

X Characterization of Product Distribution and Data Analysis

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.

Results obtained under this task are described in Chapters III-VII and Chapter IX of this report, in sections titled Reaction Studies. The information provided includes the following: lumped hydrocarbon product distribution, product yields (hydrocarbons and oxygenates), carbon number distribution (in the form of Anderson-Schulz-Flory plots), and total olefin and 2-olefin content as a function of carbon number.

XI CONCLUSIONS

The overall objectives of this contract were to: (1) demonstrate repeatability of performance and preparation procedure of two high activity, high alpha iron F-T 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). The major conclusions are:

1. Repeatability of performance of two catalysts designated B (100 Fe/5 Cu/6 K/24 SiO₂ containing 55.4 wt% of iron) and C (100 Fe/3 Cu/4 K/16 SiO₂ containing 59.7 wt% of iron) synthesized during the previous DOE Contract DE-AC22-89PC89868 was successfully demonstrated. The catalyst B was more stable in the original test (SB-1931) than in the two recent tests (SB-3354 and SB-0665), whereas the opposite trend was observed in tests with the catalyst C (runs SB-0261, SB-0045 and SA-0705). Hydrocarbon product distributions and olefin selectivities in multiple tests with the same catalyst were reproducible.

2. Performance of catalysts B and C is comparable to, or exceeds, that obtained in the two most successful bubble column slurry reactor (BCSR) tests conducted by Mobil and Rheinpreussen. In Mobil's run CT-256-13 at synthesis gas conversion of 82%, methane and C₁+C₂ selectivities were 2.7 and 5.6 wt%, respectively, whereas the catalyst productivity was about 0.26 g HC/g-cat/h (Test conditions: 257°C, 1.48 MPa, 2.3 Ni/g-Fe/h, H₂/CO = 0.73). In Rheinpreussen's demonstration plant unit the C₁+C₂ selectivity was 6.8% at the synthesis gas conversion of 89%, and the catalyst productivity was about 0.33 g HC/g-cat/h (Test conditions: 268°C, 1.48 MPa, 3.1 Ni/g-Fe/h, H₂/CO = 0.67).

In run SB-3354 with catalyst B (TOS = 97 h) the following results were obtained at 260°C, 1.48 MPa, 3.2 Ni/g-Fe/h, H₂/CO = 0.67: Methane and C₁+C₂ selectivities were 3.2

and 5.3 wt%, respectively, and the catalyst productivity was 0.26 g HC/g-cat/h at the synthesis gas conversion of 71.5%.

The performance of catalyst C in run SB-0045 at the reaction pressure of 1.48 MPa and 215 hours on stream, was very similar to that obtained in Mobil's run CT-256-13. However, the productivity of catalyst C was improved at reaction pressure of 2.17 MPa and gas space velocity of 3.4 NI/g-Fe/h (TOS = 336 h). Methane and C₁+C₂ selectivities were 2.6 and 5.4 wt%, respectively, and the catalyst productivity was 0.36 g HC/g-cat/h at the synthesis gas conversion of about 80%. The latter productivity is higher than productivity's obtained in Mobil's and Rheinpreussen's bubble column slurry reactor tests, primarily due to the use of higher reaction pressure and higher gas space velocity in the present study.

3. The use of higher reaction pressure and proportionally higher gas space velocity, to maintain constant gas residence time in the reactor, was successfully demonstrated in several tests with catalyst C (runs SB-0045, SA-0075, SA-1665, SA-0946 and SA-2186). Slurry F-T reactors have normally operated at pressures less than 1.5 MPa, whereas the coal gasifiers which generate the synthesis gas operate at pressures between 2 and 3 MPa. The use of higher operating pressures and higher gas space velocity increases reactor productivity and improves the process economics. Space-time-yields were increased up to 48% by increasing reaction pressure from 1.48 MPa to 2.17 MPa, while maintaining the gas contact time and synthesis gas conversion at a constant value. No adverse effects of operation at higher pressure on catalyst activity were observed in several of these tests (up to 250 hours of testing at 2.17 MPa).

4. Repeatability of performance of catalysts B and C was demonstrated in multiple tests with catalysts from different preparation batches. Three STSR tests were conducted with catalyst B, and four tests with catalyst C. In general, catalysts from different preparation batches (100-400 g of catalyst batches) had similar performance (activity and selectivity) and

reproducibility of catalyst preparation procedure on a laboratory scale has been successfully demonstrated.

5. The addition of CaO promoter to baseline catalysts B and C (catalysts with nominal compositions $100 \text{ Fe}/3 \text{ Cu}/4 \text{ K}/x \text{ Ca}/16 \text{ SiO}_2$ and $100 \text{ Fe}/5 \text{ Cu}/5 \text{ K}/x \text{ Ca}/24 \text{ SiO}_2$, where $x = 2$ or 6) was not found to be beneficial for their performance. The addition of larger amount of CaO ($x = 6$) resulted in markedly lower catalyst activity, whereas selectivity of the two catalysts with $x = 6$, was similar to that of the corresponding baseline catalysts (fixed bed reactor tests). The two catalysts with $x = 2$ were also tested in slurry reactors.

