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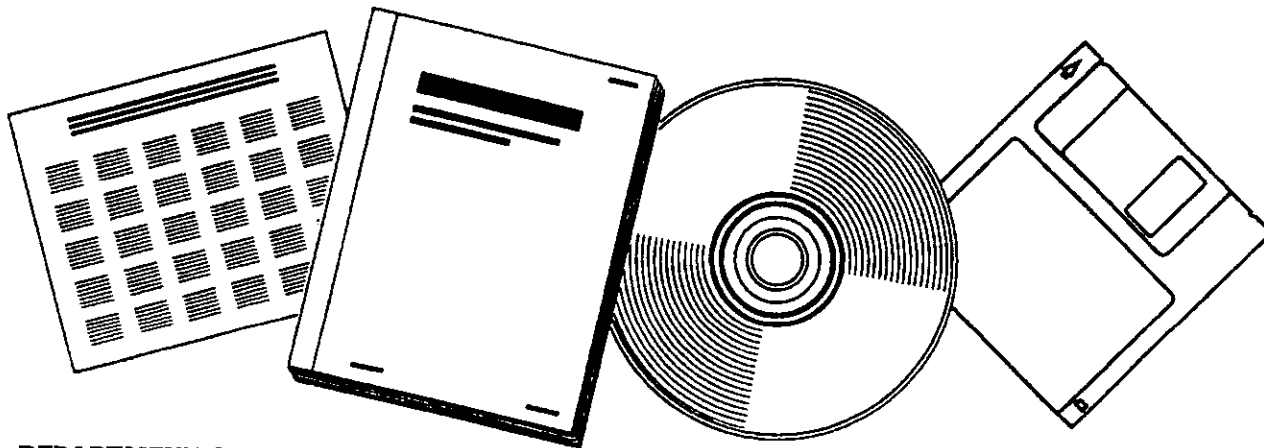Information is our business.

FISCHER-TROPSCH SYNTHESIS IN SUPERCRITICAL FLUIDS. FINAL REPORT

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FISCHER TROPSCH SYNTHESIS IN SUPERCRITICAL FLUIDS

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FINAL REPORT

by

Aydin AKGERMAN and Dragomir B. BUKUR
Co-Principal Investigators
Chemical Engineering Department
Texas A&M University
College Station, TX 77843-3122

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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,

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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

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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.

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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.

$$r_{H_2+CO} = k p_{H_2} \qquad (1)$$

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 (H₂/CO consumption ratio) is constant along the reactor length, the apparent rate constant can be expressed in terms of measurable quantities as:

