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Progress Report to

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on

FISCHER-TROPSCH SYNTHESIS IN SUPERCRITICAL REACTION MEDIA

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Our goals for this quarter were to complete construction of the reactor and analytical units for carrying out Fischer-Tropsch (F-T) synthesis in liquid (*n*-hexadecane) and in supercritical *n*-hexane phases. Due primarily to the students' preoccupation with course work (which is usually heavy during the fall semester), progress during this quarter was slower than expected.

a . Construction of Reactor Unit

This phase is being spearheaded by one of the two graduate students currently associated with the project (David Bochniak). Upon further review we found that work reported by Yokota, Hanakata and Fujimoto (1991) raised some important questions about their reactor design and operation. Based on communication with Prof. Fujimoto, the initial reactor design was revised resulting in a delay of parts acquisition and reactor assembly. Some of the changes are as follows: the flow direction has been changed from a downflow to an upflow mode as in a cocurrent bubble column reactor. Also, a preheating/mixer section packed with quartz wool will be placed upstream of the reactor section. These modifications should facilitate better interfacial contact between the syngas and either the liquid or the supercritical reaction medium. The profile thermocouple probe will be introduced at the exit end of the reactor extending into the preheater section.

Materials purchased during this quarter include a pressure regulator for the syngas cylinder, cables and hardware required for interfacing the flowmeters, thermocouples and pressure transducers to the Camile® data acquisition system. A 486/MS-DOS computer that is compatible with the data acquisition system has also been received. Materials under order include the reactor tube, an OMEGA profile thermocouple, gas cylinders, and mass flow controller for syngas addition. The sand bath surrounding the reactor will be fabricated in house. An exhaust vent for the reactor unit is being constructed by the local facilities operations department and is expected to be completed by the time the reactor is ready for testing. Dr. Udaya Rao of PETC has agreed to send Rührchemie Fe-based and Co-based F-T catalysts to be used in our experimental investigations.

b. Analytical

This phase is handled by the second graduate student (Kirk Snavely). As explained in the last report, we had initially planned to adopt the analytical method

reported by Dictor and Bell (1984) 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 is attractive for its simplicity. The entire product stream is analyzed on a 50 m capillary column using an FID. With the gas sampling valves in the load position, the vent from the sampling valve to the capillary column is run through a water-cooled condenser and the noncondensed light gases are routed through a second sampling valve connected to a 2.7 m column packed with Chromosorb 106 and analyzed by a TCD. Both columns are mounted in a single GC. Consequently, the maximum oven temperature is set by the physical limit of the packed column packing material (235°C in this case).

Conversations with research chemists and sales representatives now suggest that use of a single column oven is impractical. Sally Kail, formerly of PETC and now a research chemist at Supelco, suggested use of a 100 m column rather than a 50 m column to get the detailed analysis of C_1 to C_{20} which we desire, and to ramp the temperature to 320 °C, the upper temperature limit of the capillary column, in order to elute up to C_{40} in a reasonable amount of time (4 to 6 hours). To characterize the F-T wax, single-carbon resolution of C_{20} to C_{40} compounds is needed. The operating temperature limit of 320 °C is beyond the operating range of all packed and PLOT columns sold by vendors such as Supelco and Chrompak. Capillary columns will not resolve the permanent gases (H_2, CO, CO_2, H_2O). Hence, in the interest of minimizing analysis turnaround time, two GC's connected in series will be used: one for the capillary column, ramped to 320 °C, and one for the packed columns, operated at a lower temperature.

The first GC will be set up similar to the specifications of Dictor and Bell (1984). The inlet to the Supelco DH capillary column (100 m) will be connected to a standard injector-splitter system. Split ratio is 100:1. Injector temperature will be 310 °C. FID temperature will be 300 °C. The sample valve and independently heated capillary injector are housed in an oven capable of sustained operation at 200 °C. Sample loop size is 2 ml. Head pressure will be 25-30 psig to maintain a He carrier gas flow rate of 1 to 2 cm^3/min. Make-up He flowrate will be 30 cm^3/min. For analysis, the temperature will be held at 35 °C for 15 min., then ramped at 2 °C/min to 320 °C and held until C_{40} elutes (approximately 4 to 6 hours for total analysis.

The second GC is downstream of a low dead volume water-cooled condenser operated at 2 °C. The noncondensable gases in the product stream are analyzed on parallel packed (Porapak R) and PLOT columns in this GC, each with its own sampling valve, as proposed by Hackett and Gibbon (1989). The backflush valve for the 50 m PLOT column used by Hackett and Gibbon and the temperature-controlled valve oven are not needed in this setup, however, as C_{10+} components are removed by the condenser. Although Dictor and Bell report a maximum carbon number of C_5 in their packed column chromatogram, Huff and Satterfield (1982) reported significant quantities of C_{5+} up to C_{10} in the noncondensable gases from a cold trap operated at 2 °C. Thus, the PLOT column must be able to resolve components up to C_{10}. The Porapak R column uses Ar carrier gas flowing at 15 ml/min; analysis takes place on a TCD at 150 °C. Sample loop size is 0.2 ml. The PLOT column uses He carrier gas flowing at 3 ml/min, with a make-up of 30 ml. Sample loop size for this column is 0.1 ml. The proposed analytical scheme is thus a combination of those proposed by Dictor and Bell (1984) and Hackett and Gibbon (1989).

We believe that the stated revisions to reactor design and product analysis scheme will improve the quality and reliability of our experimental investigations aimed at determining the effects of liquid vis-a-vis supercritical reaction medium on reaction rates and product selectivity during F-T synthesis on Fe and Co-based catalysts. Our goal for the next quarter is to complete the installation of the reactor and analytical units.

REFERENCES

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