

Prospect of Success in Scaling-up Fischer-Tropsch Synthesis Reactor Operates in Near-Critical and Supercritical Phase Media

Nimir O. Elbashir

Texas A&M University at Qatar, P.O. Box 23874 Doha, Qatar

Abstract

Conducting Fischer Tropsch synthesis (FTS) reactions in supercritical fluid (SCF) media has been demonstrated to have certain advantages over the traditional routes because of the unique characteristics of the supercritical phase (combination of liquid-like heat capacity and solubility for optimum temperature distribution and in situ extraction of heavy hydrocarbons from the catalyst pores and gas-like diffusivity for higher conversion). The pioneer study in this field was conducted by Karu Fujimoto and his team at the University of Tokyo (published in a short communication in *Fuel* volume 68, 1989). Series of studies then followed led by Bala Subramanian team at the University of Kansas, Drago Bukur team at Texas A&M, Burt Davis at the University of Kentucky, and Christopher Roberts team at Auburn University. The aforementioned studies concluded several advantages of operating FTS in SCF media versus operation in conventional media due to the followings: (1) in-situ extraction of heavy hydrocarbons from the catalyst pores resulting from high solubility in the supercritical phase, (2) elimination of interphase transport limitations thus promoting reaction pathways toward the desired products, (3) enhancement of α -olefins desorption that promote the chain growth process prior to secondary reactions, and (4) excellent heat transfer compared to gas-phase reaction that results in more long chain products. This paper covers a brief review on major studies conducted in the field of SCF-FTS. It also looks at the prospectus in designing a high-pressure fixed-bed reactor setup to facilitate FTS operation under near-critical and supercritical solvent condition. The design of the reactor considers utilizing the high pressure operation under SCF-FTS in separation of hydrocarbon products from supercritical solvent as well as in hydrocarbon fractionation.

1. Introduction

Fischer-Tropsch synthesis (FTS) continues to receive attention as an alternative for the production of ultra-clean transportation fuels, chemicals, and other hydrocarbon products through the heterogeneous catalytic conversion of readily available syngas (a mixture of H_2 and CO) resources. Diesel fractions from FTS have unique characteristics that include very low sulfur and aromatic content, high cetane index and exceptional clean burning in compression-ignition engine. Compared to crude oil derived diesel, FTS diesel fuel has been shown to reduce the emissions of carbon monoxide, nitrogen oxides, hydrocarbons and other particulates. More important for the FTS process is that it can take full use of rich sources of natural gas and coal as a supplement to decreasing oil resources. FTS performance in industrial fixed-bed-reactors (gas-phase) suffers from local overheating of the catalyst surface and high degrees of methane selectivity, thereby decreasing yield of desired products (Lang, et al. 1995, Kolbel and Ralek 1980). Sasol (a South African's oil company) play a major role in developing industrial technologies of FTS reactors and reaction systems subsequently participated in the development of slurry bubble reactors (liquid-phase) to overcome the limitations of fixed-bed-reactor FTS (Geertesma 1990). Such operation provides an excellent temperature distribution for this highly exothermic reaction since the paraffinic solvent (e.g. octacosane C_{28} hydrocarbon) used as a reaction medium has a thermal mass over 500 times greater than that of the gas-phase operation in a fixed-bed-reactor. Nevertheless, the disadvantages of FTS slurry reactors are the backmixing of gas phase that bubbles through the slurry which normally results in significant drop in conversion per pass as well as catalyst attrition and the technical difficulty associated with catalyst separation from slurry phase.

The above obstacles in industrial gas-phase FTS (fixed-bed-reactor) and liquid-phase FTS (slurry-reactor) have directed research efforts on FTS towards the application of supercritical fluid solvents in order to improve product control in the liquid fuels range. Utilization of supercritical fluids (SCF) in industry has received considerable attention since the early 1980s started with the development of technologies for extraction of commodity chemicals

and synthetic fuels. By the mid 1980s, research on new applications of SCF shifted towards more complex and valuable substances that undergo a much broader range of physical and chemical transformations. A great deal of innovation took place in studies of reactions, separations, and materials processing of polymers, foods, surfactants, pharmaceuticals, and hazardous wastes (Johnson, and Penninger 1989). Supercritical fluid solvents combine the desirable properties of gas-like diffusion with liquid-like heat transfer and solubility, thus overcoming several of the current industrial limitations (Baiker 1999) (see Figure 1). Fine adjustments in operating conditions near the critical point can result in superior control of the FTS process, including tunable product distributions (Elbashir and Roberts, 2005).

2. Review on Research Activities in Application of Supercritical Fluids in Fischer-Tropsch Synthesis

The pioneer study on the application of SCF's in FTS reaction of Yokota and Fujimoto (a research group from the University of Tokyo, Japan) was first published in a short communication in 1989 (Yokota, and Fujimoto, 1989).

