

Supercritical Fluids as an Alternative Reaction Medium for Fischer-Tropsch Synthesis

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Introduction

Supercritical fluids (SCFs) offer several advantages over traditional solvents as reaction media for catalytic reactions including the ability to manipulate the reaction environment through simple changes in pressure to enhance solubility of reactants and products, to eliminate interphase transport limitations, and to integrate reaction and separation unit operations. Supercritical fluid solvents offer attractive physical properties including; low viscosity and high diffusivity resulting in superior mass transfer characteristics; low surface tension enabling easy penetration into the pores of a solid matrix (catalyst) for extraction of nonvolatile materials from within the pores; high compressibility near the critical point inducing large changes in density with very small changes in pressure and/or temperature enabling separation of the dissolved material easily and completely.

The unique properties of SCFs can be exploited in various ways for the design of heterogeneous catalytic reaction systems. As a result, several classic industrial processes are conducted under SCF conditions such as ethylene polymerization, ammonia synthesis and methanol synthesis. As an example of the potential of SCF reaction solvents, Li Fan et al. investigated the effect of supercritical conditions on alkylation reactions on Y-type zeolites. Reactions under SCF conditions exhibited both higher catalyst activity along with longer lifetimes compared to the reaction in the liquid or gas phase. SCF solvents offer many opportunities for heterogeneous catalysis in C1 chemistry.

The advantages of SCF-phase Fischer-Tropsch synthesis (SCF-FT) include gaslike diffusivities and liquid-like solubilities, which together combine the desirable features of the gas- and liquid-phase FT synthesis routes. These advantages can be attributed to the SCF offering high diffusivities and improved heat transfer (relative to a liquid) and high solubility (relative to a gas). The supercritical phase reaction can also (1) reduce production of undesirable products; produce less methane because of better distribution of heat in the reactor; (2) produce more long-chain olefins as a result of the enhanced solubility of these higher hydrocarbons in the SCF; (3) mitigate deactivation of the catalyst through better heat and mass transfer; (4) provide in-situ extraction of heavy hydrocarbons from the catalyst surface and their transport out of the pores thereby extending catalyst lifetime; (5) enhance pore-transport of the reactants such as hydrogen to the catalyst surface thereby promoting desired reaction pathways; (6) enhance desorption of the primary products preventing secondary reactions that adversely affect product selectivity.

Objective

The objective of our project is to establish optimum operating conditions for FT synthesis within the supercritical region itself and to investigate the product selectivity alteration when FT synthesis is operated in a SCF medium vs. a liquid or gas medium. We are also evaluating the feasibility of maintaining catalyst activity by continuous in situ extraction of products with the SCF medium. We plan to establish an optimum method to increase the selectivity to desired products such as diesel and high-octane gasoline to improve the economics of FT synthesis.

Our recent work

We have finished our design, development and construction of a continuous fixed-bed reactor system for fundamental investigations of SCF-based FT synthesis. We have completed all aspects of the design and construction of the reactor, which is equipped with a safety alarm detector system, computer controlled gas supply and on-line GC analysis systems and methods for evaluation of products up to C20 hydrocarbons and oxygenates. The high-pressure fixed-bed reactor allows a wide range of temperatures (up to 400°C), pressures (up to 200 bar), gas and SCF flowrates and catalyst loadings to be studied. We have performed studies of the SCF-FT synthesis reaction under supercritical hexane conditions by employing traditional Fe and Co catalysts (some results are discussed below) and comparisons were made to conventional gas phase and liquid phase FT synthesis.

Experimental

The reaction conditions employed in our previous experiments are shown below.

<i>Reactor</i>	Fixed bed: 1.27cm(0.5in)*25.4cm(10in) with an effective volume of 32 cm ³
<i>Catalyst</i>	15%Co-0.5%Pd-Al ₂ O ₃
<i>Solvent</i>	Hexane (Pc=29.7bar, Tc=233.7°C); Flowrate: 1.0 ml/min
<i>Syngas</i>	Space velocity: 50 sccm/g cat; Ratio: H ₂ /CO = 2.0
<i>Pretreatment</i>	Reducing gas type: CO; Flowrate: 50sccm Time: 20 hr; Temperature, Pressure: 280°C, 1atm.
<i>Reaction</i>	Temperature: 240°C(1.01Tc); Pressure: 1000psi (2.32Pc)
<i>Condition</i>	Time: until steady state is achieved and kept at steady state for at least 10h

