Appendix I. Fixed Bed and Slurry Reactors and Product Analysis System

Fixed Bed Reactors and Operating Procedures

A simplified flow diagram of a fixed bed reactor system is shown in Figure A-1. Inert (N_2 or He) and (H_2, CO, premixed synthesis gas) are delivered to the reactor through thermal mass flow controllers equipped with a digital meter readout. Two traps are located upstream of the flow controllers, one filled with alumina and heated to 300°C so as to decompose any carbonyls and the other filled with Cu/alumina catalyst to remove trace oxygen. The reactor is made of 1/2" OD stainless steel 316 tubings of 15 or 30 cc volume heated externally via heating blocks. Bed temperatures are monitored through six radially installed thermocouples. The reactor effluent passes through a high pressure trap maintained at 140-210°C, a heated back pressure regulator, and a low pressure trap immersed in ice bath. The gas effluent from the low pressure trap can be sampled for analysis via the sample port and the flow rate is measured by a wet test meter as well as a soap bubble meter.

The catalyst is crushed and sieved to the desired particle size range before loading into the reactor. Reactor is then pressurized and leak tested overnight with He and brought to activation conditions under He atmosphere. Depending upon the activation route being used, the appropriate gas or gas blend is introduced and a temperature program initiated. Following activation, any process parameters not at run condition are adjusted and the flow of synthesis gas is initiated.

Material balance periods are typically 4-8 h duration. Reactor effluent is diverted to tared sample traps (high and low pressure). During this period gas flow rate is measured and gas effluent analyzed periodically. At the completion of the balance, product flow is diverted to the waste traps. The steady state product traps are removed from the system and are allowed to equilibrate at room temperature and their weight

