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Progress Report to

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on

FISCHER-TROPSCH SYNTHESIS IN SUPERCRITICAL REACTION MEDIA

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Introduction

The goal of this research is to thoroughly investigate the feasibility of using supercritical fluid (SCF) solvent medium for carrying out Fischer-Tropsch (FT) synthesis. Specifically, the following questions will be addressed: What is the extent of reaction rate enhancement in SCF vis-a-vis liquid reaction medium? Is it possible to maintain catalyst activity or to extend catalyst life by continuous *in situ* extraction of the olefins (before they are transformed into longer chain hydrocarbons) with the SCF reaction medium? How is product selectivity altered in an SCF phase reaction as compared to liquid-phase reaction? Do optimum supercritical operating conditions (between low density gas-phase and dense liquid-phase conditions) exist at which catalyst activity is *maintained* at a maximum value?

These questions will be addressed via systematic experimental investigations of FT synthesis over supported Fe and Co catalysts in a CSTR and in a fixed-bed reactor at typical synthesis temperatures (240-260°C). The SCF medium to be employed is *n*-Hexane (P_c = 29.7 bar; T_c = 233.7°C), while *n*-Hexadecane will be employed as the liquid reaction medium. Overall conversion, product distribution and catalyst deactivation will be measured in each case for various feed H_2/CO ratios ranging from 0.5 to 2. Product analyses will be carried out using GC/TCD, GC/FID and GC/MS systems. The fresh and used catalysts will be characterized with respect to active metal dispersion, surface area and pore size distribution.

Summary of Progress

Two graduate students were recruited to work on this project. Kirk Snavely joined the research program on August 15, 1992 while David Bochniak started research on September 1. Both students are reviewing the state-of-the-art in F-T technology while simultaneously attending to the task of establishing the experimental infrastructure to address the proposed investigations.

a . Construction of Reactor Unit

This phase is being spearheaded by one of the two graduate students currently associated with the project (David Bochniak). A schematic of the packed-bed reactor unit is provided in Figure 1. Using premixed high-pressure cylinders of H_2 and CO, in ratios ranging from 1:2 to 2:1 respectively, the synthesis will pass through a gas regulator and flowmeter sequentially. The gases will be mixed with n-hexane from a HPLC pump. Syngas space velocities ranging from 37 cc/gcat·min to 170 cc/gcat·min have been planned in the initial design. The mixture is then preheated and fed to the reactor. The gases, regulator and flowmeter are to be ordered within the next two weeks.

In the reaction unit (see Fig. 1), the syngas and supercritical n-hexane will pass through a fixed bed of catalyst in a downflow mode. The reactor is to be 25 cm in length, 1.2 cm inner diameter, of 316 stainless steel and located in a sand bath that has been ordered. The temperature of the catalyst bed will be measured by an OMEGA profile thermocouple probe and continuously recorded using the Camile® 2500 data acquisition system that was purchased recently. Pressure drop across the catalyst bed will be measured with a pressure transducer interfaced with the Camile data acquisition system. Literature information is being sought on the phase behavior of typical product compounds in supercritical n-hexane to determine if there will be any phase separation at the expected operating conditions. The choice of reactor operating conditions will depend upon this information. We plan to complete reactor installation before December 31, 1992 and begin testing the reactor shortly thereafter.

b. Analytical

This phase along with catalyst preparation are handled by the second graduate student (Kirk Snavely). Rather than condensing liquid products and analyzing them off-line (as originally proposed), we plan to adopt the analytical method reported by Dictor and Bell (*Ind. Eng. Chem. Fundam.*, 1984, 23, pp. 252-256)which analyzes all F-T synthesis products (complete analysis of C_1 to C_{32} hydrocarbons and oxygenates in 2.5 hours) on-line. This method minimizes loss of product due to evaporation and subsequent reaction associated with conventional analysis methods. A bleed stream from the reactor effluent flows continuously through the following sequence: a sampling valve either to the GC capillary column/FID assembly or to a water-cooled condenser, whose noncondensible effluent stream flows through a second sampling valve to the GC packed column/TCD assembly. The capillary column(Petrocol DH100) provides resolution of C_1 to C_{32} compounds while the packed column (chromosorb 106) is used specifically for resolving CO_2, H_2O, and H_2. Because the molar flow rates of light gases leaving the condenser are the same as those in the reactor bleed stream, the C_4 response peak is used to link the capillary column and packed column chromatograms. A Hewlett-Packard gas chromatograph configured as explained above will be ordered before Nov. 15. An HP5871 MSD is available for compound identification.