At reaction pressure of 1.48 MPa, selectivity of gaseous hydrocarbons on CaO containing catalysts was higher than that of the corresponding baseline catalysts. However, at reaction pressure of 2.17 MPa the gaseous hydrocarbon selectivity decreased on the CaO containing catalysts, and was nearly the same as that of the baseline catalysts at 1.48 MPa. The CaO promoted catalysts may be suitable for operation at higher reaction pressures.

6. The effect of use of two different sources of potassium on the performance of catalysts B and C was studied in fixed bed and slurry bed reactors. In our standard catalyst preparation procedure silicon oxide is introduced by addition of a dilute potassium silicate (K_2SiO_3) solution to the iron/copper precipitate. This procedure introduces potassium in the excess of the desired amount. Potassium is completely removed by washing of the precipitate. Addition of the desired amount of potassium promoter is accomplished via "incipient wetness" method, using KHCO_3 dissolved in water. An obvious alternative to the above procedure is to utilize potassium from K_2SiO_3 as the source of potassium, i.e. discontinue with washing when the residual amount of potassium equals the desired amount of promoter. Catalysts B and C were synthesized using potassium silicate as the source of the potassium promoter, and performance of these catalysts was compared with those synthesized using our usual procedure (Section IV-2). On the basis of results obtained in these tests it was concluded that the baseline procedure utilizing impregnation of Fe-Cu-SiO₂ precursor with the aqueous solution of KHCO_3 is the

preferred method of catalyst preparation. The second procedure, which avoids the impregnation step, provides satisfactory results, and may be used as an alternative.

7. Significant improvements in activity of the catalyst C (from batch-4) were obtained through the use of different pretreatment procedures. The initial activity (measured by a value of the apparent reaction rate constant, k) of the catalyst reduced with hydrogen at 250°C for 4 hours (run SB-3425) was about 40% higher than that of hydrogen reduced at 240°C for 2 hours (baseline reduction procedure). However, the catalyst activity decreased with time and at about 300 h its apparent rate constant ($k = 250$ mmol/g-Fe/MPa/h) was similar to the value obtained in run SA-1665 employing the baseline reduction procedure.

The CO pretreatment (SA-0946), syngas pretreatment (SA-1626) and TAMU pretreatment (SA-2186) also resulted in improved catalyst activity, relative to the standard reduction procedure. The initial values of the apparent reaction rate constant, after these pretreatments, were 300-400 mmol/g-Fe/MPa/h, corresponding to 20-60% increase in activity relative to the standard procedure. Activity of the CO and TAMU pretreated catalysts increased with time, and at 400 hours the values of the apparent reaction rate constants were 360 and 430 mmol/g-Fe/MPa/h, respectively. As the result of the improvement in the catalyst activity, while maintaining low methane and gaseous hydrocarbon selectivities, the catalyst productivities in these two tests were markedly higher than those obtained in Mobil's and Rheinpreussen's slurry bubble column reactor tests. The catalyst productivity in Rheinpreussen test was 0.49 gHC/g-Fe/h, and those obtained in runs SA-0946 and SA-2186 were 0.71 and 0.86 gHC/g-Fe/h, respectively. This represents 45-75% improvement in catalyst productivity relative to that achieved in Rheinpreussen's demonstration plant unit, and sets new standards of performance for "high alpha" iron catalysts. We believe that the performance of our catalyst B (100 Fe/5 Cu/6 K/24 SiO₂) can be also improved through the use of better pretreatment procedures.

8. The effect of calcination temperature on performance of catalysts B and C during F-T synthesis was investigated in fixed and slurry bed reactors. Both catalyst B (100 Fe/5 Cu/6 K/24 SiO₂) and C (100 Fe/3 Cu/4 K/16 SiO₂) were tested in fixed bed reactors after calcinations at 400°C and 500°C for 5 h, and after flash calcination at 700°C for 1 h, and in a stirred tank slurry reactor after flash calcination at 700°C for 1 h.

The main findings from slurry reactor tests were: (1) The activity of catalysts B and C calcined at 700°C was lower than that of these two catalysts calcined at 300°C (baseline calcination temperature); (2) Gaseous hydrocarbon selectivities were higher on catalysts calcined at 700°C; (3) Alpha olefin selectivity of C₁₀+ hydrocarbons was markedly higher on catalysts calcined at 700°C, which is of potential significance, since alpha olefins are valuable products; and (4) Oxygenates yields were about four times higher on the catalysts B and C calcined at 700°C, than on the catalysts calcined at 300°C.

9. Although catalysts B and C have desirable activity and selectivity characteristics, they may not have a sufficient mechanical strength and attrition properties required for utilization in commercial bubble column slurry reactors. Three catalysts 100 Fe/5 Cu/4.2 K/20 Al₂O₃ (run SA-0097), 100 Fe/5 Cu/6 K/139 SiO₂ (SB-0627) and 100 Fe/5 Cu/9 K/139 Al₂O₃ (SB-2337) were evaluated in slurry reactor tests as potential alternatives to our baseline catalysts B and C. The performance of the three alternative catalysts was inferior in comparison to our baseline catalysts. The alternative catalysts had lower activity, faster deactivation rate, and produced more gaseous hydrocarbon products than the baseline catalysts.