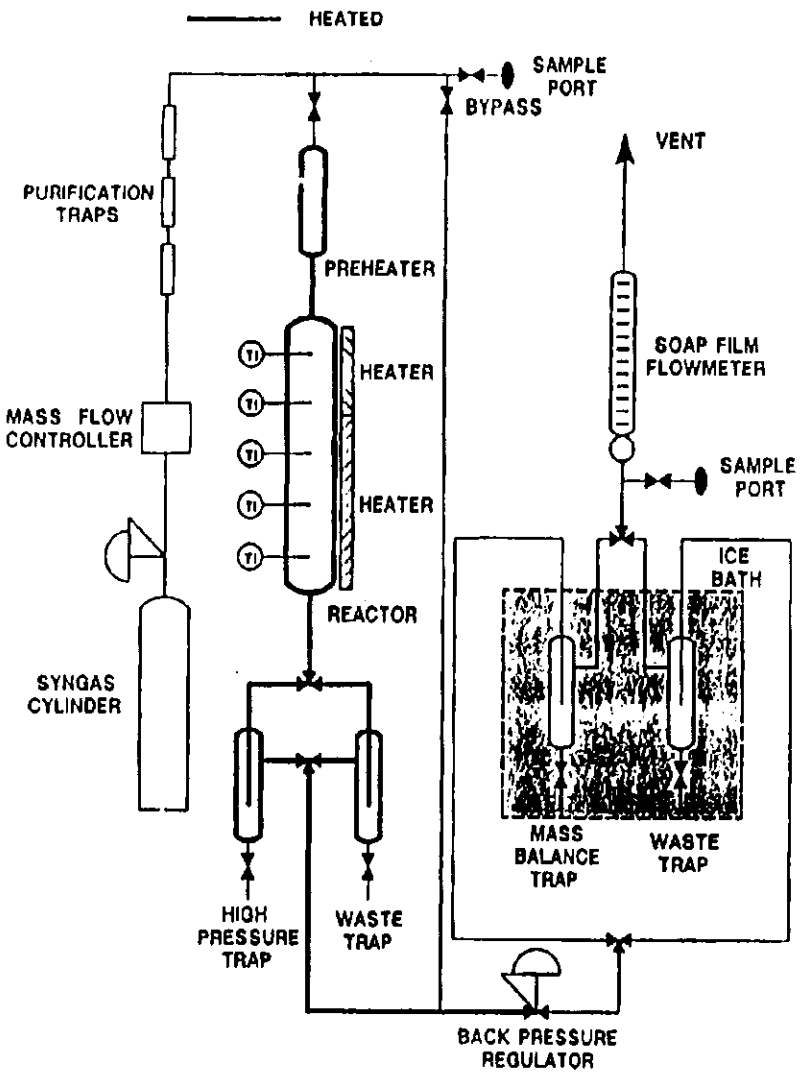

Figure A-1. Fischer-Tropsch Synthesis Reactor Assembly

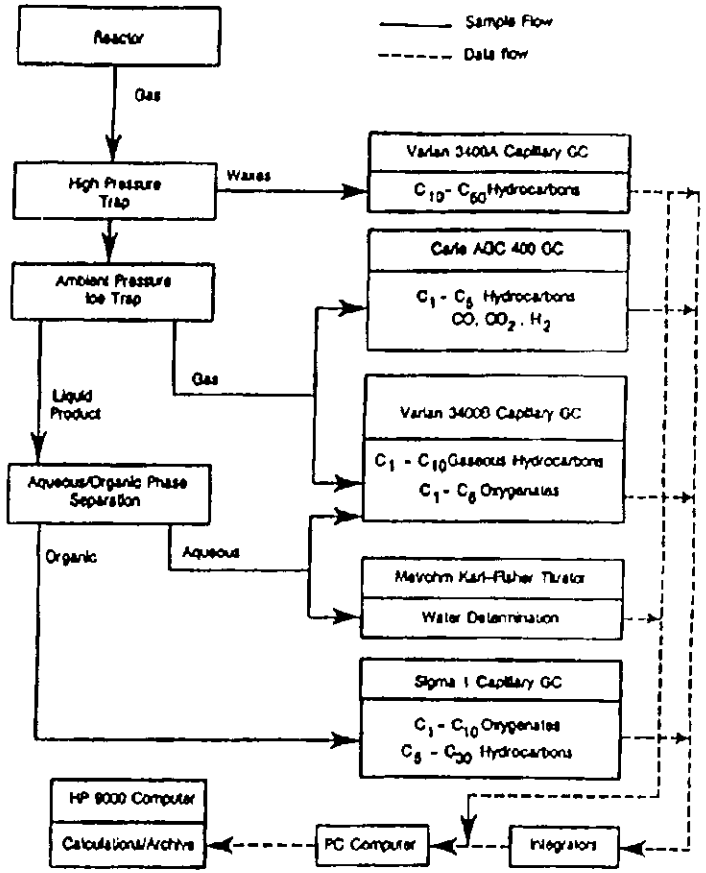

Figure A-2. Analysis of Fischer-Tropsch Synthesis Products with Automated Data Acquisition and Reduction

recorded. The contents of the traps are then drained and seperated into aqueous and organic layers.

Product Analysis System

A versatile analytical and computerized data handling system consisting of four gas chromatographs linked to a data acquisition system is used for product analysis (Figure A-2). In the gas effluent from the reactor unreacted H_2, CO and product CO_2 and C1-C5 hydrocarbon gases are analyzed on the Carle AGC-400 Series gas chromatograph. Small amounts of C_6 and higher hydrocarbons and light oxygenates that are not condensed in the cold trap are analyzed by a Varian 3400 GC. The liquid product is seperated into aqueous and organic fractions. The aqueous layer is analyzed for C1-C6 alcohols, C2-C4 aldehydes, C3-C6 ketones and carboxylic acids. The water content is determined by Karl-Fischer titrator. The organic fraction is analyzed in a Sigma 1 GC for C4-C30 hydrocarbons, C4-C11 alcohols, C3-C6 ketones, and C2-C6 aldehydes. The wax fraction is dissolved in CS_2 or other organic solvents and is analyzed on the Varian 3400 for hydrocarbons up to C50.

Several integrators are used to collect and integrate the data from all the GC's. The results are then transferred to a HP-9000 series minicomputer for further analysis and reduction. The mass balance program uses pull up templates to prompt the operator to enter the needed information. The calibration data for each GC are stored in databases files. The program is designed to handle up to 50 classes of products with up to 100 members in each class. Five types of streams: feed gas, aqueous liquid product, organic liquid product, reactor tail gas, and reactor wax are considered by the program. Using measured sample weights, the program can calculate individual species flow rates and arrive at total inlet and outlet weight and mole fractions of all identified compounds. The material balance program calculates mass and atomic balance closures, yields, and selectivities of products, and lumps poducts according to carbon

numbers. The program also calculates the Schulz-Flory chain growth parameter and produces Schulz-Flory plots.

Slurry Reactors and Operating Procedure

Two continuous 1 liter stirred slurry-phase reactors were used for catalyst testing and the schematic representation of one of these units is shown in Fig. A-3. Inlet CO and H_2 streams are passed through a series of oxygen removal, drying and carbonyl removal traps. The gas flow rate and H_2 to CO feed ratio are controlled using a mass flow controller for each feed gas. Alternatively, premixed synthesis gas at a fixed H_2 to CO feed ratio may be used, in which case only a single mass flow controller is required. The reactor is fully baffled, and the gas inlet point is directly beneath the flat-bladed impeller to maximize gas shear.

Products, together with unreacted syngas, are taken overhead through a heated partial reflux condenser, maintained at a temperature of about 200°C to return vaporized slurry oil to the reactor and minimize the carryover of high boiling products. The slurry level in the reactor is controlled by withdrawing accumulated slurry oil at the end of each mass balance period. The rise in slurry level is due to the accumulation of high molecular weight products in the reactor during synthesis. By determining the amount of slurry oil withdrawn to maintain a constant level at a particular set of process conditions, the higher molecular weight hydrocarbons that do not distill with the gas phase product can be quantitatively included in the material balance. This procedure is essential for obtaining an accurate overall product distribution.