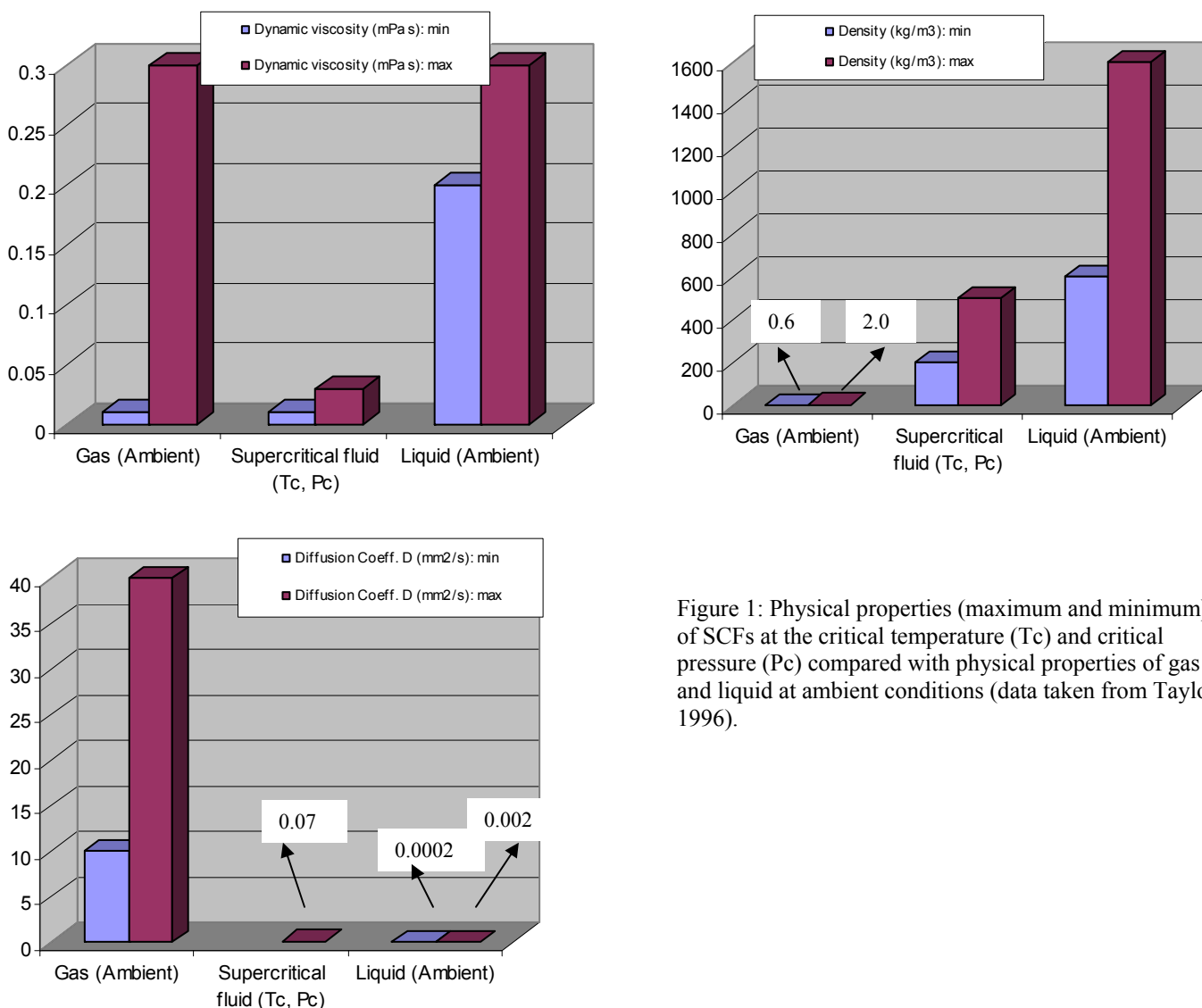


Figure 1: Physical properties (maximum and minimum) of SCFs at the critical temperature (T_c) and critical pressure (P_c) compared with physical properties of gas and liquid at ambient conditions (data taken from Taylor 1996).

In a later study they reported detailed results comparing the performance of the FTS reaction in supercritical phase to the conventional FTS processes (gas-phase and liquid-phase) (Yokota, et al. 1990). They demonstrated that conducting FTS reactions using SCF media offers unique characteristics, such as high diffusivity of reactant gases, effective removal of reaction heat and *in situ* extraction of high molecular weight hydrocarbons (wax).

Since then Fujimoto's research group reported numerous studies on SCF-FTS addressing influence of the catalyst type and characteristics [examples are 20, 21], selective synthesis of wax and heavy hydrocarbons (e.g. Fan et al. 1997, Tsubaki, and Fujimoto 2000, Tsubaki, et al.2002, Xiaohong et al. 2005) to and influence of the type of solvents on SCF-FTS reaction performance (examples is Wen-sheng, et al 2007). Bukur's and his workers supported the previous findings of the enhancement in α -olefin selectivity when conducting FTS reactions under SCF media (Lang, et al . 1995, Bukur, 1997). Their findings show that the total olefin and 2-olefin selectivities were essentially independent of reaction temperature but changed significantly when conditions were changed from conventional gas-phase and near-critical operations to supercritical operation. Subramaniam and his coworkers developed an on-line GC method for analysis of C₁-C₃₀ products from FTS reactions (Snavey, and Subramaniam 1997) . In another study, they also addressed the influence of pressure on the SCF-FTS operation, particularly its effect on the catalyst effectiveness factor and pore diffusivity (Bochniak, and Subramaniam 1998). Other contributions in the SCF-FTS field have come from Davis and his coworkers (Jacobs, et al 2002 and 2003. In the studies of Jacobs et al. they addressed the issue of catalyst stability in SCF-FTS reaction over 25% Co/Al₂O₃ under SCF-FTS. Roberts and his coworkers have continued these efforts in exploring the advantages of operating FTS reaction under supercritical hexane and supercritical pentane medium over alumina supported cobalt catalysts (15%Co-Pt/Al₂O₃ and 15% Co/Al₂O₃) (Huang and Roberts 2003, Huang et al 2004, Elbashir and Roberts 2004a,b, 2005, Elbashir, et al 2005). Fan's research group at the Institute of Coal Chemistry in China has also reported improved selectivity of heavy hydrocarbons as a result of co-feeding the C₁₄ olefins with the reactants mixture (Zhou, et al. 2002). Other research groups focused on the phase behavior and critical properties of SCF-FTS reaction mixtures, such as solvent-reactants (CO and H₂) mixtures (e.g. Joyce, et al. 2000), solvent-product mixture (e.g. Joyce, et al. 1999, 2000), and solvent-reactant-products mixture (Elbashir and Roberts, 2005a). Positive effects of SCF-FTS operation on cobalt catalysts *in situ* characteristics and stability was addressed by Elbashir et al. 2005. Measuring the phase behavior based on thermodynamic modeling of a mixture composed of supercritical solvent and hydrocarbon product was also reported in literature (Polishuk et al. 2004).

2.1 Selection of Supercritical solvent for FTS reaction

Only hydrocarbons (e.g. propane, n-pentane, n-hexane and hexanes, n-heptane and n-decane) have so far been used as supercritical solvents for the FTS reactions (references listed in previous section). Hydrocarbon solvents are preferred than the environmentally favored supercritical solvents (supercritical CO₂ and supercritical H₂O) for FTS conditions because their critical properties (specifically temperature) are within the activity range of the Co, Fe and Ru catalysts used in the FTS reaction. Table 1 shows a summary of the critical properties of light hydrocarbons (C₂-C₈) compared to the well known green solvents ScCO₂ and supercritical water. The criteria for selecting appropriate solvents for SCF-FTS were previously addressed by Fan and Fujimoto (1999) as follows:

1. The critical temperature and pressure should be slightly lower than the typical reaction temperature and pressure. In this case, selecting CO₂ as the SCF is not appropriate since its critical temperature (30.9 °C) is much lower than that needed for the FTS reaction (approximately >180 °C for Co and Ru based-catalysts and >200 °C for Fe based-catalysts), while its critical pressure (73.8 bar) was considerably higher than that used for either a gas phase or a liquid phase FTS reactor (approximately 20 bar).
2. The solvent should not poison the catalyst and should be stable under the reaction conditions. The low molecular weight paraffins chosen for SCF-FTS studies are both unreactive and stable. Also, the paraffins (i.e. SCF solvents) are not coke precursors, even under the mild temperatures of FTS (Jacobs et al., 2003).
3. The solvent should have a high affinity for aliphatic hydrocarbons in order to extract the wax from the catalyst surface and reactor. As shown in Table 2.1, most of the solvents that are used in SCF-FTS operations have this ability.

