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on

**FISCHER-TROPSCH SYNTHESIS IN
SUPERCRITICAL REACTION MEDIA**

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Fischer-Tropsch Synthesis in Supercritical Media

Introduction

The goal of the proposed research is to develop novel reactor operating strategies for the catalytic conversion of syngas to transportation grade fuels and oxygenates using near-critical (*nc*) fluids as reaction media. This will be achieved through systematic investigations aimed at a better fundamental understanding of the physical and chemical rate processes underlying catalytic syngas conversion in *nc* reaction media. Syngas conversion to fuels and fuel additives on Fe catalysts (Fischer-Tropsch synthesis) was investigated.

Specific objectives are to investigate the effects of various *nc* media, their flow rates and operating pressure on syngas conversion, reactor temperature profiles, product selectivity and catalyst activity in trickle-bed reactors. Solvents that exhibit gas to liquid-like densities with relatively moderate pressure changes (from 25 to 60 bars) at typical syngas conversion temperatures (in the 220-280°C range) will be chosen as reaction media.

Interest in syngas conversion technology is primarily dictated by the ability to produce liquid fuels via indirect coal liquefaction and the potential use of methanol as a fuel intermediate for producing other oxygenates such as methyl tertiary butyl ether (MTBE) and tertiary amyl methyl ether (TAME). A major future application of methanol synthesis is in Integrated Gasification Combined Cycle (IGCC) power plants, wherein methanol is produced during periods of low power demand and burned as an auxiliary fuel in combined-cycle gas turbines during periods of peak demand (Kornosky, 1992). The main research thrusts in syngas conversion to fuels and oxygenates have been the development of catalysts and reactor technology aimed at selectively *and* economically producing liquid fuels.

The Fischer-Tropsch synthesis is a highly exothermic reaction whereby carbon monoxide and hydrogen react to form hydrocarbons.



In addition to being a synthesis reaction, the Fischer-Tropsch reaction is a polymerization reaction as well. Hydrogen and carbon monoxide form monomer building blocks that join to form longer-chained molecules. This chain growth contributes to the exothermicity of the overall reaction. Consequently, when carried out in a gas-phase in a fixed-bed reactor, hot spots may form in the catalyst bed leading to deactivation of the catalyst by formation of carbon and by sintering. Additionally, the FT reaction produces low volatile, high molecular weight hydrocarbons (or wax) that accumulate on the catalyst surface and eventually lead to pore-plugging.

In order to provide better heat transfer and temperature control, a slurry phase technology in which catalyst particles are suspended in mineral oil was developed for FT synthesis (Kölbel and Ralek, 1980). However, reduced diffusivities in liquid-filled pores causes the overall reaction rate in the slurry-phase reaction to be much lower than in the case of the gas-phase reaction. In the case of methanol synthesis, the syngas conversion is also limited by thermodynamic equilibrium due to accumulation of methanol in the reaction zone. Clearly, the ideal reaction medium for the exothermic syngas conversion processes should possess liquid-like densities and heat capacities for efficient product desorption and heat removal, yet gas-like diffusivities for enhanced product removal and reaction rates. Near-critical reaction media offer such a unique combination of physical and transport properties.

While an *nc* solvent has liquid-like density and solvent power, the transport properties (momentum, thermal and mass diffusivities) are intermediate to that of a gas and a liquid. In the

vicinity of the critical point, these physical properties can be continuously varied between gas-like and liquid-like properties with relatively small changes in pressure and/or temperature (Paulaitis et al., 1983; Subramaniam and McHugh, 1986). Thus, *nc* reaction media offer an optimum combination of solvent and transport properties that is better suited than either gas-phase or liquid-phase reaction media for efficient heat removal *and* for enhanced transport rates of reactants/products in the catalyst pores. The easily-tunable densities of *nc* media (with relatively small variations in pressure) may thus be exploited for varying the relative transport rates of products and, thereby, for manipulating product selectivity.

The project objectives are addressed via systematic experimental investigations of syngas conversions in a trickle-bed reactor. FT synthesis was studied over a Ruhrchemie Fe catalyst at typical synthesis temperatures (240-260°C) employing *n*-hexane ($P_c = 29.7$ bar; $T_c = 233.7^\circ\text{C}$) as *nc* medium. The proposed research is aimed at determining operating pressure and temperature in the *nc* region that yield an optimum combination of liquid-like physical properties (densities and heat-capacities) yet gas-like transport properties (diffusivities and viscosities). Accordingly, overall syngas conversion, product selectivity and catalyst deactivation rates will be studied for both CO-rich and H₂-rich syngas compositions at various pressures in the *nc* region. On-line product analyses are carried out using an automated GC/FID/TCD system. The fresh and used catalysts are characterized with respect to surface area and pore size distribution.

2. Literature Review

2.1 FT reactor technology

Due primarily to excellent heat transfer characteristics as compared to fixed-bed operation, slurry phase reactors have been the major focus of research in FT reactor technology. A concise summary of FT catalysis and slurry reactor technology may be found elsewhere (Rao and Gormley, 1990; Srivastava *et al.*, 1990). Recent research in slurry reactor technology has been aimed at better understanding reactor hydrodynamics and transport characteristics (see for example, Stern *et al.*, 1985; Satterfield and Stenger, 1985; Deckwer *et al.*, 1986; Bukur *et al.*, 1990a; Zhou *et al.*, 1992). In August 1992, a pilot-plant slurry reactor unit with a target for producing roughly 1 T/day of liquid fuels was commissioned in LaPorte, Texas. This demonstration unit is capable of processing 6,000-13,000 NL syngas/hr/kg Fe. For a feed H₂/CO ratio of 0.5 and syngas throughput of 2,400 NL/h/(kg Fe), preliminary plant data indicate a CO conversion of 50-70% at 265°C and 290 psig with 65% CO₂ selectivity, 3-5% C₁ selectivity and 1-2.5% C₂ selectivity after 70-140 h on line (Bhatt, 1994). These operating conditions and product selectivities provide a benchmark for assessing the performance of the reactor technology based on *nc* reaction media.

