

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

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Introduction

The Fischer-Tropsch (F-T) synthesis reaction conducted in the solid-catalyzed gas-phase reaction system is inevitably accompanied by local overheating of the catalyst surface as well as by production of heavy wax, which may lead to the deactivation of catalyst and also the increase of methane selectivity. The slurry phase F-T reaction process, in which the slurry is composed of fine powdery catalyst and mineral oil, is used as an alternative reaction medium and has been developed to overcome defects of the gas-phase process [1]. However, the diffusion of syngas into the micropores of the catalysis is slow in the slurry phase such that the overall rate is markedly lower than that in the gas-phase reaction [2]. Further more, the concentration of solid catalyst particles in the slurry medium must be limited to low levels in order to maintain slurry fluidity. Other disadvantages of slurry reactors are the accumulation of high molecular weight products and the in situ separation of fine catalyst particles from the heavy products. These considerations have driven research on F-T synthesis to the application of supercritical conditions, which combines the desirable properties of gaslike diffusivity and liquidlike solubility.

It is well known that a supercritical fluids have unique characteristics in their molecular diffusion and solubility parameters [3]. As a result, supercritical fluids possess properties that make them attractive media for chemical reactions. Conducting chemical reactions at supercritical conditions affords opportunities to manipulate the reaction environment by manipulating pressure to enhance the solubility of reactants and products, to eliminate interphase transport limitations on the reaction rates, and to integrate reaction and separation unit operations. For the application of supercritical FT synthesis, there are at least four distinct advantages [4-7]: (1) the in-situ extraction of heavy hydrocarbons from the catalyst surface and their transport out of the pores before they are transformed to consolidated coke, thereby extending catalyst lifetime; (2) the enhancement of the pore-transport of syngas to the catalyst surface thereby promoting desired reaction pathways; (3) the enhanced desorption of primary products preventing secondary reactions that adversely affect product selectivity; (4) and the

elimination of interphases, which may exist in multicomponent systems under ordinary conditions which can result in significantly enhanced mass transfer under supercritical conditions.

Outcomes

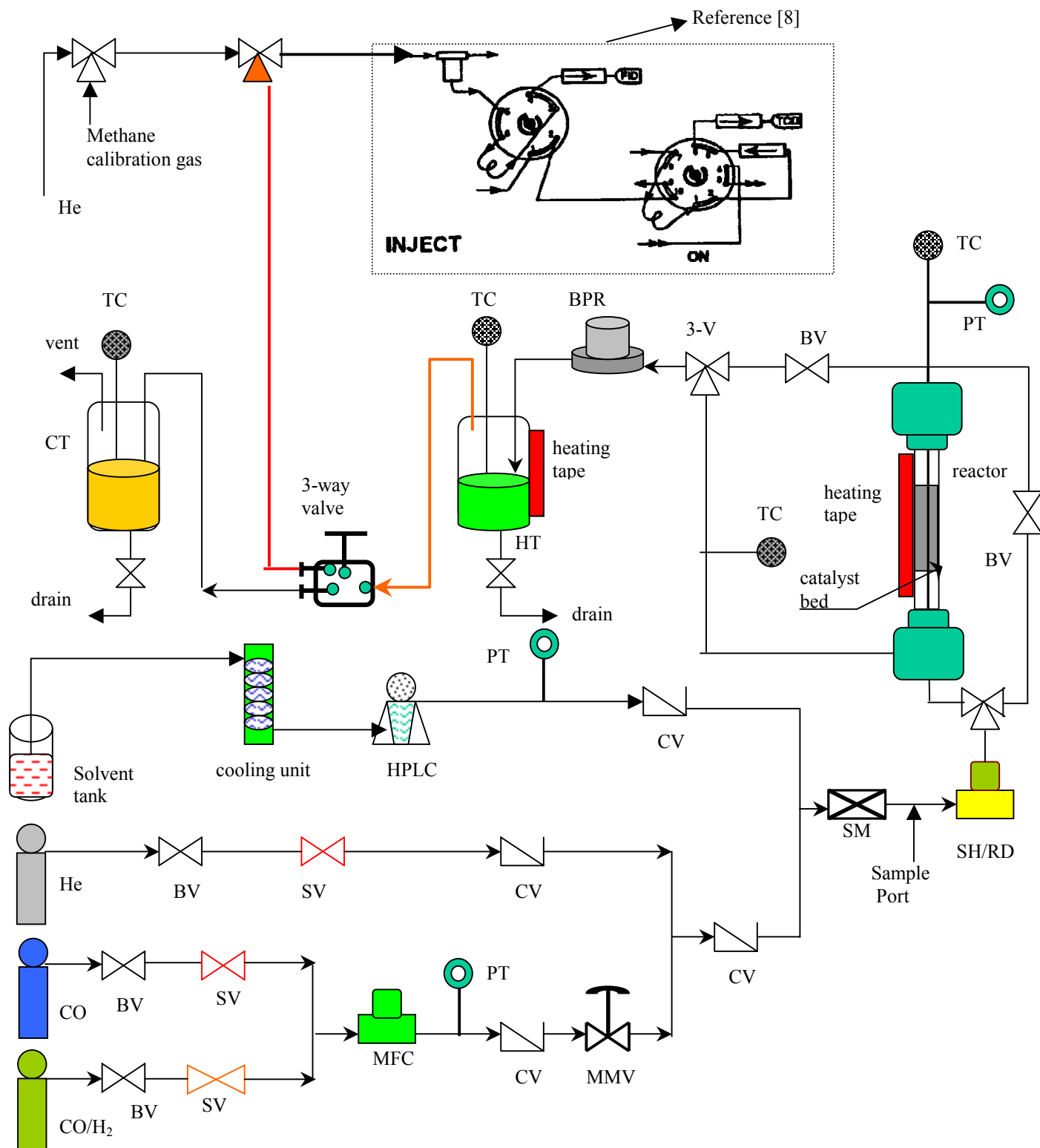
An optimum operating condition for the F-T synthesis reaction is expected within the SCF solvent region. Comparison of the conversions and product selectivities in the SCF media will be made with those in traditional gas- and liquid-phase operation. The unique and adjustable properties of the SCF reaction medium will provide several advantages in the F-T synthesis of fuels and oxygenates including: (1) increased heat transfer from the catalyst surface, compared to gas phase F-T, leading to improved product selectivities, (2) enhanced mass transport into and out of the catalyst pores that will improve overall product yields and selectivities, (3) and enhanced desorption and in situ extraction of desired products which will improve catalyst lifetimes.