In earlier study, Jacobs, et al.(2003) suggested that using solvent mixture composed of 55 volume% hexane/45 volume% pentane should give favorable liquid-like densities, while still maintaining gas-like transport properties at a pressure of approximately 82.4 bar. They used a Hysys 2.1 process simulator for the determination of the critical properties of this solvent mixture and the effect of pressure on its density, as shown in Figures 1 & 2, respectively. Fan and Fujimoto (1999) reported SCF-FTS performance in both hexane

environment and pentane environment. They concluded that operating an FTS reaction under supercritical pentane ($T_c = 196.7\text{ }^\circ\text{C}$, and $P_c=33.6\text{ bar}$) environment is preferred for wax synthesis experiments where the reaction temperature is low, while for the production of light hydrocarbons and middle distillates that require a high reaction temperature hexane can be chosen as supercritical solvent ($T_c = 233.3\text{ }^\circ\text{C}$, and $P_c=29.7\text{ bar}$). Huang, et al. (2004) reported a comparison between the performances of Sc-pentane-FTS and Sc-hexane-FTS over an alumina supported catalyst and under similar reaction temperatures and densities. In order to achieve the same density condition at $240\text{ }^\circ\text{C}$ ($\rho\approx 0.33\text{ g/cm}^3$), higher pressures are required in pentane (38 bar in hexane vs. 65 bar in pentane).

Table 1 Critical properties of hydrocarbon solvents compared to those of CO_2 and water. Solvents highlighted are commonly used in SCF-FTS. Data obtained from *NIST Scientific and Database* website <http://webbook.nist.gov/chemistry/name-ser.html>.

Solvent	Critical Temp. $T_c, ^\circ\text{C}$	Critical Pressure P_c, bar	Critical Density $\rho_c, \text{g/cm}^3$
<u>Green solvents</u>			
Carbon dioxide (CO_2)	30.9	73.75	
Water (H_2O)	373.9	220.6	
<u>Hydrocarbons</u>			
Propane (C_3H_8)	96.6	42.5	2.244
n-Butane (C_4H_{10})	151.85	38.0	2.273
n-Pentane (C_5H_{12})	196.65	33.6	2.318
n-Hexane (C_6H_{14})	233.3	29.7	2.331
n-Heptane (C_7H_{16})	266.85	27.84	2.350
n-Decane ($\text{C}_{10}\text{H}_{22}$)	344.84	21.1	2.286

2.2 Catalyst activity and stability during supercritical FTS operation

Deactivation of a catalyst during conventional FTS reaction results in a drop in syngas conversion and hydrogenation activity and has been attributed to many reasons; the poisoning or blocking of catalytic active sites by products or carbonaceous species (Madon and Igelisa 1994, Anderson et 1949), or the partial reoxidation of the catalyst (especially cobalt-based catalysts) at the surface by water or the oxygen produced by CO dissociation (Jager, and Espinoza, 1995; Henrici-Olive 1976). Effective in situ extraction of heavy hydrocarbon products from the catalyst pores was assumed to decrease significantly due to the deactivation of FTS catalysts (Jacobs, et al. 2003). However, stability in catalyst activity was observed even over a long time-on-stream (TOS) FTS operation when conducting the reaction in supercritical fluid medium (Elbashir, et al. 2005). This was early explained by the model proposed by Yokota et al.(1990). The model shows that the desorption and diffusion of FTS products are well-balanced in the supercritical phase. Therefore, the overall mass transfer of the products is most effective, which inhibits secondary reactions during the chain propagation. Lang, et al. (1995) demonstrated that operating FTS under supercritical propane over a precipitated iron catalyst stabilize the catalyst activity for a relatively long period of time (120 hr) with higher CO conversion and H_2/CO usage ratio than for the conventional gas phase reaction. They also showed that returning to the gas-phase reaction after operating in SCF sustains the catalyst activity for more than 250 hr in total.

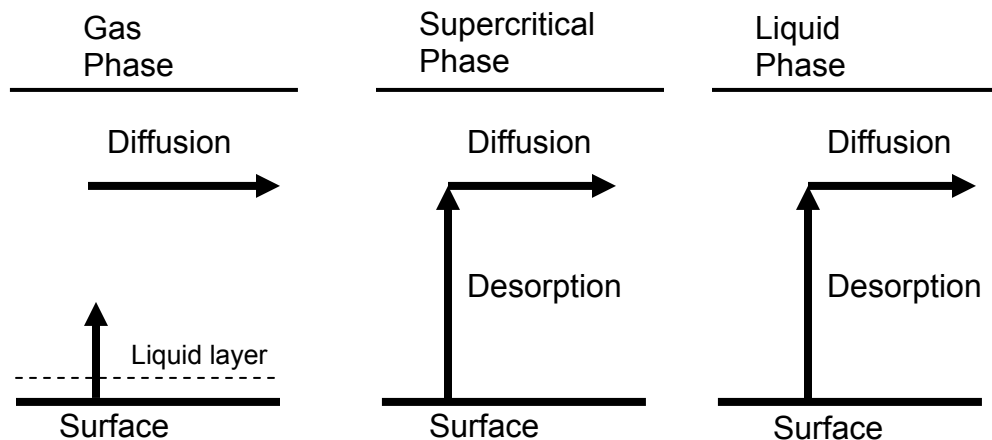


Figure 2 Model of overall diffusion of the products in three reaction phases. Source [15].

Huang and Roberts (2003) have also shown that activity in SCF-FTS is higher than in gas-phase FTS despite the fact that mass transport and product bulk diffusion rates are higher in the gas phase than in the supercritical phase. Their steady state data (20 h for SCF and 30 h for gas -phase) show that operating FTS in Sc-hexane yields higher CO conversions (ca. 70%) relative to the gas-phase FTS (ca. 50%). In addition, their findings show that steady-state operation was achieved more rapidly under SCF-FTS than in gas-phase FTS. They attributed these results to the higher solubility and in situ extractability of the SCF, resulting in suppressed coke formation inside the catalyst pores. Moreover, the liquid-like gas membrane resistance that occurs on the catalyst surface in gas-phase FTS could be reduced under supercritical-phase operation by the solubility-driven removal of heavy hydrocarbons (Huang and Roberts, 2003). By using a tailor-made wax, Jacobs et al. 2003 were able to simulate the extraction process of heavy wax from inside the catalyst pores for the three phases. Their findings show that wax can easily and quickly be extracted from the catalyst pores in both the supercritical phase and liquid-phase (up to 80% extraction within 1 hr), while little was extracted during gas-phase operation. In another study Elbashir et al. 2005 showed that the correlations of catalyst activity and selectivity with the catalysts surface characteristics reveal that pore radius of the catalyst has an influence on both syngas and CO conversions in gas-phase FTS. However, no such correlation was observed in the case of SCH-FTS, indicating an alleviation of that mass transfer limitations typically controlled by interparticle characteristics of the catalyst. This is attributed to the higher solubility of heavy products in the SCH medium that inhibits the condensation of those products inside the catalyst pores and enhances their in situ extraction. The XRD and magnetic characterizations of the used catalysts reveal that in situ reducibility of the Co_3O_4 to hcp Co^0 or fcc Co^0 is taking place during the FTS reaction. However, minimal in situ reduction was observed in the case of gas-phase FTS, whereby significant changes in the reduced cobalt electronic state and support (alumina, and silica) phase were detected under SCH-FTS conditions. The outcome of their XRD and magnetic characterizations of the used catalysts show that in situ reducibility of the cobalt oxide takes place during the FTS reaction in both GP-FTS and SCH-FTS conditions. In the latter, the in situ reduction of Co_3O_4 gave active crystal-lines of hcp and fcc Co^0 that were found to be very stable for a long TOS (15 days). As a result, the activity and selectivity of the catalyst in the SCH medium is more stable and recoverable than that under GP-FTS conditions.