Since our major objective is to investigate the effect of supercritical reaction medium on F-T synthesis, catalyst preparation is not being given priority at the present time. After the experimental infrastructure is established, we shall prepare supported Co-based catalysts following technique of Yokota and Fujimoto (*J. Jpn. Pet. Inst.* 1983, 26 , pp. 258). Dr. Udaya Rao at DOE/PETC has agreed to provide us with Fe-based catalysts to commence our investigations.

Our goal for the next quarter is to complete the design and installation of the reactor and analytical units.

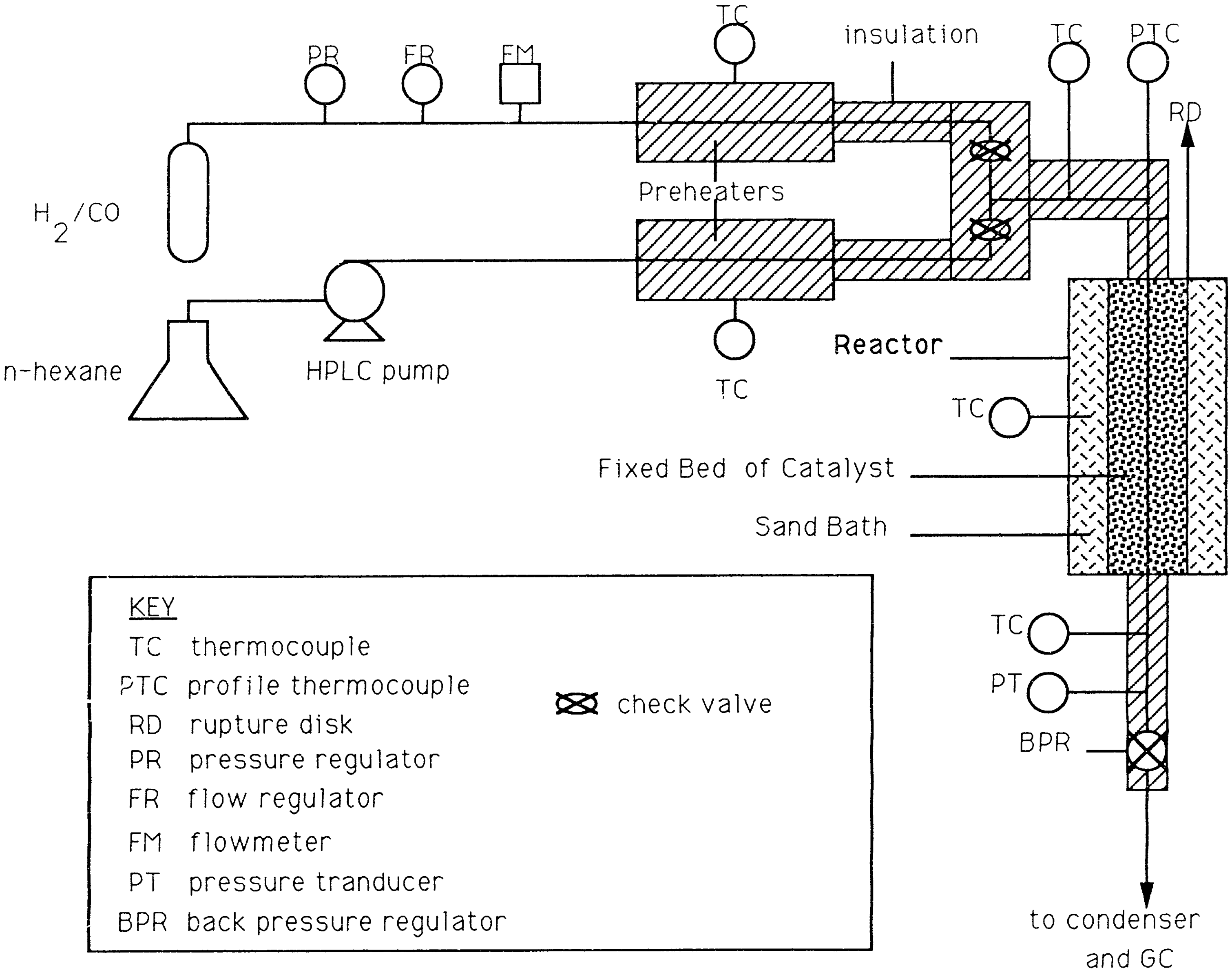

Figure 1. Schematic of Reactor Unit

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