Current Status of the SCF Project

Recently, we have developed a continuous fixed-bed reactor system equipped with an on-line GC analysis system. This reactor will be used to perform continuous catalytic reaction studies of SCF-FT synthesis in both CO₂ and hydrocarbon solvents over a variety of solvent conditions, reaction feed compositions, flowrates and catalyst materials. The function checks and tests of the entire reaction system have been accomplished. In addition, a detailed and accurate on-line analysis strategy for the gas and liquid phase products has been developed, and the corresponding calculation methods of the syngas conversion, product selectivity and carbon number distribution have been created.

Schematic Diagram of the SCF Fischer-Tropsch Reaction and Analysis System

BPR: back pressure regulator; BV: ball valve; CT: cold trap; CV: check valve
 MFC: mass flow controller; MMV: micrometering valve
 HT: hot trap; PT: pressure transducer; SM: static mixer
 SV: solenoid valve; SH/RD: safety head/rupture disc
 TC: thermocouple



Experimental Conditions

Reactor	<ul style="list-style-type: none"> Fixed bed(1.27cm(0.5in)*25.4cm(10in) with an effective volume:32 cm³)
Catalyst	<ul style="list-style-type: none"> <ul style="list-style-type: none"> Traditional Fe&Co supported on SiO₂ and Al₂O₃ with promoter potassium: Fe/Cu/K₂O/SiO₂ <ul style="list-style-type: none"> Recent Ru on Al₂O₃, Co-Ni on ZrO₂ <ul style="list-style-type: none"> Others
Supercritical Solvent Medium	<ul style="list-style-type: none"> <ul style="list-style-type: none"> Pure SCF Solvents: CO₂ (Pc=72.9atm, Tc=304.2K) , acetone (Pc=47atm, Tc=508.1K) ethane (Pc=48.8atm, Tc=305.4K) , hexane (Pc=29.7bar, Tc=233.7°C), propane (Pc=42.5atm, Tc=369.8K), n-pentane (Pc=33.7atm, Tc=469.6K) propylene (Pc=46.2atm, Tc=365.0K), <ul style="list-style-type: none"> Mixtures of SCF Solvents: Mixtures of CO₂ + C_nH_{2n+2} Mixtures of C_nH_{2n+2} Flowrate:1.0 ml/min
Syngas	<p>Space velocity: 50 sccm/g cat</p> <p>Ratio: H₂/CO:0.1~ 1.0</p>
Pretreatment	<p>Reducing gas type: CO, H₂, CO/H₂</p> <p>Flowrate: 50sccm</p> <p>Time: 20 hr</p> <p>Temperature, Pressure: 280°C, atmospheric pressure</p>
Reaction Conditions	<p>Temperature: 1.1-1.5Tc</p> <p>Pressure: 1.2-2.4Pc</p> <p>Time: the reactions are run for 10hrs once steady state has been reached</p>
Targeted Results	<p>Syngas(H₂+CO) conversion, Carbon number distribution(selectivity)</p> <p>Catalyst activity(volume, surface area)</p>