Yokota and Fujimoto (1991) performed FT synthesis over Co-La/SiO₂ catalysts in a packed-bed reactor using N₂ (gas-phase), *n*-hexadecane (liquid-phase) and *n*-hexane (supercritical phase) as reaction media. The total pressure in their experiments was roughly 45 bars, with the syngas partial pressure being 10 bars and the reaction medium constituting 45 bars. For identical syngas composition (H₂/CO = 2) and syngas space velocity (100 sccm/g cat.), Yokota and Fujimoto report that supercritical *n*-hexane provides faster reaction rates and higher olefin selectivity relative to the liquid-phase reaction medium. The catalyst bed temperatures for the various runs ranged from 220-240°C.

Bukur and coworkers (1994) investigated FT synthesis on a Ruhrchemie Fe catalyst using N₂ and supercritical propane ($P_c = 42.5$ bars ; $T_c = 96.7^\circ\text{C}$) as the reaction medium. The catalyst temperature was 265°C and the total pressure was roughly 70 bars, with the syngas (H₂/CO = 0.67) partial pressure being 25 bars. Bukur and coworkers reported that while the overall conversion in the two cases was similar, the olefin selectivity was higher in the C₇₊ range when using propane as the reaction medium. Fan *et al.* (1992) investigated reaction rates and product

distribution during supercritical phase FT synthesis on γ -Al₂O₃ supported Ru catalysts with mean pore sizes of 11.4, 20, 27 and 33.5 nm. While more or less similar C₂-C₁₀ olefin yields were observed with all these catalysts, significantly higher C₁₀-C₂₀ olefin yields were observed in the case of the larger pore (27 and 33.5 nm) catalysts. This increase was attributed to enhanced mass-transfer rates in the larger pores, and consequently, a lower degree of secondary hydrogenation.

Yokota and Fujimoto (1991), Fan *et al.* (1992) and Bukur and coworkers (1994) reported FT rates and product selectivity with a supercritical reaction medium at only one pressure. As seen in Figure 1, increasing the pressure from 29-50 bars at 240°C produces significant increases in n-hexane density from gas-like to liquid-like values. Additionally, the transport properties vary by a few orders of magnitude near the critical point. These relatively large changes in physical and transport properties in the *nc* region should produce significant changes in the reaction rates, the reactor temperatures and product selectivity. This research was aimed at systematically investigating such changes.

2.2 Optimum operating conditions in the supercritical region

As reactor pressure is isothermally increased, the phase behavior of the reaction mixture (dominated by chosen *nc* reaction medium) and the rates of the physicochemical processes vary. At pressures below the critical pressure of the reaction medium, the reaction mixture exists as a low-density homogeneous gas phase. While the transport rates of the reactants and products are relatively high, the intrinsic reaction rates, product desorption rates and heat capacity of the reaction medium are relatively low. As the reactor pressure is increased above the critical pressure of the reaction medium, the phase behavior becomes complex due to the wide differences in the critical properties of CO, H₂, the reaction medium and the products. In such a case, two phases may form as shown in Figure 2; a low density phase dominated by syngas, and a dense phase dominated by the supercritical reaction medium. The syngas diffuses through the dense phase into the catalyst while the products that diffuse outward.

With increasing pressure in the supercritical region, the density and heat capacity of the hexane-dominated phase increase. The decrease in mass transfer rates at the higher pressures is offset somewhat by the increase in the intrinsic reaction rates. At sufficiently high pressures, however, the dense phase becomes liquid-like leading to severe mass transfer limitations. It should be clear therefore that an optimum pressure exists at which the ideal combination of gas-like transport properties and liquid-like physical properties are realized.

The existence of optimum operating conditions in the supercritical region for solid-catalyzed reactions was shown by us for 1-hexene ($P_c = 31.7$ bar; $T_c = 231^\circ\text{C}$) isomerization on a Pt/ γ -Al₂O₃ catalyst. The reaction was performed at 280°C. Since the critical temperature of 1-hexene and its product isomers is similar, the temperature of the reaction mixture is near-critical ($1.1 T_c$). Employing a single-pellet model, we showed that for an isothermal increase in pressure along this *nc* isotherm, there exists an optimum density at which catalyst activity is maximized (Baptist-Nguyen and Subramaniam, 1992). At lower-than-optimum densities, the catalyst undergoes deactivation due to a lack of extraction of the coke-forming compounds; at higher-than-optimum densities, the catalyst activity decreases due to pore-diffusion limitations in liquid-like supercritical reaction mixtures. These model predictions were confirmed by experiments recently (Ginosar and Subramaniam, 1994; Subramaniam and Jooma, 1995).