2.3 Hydrocarbon product distribution and control of selectivity in SCF-FTS

Deviations from the standard Anderson-Shulz-Flory (ASF) model (Herrington, 1946; Friedel, and Anderson 1950) that describes the hydrocarbon product distribution in FTS reaction as polymerization process for an intermediate species contain one carbon molecule model product distribution model were targeted by many studies as a mean of controlling the selectivity of the FTS reaction. The main objectives of those studies is to find catalytic systems, reaction conditions, and operation modes that would result in maximizing the production of hydrocarbons within specific carbon number ranges (e.g. $\text{C}_5\text{-C}_{11}$ for the gasoline fraction, $\text{C}_{12}\text{-C}_{19}$ for the diesel fraction, or higher carbons for the heavy wax range). Success in deviating the product distribution from the standard ASF model represents a breakthrough in FTS technology, allowing high selectivity towards desired products such as desired transportation

fuels (e.g. diesel fuels) (Dry 2001). Several studies report an enhancement in chain growth probability and increase of selectivity towards high value added chemicals (e.g. α -olefins) in SCF-FTS compared to conventional gas-phase FTS and liquid-phase FTS (Yokota et al., 1990; Bukur, et al. 1997; Huang and Roberts, 2003; Elbashir and Roberts 2005). Higher productivity of α -olefins, the primary product in the FTS chain growth process, indicates suppression of secondary reactions such as hydrogenation to paraffins, isomerization and oxygenations. α -olefins are also known to incorporate in the chain-growth process and behave similarly to the FTS building blocks by either initiating a new chain or becoming a part of a growing one.

Deviations from the standard ASF distributions were observed when conducting FTS reactions in supercritical phase solvents. Tsubaki, et al. 2002 reported a non-ASF product distribution in the supercritical pentane phase at a reaction temperature of 200 °C over a silica supported cobalt catalyst. The authors reported a hydrocarbon product distribution that showed that the formation rate of hydrocarbons from C₇-C₂₈ was totally independent of the carbon number, with an α -value (chain growth probability) higher than 0.96. They suggested that the high ability of the olefins (C_nH_{2n}) formed to readsorb in the supercritical phase and initiate new chain-growth processes acts to increase the formation rate of heavy hydrocarbons.

However, another study Jacobs et al. 2003 that employed mixed supercritical solvents (55% hexane-45% pentane) with an alumina supported cobalt catalyst at 220 °C and over a wide range of pressures (from 23 bar to 54.5 bar) showed that hydrocarbon distributions beyond C₁₀ followed closely the ASF distributions model. Elbashir and Roberts (2005) reported significant deviation from the standard ASF model within Sc-hexane-FTS in near-critical and supercritical conditions (controlled by tuning the reaction temperature and/or pressure) over an alumina supported cobalt catalyst. The degree of deviation from the ASF model was found to vary from near-critical to supercritical and from liquid-like density to gas-like density. They suggested that the hydrocarbon product distribution in Sc-hexane FTS should be represented by more than one chain growth probability for the different ranges of hydrocarbons. Very high chain growth probability (α -value \approx 0.95) was observed within the middle hydrocarbon distillates (i.e. C₅-C₁₅). This phenomenon was attributed to the enhanced α -olefin incorporation in the chain growth process and a model for the reaction network and chain growth pathway was proposed accordingly (Elbashir and Roberts 2005). Successes in controlling FTS hydrocarbon product distribution could lead to next generation of technology that provides selective control of fuels fractions and value-added chemicals (Elbashir and Roberts 2004a, Elbashir, et al. 2008).

2.4 Phase behavior of SCF-FTS reaction mixture

Few studies have dealt with the phase behavior of the reaction mixture within supercritical phase FTS (Gao, et al. 2001; Joyce et al. 1999 and 2000). Joyce and his coworkers 1999 studied the vapor-liquid composition for a mixture of hexane (supercritical solvent) + C₁₆ (FTS wax) at three different temperatures (199, 252, and 300 °C). Hexadecane and hexadecene (C₁₆ hydrocarbons) was used to simulate the changes in the phase behavior of hexane as the percentage of heavy hydrocarbons in the product stream increased. Their findings showed that for a 0.0326 mole fraction of C₁₆ in the hexane+hexadecane mixture, the critical pressure and temperature of the mixture were 33.76 bar and 252 °C, respectively. These results can be considered as a significant change in the critical properties of the dominant hexane medium, since the critical pressure and temperature of pure hexane are 32.4 bar and 234.5 °C, respectively. In another study, Gao et al. 2001 reported the phase behavior of the hexane (above 94% by mole) + reactant (CO, and H₂) mixture at different moles ratios. They reported that the critical temperature and critical density of the solvent-reactant mixture decreased as the concentration of CO and H₂ increased, hence the critical pressure increases with CO+ H₂ concentration. More recently, Polishuk et al. 2004 used thermodynamic modeling to predict the critical and the near-critical data for very asymmetric systems that represent the FTS product spectrum, such as propane—*n*-hexatetracontane. They used the global phase diagram approach (GPDA) and the predictive Soave–Redlich–Kwong model (PSRK), to describe the experimental data in the binary homologous series of *n*-alkanes. Their results showed that the reliability of GPDA in comparison with PSRK becomes evident when predicting the data of asymmetric systems.

Elbashir and Roberts (2005) were the first to report experimental measurement of the critical point of a typical product stream of supercritical FTS reaction mixture trapped by the outlet of a fixed-bed FTS reactor over cobalt-based catalyst. A variable-volume-view cell was used to measure the critical properties of stream composed of unreacted syngas, supercritical solvent (hexanes), and hydrocarbon products up to C₃₀. Their findings showed that

the critical properties of the mixture is different from that of the supercritical solvent while most studies in the field assumed near-critical and supercritical FTS phase solely based on the critical properties of the solvent. Nevertheless, there is still a need for in depth studies on phase behavior of supercritical phase FTS reaction mixture as it changes from reactor bed entrance (only solvent and syngas are present) and then at the catalysts bed whereby the presence of solid particles with extremely high heat capacities in addition to the presence of synthesized hydrocarbons may drastically change the critical properties of the mixture. Furthermore, measurement of the phase behavior of the product stream leaving the catalyst bed is also important for the separation/recycle of solvent as well as for separation/upgrading of hydrocarbons product stream.