In general, all major objectives of this contract have been achieved. Significant improvements in catalyst productivity were achieved through the use of higher operating pressure (2.17 MPa) and use of different pretreatment procedures. Catalyst productivities achieved in runs SA-0946 and SA-2186, 0.71 and 0.86 gHC/g-Fe/h, respectively, have established new standards of performance for "high alpha" iron catalysts.

XII Acknowledgments

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Appendix 1

Catalysts Preparation Procedure

A1-1 Co - Precipitation Procedure

Desired compositions of copper-promoted iron-based catalysts were prepared by continuous co-precipitation, using an apparatus and a technique similar to that employed by previous investigators (Kölbel and Ralek, 1980; Deckwer et al., 1982). Unlike conventional batch precipitation, this approach ensures that precipitation occurs at a constant, rather than continuously changing, pH, resulting in much more uniform and predictable particle size and pore/structure.

In the present case, an aqueous solution containing $\text{Fe}(\text{NO}_3)_3$ ($\sim 0.6 \text{ M}$) and a concentration of $\text{Cu}(\text{NO}_3)_2$ that corresponds to the desired Fe/Cu ratio in the final catalyst, and a second solution containing aqueous NH_3 ($\sim 2.7 \text{ M}$) are maintained in stirred vessels at $84 \pm 2^\circ\text{C}$. The two solutions are separately conveyed by fluid pumps to a stirred tubular reaction vessel that is thermostated at $82 \pm 2^\circ\text{C}$. Precipitation (to form FeOOH and $\text{Cu}(\text{OH})_2$) occurs continuously as the two solutions are pumped upward through the vessel, while an in-line pH electrode is used to monitor the pH of the reactor effluent, which is maintained at 6.0 ± 0.2 . Collection of the slurried precipitate is made in ice-cooled vessels and is continued until one of the two solutions is consumed. The precipitate is then thoroughly washed by vacuum filtration to remove excess NH_3 and NO_3^- , using ~ 10 liters of deionized and distilled water per 100 g (dry weight) of the final catalyst. The washed precipitate is then used for the preparation of final catalysts.

A1-2 Addition of Silicon Oxide

The wet Fe/Cu precipitate is mixed with deionized and distilled water to make a uniform slurry. Dilute potassium silicate solution containing a desired amount of silica (SiO_2) was added to the slurry very slowly. During potassium silicate addition the pH was

maintained at about 9.0. Once the addition of potassium silicate was over and the pH was stabilized, a 10% dilute nitric acid was added drop by drop until the pH reaches ~ 6.0 - 6.5 with constant stirring. Stirring was continued for additional four hours after the addition of nitric acid. Immediately after completing the stirring procedure the resulting silica containing slurry was filtered, washed (to remove the K^+ ions) and vacuum oven dried at 50°C for 48 h and then at 120°C for 24 h.

A1-3 Addition of Aluminum Oxide

The method used to prepare the alumina containing precipitated iron catalysts employed an Fe/Cu precipitate of the desired composition (100 Fe/5 Cu) that had been already vacuum dried. Under an atmosphere of dry nitrogen (to prevent exposure to atmospheric water) an appropriate amount of liquid sec-butoxide was dissolved in a volume of 2-butanol needed to just fill the pores of the precipitate sample (incipient wetness method). The required amount of dried Fe/Cu precipitate was added to the butoxide solution, and the resulting slurry was stirred for 16 hours to ensure complete pore filling by viscous alkoxide solution. Excess alcohol solvent was then removed by heating the mixture in a vacuum oven for 6 h at 60°C. Hydrolytic decomposition of the impregnated aluminum sec-butoxide to form Al_2O_3 was accomplished by exposure of the material for 16 h at 25°C to air that was saturated with water vapor. The alumina-containing catalysts after being thoroughly washed and dried in a vacuum oven for 16 h at 120°C, were impregnated with $KHCO_3$ (see below) and were re-dried to yield the final catalysts.

A1-4 Impregnation by Potassium

Addition of the desired levels of potassium promoter to Fe-Cu-SiO₂ (or Fe-Cu-Al₂O₃) catalyst precursors was made by pore filling technique, using dried precipitate that has been crushed to < 30 mesh. In this method, the required amount of $KHCO_3$ is dissolved in a volume of water that is ~ 5% larger than that needed to just fill all of the pores of the solid.

The solution is then added to a weighed sample of the dried catalyst, resulting in the so-called "incipient wetness" condition. Excess solvent (water) is then removed by vacuum-aided evaporation, with continuous rotational agitation. The final product is dried further in a vacuum oven at 120°C for 16 h. This procedure ensures uniform and complete distribution of the potassium salt throughout the catalyst pore structure.

A1-5 Potassium from Potassium Silicate (K_2SiO_3) Source

In some of the iron based F-T synthesis catalysts the source of potassium was potassium silicate. For the preparation of these catalyst formulations the wet precipitate (cake) was utilized after the addition of potassium silicate to the Fe-Cu precipitate slurry. After the addition of potassium silicate, the potassium content in the slurry is usually higher than the desired potassium content. Excess potassium was removed by decantation of appropriate amounts of water from the slurry, and the remaining water was removed by vacuum aided evaporation. Then the final solids were dried in a vacuum oven at 50°C for 48 h and at 120°C for 24 h.