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

where: F - H₂/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 (cm³·MPa)/(mol·K)); s - gas hourly space velocity (cm³ (STP)/(g-Fe·h)); U - usage ratio at the exit from the reactor; X_{H_2+CO} - syngas conversion; y^0_{SG} - mole fraction of syngas in the feed (y^0_{SG} = 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.
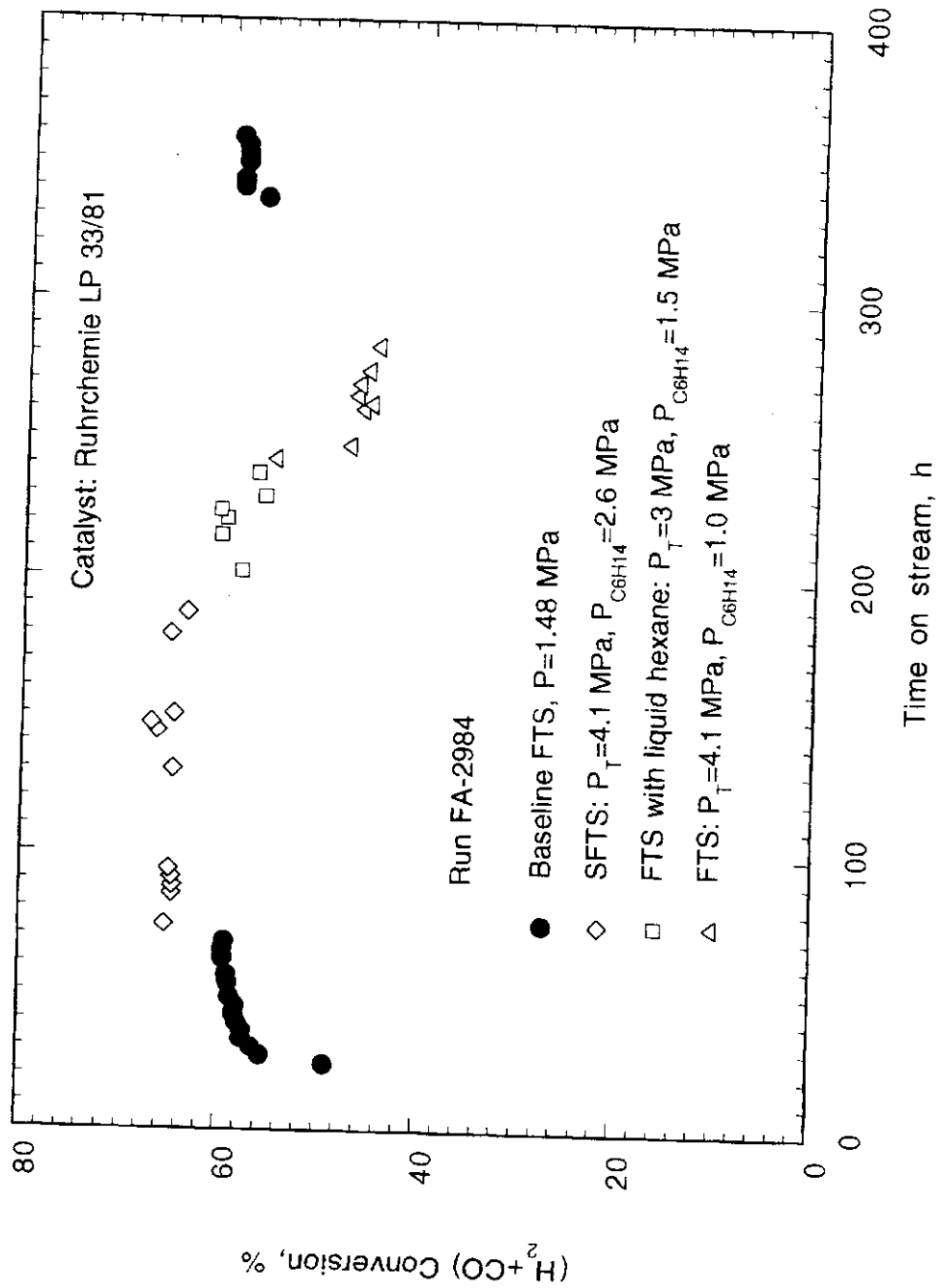
Figure 1. Variation in synthesis gas conversion with process conditions and time on stream during Run FA-2984.

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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.

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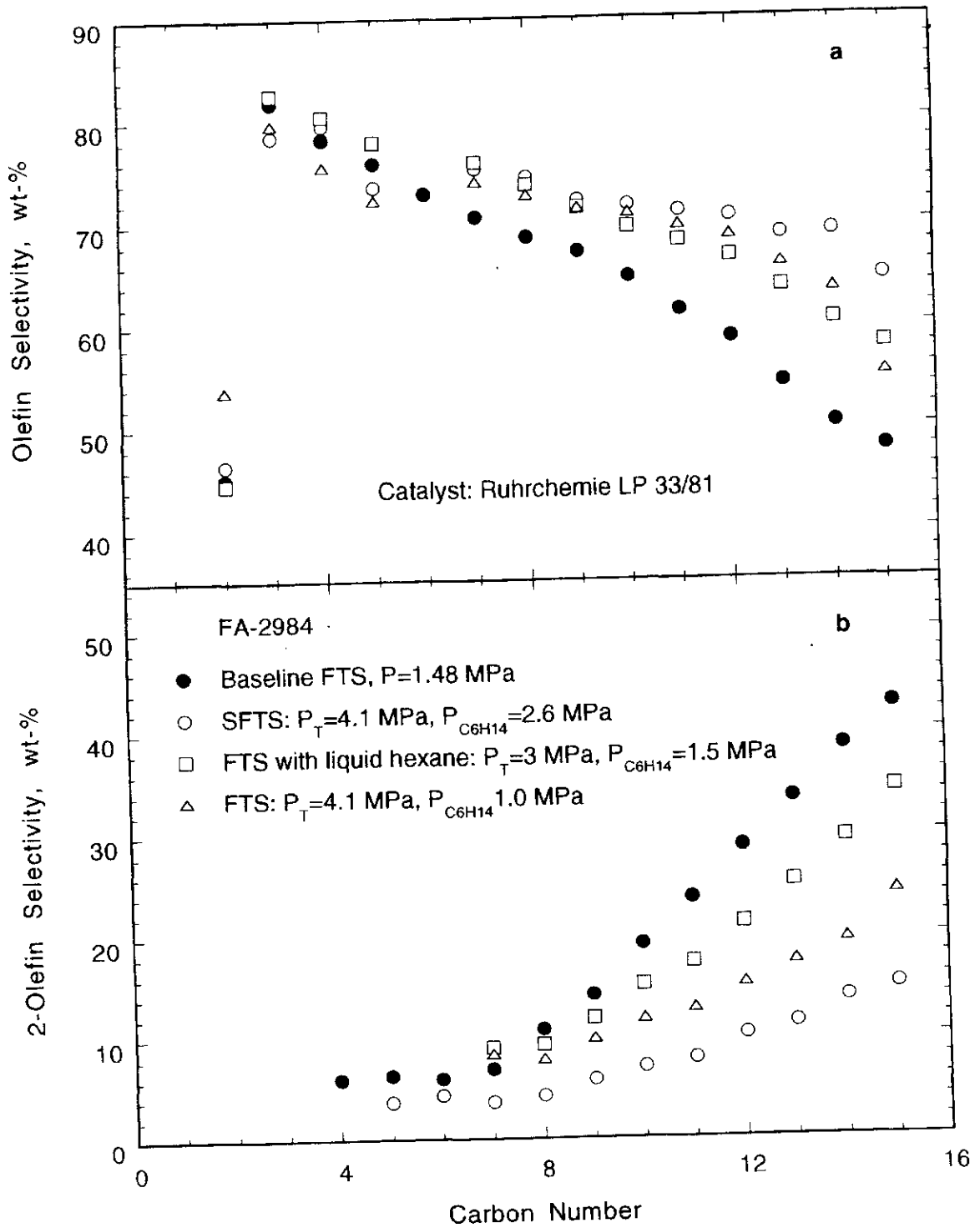
Figure 2. Olefin and 2-olefin selectivities during different periods of Run FA-2984.