At a space velocity of 135 g hexene/g cat/h, end-of-run (8 h) isomerization rates are roughly twofold higher and deactivation rates are threefold lower in near-critical ($\rho_r = 0.85$) when compared to subcritical ($\rho_r = 0.42$) reaction mixtures (Fig. 3). Coke laydown is more than twofold lower when compared to subcritical conditions (Fig. 4). Consequently, *nc* reaction mixtures are found to maintain more than 70% of the accessible surface area and pore volume (Fig. 4). Pore-size

distribution data from coked catalysts revealed that the *in situ* extraction of coke-forming compounds by supercritical reaction mixtures alleviates pore-choking and prevents pore-plugging that otherwise occurs at subcritical conditions. Although coke laydown continues to decrease at higher supercritical densities, the isomerization rates are lower and the deactivation rates are higher due to pore diffusion limitations in dense (i.e., liquid-like) supercritical reaction mixtures. Thus, *nc* reaction mixtures provide an optimum combination of solvent and transport properties that is better than either subcritical (gas-like) or dense supercritical (liquid-like) mixtures for maximizing the isomerization rates *and* for minimizing catalyst deactivation rates.

The improved pore accessibilities in supercritical reaction mixtures favored the intermediate product (2-hexenes) due to enhanced desorption and transport of the products in the supercritical reaction mixtures. Thus, the ability to fine-tune hydrocarbon desorption and transport with *nc* media provides another means to manipulate pore-accessibilities and product distribution. We proposed to measure reaction rates and product selectivity on a Ruhrchemie Fe catalyst at roughly 240°C and at various pressures ranging from subcritical to supercritical values of the chosen *nc* medium. Such investigations are needed to better understand the underlying physicochemical processes and to determine optimum operating conditions for FT synthesis in *nc* media.

3 Experimental

3.1 Experimental Setup

Figure 5 shows the reactor and analytical units assembled for investigating FT synthesis in *nc* reaction media. The feed preparation section consists of a Brooks 5850 mass flow controller for syngas introduction, a pump for solvent introduction, preheaters, check valves, static mixer, and a safety head. The internal surfaces of the heated reactor and other reactor fittings are alonized to prevent: (a) catalytic activity of the reactor material; (b) carbon deposition via the Boudouard reaction at temperatures exceeding 200°C (Huff and Satterfield, 1982); (c) methane formation which inhibits the formation of especially higher alcohols (Stiles *et al.*, 1991); and (d) the formation of Fe and Ni carbonyls which are detrimental to catalyst activity. Furthermore, glass-lined tubing is employed for all post-reactor lines exposed to temperatures above 100°C.

The reactor is a 10" long, 0.5" i.d. tubular reactor. An Omega profile-thermoprobe with eight thermocouples is used to obtain the axial temperature profile in the tubular reactor. Stepping-motor-driven Autoclave® micrometering valves have been installed for pressure control of the reactor and of the syngas feed stream. The nearly 14,000 steps from the fully-open to the fully-closed valve positions allows fine control of the reactor pressure. The heated effluent line from the micrometering valve is routed to the GC for on-line analysis of the reactants and products.

All the measurement and control devices in the reactor unit (viz., thermocouples, pressure transducers, stepping motor controls for driving the micrometering valves, heaters, and the mass flow controller) are interfaced with the Camile® 2500 Data Acquisition and Control Unit (CDACS). Programmed sequences developed for reactor startup, operation and shutdown enhance the ability to accurately repeat experimental procedures.

3.2 Catalyst Pretreatment

The Ruhrchemie iron catalyst (percent weight composition: Fe₂O₃-82.8%, SiO₂-13.3%, K₂O-2.56%, CuO-3.8%) was stored in jars under a nitrogen blanket which were in turn kept in a dessicator. Then, for each reaction, a portion of the catalyst, usually about 1.1g, was removed for the run. This catalyst sample was dried in a Micromeritics FlowPrep 060 unit by flowing nitrogen

over the catalyst at 150°C for at least 2 hours or until the weight of the catalyst stopped decreasing. The catalyst was reweighed and generally found to lose about 10 wt. %.

The catalyst was next loaded into the reactor and held in place by glass wool and a 10 μ m titanium frit. High-purity helium (Linde, 99.9995%), was passed over the catalyst at approximately 50 sccm and 6.9 bar while the temperature of the bed was being ramped to 150°C. After the temperature of the entire reactor surpassed 150°C, flow was switched from helium to commercial-grade carbon monoxide (Scott Specialty Gases, 99.3%). The carbon monoxide flow was controlled by a Brooks 5850E mass flow controller at 50 sccm/gcat. Again, the pressure was controlled at 6.9 bar while the catalyst bed was further heated, this time to 280°C. After the *entire* catalyst bed was at or above 280°C, all the conditions were held constant for 18 hours. Thereafter, the flow of carbon monoxide was halted and replaced with helium while the temperature of the catalyst bed was reduced to 240°C and the reaction procedure commenced.

3.2 Reaction Procedure

Following the pretreatment procedure, the catalyst was exposed to helium at 240°C and 6.9 bar. The first step in the reaction sequence was to stop the helium flow and start feeding hexane (Fischer, HPLC grade) by a Waters Associates 6000 HPLC pump at a flowrate of 1.0 ml/min. Hexane was the reaction medium for all investigations. This process was continued until both the temperature of the catalyst bed (240°C) and the pressure within the reactor (variable) were at the desired values for the particular experiment. Then, the flow of syngas (Air Products, H₂-66.9%, CO-33.1%) was added at a rate equivalent to 100 sccm/gcat.