A1-6 Addition of Calcium Oxide Promoter

Catalysts with nominal composition 100 Fe/3 Cu/4 K/x Ca/16 SiO_2 and 100 Fe/5 Cu/5 K/x Ca/24 SiO_2 (where: $x = 2$ or 6) were prepared by impregnation of the corresponding Fe-Cu- SiO_2 precursors. Dried precursors (prepared as described above in A1-1 and A1-2) were impregnated first with calcium acetate monohydrate (in catalysts with $x = 2$) and then with potassium bicarbonate by incipient wetness method. For catalysts with $x = 6$, the dried precursors were impregnated first with potassium bicarbonate, followed by impregnation with calcium acetate monohydrate.

A1-7 Impregnation of Commercial Supports

We have prepared four supported catalysts (~ 50 g each) by impregnation with aqueous solutions of iron and promoter salts. The supports (silica - Davison grade 952; and alumina - Vista B) were sieved and calcined at 500°C in air for 5 h prior to impregnation. Catalysts containing iron, copper and potassium on silica or alumina were prepared by co-impregnation with aqueous solutions containing desired amounts of ferric nitrate, copper nitrate and potassium bicarbonate in successive steps. The total volume of impregnating solution (which contains the calculated amounts of promoters) was about 95 ml in each catalyst preparation. However, the amount of impregnating solution consumed in each impregnation step was different and varied with the support. For example during the preparation of silica supported catalysts we were able to complete the preparation of catalysts in three impregnation steps, whereas seven impregnation steps were used in preparation of alumina supported catalysts. After each impregnation step the sample was vacuum dried at 100°C for about 2 h. After the final impregnation and drying for 12 h in vacuum, the catalyst was calcined in air at 300°C for 5 h. Various steps in the catalyst preparation are shown in Figure A1-1. Nominal compositions (on mass basis) of synthesized catalysts are: (1) 100 Fe/5 Cu/6 K/139 SiO₂, (2) 100 Fe/10 Cu/6 K/134 SiO₂, (3) 100 Fe/5 Cu/6 K/139 Al₂O₃ and (4) 100 Fe/10 Cu/6 K/134 Al₂O₃. The corresponding weight % of iron (as metal) in the prepared catalysts is approximately 33.8%.

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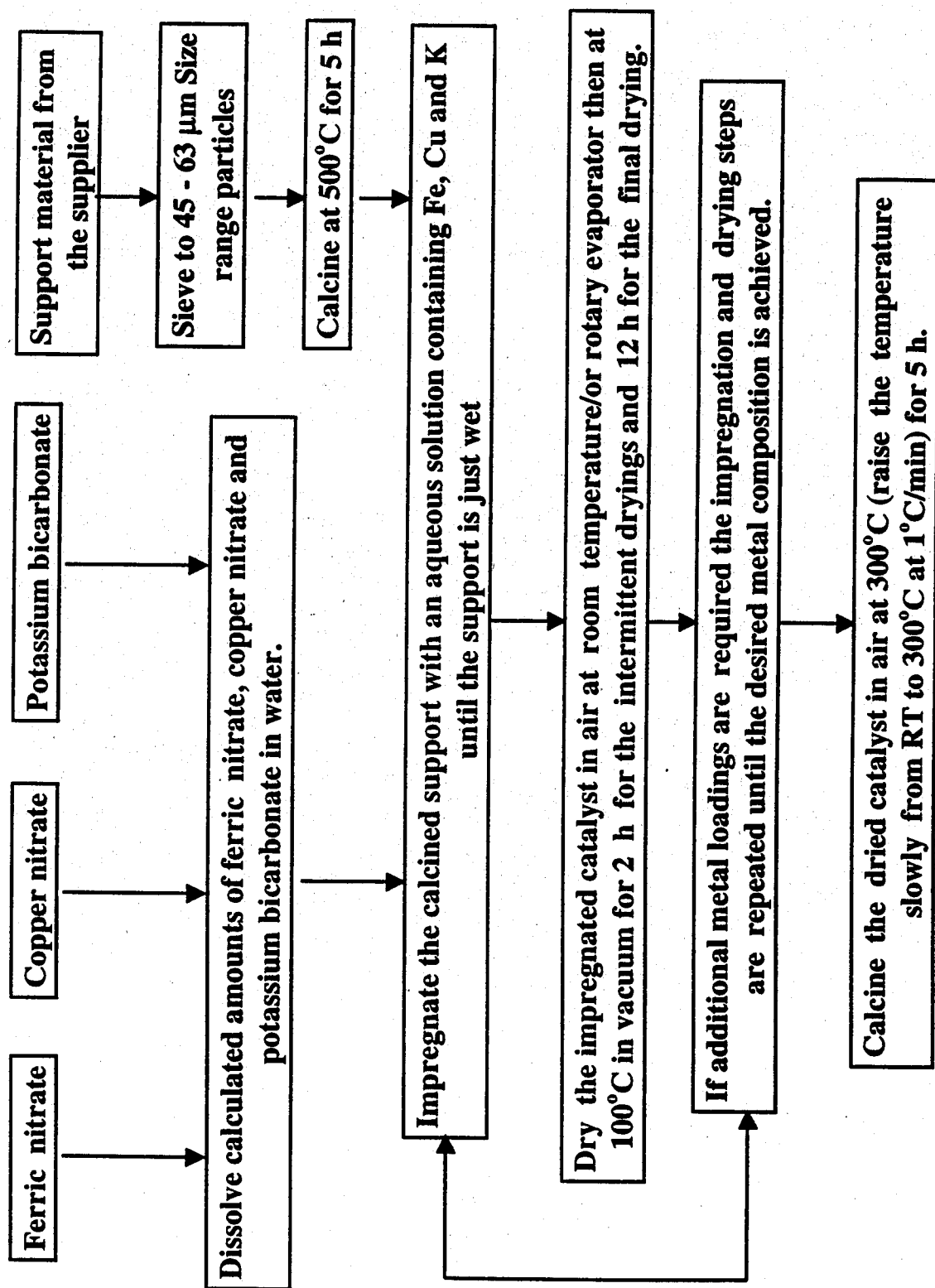