Result and Discussion

1. Product Distribution

The product distributions at 8h and 29h are shown in Figure1. From Figure 1, we can see little variation of the product distribution between 8hrs and 29hrs, which suggests that steady state can be easily approached in the supercritical conditions. In general, the lumped hydrocarbon product distribution diagram under supercritical conditions is similar in shape to that obtained under gas phase and liquid phase conditions. The SCF-FT process has a marked effect on the hydrocarbon product distribution with a shift to higher carbon number products owing to enhanced heat and mass transfer from the catalyst surface. Enhanced heat transfer from the catalyst surface will result in an increase in the median carbon number in the product distribution as is observed in these SCF-FT results. Relatively flat product distributions with similar mass percentages of the C11-C17 products were observed. The increased mass transfer in the SCF phase can result in higher diffusivities and desorption rates of high molecular weight hydrocarbons.

Hence, the heavy product can diffuse easily from the catalyst bed along with light compounds rather than remaining on the catalyst surface or pores shortening the catalyst lifetime or leading to more secondary undesired reactions.

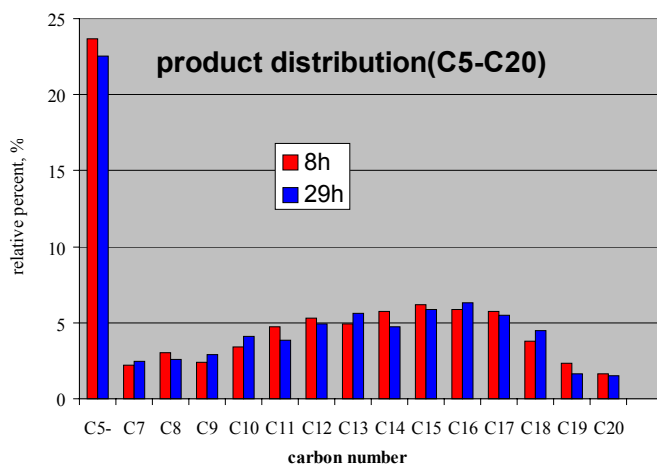


Figure 1. Product distributions at 8 and 29 hours.

2. 1-olefin Content in Hydrocarbon Product

In the conventional FT reaction, the 1-olefin products are generally produced as the primary products and are successively hydrogenated to paraffins. A decrease in the olefin content with increasing carbon number is due to the relatively lower diffusion and desorption rate of heavy hydrocarbon (high molecular weight) components from the catalyst surface or pores. The larger compounds experience greater Van der Waals forces between the molecule and catalyst surface and thus stay longer on the surface for easy hydrogenation.

In the gas-phase or liquid-phase FT process, the olefin content (the fraction of product of a given carbon number that is the olefin product) dramatically decreases with an increase of carbon number. For example, in gas phase reaction, when the carbon number is increased to 16, very little olefin is contained in the product, whereas it is a larger fraction of the C7 product.

Under SCF-FT conditions, an obvious difference in the olefin content is observed where the 1-olefin content in the SCF phase is higher than in gas- or liquid-phase. From the result in Figure 2, we can conclude that the olefin product comprises much of the product distribution relative to the paraffin products even at the higher carbon numbers. As example, at a carbon number of 16 the olefin content is as much as one third. We are currently collecting experimental data in the gas phase and liquid phase in our reactor system for direct comparison. Referring to Fujimoto's results, as presented in Figure 3, we can see an obvious difference in the olefin content where the 1-olefin content in supercritical phase is always higher than in gas- or liquid-phase. One possible explanation for this is as follows.