The stainless steel reactor was enclosed by an aluminum block which in turn was placed in a sand bath (constructed in house) through air was bubbled at 15 psig. In the aluminum block, cartridge heaters (OMEGA, Chromalox® high-density cartridge heater) were inserted. From the reactor, the product stream was heated the entire distance to the GC or to the point where the stream was directed to the cold trap. The temperature of all transfer lines was kept at 200°C by heating cords (Cole-Parmer, flexible heating cords) wrapped with fiberglass insulating tape. Leaving the reactor, the flow was directed to a hot wax trap. The trap is a 0.75" i.d., 0.25" thick aluminum block, heated by a Omega high temperature heating tape. The temperature of the trap was kept at 200°C for all runs.

Exiting the hot wax trap, the flow could be directed either to the GC (Hewlett-Packard, 5890 Series II) for on-line analysis or to the cold trap to collect the remainder of the condensable products. Permanent gases were vented from the cold trap to the roof. When the flow went to the GC, it passed through a three-way ball valve which selected from either the reaction, or a calibration gas, stream. The line exiting the hot wax trap was split, part of it going to the GC. This transfer line was wrapped with a flexible heating cord and kept at 220°C to ensure that there was no condensation in the transfer lines.) The alternate route, from the split after the hot wax trap, sent the stream to the cold trap, was not heated. The cold trap was also constructed from an aluminum cylinder bored to an i.d. of 0.75" and with a wall thickness of 0.25".

To provide cooling to the cold trap, the trap was wrapped with 0.25" copper tubing, through which an ethylene glycol/water mix was recycled through a cooling bath (Brinkman, RM6). The cold trap was periodically drained during the course of a run. Each run, after the syngas flow was initiated, was continued for about 8 hours, with samples sent to the GC after the first 20 minutes and approximately every two hours thereafter. Liquid samples were also taken sporadically from the cold wax trap for later, off-line analyses.

At the end of a run, the syngas flow was first halted and hexane left running through the reactor, cooling the catalyst. After the reactor had cooled and the pressure dropped accordingly, the hexane flow was stopped and helium was passed through the reactor to both cool the catalyst

bed and to flush out the remaining hexane. The temperature of the transfer lines was left at reaction conditions to avoid any condensation in the lines during shutdown. After one hour of helium flow, power to all heaters was stopped. The helium was usually left flowing through the reactor overnight.

The last part of the experimental procedure was the removal of the catalyst from the reactor. The catalyst particles were collected in a aluminum measuring dish after it was found that something about the catalyst after reaction caused plastic weighing boats to melt. The catalyst was then loaded again into the Micromeritics® FlowPrep 060 for drying. The catalyst was typically dried after reaction for at least 24 hours before being subject to micromeritic analysis.

3.3 Control

The Camile® 2500 data acquisition and control system (CDACS) was used extensively for these investigations. Not only were the mass flow controller, pressure regulating device, and all heaters controlled by the CDACS but several procedures, including pretreatment sequences and safety shutdowns were automated as well. The CDACS was also used for logging data during experiments.

The Brooks 5850E mass flow controller was wired directly to the CDACS unit. Wiring the mass flow controller in such a manner also permitted a separate override for the flow through this device to be installed in the CDACS system.

CDACS also was part of the pressure regulating unit. This consisted of an Autoclave Engineers 30 VRMM micrometering valve driven by a stepping motor assembly. The principle behind the design was for the valve to open or close to maintain reactor pressure at a desired set point using the pressure measured by a pressure transducer (Validyne, DP15-42). The stepping motor assembly is composed of a gear (mounted on the valve stem) interfaced with a worm gear driven by a stepping motor. The signal to the motor was delivered by a 15V power supply through a HC11 evaluation board. This board contained a chip with code written by Mr. Edwin Atchison, the technician of the Chemical and Petroleum Engineering Department at the University of Kansas.

The program received an output from a PID control loop from the CDACS unit and would in turn send an appropriate signal to the stepping motor. The code written was flexible in that there were several adjustable values which would change the signal sent to the motor based on what output was received from CADCS. The pressure control achieved by this process was excellent, both for pretreatment and reaction. In both cases, control was reached within the error of the transducer used.

The CDACS controlled all the heaters. The heaters used were of several types: flexible heating cords for the preheating section and transfer lines, high-density heating tape for the hot wax trap and cartridge heaters for the reactor block. A time-proportioned signal was delivered to a solid-state relay which in turn activated the heater. This method of controlling very different types of heaters allowed for control of temperatures within $\pm 2^\circ\text{C}$ in all cases.

The procedures for pretreatment and shutdown used an aspect of the CDACS whereby a series of actions, combined into a *phase*, will be executed until some condition, set by the user is reached. The system marches through these phases until the entire process, called a *sequence*, is complete. Thus, processes were automated which allowed for extended periods of unattended operation, continuous safety oversight and process reproducibility.

3.4 Catalyst Characterization

Since part of the present investigations centered on the deactivation of the catalyst used, a catalyst characterization unit was used. With the surface area and pore volume measured by this unit, useful information was available as to the extent of coking, thereby providing insight into the efficacy of using supercritical operating conditions for the Fischer-Tropsch reaction. A Micromeritics®, Gemini II 2370 Surface Area Analyzer was used to measure the surface area and pore volume of the catalyst used in a run. Measurements were made of the fresh, pretreated (only), and pretreated and reacted catalyst.