Figure A1-1 Steps in preparation of alumina or silica supported catalysts.

Appendix 2 Catalyst Characterization Equipment and Procedures

A2-1 Elemental Analysis

Catalyst bulk compositions were determined by Atomic Absorption Spectroscopy (AAS) using a Varian SpectrAA-30 spectrophotometer. For AAS analysis, a required amount of catalyst was dissolved in an acid mixture of hydrochloric (HCl) and hydrofluoric acid (HF) followed by dilution with distilled water to 100 ml. Portions of this sample were properly diluted and then the amounts of Cu, K, and Fe were determined by AAS. The composition of silica was determined either directly by the AAS method or by calculation method. In the latter method, the composition of silica in the catalyst was estimated indirectly using the measured amounts of Fe, Cu, and K and by assuming that oxides of these elements were in the form of Fe_2O_3 , CuO , and K_2CO_3 . The weight percent of SiO_2 was calculated from the equation:

$$\begin{aligned} W_{\text{SiO}_2} &= 100\% - W_{\text{Fe}} (M_{\text{Fe}_2\text{O}_3}/2M_{\text{Fe}}) - W_{\text{Cu}} (M_{\text{CuO}}/M_{\text{Cu}}) - W_{\text{K}} (M_{\text{K}_2\text{CO}_3}/2M_{\text{K}}) \\ &= 100\% - 1.43 W_{\text{Fe}} - 1.25 W_{\text{Cu}} - 1.77 W_{\text{K}} \end{aligned}$$

where: w_i is the weight percent of element i determined by AAS, M_i is the molecular (or atomic) weight of species i .

A2-2 BET Surface Area, Pore Volume and Pore Size Distribution Measurements

The BET surface area and pore volume measurements of the catalysts after calcination were obtained by nitrogen physisorption at 77 K using Micromeritics Digisorb 2600 system. The samples (~ 1-2 g) were degassed at 150°C for 12 h prior to each measurement. Surface area only was also determined using Pulse Chemisorb 2705 instrument (Micromeritics Inc.). Catalyst samples were outgassed in a flow of nitrogen (~ 30 cm^3/min) at 200°C for 3 to 12 h prior to each measurement.

A2-3 X-Ray Diffraction Measurements

Powder X-ray diffraction patterns of catalyst samples before pretreatment, after pretreatment, and after Fischer-Tropsch synthesis reaction (used catalysts) were obtained on a Scintag XDS-2000 diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) starting from $2\theta = 28^\circ$ to 68° at a rate of $1^\circ/\text{min}$. The pretreated and used catalyst samples from fixed bed and slurry reactor tests were handled in an inert atmosphere to prevent catalyst oxidation prior to and during XRD measurements.

Handling of Slurry Reactor Samples - No Extraction

A small portion (7-8 g) of a slurry sample withdrawn from the reactor was transferred into a small cylindrical vessel (sampling cylinder) which can be sealed air-tight. The sampling cylinder was transferred to a glove box filled with inert gas (Argon). The slurry samples for XRD analyses were removed in an inert atmosphere and washed with dry and warm Varsol solvent, until the filtrate (Varsol) was clear. After this the solid residue (catalyst plus some wax) is transferred into a sample holder or stored in a sample vial. The sample holder is sealed in the glove box and then placed directly in the X-ray diffractometer. The sample holders are made out of Plexiglas which does not yield any diffraction peaks. The above procedure prevents exposure of catalyst samples to an oxidizing environment.