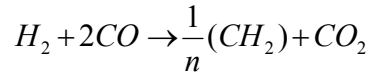
2.5 Kinetics and modeling of reaction pathways in supercritical FTS

Few studies reported mechanism and kinetics modeling of SCF-FTS (Bochniak, and Subramaniam 1998; Fan, et al. 1992; Elbashir and Roberts 2004b). Fan et al. 1992 suggested the following empirical power rate law for Sc-hexane-FTS over Ru catalysts of different pore diameter and pore size:

$$r = k P_{H_2}^x P_{CO}^y$$

where k is the rate constant and x and y are the exponential constants. They referred to previous FTS kinetic models (Vannice, 1976; Karn et al. 1965) that suggested that the rate of an FTS reaction on ruthenium catalysts is first order in H_2 . As a result, they were able to calculate the apparent rate constant for each catalyst (of different pore diameter and size) and defined the catalyst effectiveness factor as the ratio between the rate of reaction in supercritical fluid to that in gas phase reaction.

Bochniak and Subramaniam 1998 used the diffusion-enhanced readsorption model (Madon et al. 1991) to explain the deviation of product distribution in supercritical hexane from the standard ASF model. In order for them to explain the increase in syngas conversion with reactor pressure in a supercritical fluid medium, they correlated the effectiveness factor (ηk s) with the pressure. The effectiveness factor was derived by assuming a plug-flow reactor and that the syngas conversion is pseudo first order reaction in H_2 (they referred to Anderson's [51] model for syngas conversions below 60%). The general stoichiometric equation (below) was used to derive the effectiveness factor



The derived effectiveness factor was then found to be;

$$\eta k = \left(\frac{F_{S0}}{F_T F_{S0} W} \right) \left(-F_0 \ln(1 - x_A) + 2F_{A0} \{ \ln(1 - x_A) + x_A \} \right)$$

The calculated effectiveness factor (ηk) was found to increase with pressure in the system, which they attributed to the alleviation of pore diffusion limitations (viz., maintenance of wider pore channels) as a result of enhanced extraction of heavier hydrocarbons from the catalyst pores by the liquid-like densities, yet significantly better-than-liquid diffusivities, of n-hexane (Bochniak and Subramaniam, 1998).

Both of the suggested rate equations for the SCF-FTS (Bochniak and Subramaniam 1998; Fan et al. 1992) rely on gas-phase and liquid-phase kinetic models, which result in very simplified rate equation formulas. Recently, Elbashir and Roberts (2004b) suggested a reaction network for SCF-FTS that takes into account the role of enhanced α -olefin incorporation in the chain growth process under SCF operation. The model assumes that operating FTS in SCF medium promotes the in situ extraction of heavy products from the catalyst pores and as a result accessibility to active sites increases. Those vacant sites (due to the enhanced extraction) were assumed to promote both adsorption of CO and H_2 and incorporation of α -olefins in the chain growth process. The kinetics model and the reaction pathway were derived from the surface reaction kinetic model (see Section 1-3.1) (Bell 1981; Kellner and Bell 1981; Uner 1998). The proposed reaction pathway shown in Figure 2.20 assumes that the characteristics of Co catalyst site very much control the initial stages of the synthesis (stages 1-3), implying the supercritical solvent has the least influence at these stages. The reaction rate equations were then derived by using the simplified assumptions of Sarup and Wojcichowski 1988 to yield the following rate expression for CO consumption:

$$-r_{CO} = \frac{k P_{CO}^{1/2} P_{H_2}^{1/2}}{[1 + K_1 P_{H_2}^{1/2} + (K_2 + K_3) P_{CO}^{1/2} + K_4 P_{CO}]^2}$$

This model was found to be in a good agreement with the experimental results obtained from the gas-phase FTS, though, it poorly predicted the behavior under Sc-hexane-FTS. The authors (Elbashir and Roberts 2004b) suggested improving the kinetic model to predict SCH-FTS behavior by including thermodynamic nonidealities into the rate expression, and quantifying the influence of modified active site (evacuated ones, S^*).

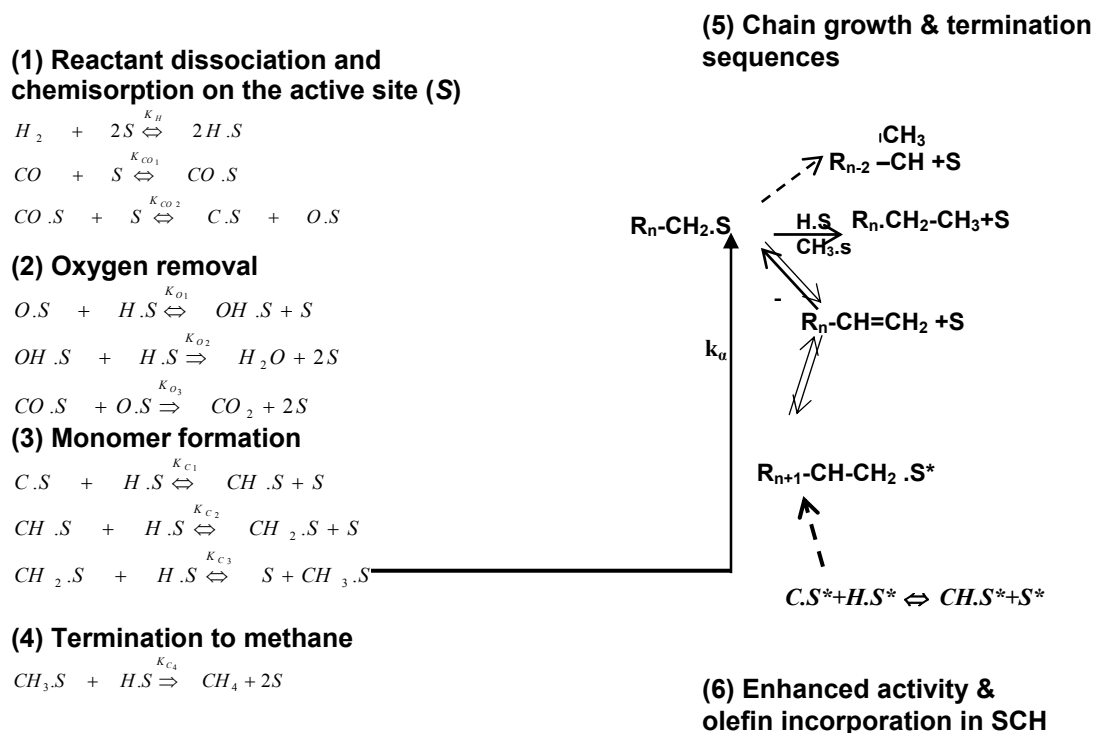


Figure 3 FTS reaction network including the enhanced activity and olefin incorporation sites. Source (Elbashir and Roberts 2004b).

