Reactor

Paper published in Industrial & Engineering Chemistry Research, Vol. 34, pp. 72-77 (1995).

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APPENDIX II

Effect of Process Conditions on Olefin Selectivity during Conventional and Supercritical Fischer - Tropsch Synthesis

Manuscript accepted for publication in Industrial & Engineering Chemistry Research.

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APPENDIX III

Comparison of Catalyst Performance during Conventional FTS in Fixed Bed and Stirred Tank Slurry Reactors and Supercritical FTS in a Fixed Bed Reactor

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APPENDIX IV

Experimental Apparatus Used to Measure Molecular Diffusivities by Taylor Dispersion and Effective Diffusivities by Tracer Response and Data on Effective Diffusivities

Manuscripts published in *Journal of Chemical and Engineering Data*, 1994 & 1995

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APPENDIX V

Theory for Prediction of Diffusion in Supercritical Fluids and Prediction of all the Data in the Literature (101 Systems over 1500 Data Points)

Manuscript Published in *Industrial & Engineering Chemistry Research*, 1977

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