Extracted Samples for X-ray Analysis

Catalyst samples from slurry reactor tests were separated from wax in an inert atmosphere according to the following procedure. A slurry sample (about 7-8 g), from the sampling cylinder was dispersed in 500 ml of warm and degassed Varsol and then filtered at about 80°C . The filter cake, mostly catalyst and a small amount of wax, was then rinsed with warm degassed xylene. The wet cake was dried in vacuum at ambient temperature in a pre-chamber of the glove box. After drying, the cake was put into an extraction thimble which was placed inside a small sealable plastic bag. The thimble was then transferred into the Soxhlet extraction apparatus in a glove bag filled with pure Argon. The extraction apparatus was then taken out of the glove bag and the extraction is carried out first with 200 ml xylene

for 10 h, followed by methyl ethyl ketone (MEK) for another 10 h. The top of the condenser unit was closed so that no air could enter the system during the extraction. At the end of extraction, the catalyst was transferred again to the glove box where it was removed from the thimble and sealed in sample vials and stored, or placed in specially designed sample holders for characterization by XRD.

Fixed Bed Reactor Samples

At the end of reaction tests the reactor was sealed (air-tight) in an inert gas atmosphere and then transferred to a glove box. Catalyst samples removed from the top, bottom, and /or middle portions of the reactor were analyzed separately, after magnetic separation from glass beads (used as a diluent during FT synthesis) in a glove box. Such a separation was found to increase the intensity of the XRD peaks significantly.

Catalyst Passivation Procedure after Isothermal Reductions

After an isothermal reduction in a thermal gravimetric analyzer the catalyst sample was cooled to a room temperature in helium flow (100 cm³/min). Then a small stream (at a low flow rate) of purified air was introduced into the helium stream. Gradually the air flow was increased very slowly until a final oxygen content was about 20%. The passivation process was marked by the occurrence of small exotherms (typically 2-3 K) in the catalyst bed and subsequent return to room temperature. At the end of passivation the sample was loaded into a specially designed sample holder and analyzed by X-ray diffractometer.

A2-4 Mössbauer Effect Spectroscopy

The Mössbauer measurements were conducted at the University of Kentucky (The Consortium for Fossil Fuel Liquefaction Science) using a constant acceleration spectrometer of standard design. The radioactive source consisted of 50 - 100 mCi of ⁵⁷Co in a Pd matrix. The samples were in powdered form and were mounted in Plexiglas compression holders to present a thin aspect to the gamma ray beam. Calibration spectra of metallic iron were obtained simultaneously at the other end of the drive. The spectra were analyzed by least-

squares regression of a sum of Lorentzian lines to the experimental data. The hyperfine parameters (the isomer shift, the quadrupole splitting, and the magnetic hyperfine field) were obtained from the estimated line positions. Iron phases were identified by matching the observed values of the hyperfine parameters to those from literature .

A2-5 Temperature Programmed Reduction (TPR) Measurements

Temperature-programmed reduction (TPR) studies were performed using 5% H₂/95 %N₂ as reductant. In a typical TPR experiment about 10 to 20 mg of catalyst was packed in a quartz reactor and purged with helium to remove the moisture from the catalyst sample. Then the catalyst sample was heated in a flow of 5% H₂/95 %N₂ (flow rate of 40 cm³/min) from room temperature to 800-900°C at a heating rate of 20°C/min. Consumption of the H₂ was monitored by a change in the thermal conductivity of the effluent gas stream. A dry ice/acetone bath was used to remove water formed during hydrogen reductions. In order to quantify the degree of reduction, CuO standard was used for the calibration of the peak areas. All experiments were conducted in Pulse Chemisorb 2705 unit (Micromeritics Inc.) equipped with thermal conductivity detector and temperature programmable furnace for TPR/TPD studies.

A2-6 Isothermal Reductions by Thermogravimetric Analysis

Isothermal reduction in thermogravimetric analysis (TGA) experiments was conducted using approximately 20 mg catalyst samples. The catalyst sample was purged with helium (40 cm³/min) and temperature was ramped at a rate of 5°C/min from room temperature to a desired reduction temperature. Then the helium flow was switched to a reductant (hydrogen, carbon monoxide or synthesis gas) at 40-100 cm³/min, and the temperature was maintained at a constant value for a total period of up to 8 hours. The degree of reduction was calculated from the weight loss vs. time data. Experiments were conducted in a simultaneous TGA/DTA apparatus (TA Instruments, Model SDT 2960).

Appendix 3 Fixed and Slurry Bed Reactors and Product Analysis System

A3-1 Fixed bed reactor

Two fixed bed reactors were for screening tests of F-T catalysts. A simplified flow diagram of one of the existing reactors is shown in Figure A3-1. The reactor is a conventional downflow fixed bed reactor (1.3 cm inside diameter, effective length of 30 cm). Bed temperature is monitored through six thermocouples placed along the reactor. The reactor is heated externally with heating tapes wound around periphery of alumina blocks surrounding the stainless steel reactor. The reduction gas, an inert gas (helium or nitrogen), and/or a premixed synthesis gas passes through a series of oxygen removal, alumina, and activated charcoal traps to remove trace impurities. The gas flow rate is controlled using calibrated mass flow controllers, and the feed was preheated before entering the reactor. After leaving the reactor, the exit gas passes through a high pressure trap, which is maintained at about 90 - 150°C, to condense high molecular weight products. After releasing pressure through a back pressure regulator, the gas passes through a low pressure ice trap to collect any remaining condensibles. The flow rate of the tail gas exiting the system is measured frequently with a soap film flow meter.