3. Prospectus for Design of Advanced Fischer-Tropsch Reactor for Operation in Near Critical and Supercritical Solvent Medium

One of the most known strategies for design of FTS process was developed by Krishna and Sie (1994) who identified three parameters that have to be systematically analyzed prior to selection of the right multiphase reactor. They started with the catalyst design as the first strategy for reactor selection followed by injection and dispersion strategies, and finally the evaluation of reactor hydrodynamic characteristics. Based on their concept, the ideal reactor for a process should be decided independently for each level of these aforementioned strategies. Their approach has been considered as a powerful technique in identifying ideal reactor configuration (e.g., de Deug et al 2003) and it has been applied in the design of a novel slurry bubble reactor operated in well-mixed gas flow regime (Krishna et al. (2005) US Patent 6914082).

Elbashir, et al. (2008b) described an approach to optimizing the design of advanced FTS catalytic reactor for near-critical and supercritical operation. In order to systematize the design of advanced FTS, they proposed an approach that integrates process synthesis, process simulation, and tailored experiments. Process synthesis techniques (e.g,

El-Halwagi 2006) are used to generate process configurations from various building blocks including solvent selection and mixing with syngas, reaction, compression, upgrading, separation, and solvent recovery and recycle. The procedure Elbashir, et al (2008b) suggested can lead to innovative design. An example is an advanced FTS process shown in Figure 4. This process is composed of six major units including: static mixer for syngas and solvent that operate under controlled temperature and pressure to ensure proper mixing prior feeding mixture to catalyst bed; single tube fixed bed reactor of specially designed interior to sustain catalyst-bed under high pressure/high temperature operating conditions (45 bar – 85 bar and 200 – 400 °C); a compressor for generation of high pressure needed for this process; pressure release valves to utilize pressure drop in flashing unreacted syngas and light hydrocarbon; flash distillation column for separation of syngas, light hydrocarbons, and solvent from product mixture; fractional distillation column for separation of middle distillate hydrocarbons from wax; and a mixing tank for fresh/recycled solvent with multiple controlled valves. Their strategy to design this advanced FTS process has many similarities to Krishna and Sie (1994) approach; however, it considers each of the aforementioned units as a separate process during optimization. The performance of the synthesized systems is evaluated via process simulation to provide input/output relations that are used to refine and analyze the synthesis results. The generated designs are tested experimentally. Needed refinements are fed back to the synthesis and simulation steps. The process is continued until sufficient design alternatives are generated.

They (Elbashir, et al. 2008b) measured ability to separate the supercritical solvent (considered in this case as a hydrocarbon mixture of C₅-C₇ with hexanes representing the major component of the mixture) from the hydrocarbon mixture of liquid-like properties is simulated by a flash distillation column using the property method NRTL-RK whereby all parameters are taken from ASPEN (used to determine gas composition as function of changes in both pressure and temperature). Their data shows that solvent recoverability increases as pressure decreases at fixed temperature, while better recoverability is obtained at the higher temperature. It is noteworthy to mention here that at relatively high temperature such as 250 °C syngas conversion reached 85% as well as productivity of light hydrocarbon fractions (including fractions that represent the solvent C₅-C₇) which will obviously affect solvent recoverability calculations. More importantly, their data shows that the concentrations of middle distillate and heavy hydrocarbons fractions (C₁₀₊) collected at the bottom of the flash distillation column increased as pressure decreased from 45 bar to 25 bar for all studied temperatures. This finding supports the basic concept of our design since it proves that by fine tuning temperature and pressure in the flash distillation column we could recover the supercritical solvent and the light hydrocarbon fractions without affecting the other hydrocarbon products of interest.

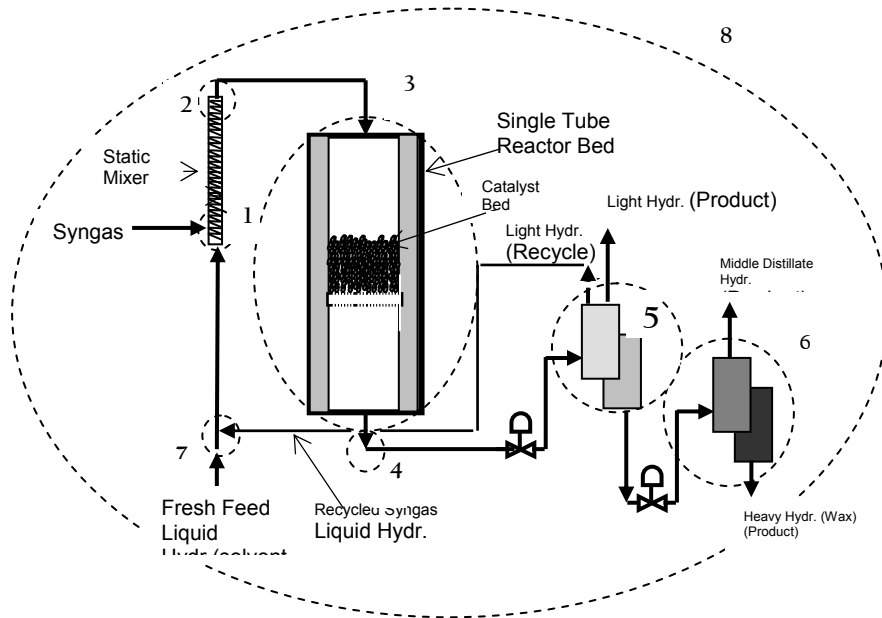


Figure 4: Diagram describing an advanced Fischer-Tropsch synthesis process for operation in near critical and supercritical phase media (Source Elbashir, et al. 2008b).

4. Conclusions

Despite intensive research efforts in the implementation of SCF in FTS as summarized in this paper this technology has not yet moved beyond the lab-scale reactor operation. The scale-up of SCF-FTS to a pilot plant is still a challenge because product yield and selectivity of a large scale reactor requires a deep understanding of phase behavior of reaction mixture, reaction kinetics, and catalytic system and its FTS chemistry. In general, application of SCF technology in reaction engineering has long way to go before commercialization. Optimizing the design of such complex process requires multi-disciplinary specialties since the introduction of the supercritical solvent as a new parameter to influence FTS performance shifts the problem from a classical catalytic reaction engineering process to one combined with a thermophysical puzzle (Elbashir and Roberts, 2005). Nevertheless, better understanding of the phenomena associated with operating under near-critical and supercritical conditions, combined with the optimum utilization of those properties in improving the process performance could lead to breakthroughs in advancing SCF-FTS technology.

The new design approach that has been proposed by Elbashir et al 2008b for developing reactor configuration for FTS process in presence of supercritical solvents represented has been described. Their strategy to optimizing the design of advanced FTS catalytic reactor using components of process synthesis, process simulation, and tailored experimentation could lead to innovative FTS process.

Acknowledgment

The author would like to express his gratitude to Prof. Mahmoud El-Halwagi at Texas A&M and Prof. Christopher Roberts at Auburn University for their thoughtful contribution to this study.