During the system startup, or during an unsteady period, the reactor effluent passes through the unsteady state trap, which operates at ambient temperature and system pressure. The gas flows through the back pressure regulator to an unsteady state ice trap, and then to the system outlet where the gas flowrate is measured. During a mass balance period, the flow is diverted through the high and low pressure steady

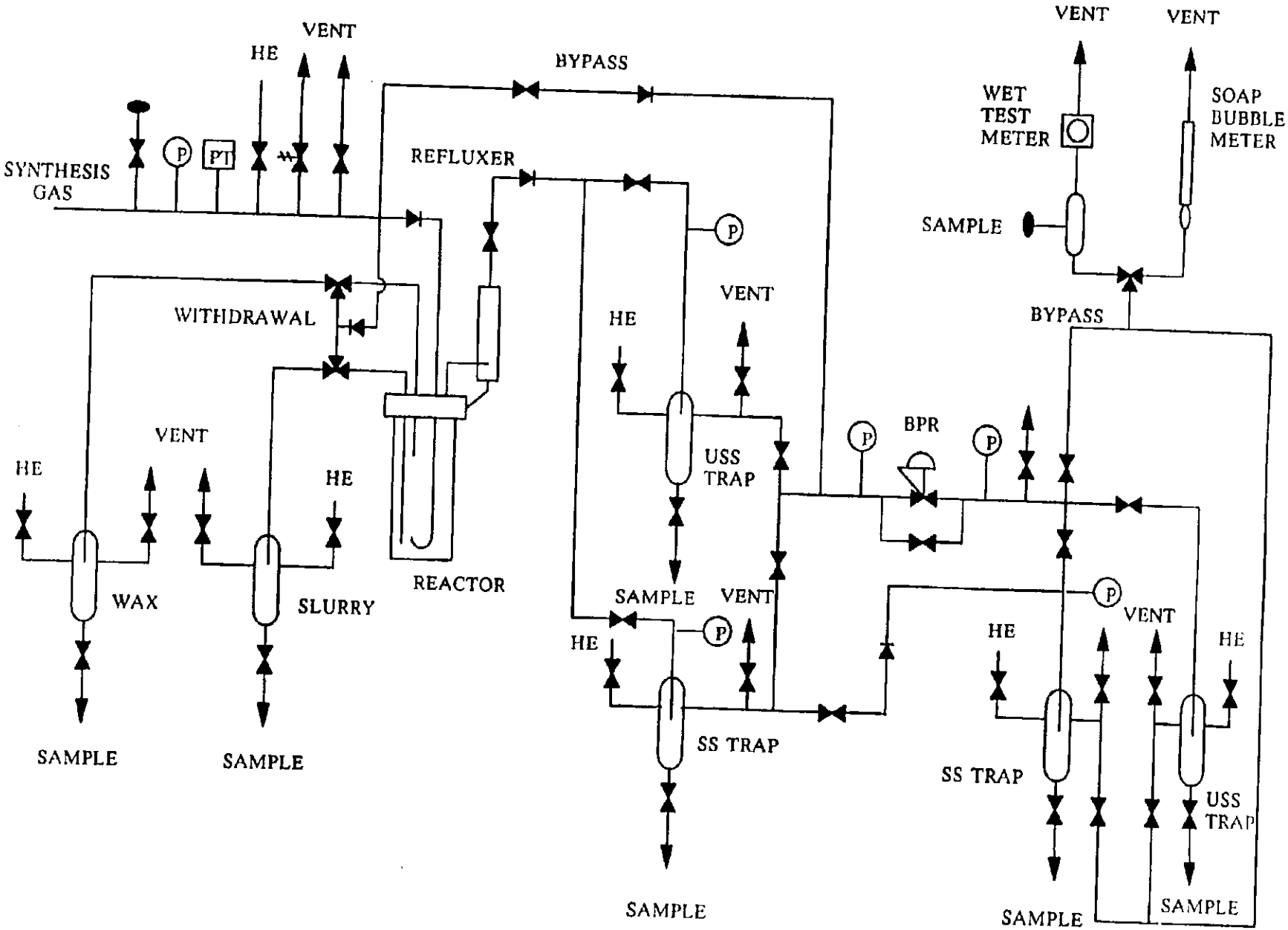

Figure A-3. Slurry Reactor System Schematic

state traps. The high pressure steady state trap is operated at 60–100°C and system pressure, and the low pressure trap is operated at 0°C and ambient pressure. Before draining, the pressure in the high pressure trap is relieved through the ice trap to minimize product loss due to flashing.

The whole system is designed to run continuously and automatically when unattended. After any change in process parameters, the reactor system is allowed to equilibrate for at least 14 to 16 hours before obtaining material balances over an additional 6–8 hour period. Due to the complexity of the Fischer-Tropsch product, equilibration of the reactor and the product collection system and a flexible quantitative analysis scheme incorporating all product, including waxes, are required to produce good mass balances and prevent misleading results.