During mass balance periods liquid products are allowed to accumulate in high and low pressure mass balance (steady state) traps. At the conclusion of the mass balance period, flow is directed to waste traps placed in parallel with the mass balance traps, and liquid products from the mass balance traps are collected and weighed. After startup, and following any change in process conditions, the reactor is allowed to operate undisturbed for 20 - 40 hours in order to achieve steady conditions before the next mass balance is performed. High molecular weight hydrocarbons (wax), collected in the high pressure trap, and liquid products, collected in the ice trap, are analyzed by gas chromatography.

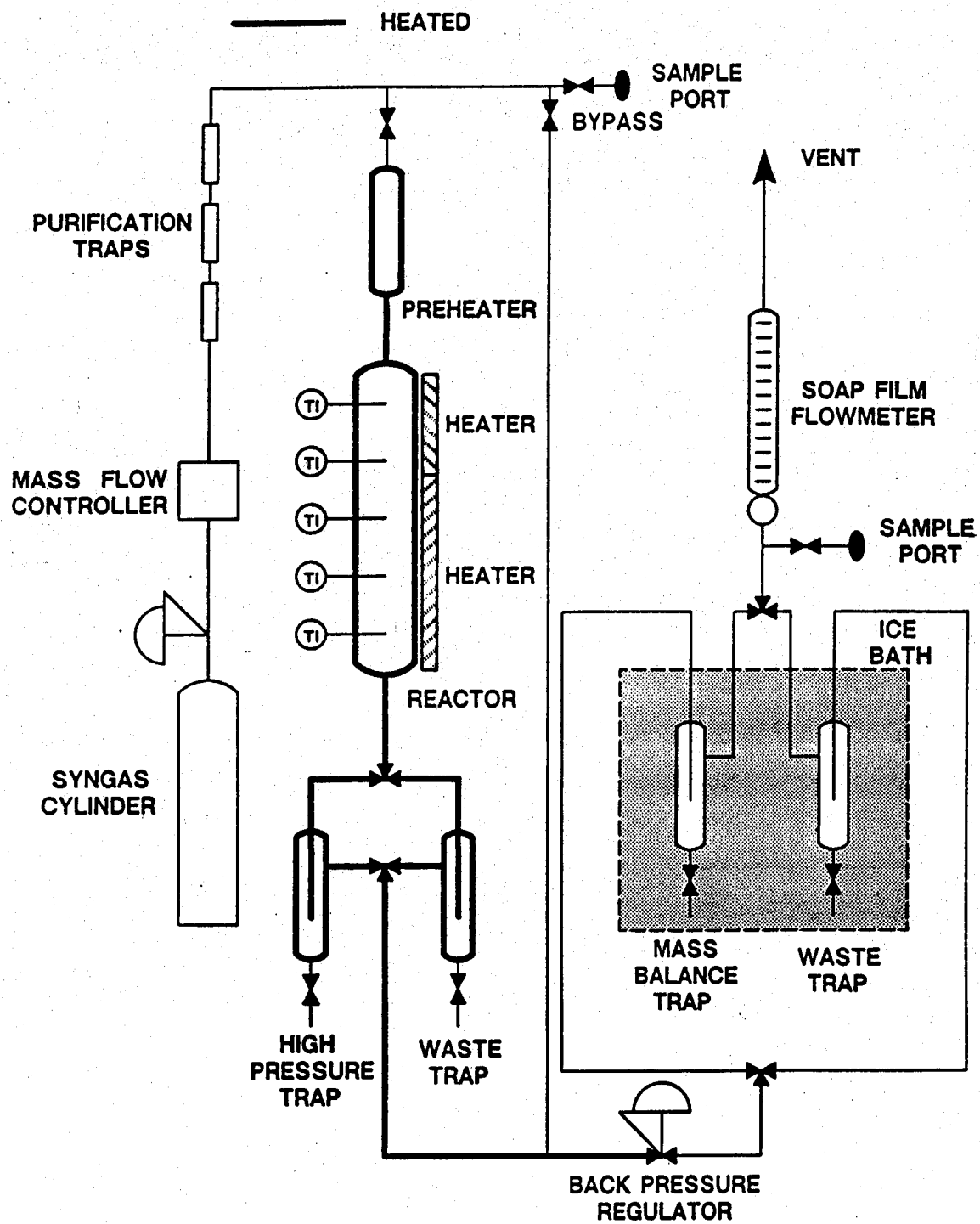


Figure A3-1 Schematic diagram of fixed bed reactor system used for catalyst testing.

A3-2 Stirred Tank Slurry Reactor

A schematic representation of a 1 liter stirred tank slurry-phase reactor (Autoclave Engineers, Inc.) is shown in Figure A3-2. Inlet CO and H₂ streams are passed through a series of oxygen removal, drying and carbonyl removal traps. The gas flow rate and H₂ to CO feed ratio are controlled using a mass flow controller for each feed gas. Alternatively, a premixed synthesis gas at a fixed H₂ 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 line. The slurry level in the reactor is controlled by withdrawing accumulated slurry oil at the end of each mass balance period through a porous metal filter. 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. Slurry samples can be also withdrawn from the reactor through a dipleg tube for subsequent catalyst characterization.