3.5 Analytical

The FTS yields a complex mixture of C_1 to C_{40+} hydrocarbons and C_1 to C_{16+} oxygenates, in addition to H_2O , CO_2 and unreacted syngas. The analytical method was designed to measure conversion, yield and selectivity. A sustained level of conversion would demonstrate catalyst activity maintenance, that could make supercritical FTS in a fixed-bed reactor more profitable than gas phase FTS in a fixed-bed reactor. A high rate of reaction or yield would demonstrate optimal transport properties that could make supercritical FTS in a fixed-bed reactor more profitable than liquid phase FTS in a slurry reactor. Selectivity measurement would highlight the fractions of interest, which include C_5 to C_{10} (gasoline range), C_{10} to C_{20} (diesel range) and C_{20+} (FT wax).

On-line analysis was chosen to avoid the pitfalls of off-line sampling for Fischer-Tropsch synthesis products, as outlined in Dictor and Bell's article (Dictor et.al., 1984). The disadvantages of off-line sampling include problems with quantitation, sample handling, and kinetics and transient studies. Quantitation requires accurate volumetric measurement be made of each phase, and the addition of phases (aqueous, organic and vapor) to yield the full product spectrum. Significant vaporization and oxidation of products, as well as further reaction, can occur during storage and handling. A time period on the order of days is required to collect sufficient sample when performing low conversion kinetics studies. Even the time period for collection with significant conversion is too long for some transient behavior studies.

The on-line analytical system arrived upon combined ideas from Dictor & Bell as well as Hackett & Gibbon (Hackett et.al., 1989) (Fig. 6). It consisted of a single gas chromatograph with high resolution capillary column/FID in parallel with a packed column/TCD (Dictor & Bell's contribution). In order to obtain the high resolution required for the complex FT product, the Supelco Petrocol DH capillary column was chosen. This 100 m x 0.25 mm nonpolar column is normally used for detailed analysis of gasoline, and was used in the FTS application to determine selectivity of alkane vs. alkene and hydrocarbon vs. oxygenate.

The sample was injected directly onto the capillary column rather than being split, and the sample line was located between a hot trap (for removing C_{20+}) and cold trap (for collecting remaining condensables). These last ideas along with the use of external standardization for calibration were borrowed from Hackett & Gibbon (1989). Atmospheric balancing was used for the external standard calibration. Peak identification is facilitated by a table of retention indices of over 300 compounds present in unleaded gasoline, as measured on Petrocol DH columns (White et al., 1992). An HP 3365 Chemstation software is used to control GC operation and peak integration.

Several temperature programs were tested using FTS organic samples obtained from Texas A&M, University of Kentucky and UOP. A program starting at ambient temperature and ramping at $2^\circ C/min$ proved optimal for resolving oxygenate from the hydrocarbon matrix in the TA&M product (upper chromatogram of Fig. 7). Cryogenics were required to obtain satisfactory oxygenate resolution in the UK and UOP products, as the background hydrocarbon matrix for

these samples was more complex in the lower carbon number range (lower chromatogram of Fig. 7).

The on-line product from supercritical FTS also required cryogenics, as it turned out, and good resolution of most of the alcohols was obtained (Fig. 8). In Figure 8, carbon numbers are indicated above the peaks of normal alkanes. Table 1 lists the product distribution for the chromatograms in Figure 4. Resolution of hydrocarbons was excellent for C_1 to C_5 , and coelution of trans-2-ene with normal paraffin occurred only after C_{12} . The large tail on the hexane solvent peak was a result of direct injection, which was preferable to split injection given the small fraction of hydrocarbons in the product. Sample size was kept at 50 μ l to avoid overloading the column, which has a sample capacity of 50 to 100 ng.

A Hewlett-Packard 5970 quadrupole mass spectrometer was used in GC/MS of off-line samples for positive identification of sample components. A spectral library was unavailable, so identification was limited to some major components, whose mass spectra were interpreted manually. In this way, the fingerprint of 1-alcohol, 1-alkene, normal alkane, and trans- and cis-2-alkene common to each carbon number was verified (see the fingerprint noted for C_8 in Fig. 8).

Syngas ($CO+H_2$) conversion was initially measured on a Supelco Carboxen-1000 packed column (5 ft x 1/8"), with a 6 ft x 1/8" ss pre-column packed with 80/100 mesh Hayesep D to backflush C_{3+} . The upper temperature limit of 225°C for the Carboxen column limited the temperature program of the column oven as well. This relatively low temperature caused problems with adsorption of heavy hydrocarbons on the capillary column, later manifested as large humps in the baseline which appeared occasionally on chromatograms of the product (sporadic desorption of the heavy compounds). The Hayesep D column provided adequate resolution with the cryogenic program mandated by the capillary column, and had an upper temperature limit of 290°C, so the Carboxen was removed and replaced with a piece of 1/16" x 0.030" i.d. piece of Silcosteel tubing. With the column oven ramped to 280°C, there were no further spikes in the baseline at high temperature, and analysis time was shorter.

Analysis of hydrogen proved to be a sticky problem. The thermal conductivity detector required for the measurement of permanent gases in the FTS product responds to the difference in conductivity between the carrier gas and sample component eluting from the column. The thermal conductivity of sample gases other than hydrogen is much less than that of helium, making helium the carrier gas of choice for these components. The thermal conductivity of hydrogen is greater than that of helium. Unfortunately, the thermal conductivity of the hydrogen-helium mixture is less than that of helium for low concentrations of hydrogen, making the TCD response to hydrogen nonlinear when helium is used as the carrier gas. For a sample size of 100 μ l, the response was linear for concentrations greater than 30% H_2 . Fortunately this proved adequate when 2/1 H_2/CO syngas was used, as the product concentrations fell within this linear range. However, the 1/2 H_2/CO syngas fell outside of the linear range, requiring a new set of parameters.

