

II INTRODUCTION

Several technologies are currently available or are under development for conversion of coal-derived synthesis gas to liquid transportation fuels or fuel precursors. Technologies that have been commercially proven include fixed and fluidized bed Fischer-Tropsch synthesis, methanol synthesis (fixed bed and slurry phase), and Mobil's methanol to gasoline (MTG) process. Of these technologies, Fischer-Tropsch (F-T) hydrocarbon synthesis produces the widest slate of products and has been in operation for the longest period. F-T hydrocarbon synthesis was first developed and practiced in Germany during the 1930's and 1940's using cobalt catalysts. Subsequently, the process was commercialized on a large scale by Sasol in South Africa. The Sasol process includes both tubular fixed bed and circulating fluidized bed operation and uses promoted iron catalysts (Dry, 1981).

Of the various indirect liquefaction technologies, Fischer-Tropsch synthesis offers many advantages. While hydrocarbon production is generally non selective and is governed by the so-called Schulz-Flory distribution, the Fischer-Tropsch process has the ability to produce a range of gaseous and liquid hydrocarbon products that can be easily upgraded via conventional refining operations. The fluidized bed reactors at Sasol, for example, maximize gasoline yields while the fixed bed process produces predominantly diesel fuel and hydrocarbon waxes.

In the late 1940's, slurry phase Fischer-Tropsch technology was developed in Germany (Kölbel and Ralek, 1980). Slurry processing provides the ability to more readily remove the heat of reaction, minimizing temperature rise across the reactor and eliminating localized hot spots. As a result of the improved temperature control, yield losses to methane are reduced and catalyst deactivation due to coking is decreased. This, in turn, allows much higher conversions per pass, minimizing synthesis gas recycle, and offers the potential to operate with CO-rich synthesis gas feeds without the need for prior water-gas shift. Due to the simpler reactor design, capital investment in a slurry phase F-T reactor is expected to be

substantially smaller than in conventional fixed or fluidized-bed systems. In May 1993 the commercial Slurry Bed Reactor (5 m in diameter, 22 m high) was commissioned by Sasol, as replacement for its tubular fixed bed reactors (Jager and Espinoza, 1995).

II-1 Objectives and Scope of Work

The slurry phase F-T processing is a very promising alternative to conventional vapor phase processes, but additional improvements are needed in the catalyst performance (higher activity, minimization of methane and low molecular weight hydrocarbon yields, and better catalyst stability). This can be achieved in several ways: (a) through development of new improved catalysts; (b) use of novel reactor configurations; (c) use of suitable catalyst pretreatment (activation) procedures or through combination of these methods, as demonstrated in studies at Texas A&M University (TAMU) sponsored by DOE (Contracts DE-AC22-85PC8011 and DE-AC22-89PC89868). Some of the iron based catalysts synthesized and tested at TAMU, have proven to be more active than any other known iron F-T catalysts developed for maximizing production of high molecular weight hydrocarbons (Bukur et al., 1994).

The overall objectives of this contract are to: (1) demonstrate repeatability of performance and preparation procedure of two high activity, high alpha iron Fischer-Tropsch catalysts synthesized at TAMU during the DOE Contract DE-AC22-89PC89868; and (2) seek potential improvements in the catalyst performance through variations in process conditions, pretreatment procedures and/or modifications in preparation steps (e.g. means of introduction of promoters and calcination conditions). In order to achieve these objectives the work is divided into a number of tasks, which are described below together with the time schedule for their execution.

Task 1. Project Work Plan (April 1-April 30, 1994)

The objectives of this task are: (1) Prepare in detail all activities which shall be performed for the successful completion of the work for the entire duration of the contract; and (2) Provide a project work chart showing the key personnel/groups planned for each task, and the percentage of their time to be devoted to individual tasks.

Task 2. Engineering, Modification and Training of New Personnel (April 1-September 30, 1994)

The objective of this task is to perform the engineering design, procurement of new equipment, installation of the instruments and auxiliary gas supply lines and to provide training for new personnel prior to catalyst testing in laboratory reactors.

Task 3. Testing of Previously Synthesized Catalysts (October 1, 1994 - March 31, 1995)

The purpose of this task is to verify reproducibility of results obtained previously at TAMU with catalysts designated B (100 Fe/5 Cu/6 K/24 SiO₂) and C (100 Fe/3 Cu/4 K/16 SiO₂). The catalysts from the same preparation batch shall be used, and the same pretreatment and process conditions shall be employed as in the previous slurry reactor tests of these two catalysts.

Task 4. Reproducibility of Catalyst Preparation (October 1, 1994 - September 30, 1995)

The objective of this task is to demonstrate reproducibility of catalyst preparation procedure on a laboratory scale. Catalysts B and C will be synthesized following procedures developed at TAMU. Catalysts with satisfactory physico-chemical properties will be initially tested in a fixed bed reactor for screening purposes (5 day tests). Following this the two catalysts will be tested in a stirred tank slurry reactor (STSR) using standard pretreatment and process conditions. The activity, selectivity, deactivation behavior of these new catalyst batches will be compared to that of the catalysts from the original (existing) batches. ✓

Task 5. The Effect of Source of Potassium and Basic Oxide Promoter (October 1, 1994 - December 31, 1995)

The objective of this task is to determine effects of two different sources of potassium and addition of another promoter on the catalyst performance. Catalysts B and C will be synthesized using potassium silicate solution as the source of potassium promoter, and performance of these catalysts will be compared with that of catalysts synthesized using our standard procedure (i.e. using potassium bicarbonate as the source of potassium promoter).