Analytical Procedure

Two gas chromatographs (GCs) are being used in the on-line analysis system. The first involves a Varian 3300 GC equipped with a capillary column (DB-5) and FID for the analysis of C₁-C₂₀ hydrocarbons and oxygenates. The second consists of a Varian CP-3800 GC with a packed column and TCD for the analysis of permanent gases and C₁-C₅ hydrocarbons and oxygenates.

Analytical Conditions

Sample	Size	50uL gas, Capillary Column GSV 100uL gas, Packed Column GSV
Column	Capillary Packed Analytical	DB5 HayeSep D
Injection Source	Source Hold Time	Packed and Capillary GSVs 20 seconds
Zone Temperatures	Capillary Injector Valve Oven TCD FID Sample transfer Line	250°C 250°C 140°C 300°C 220°C
Column Oven Parameters	Oven Equilibration Time Oven Maximum Temperature Oven	 3 minutes 290°C on
Column Oven Temperature program	-25°C(0 minute) to 280°C at 4C/min. , hold	
Detector Information	TCD: Reference GAS Flow Rate(30°C)	40cc/min
	FID: make-up GAS Flow Rate(30°C) N ₂ ,	30cc/min
	H ₂ Flow Rate(30°C),	30cc/min
	Air Flow Rate(30°C),	300cc/min
Pressure and Flow	Capillary Column: carrier gas flow rate(30°C): He	13cm/s
	Pressure Program: 25psig(27min.) to 70psig at 5psig/min, hold	
	Packed Column: Carrier Gas: Helium	

Quantitative Analysis

Concentration Calculations: All of the expected components that are being analyzed by the packed column are gases at standard conditions and appropriate gas standards have been

obtained and used to calibrate the analytical equipment. Hence, external standard curves could be generated for each compound in the packed column chromatogram. In the capillary chromatography, only the hydrocarbons up to pentane have been obtained within gas mixtures. None of the oxygenates are gases at standard conditions. An alternate we are exploring involves relating the quantities of nongaseous hydrocarbons and oxygenates to a light hydrocarbon. A technique has been devised for using the external standard curve of methane to calculate quantities for all compounds present in the capillary column chromatogram, which involve converting the peak area of any peak in the capillary chromatogram to an “equivalent” methane peak area. For example, for the hydrocarbon concentration:

$$A_1^e = \left(\frac{M_{CH_4}}{M_2} \right) A_2 = A_{CH_4}^e$$

Thus the peak area is multiplied by the ratio of molecular weights of methane to the component of interest and the resulting equivalent area is fed to calibration equations for methane.

Current Experimental Plan

- ◆ SCF-based FT reactions are to be performed with SCF CO₂ and SCF alkanes using temperatures that range from 100 to 250 °C, pressure from 70 to 200 bar, syngas and SCF solvent feed composition from 1:1 to 1:5 and H₂/CO from 0.5 to 2. Solvent/syngas flowrates will be varied at each of the desired operating conditions. A variety of FT catalysts are to be used in these reactions including iron and Co-based catalysts, as well as ruthenium catalysts. The reaction products are analyzed to determine the effect of the SCF reaction parameters and catalysts on product conversions and selectivities.
- ◆ The influence of the SCF solvents on the adjustable solubilities of the products is to be determined. Specifically, in the case of mixed supercritical solvent systems, the determination of phase boundaries using a high temperature and high pressure view cell are being performed to ensure single-phase operation throughout the FT system.

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