Initially, the H_2 peak was driven in the negative direction by concentrating the hydrogen using larger sample loops and by using higher detector temperatures. Replicate studies showed that the response, while being completely negative, was also parabolic over the concentration range of interest, even for 1 ml sample size (left curve of Fig. 9). The other end of the hydrogen-helium range was tried, using small sample loops to dilute the hydrogen and low TCD temperatures to drive the peak positive and increase sensitivity of detection.

A combination of 10 μ l sample size and 130°C detector temperature gave a positive response to hydrogen over the entire range of interest, but the response was also parabolic and the peak areas were comparable to those obtained for 250 μ l sample size using argon as a carrier gas, which gave a linear response. In addition, the flow restriction imposed by the 10 μ l sample loop may have been the reason for the lack of repeatability of capillary column chromatograms seen in a trial on-

line run. The restriction may have prevented the contents of the upstream capillary column sample loop from equilibrating with atmospheric pressure in the twenty seconds given for atmospheric balancing prior to sampling. The main reason for using helium over argon as a carrier gas was to increase sensitivity for the detection of CO₂ and H₂O, used to measure the extent of the water-gas shift. With H₂/CO ratio of 1/2, linearity was required only up to 30% H₂, and this was obtained using a 30 μl sample loop, which also gave more sensitivity to water gases than 250 μl argon (Fig. 10).

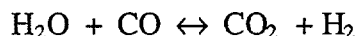
Whether helium or argon was used as a carrier gas, the addition of an internal standard to the reactant was desirable for conversion measurement, as conducted by Nijs and Jacobs (1981). The internal standard would be an inert gas (argon in the case of helium gas and vice versa) and the ratios of H₂ and CO to the inert in the feed and product could be used to directly calculate conversion, with no need to measure flows. The resolution of the added inert from the other permanent gases necessitated the replacement of the Silcosteel jumper with another Hayesep D column, identical to the precolumn and purchased previously when detector overload to CO was mistaken as column deterioration. The combination of the two Hayesep columns in series gave adequate resolution of internal standard using either argon or helium as a carrier gas.

4. Results

The measures used in our investigations to evaluate FT synthesis with supercritical media are conversion, selectivity, the Anderson-Schultz-Flory parameter (α), and micromeritic information (surface area and pore volume). In keeping with our objectives, temperature, syngas space velocity, syngas ratio (H₂/CO ratio), catalyst type, catalyst loading, syngas flowrate, and for our process, hexane flowrate were held constant at values listed in Table 2.

Temperature was not held constant but instead a constant rate of heat introduction was supplied to the catalyst bed. As a consequence, temperatures ranged from 240°C-270°C (1.01-1.07 T_r) over the range of experiments conducted. It was the pressure that was varied between runs. For the present set of experiments, pressure ranged from 20 to 60 bar. Since the reaction medium was hexane ($T_c = 31.3$ bar), experiments at pressures above 31.3 bar are considered "supercritical" and those experiments below 31.3 bar are considered "subcritical". These designations may not truly describe the reaction *mixture*. However, the above terms can probably at least describe the reaction medium which surrounds the catalyst pellet and through which the reactants diffuse to reach the catalyst surface and which solubilizes products from the catalyst surface and absorbs the heat of reaction (Fig 2).

The best determinant for the Fischer-Tropsch reaction is the syngas conversion. Fig. 11 is a graph of the conversions obtained from different runs. These ranged from 0% at 20 bar, rose to 46% at 50 bar and decreased to 20% at 60 bar (Fig. 11). The carbon monoxide (CO) conversion, on the other hand, also displayed on Fig. 11, was 0% at 20 bar, and continually rose to 64% at 60 bar. When these two conversions are examined simultaneously, the degree to which the water gas-shift (WGS) reaction



takes place can be found. While these results do show a significant effect of pressure, further ongoing tests are necessary to draw concrete conclusions.

Selectivity can be viewed from any of a number of biases. Here, the biases chosen were that of olefin selectivity and alcohol selectivity. Olefin selectivity, versus paraffins, was considered important since one measure of the usefulness of operating at supercritical conditions would be the increased ability to solubilize the primary products (olefins) from the catalyst before they undergo

further reaction. Due to the lack of reaction at 20 bar, olefin selectivity could only be measured from 31-60 bar (Fig. 12). There was a clear increase in the olefin selectivity as the pressure was increased from 31-39 bar for hydrocarbons up to C_6 . In the same hydrocarbon number range, there was a clear decrease in the selectivity to olefins from 39 to 60 bar. In the C_{7+} range, there is little discernible difference in the olefin selectivity at any pressure.

Another performance measure is the alcohol selectivity. Alcohols, and oxygenates in general, are of interest, as additives to transportation fuels. This is especially important given that oxygenates in gasoline was mandated by the 1990 Clean Air Act to increase effective January 1, 1995 (Stiegel, 1992). If supercritical fluid operation could solubilize more oxygenates, then it would be of great benefit. However, as far as the present runs are concerned (Fig. 13), supercritical operation exhibited no pressure effects other than to produce more higher carbon number alcohols at higher pressure. This could be attributed to pressure effects only (Advances in Catalysis, Emmett (ed.), 1956) and may not necessarily have been due to increased solubility.