The effect of CaO promotion on performance of catalysts B and C (two levels of promotion per catalyst) shall be investigated. Synthesized catalysts will be tested first in a fixed bed reactor, and if the satisfactory results are obtained the most promising catalyst formulations will be tested in the STSR.

Task 6. Pretreatment Effect Research (October 1, 1995 - November 30, 1996)

The effect of four different pretreatment procedures, in addition to the baseline procedure, on the performance of catalyst B (or C) will be studied in a STSR. In addition to STSR tests, the pretreatment effects will be studied by thermogravimetric analysis (TGA), and temperature programmed reduction (TPR). Iron phases in the catalyst will be determined by X-ray powder diffraction (XRPD).

Task 7. Calcination Effect Research (October 1, 1995 - July 31, 1996)

The effect of calcination temperature (300-500°C) on the catalyst physical properties and performance during F-T synthesis shall be studied in a fixed bed reactor and a STSR. In addition to the baseline calcination temperature of 300°C, the calcination temperatures of 400 and 500°C will be employed in a fixed bed reactor with flowing air. Also, the effect of rapid heating (flash calcination) on performance of catalysts B and C shall be investigated. ✓

Task 8. Catalyst Characterization (December 1, 1994 - July 31, 1997)

The goal of this task is to: (a) provide basic characterization of all catalyst prepared (atomic absorption analysis, surface area, X-ray diffraction); (b) determine bulk iron phases after the pretreatment and during Fischer-Tropsch synthesis in slurry reactors by XRD and Mössbauer spectroscopy (at University of Kentucky); and (c) study reduction behavior of iron F-T catalysts by isothermal and temperature programmed reduction (TPR). These studies may lead to activity-structure relationships, and better understanding of the factors which influence catalyst activity, selectivity and longevity.

Task 9. Testing of Alternative Catalysts for Slurry Reactors (January 1 - June 30, 1997)

Although catalysts B and C have desirable activity and selectivity characteristics, they may not have a sufficient mechanical strength and attrition resistance properties required for utilization in commercial bubble column slurry reactors. We propose to evaluate the performance of up to three alternative catalysts containing either silica and/or alumina as a binder/support in the STSR tests. Mechanical strength and attrition resistance of these catalysts will be determined in collaboration with other DOE contractors.

Task 10. Characterization of Product Distribution and Data Analysis (June 1 - August 31, 1997)

The objective of this task is to perform detailed gas chromatographic analysis of selected liquid and wax products collected during the STSR tests (Tasks 3-7 and 9), and provide information on the effects of time on stream (catalyst aging), process conditions, pretreatment conditions and/or catalyst promoters on product distribution.

A brief description of activities conducted under Task 2. Engineering, Modification and Training of New Personnel is provided in the section II-3, whereas results from Tasks 3 - 10 are described in Chapters III-X of this report. ✓

II-3 **Engineering Modification and Training of New Personnel**

During the course of work on this task we have obtained quotes for major equipment and prepared bid specifications for the following items: Thermal Gravimetric/ Differential Thermal Analyzer (TGA/DTA Apparatus); Temperature Programmed Pulse Chemisorption Unit equipped with thermal conductivity detector for temperature-programmed reduction studies, Carbon Monoxide/ Flammable Gas Detector/Monitor System; Gas cylinder cabinet for storage of toxic and flammable gases and Macintosh computer (Mac Quadra 660 AV 8 MB RAM, 230 MB hard disk) and a Laser printer (Hewlett Packard, 4 ML).

After reviewing the bids the following equipment was purchased: Thermal Gravimetric/ Differential Thermal Analyzer (TGA/DTA Apparatus) - TA Instruments, Carbon Monoxide/ Flammable Gas Detector/Monitor - MSA; Pulse chemisorption, temperature programmed reduction/desorption (TPR/TPD) apparatus (Micromeritics Inc.; TPR/TPD Pulse Chemisorb 2705). All instruments were installed and calibrated with appropriate standards. A gas cylinder cabinet (with CO and H₂ cylinders, or syngas mixture) was connected to a fume hood vent in our Catalyst Characterization Laboratory (Room 35B of Zachry Engineering Center).

During the first six months of the contract tests of the existing gas chromatographs for gas, liquid and hydrocarbon wax product analysis, were completed using the calibration standards. A Carle gas chromatograph, used for analysis of gaseous hydrocarbons, synthesis gas and carbon dioxide, was moved to a laboratory in which our reactors are located (Room 326B). Also, tubing and valves connecting the GC and the two slurry reactors were installed, which will enable us to use it as an on-line gas chromatographic system. Two slurry reactor systems were pressure tested, and mass flow meters were calibrated for future tests. Dr. Xiaosu Lang trained new personnel in the usage of existing computer software for data reduction and analysis, gas chromatographs and fixed bed and slurry reactor systems.

II-4 References

- Bukur, D. B., Nowicki, L. and Lang, X., "Fischer-Tropsch Synthesis in a Stirred Tank Slurry Reactor", *Chem. Eng. Sci.*, **49**, 4615-4625 (1994).
- Dry, M. E., 1981, "The Fischer-Tropsch synthesis" in *Catalysis - Science and Technology; Volume 1*, pp. 160-255. Springer - Verlag, New York.
- Jager, B. and Espinoza, R. , *Catalysis Today*, **23**, 17-28 (1995).
- Köbel, H. and Ralek, M., 1980, "The Fischer-Tropsch synthesis in the liquid phase" *Catal. Rev. - Sci. Eng.* **21**, 225-274.