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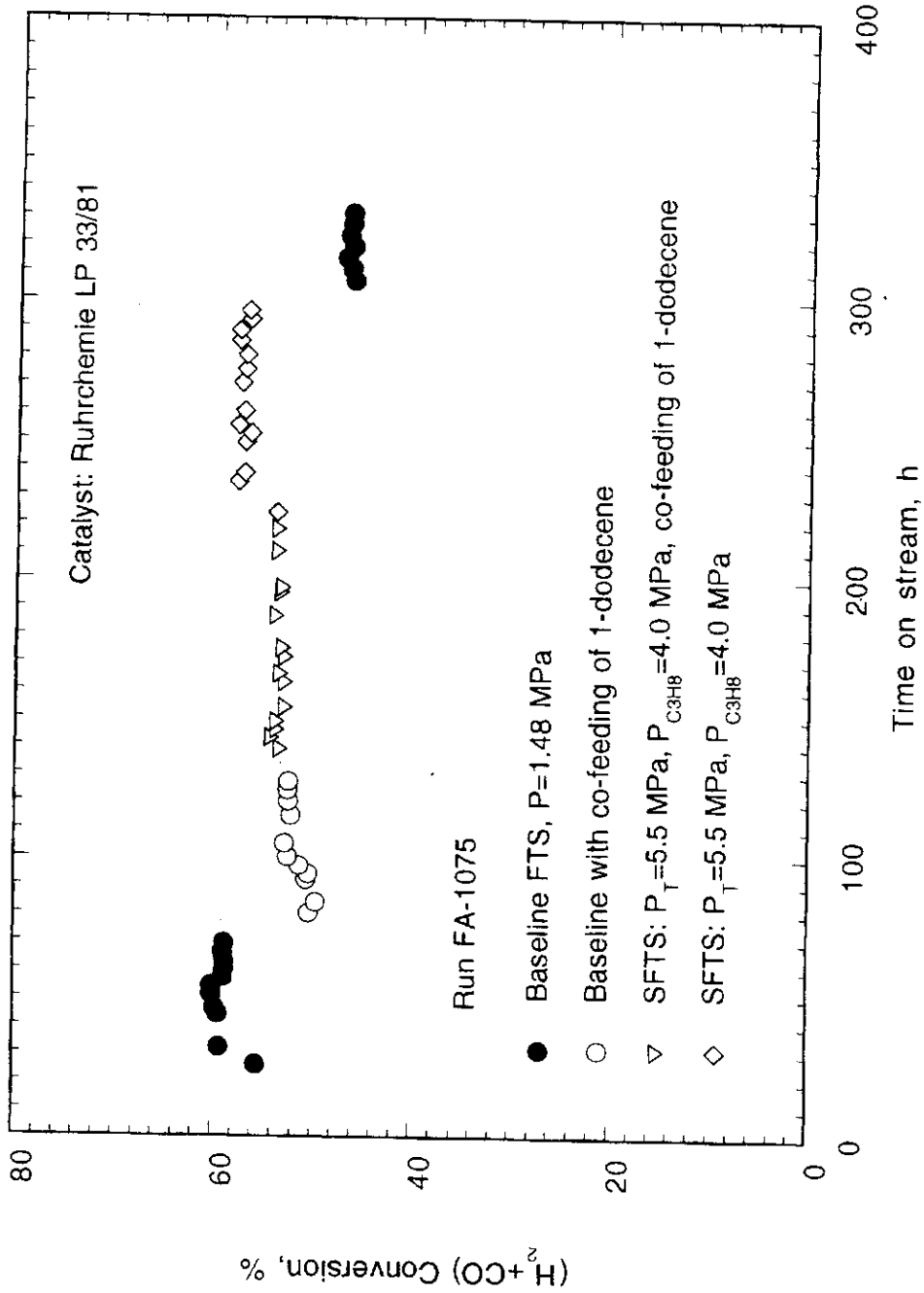
Figure 3. Variation in synthesis gas conversion with process conditions and time on straem during Run FA-1075.