Results of the ASF parameter, α , were ambiguous, as in the case of conversions. Due to the changing nature of the catalyst during a reaction, the product distribution changes as well. This was manifest in the α as well (Fig. 14). For reaction at 31 and 50 bar, α gradually increased with time on-stream. However, in runs at 39 and 60 bar α either decreased or oscillated between on-line injections. At 20 bar, α was not even calculated since there was negligible conversion. At the end of a run, α was 0.59 for reaction at 31 bar, decreased to 0.48 at 39 bar and increased to 0.64 for both 50 and 60 bar (Fig. 15).

Runs were only conducted for an 8 hour time period. As a result, although the activity of the catalyst stabilized with time into a run, the steady-state activity of the catalyst was never reached. Additionally, the curves are not quite linear as expected. While this phenomenon was reported previously (Donnelly and Satterfield, 1989), its occurrence in our case may be due to the non-attainment of steady-state. Extended runs are planned to find the value of α which can describe the entire product distribution for FT reaction at a given pressure.

Micromeritic measurements were also made to obtain information on the physical characteristics of a catalyst after reaction. Table 3 summarizes the measurements taken after each of the five runs performed. The fresh catalyst information is an average of four measurements, whereas the pretreated (only) catalyst information is based on 6 measurements. The analyses of catalyst that undergone reaction are single measurements, except for the case of the 20 bar experiment measurements which are an average of three measurements. Unfortunately, all the information that can be gleaned from this data is that reaction at 20 and 50 bar caused the catalyst to lose much of the original surface area and pore volume. On the other hand, reactions at 31, 39 and 60 bar yielded catalyst that had lost less of both surface area and pore volume. In fact, results of the last three cases are probably all within experimental error of each other. Interestingly, in some cases, 39 bar and 60 bar experiments, the pore volume of the catalyst is actually *greater* after reaction than after just pretreatment. Whether this is caused by removal of species formed during pretreatment is being investigated further.

5. Concluding Remarks

A state-of-the-art reactor unit with provisions for on-line product analysis was assembled and successfully tested for investigating high pressure reactions. The reactor is rated to 400 bar at 350°C. Our investigations of FT synthesis on a Ruhrchemie catalyst indicates that for fixed syngas composition ($H_2/CO = 2$), syngas space-velocity (100 sccm/g cat) and *n*-hexane flow rate (1 cc/m), changes in total pressure from 39-60 bars increased CO conversions from 25 to 60% and the AFS chain growth factor α from 0.48 to 0.64. Also, the olefin selectivity in the C_1 - C_6 range showed a maximum in this pressure range.

We are encouraged by the fact that the maximum CO conversion (~60%), C₁ selectivity (3%) and (C₅-C₂₀) production rates are in the same range as targeted in the LaPorte, Texas slurry reactor demonstration unit. However, interpretation of the pressure effects and the determination of optimum operating conditions are complicated by the fact that the reactor temperature in virtually all the runs exhibited an increasing trend from 240-270°C. Our present investigations address these issues. We are currently investigating reaction rates and product selectivity on a Ruhrchemie Fe catalyst at roughly 240°C and at various pressures ranging from subcritical to supercritical values of the chosen *nc* medium. For a fixed syngas throughput (roughly 6 NL syngas/h/g Fe), the feed rate of the *nc* medium will be chosen such that isothermal reactor operation is achieved (Besides providing increased heat capacity, the *nc* medium also acts as a diluent moderating the reaction rate and hence heat generation rates). The ongoing investigations should thus help us to better understand the underlying physicochemical processes and to determine optimum operating conditions for FT synthesis in *nc* media.

We are confident that successful completion of the ongoing studies will lead to an advanced and economical processes for producing fuels and fuel additives from syngas -- an FT process with extended catalyst life and desirable product selectivity (i.e., lower C₁-C₄ yields and higher yields of olefins and oxygenates). The supercritical concept is also applicable for methanol synthesis with extended catalyst life and enhanced reaction rates, and for exothermic hydrogenation reactions in general. This funding has clearly helped us establish an experimental infrastructure for systematic investigation of these novel possibilities.

6. References

- Baptist-Nguyen, S. and B. Subramaniam, *AIChE J.*, **38**, 1027 (1992).
- Bhatt, ACS Meeting Presentation, San Diego, CA, March 1994.
- Bochniak, D. B., Snavely, W. K. and B. Subramaniam, Paper 121a, AIChE Annual Meeting, San Francisco, CA, Nov 1994.
- Bukur, D. B., S. A. Patel and X. Lang, *Appl. Catal.*, **61**, 329 (1990a).
- Bukur, D. B., Patel, S. A. and J. G. Daly, *AIChE J.*, **36**, 1731 (1990b).
- Bukur, D. B., Univ. Coal Research Contractors' Conference, Pittsburgh, June 1994
- Advances in Catalysis, IV: Hydrocarbon Synthesis, Hydrogenation, and Cyclization, Emmett, Paul H., (ed.), Reinhold Publishing, New York, pp. 228-233, (1956)
- Chantong, A. and F. E. Massoth, *AIChE J.*, **29**, 725 (1983).
- Deen, W. M., *AIChE J.* **33**, 1409 (1987).
- Deckwer, W. D., Kokiun, R., Sanders, R. and S. Ledakowicz, *I&EC Proc. Des. Dev.*, **25**, 643 (1986).
- Dictor, R.A. and Bell, A.T., *On-Line Analysis of Fischer-Tropsch Synthesis Products*, Industrial Engineering and Chemistry Fundamentals, **23**, 252 (1984)
- Donnelly, T. J., and Satterfield, C. N., *Applied Catalysis*, **56**, 231-251, (1989)
- Erkey, C., and A. Akgerman, *AIChE J.*, **36**, 1715 (1990).