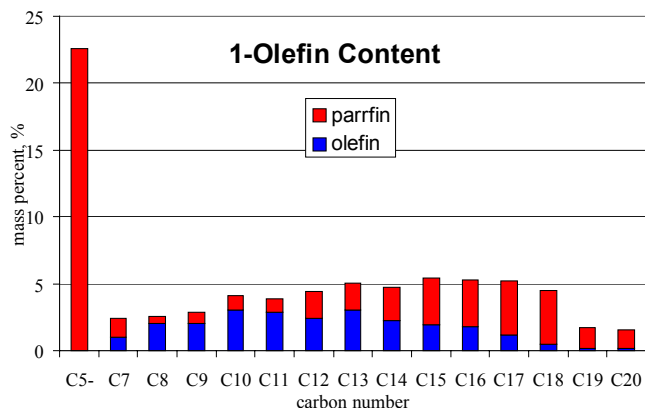


Figure 2: 1-olefin Mass Percentages in Supercritical Phase FT Reaction

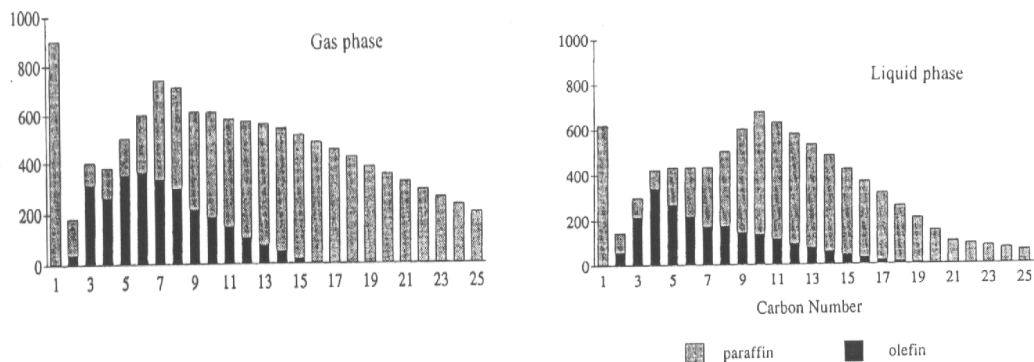


Figure 3: 1-olefin Contents in Gas- and Liquid-Phase FT (From Fujimoto)

The heavier hydrocarbons (e.g. C16+) olefins are more strongly adsorbed on the catalyst surface during the reaction and, in the case of gas-phase FT, hardly de-absorbed into the gas phase. However, in the SCF-FT process, the SCF readily extracts these heavy olefins from the catalysts surface and transports them effectively out of the catalyst bed reducing opportunity for the subsequent hydrogenation. In liquid phase, the olefin product should be extracted quickly by the liquid media. However, the much slower mass transfer prohibits the olefin product from flowing out of the catalyst bed inducing a long residence time and enhanced opportunity for hydrogenation. Therefore, the degree of olefin hydrogenation is higher in both the gas and liquid phases than in the SCF hexane phase. The decrease in the olefin content with the increasing carbon number in each reaction-phase should be attributed to the increase in the hydrogenation

rate relative to the diffusion rate with the increasing carbon number. This is due to the longer residence time on the catalyst surface derived from the slower diffusion rate of these olefins.

These results suggest the SCF-FT reaction rate is not diffusion controlled, whereas the secondary olefin hydrogenation and isomerization reactions are diffusion limited. The SCF-FT process results in higher diffusivity and more rapid removal of high molecular weight 1-olefins and suppresses secondary hydrogenation and isomerization reactions. The observed increase in olefin content in SCF phase is in agreement with results obtained by Bukur et al.

Future Plan

- Perform detailed SCF-FT reaction studies on traditional Fe and Co catalysts in the SCF solvents: propane, n-pentane, hexane, and mixtures of these solvents at temperatures up to 300°C and pressures up to 200 bar. Analyze reaction products to determine the effect of the reaction parameters and catalysts. A variety of solvent/syngas flow rates and feed compositions will be explored.
- A variety of catalyst materials will be examined including traditional iron and cobalt based catalysts as well as alumina-supported ruthenium catalysts, Co-Ni-ZrO₂ and K-MoO₃-Al₂O₃.
- Perform comparative studies of FT reactions (with the catalysts of interest here) under liquid and gas phase conditions in order to make comparisons of the syngas conversion, product selectivity, reaction rates and catalyst activity in SCF, liquid, and gas phase media.
- Analyze and simulate the experimental data; conduct kinetic mechanism analysis of reaction pathways using labeled molecules during steady-state; determine the apparent activation energies of SCF-FT reaction system; create the modeling of product distribution for the prediction and control of FTS selectivity, specifically chain growth probability and olefin content in products, without requiring separate exploratory and development research programs for their implementation.

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