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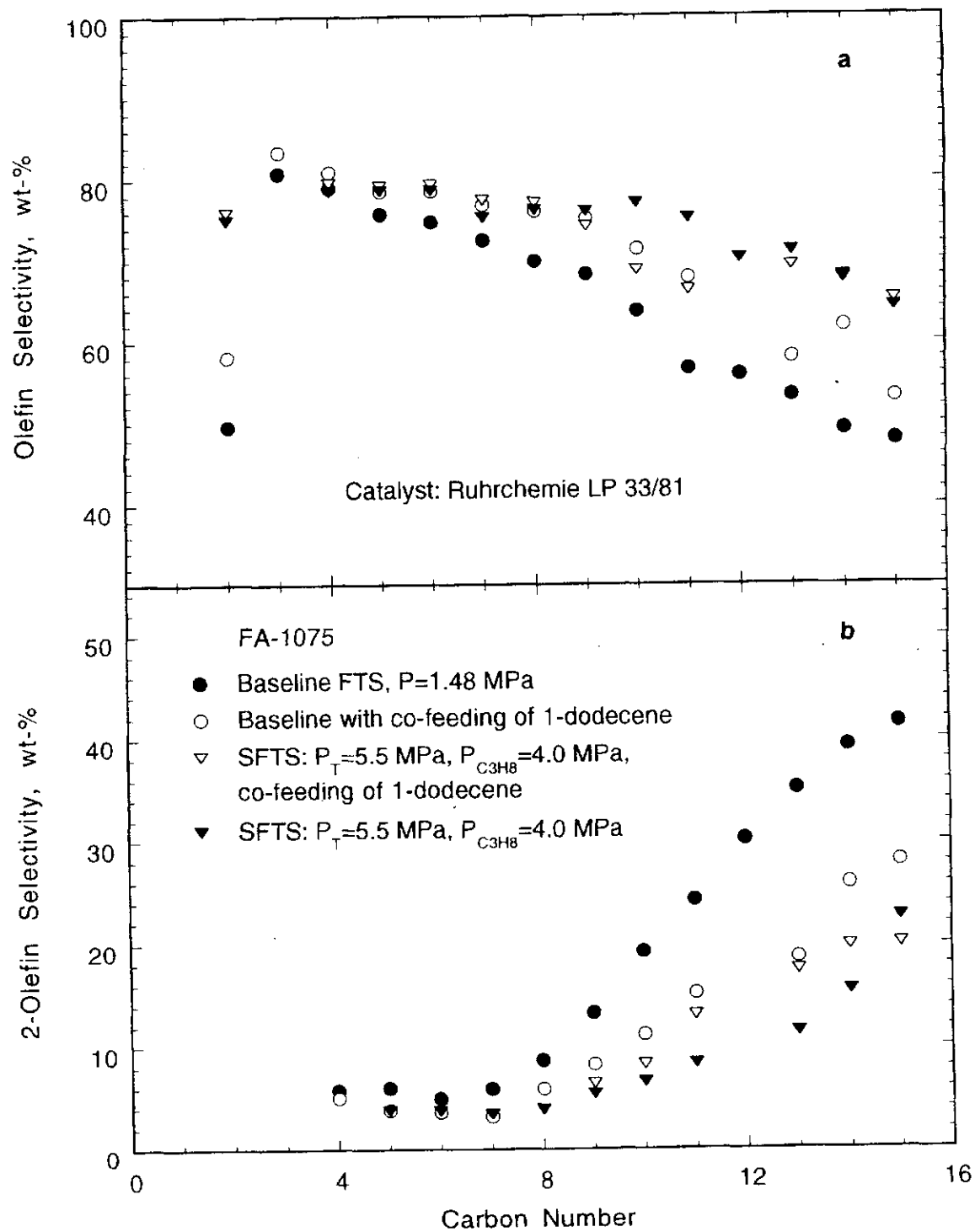
Figure 4. Olefin and 2-olefin selectivities during different periods of Run FA-1075.

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).