References

- Anderson, R. B., The Fischer-Tropsch Synthesis. 1984, Orlando, Florida: Academic Press, Inc.
- Anderson, R. B., Hall, W. K., Krieg, A., and Seligman, B., Studies of the Fischer-Tropsch Synthesis. V. Activities and Surface Areas of Reduced and Carburized Cobalt Catalysts. *J. Am. Chem. Soc.*, 1949. 71: p. 183-188.
- Baiker, A., Supercritical Fluids in Heterogeneous Catalysis. *Chem. Rev.*, 1999. 99(2): p. 453 -474.
- Bell, A. T., Catalytic synthesis of hydrocarbons over Group VIII metals. Discussion of the reaction mechanism. *Catalysis Reviews - Science and Engineering*, 1981. 23(2): p. 203-32.
- Bochniak, D. J. and Subramaniam, B., Fischer-Tropsch Synthesis in Near-Critical n-Hexane: Pressure-Tuning Effects. *AIChE Journal*, 1998. 44(8): p. 1889-1896.
- Bukur, D. B., Lang, X., Akgeman, A., and Feng, Z., Effect of Process Conditions on Olefin Selectivity during Conventional and Supercritical Fischer-Tropsch Synthesis. *Ind. Eng. Chem. Res.* 1997. 36: p. 2580-2587.
- Cagniard de LaTour, C., Supercritical fluids. *Ann. Chim. Phys.*, 1822. 21: p. 127-132.
- Dry, M. E., High quality diesel via the Fischer-Tropsch process - a review. *Journal of Chemical Technology and Biotechnology*, 2001. 77(1): p. 43-50.
- Elbashir, N. O. and Roberts, C. B., Reaction pathway and kinetic modeling of Fischer-Tropsch synthesis over an alumina supported cobalt catalysts in supercritical-hexane. *Preprints Division of Petroleum Chemistry 2004*. 49(2): p. 157-160.
- Elbashir N. O; Bukur, B. D.; Roberts, C. B. "Review on Utilization of Supercritical Fluids in Fischer-Tropsch Synthesis" 2008a. Prepared for publication.
- Elbashir N. O; B. Bao; M. M. El-Halwagi "An Approach to the Design of Advanced Fischer-Tropsch Reactor for Operation in Near-Critical and Supercritical Phase Media" 2008b. *Proceedings of the 1st Annual Gas Processing Symposium, Elsevier, in press.*
- Elbashir N. O. ; C. B. Roberts "Enhanced Incorporations of α -olefins in the Fischer-Tropsch Synthesis Chain-Growth Process Over an Alumina Supported Cobalt Catalyst in Near-Critical and Supercritical Hexane Medium" *Industrial & Engineering Chemistry Research* 2005a. 44, 505-521.

Elbashir N. O.; P. Dutta; A. Manivannan; M. S. Seehra; C. B. Roberts "Impact of Cobalt-based Catalyst Characteristics on the Performance of Conventional Gas-Phase and Supercritical-Phase Fischer-Tropsch Synthesis" *Applied Catalysis A: General* 2005b, 285, 169-180.

Huang X.; N. O. Elbashir; C. B. Roberts "Supercritical Solvent Effects on Hydrocarbon Product Distributions in Fischer-Tropsch Synthesis over an Alumina Supported Cobalt Catalyst" *Industrial & Engineering Chemistry Research* 2004. 43, p. 6369- 6381.

El-Halwagi M., 2006, Process Integration, Elsevier, Amsterdam.

Fan, L., Yokota, K., and Fujimoto, K., Supercritical Phase Fischer-Tropsch Synthesis: Catalyst Pore-Size Effect. *AIChE Journal*, 1992. 38(10): p. 1639.

Fan, L., Yoshii, K., Yan, S., Zhou, J., and Fujimoto, K., Supercritical-phase process for selective synthesis of wax from syngas: Catalyst and process development. *Catalysis Today*, 1997. 36(3): p. 295-304.

Fan, L. and Fujimoto, K., Fischer-Tropsch synthesis in supercritical fluids: Characteristics and application. *Applied Catalysis A: General*, 1999. 186(1-2): p. 343-354.

Freemantle, M., Continuous SCF reactor. *Chem. Eng. News*, 1997. 79: p. 30.

Friedel, R. A. and Anderson, R. B., Composition of Synthetic Liquid Fuels. I. Product Distribution and Analysis of C5-C8 Paraffin Isomers from Cobalt Catalyst. *J. Am. Chem. Soc.*, 1950. 72: p. 1212-1215.

Gao, L., Hou, Z., Zhang, H., He, J., Liu, Z., Zhang, X., and Han, B., Critical Parameters of Hexane + Carbon Monoxide + Hydrogen and Hexane + Methanol + Carbon Monoxide + Hydrogen Mixtures in the Hexane-Rich Region. *J. Chem. Eng. Data*, 2001. 46: p. 1635-1637.

Geertesma, A., Consideration in the the selection of Fischer-Tropsch Reactor for synfuel production, in DOE Indirect Liquification Contractors' Review Meeting Proc., G.J. Stigel and R.D. Srivastava, Editors. 1990, US Department of Energy: Pittsburg. p. 272-281.

Guisnet, M. and Magnoux, P., Deactivation by coking of zeolite catalysts. Prevention of deactivation. Optimal conditions for regeneration. *Catalysis Today*, 1997. 36(4): p. 477-483.

Henrici-Olive, G. and S., O., *Angew. Chem., Int. Ed. Engl.*, 1976. 15: p. 136.

Herrington, E. F. G., The Fischer-Tropsch synthesis considered as a polymerization reaction. *Chemistry & Industry (London, United Kingdom)*, 1946: p. 346-347.

Huang X.; N. O. Elbashir; C. B. Roberts "Supercritical Solvent Effects on Hydrocarbon Product Distributions in Fischer-Tropsch Synthesis over an Alumina Supported Cobalt Catalyst" *Industrial & Engineering Chemistry Research* 2004. 43, 6369- 6381.

Huang, X. and Roberts, C. B., Selective Fischer-Tropsch synthesis over an Al₂O₃ supported cobalt catalyst in supercritical hexane. *Fuel Processing Technology*, 2003. 83: p. 81-99.

Hyde, J. R., Licence, P., Carter, D., and Poliakov, M., Continuous catalytic reactions in supercritical fluids. *Applied Catalysis A: General*, 2001. 222: p. 119-131.

Jacobs, G., Patterson, P. M., Zhang, Y., Das, T., Li, J., and Davis, B. H., Fischer-Tropsch synthesis: deactivation of noble metal-promoted Co/Al₂O₃ catalysts. *Applied Catalysis A: General*, 2002. 233(1-2): p. 215-226.

Jacobs, G., Chaudhari, K., Sparks, D., Zhang, Y., Shi, B., Spicer, R., Das, T. K., Li, J., and Davis, B. H., Fischer-Tropsch synthesis: Supercritical conversion using a Co/Al₂O₃ catalyst in a fixed bed reactor. *Fuel*, 2003. 82(10): p. 1251-1260.

Jager, B. and Espinoza, R., Advances in low temperature Fischer-Tropsch synthesis. *Catalysis Today*, 1995. 23(1): p. 17-28.

Johnson, K. P. and Penninger, J. M. L., eds. *Supercritical Fluid Science and Technology*. ACS Symposium Series 406. 1989, American Chemical Society: Washington, DC.