- Fan, L., K. Yokota and K. Fujimoto, *AIChE J.*, **38**, 1639 (1992).
- Ginosar, D. M. and B. Subramaniam, in *Catalyst Deactivation 1994: Stud. in Surf. Sci. and Catal.*, **88**, B. Delmon and G. F. Froment (eds.), Elsevier, Amsterdam, pp. 327-334 (1994).
- Hackett, J.P. and G. A. Gibbon, *J. Chromat. Sci.*, **27**, 405-412 (1989)
- Huff, G. A. Jr. and C. N. Satterfield, *I&EC Fundam.*, **21**, 493 (1982).
- Jooma, A. and B. Subramaniam, *ACS Symposium on Supercritical Fluid Science and Technology*, Foster, N. and K. Hutchenson, Eds., in press (1995).
- Kölbel, H and M. Ralek, *Catal. Rev. Sci. Eng.*, **21**, 225 (1980).
- Kornosky, R. M., *PETC Review*, **6**, 30 (1992).
- McHugh, M. A. and V. J. Krukonis, "Supercritical Fluid Extraction: Principles and Practice", Butterworths, Boston, 1992.
- Nijs, H.H. and Jacobs, P.A., *J. Chromat. Sci.*, **19**, 40 (1981)
- Paulaitis, M. E., Krukonis, V. J., Kurnik, R. T. and R. C. Reid, *Rev. Chem. Eng.*, **1**, 179 (1983).
- Rao, V. U. S. and R. J. Gormley, *Catalysis Today*, **6**, 207 (1990).
- Satterfield, C. N., C. K. Colton and W. H. Pitchler, Jr., *AIChE J.*, **19**, 628 (1973).
- Stenger, H. G. and C. N. Satterfield, *Ind. Eng. Chem. Process Des. Dev.*, **24**, 407 (1985).
- Srivastava, R. D., Rao, V. U. S., Cinquegrane, G. and G. J. Stiegel, *Hydrocarbon Process.*, **Feb.**, 59 (1990).
- Stern, D., Bell, A. T. and H. Heinemann, *I&EC Proc. Des. Dev.*, **24**, 1213 (1985).
- Stiegel, G. J., *PETC Review*, **7**, 26 (1992).
- Stiles, A. B., F. Chen, J. B. Harrison, X. Hu, D. A. Storm and H. X. Wang, *I&EC Res.*, **30**, 811 (1991).
- Subramaniam, B. and McHugh, M. A., *I&EC Process Des. Dev.*, **25**, 1 (1986).
- Tiltscher, H., Wolf, H. and J. Schelchshorn, *Angew. Chem. Int. Ed.*, **20**, 892 (1981).
- White, C. M., Hackett, J. P., Anderson, R. R., Kail, S. and P. S. Spock, *J. High Resolution Chromatography*, **15**, 105 (1992).
- Yokota, K. and K. Fujimoto, *Ind. Eng. Chem. Res.*, **30**, 95 (1991).
- Zhou, P., Srivastava, R. D., Bose, A. C. and G. J. Stiegel, Paper 55h, AIChE Mtg., Miami Beach, FL, 1992.

List of Tables

Table 1: Product distribution for the chromatograms shown in Figure 8.

Table 2: Constant experimental conditions

Table 3: Surface Area and Pore Volumes of Ruhrchemie Iron Catalyst

Table 1. Product Distribution for the chromatograms shown in Figure 8.

Sig. 1 in C:\HPCHEM1\DATA\12NOV94\IR3.D
Capillary Column Analysis

Carbon #	Carbon # Mole %	1-Alkene + cis-/trans-		n-Alkane Mole %	
		1-Alcohol Mole %	2-Alkene Mole %		
1	1.218891	0.099721		1.11917	
2	0.485414	0.098711	0.094976	0.291726	
3	0.347866	0.029062	0.21424	0.100426	
4	0.175139	0.011384	0.103807	0.055389	
5	0.117775	0.006236	0.058209	0.030539	
6		0.003399			
7	0.04371	0.002119	0.020238	0.014181	
8	0.027457	0.000909	0.012208	0.009433	
9	0.018762	0.000771	0.007773	0.006628	
10	0.012221	0.000755	0.00511	0.004867	
11	0.008968	0.000558	0.003548	0.003859	
12	0.006659	0.000219	0.002666	0.003247	
13	0.005631	0.000211	0.00178	0.003367	
14	0.00462		0.001376	0.002999	
15	0.003641		0.00099	0.002524	
16	0.003443		0.000812	0.00254	
17	0.001851		0.000456	0.001232	
18	0.001119		8.71E-05	0.000887	
19	0.000576		0.000141	0.000436	
20	0.000266			0.000266	
SUM =		2.484011	0.254055	0.528418	1.653718

Packed Column Analysis

Injection #	Mole %			
	1	2	3	4
Time (min)	20	196	366	553
Compound				
H2	18.56534	18.27353	18.54419	19.08974
N2				
CO	7.166826	6.406703	7.709512	9.494291
CH4	1.878356	1.493036	1.136791	0.784935
CO2	4.431244	4.696458	3.701428	2.531879