Joyce, P. C., Gordon, J., and Thies, M. C., Vapor-liquid equilibria for the hexane+tetracosane and hexane+hexatriacontane systems at elevated temperatures and pressures." *Journal of Chemical and Engineering Data*, 2000. 45: p. 424-427.

Joyce, P. C., Leggett, B. E., and Thies, M. C., Vapor-liquid equilibrium for model Fischer-Tropsch waxes (hexadecane, 1-hexadecene, and 1-hexadecanol) in supercritical hexane. *Fluid Phase Equilibria*, 1999. 158-160: p. 723-731.

Karn, F. S., Shultz, J. F., and Anderson, R. B., Hydrogenation of carbon monoxide and carbon dioxide on supported ruthenium catalysts at moderate pressures. *Industrial & Engineering Chemistry Product Research and Development*, 1965. 4: p. 265-269.

Kellner, C. S. and Bell, A. T., The kinetics and mechanisms of carbon monoxide hydrogenation over alumina-supported ruthenium. *Journal of Catalysis*, 1981. 70(2): p. 418-32.

Kolbel, H. and Ralek, M., The Fischer-Tropsch Synthesis in the Liquid-Phase. *Catalysis Reviews*, 1980. 21(2): p. 225-274.

Lahtinen, J., Anraku, T., and Somorjai, G. A., Lahtinen, J.; Anraku, T.; Somorjai, G. A. C, CO and CO₂ hydrogenation on cobalt foil model catalysts: evidence for the need of CoO reduction. *Catalysis Letters*, 1994. 25: p. 241-255.

Lang, X., Akgeman, A., and Bukur, D. B., Steady state F-T synthesis in Supercritical propane. *Ind. Eng. Chem. Res.*, 1995. 34: p. 72-77.

Linghu, W., Li, X., Asami, K., and Fujimoto, K., Supercritical phase Fischer–Tropsch synthesis over cobalt catalyst. *Fuel Processing Technology*, 2004. 85(8-10): p. 1121-1138.

Madon, R. J., Reyes, S. C., and Iglesia, E., Primary and secondary reaction pathways in ruthenium-catalyzed hydrocarbon synthesis. *Journal of Physical Chemistry*, 1991. 95(20): p. 7795-804.

Madon, R. J. and Iglesia, E., Hydrogen and CO Intrapellet Diffusion Effects in Ruthenium-Catalyzed Hydrocarbon Synthesis. *Journal of Catalysis*, 1994. 149: p. 247-489.

McHugh, M. A. and Krukonic, V. J., *Supercritical Fluid Extraction*. 2nd Edition ed. 1994, Boston: Butterworth-Heinemann.

Polishuk, I., Statevab, R. P., Wisniakc, J., and Segurad, H., Simultaneous prediction of the critical and sub-critical phase behavior in mixtures using equations of state IV. Mixtures of chained n-alkanes. *Chemical Engineering Science*, 2004. 59(3): p. 633-643.

Prajapati, D. and Gohain, M., Recent advances in the application of supercritical fluids for carbon–carbon bond formation in organic synthesis. *Tetrahedron*, 2004. 60(4): p. 815-833.

Sarup, B. and Wojciechowski, B. W., Studies of the Fischer-Tropsch Synthesis on a cobalt catalyst. I. Evaluation of product distribution parameters from experimental data. *Canadian Journal of Chemical Engineering*, 1988. 66(5): p. 831-42.

Satio, S., Research activities on supercritical fluid science and technology in Japan—A review. *The Journal of Supercritical Fluids*, 1995. 8(3): p. 177-204.

Savage, P. E., Gopalan, S., Mizan, T. I., Martino, C. J., and Brock, E. E., Reactions at supercritical conditions: applications and fundamentals. *AIChE Journal*, 1995. 41: p. 1723-78.

Snavelly, K. and Subramaniam, B., On-line Gas Chromatographic Analysis of Fischer-Tropsch Synthesis Products Formed in a Supercritical Reaction Medium. *Ind. Eng. Chem. Res.*, 1997. 36: p. 4413-4420.

Subramaniam, B., Enhancing the stability of porous catalysts with supercritical reaction media. *Applied Catalysis A: General*, 2001. 212: p. 199-213.

Sun, S., Tsubaki, N., and Fujimoto, K., The reaction performances and characterization of Fischer-Tropsch synthesis Co/SiO₂ catalysts prepared from mixed cobalt salts. *Applied Catalysis A: General*, 2000. 202(1): p. 121-131.

Taylor, L. T. *Supercritical Fluid Extraction*. New York, John Wiley & Sons 1996.

Tsubaki, N. and Fujimoto, K., Product control in Fischer-Tropsch synthesis. *Fuel Processing Technology*, 2000. 62(2-3): p. 173-186.

Tsubaki, N., Yoshii, K., and Fujimoto, K., Anti-ASF Distribution of Fischer-Tropsch Hydrocarbons in Supercritical-Phase Reactions. *Journal of Catalysis*, 2002. 207(2): p. 371-375.

Uner, D. O., A Sensible Mechanism of Alkali Promotion in Fischer-Tropsch Synthesis: Adsorbate Mobilities. *Industrial & Engineering Chemistry Research*, 1998. 37(6): p. 2239-2245.

Vannice, M. A., The catalytic synthesis of hydrocarbons from carbon monoxide and hydrogen. *Catalysis Reviews - Science and Engineering*, 1976. 14(2): p. 153-191.

Yokota, K. and Fujimoto, K., Supercritical phase Fischer-Tropsch synthesis reaction. *Fuel*, 1989. 68(2): p. 255-256.

Yokota, K., Hanakata, Y., and Fujimoto, K., Supercritical phase Fischer-Tropsch synthesis. *Chemical Engineering Science*, 1990. 45(8): p. 2743-2749.

Zhou, J., Yan, S., Gao, Z., and Fan, L., Supercritical phase process for selective synthesis of heavier hydrocarbons from syngas on cobalt catalysts. *Preprints - American Chemical Society, Division of Petroleum Chemistry*, 2002. 47(1): p. 154-157.

Zhang, Y., Sparks, D. E., Spicer, R., and Davis, B. H. Steady-State Supercritical Fischer-Tropsch Synthesis on Co/SiO₂ Catalyst. in *Symposium on Advances in Fischer-Tropsch Chemistry*, 219th National Meeting, American Chemical Society. 2000. San Francisco: American Chemical Society.

Xiaohong Li, Xiaohao Liu, Zhong-Wen Liu, Kenji Asami, Kaoru Fujimoto Supercritical phase process for direct synthesis of middle iso-paraffins from modified Fischer–Tropsch reaction *Catalysis Today*, 106, Issues 1-4, 15 October 2005, Pages 154-160

Wen-sheng LINGHU, Xiao-hong LI, Kaoru Fujimoto Supercritical and near-critical Fischer-Tropsch synthesis: Effects of solvents *Journal of Fuel Chemistry and Technology*, 2007, 35, 51-56