During system startup, or during an unsteady period, the reactor effluent passes through the unsteady state trap. 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 state traps. 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

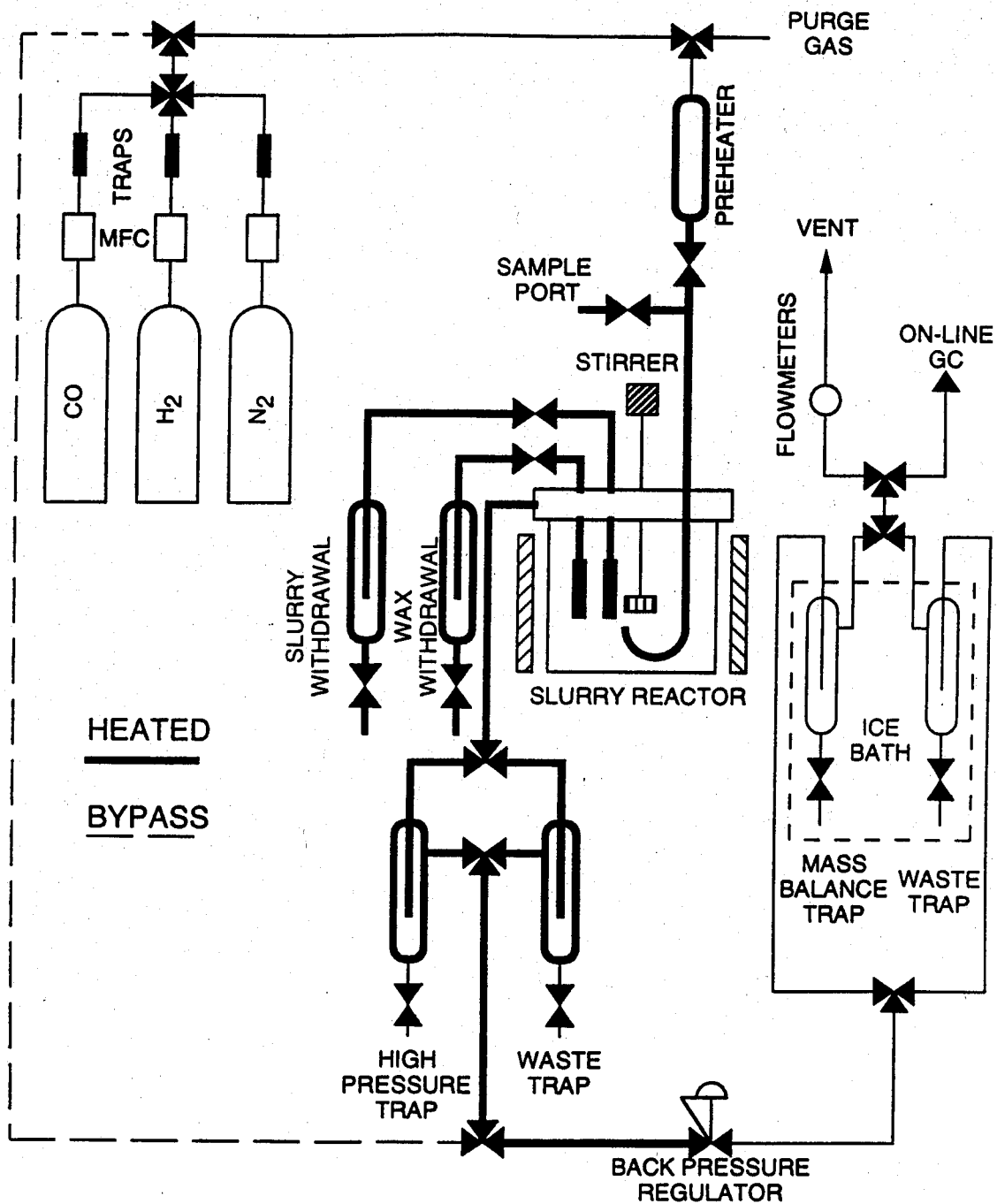


Figure A3-2 Schematic of stirred tank slurry reactor system.

equilibrate for at least 14 to 16 hours before obtaining material balances over an additional 8-12 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. All products collected in the steady state traps are analyzed by gas chromatography after physical separation into an aqueous and organic phase. Exit gas composition is determined by an on-line gas chromatograph, and wax from the reactor is analyzed on a capillary column (see below).

A3-3 Product Analysis

A versatile analytical and computerized data handling system consisting of four GC's linked to a data acquisition system is used for product analysis (Figure A3-3). In the gas effluent from the reactor unreacted H₂, CO and product CO₂ and C₁-C₅ hydrocarbon gases are analyzed on the Carle AGC-400 chromatograph. Small amounts of C₆ 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 separated 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 Varian 3400 GC for C₄-C₃₀ hydrocarbons, C₄-C₁₁ alcohols, C₃-C₆ ketones, and C₂-C₆ aldehydes. The wax fraction is dissolved in CS₂ 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 PC for further analysis and reduction. Mass balance program uses pull up templates to prompt the operator to enter the needed information. 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

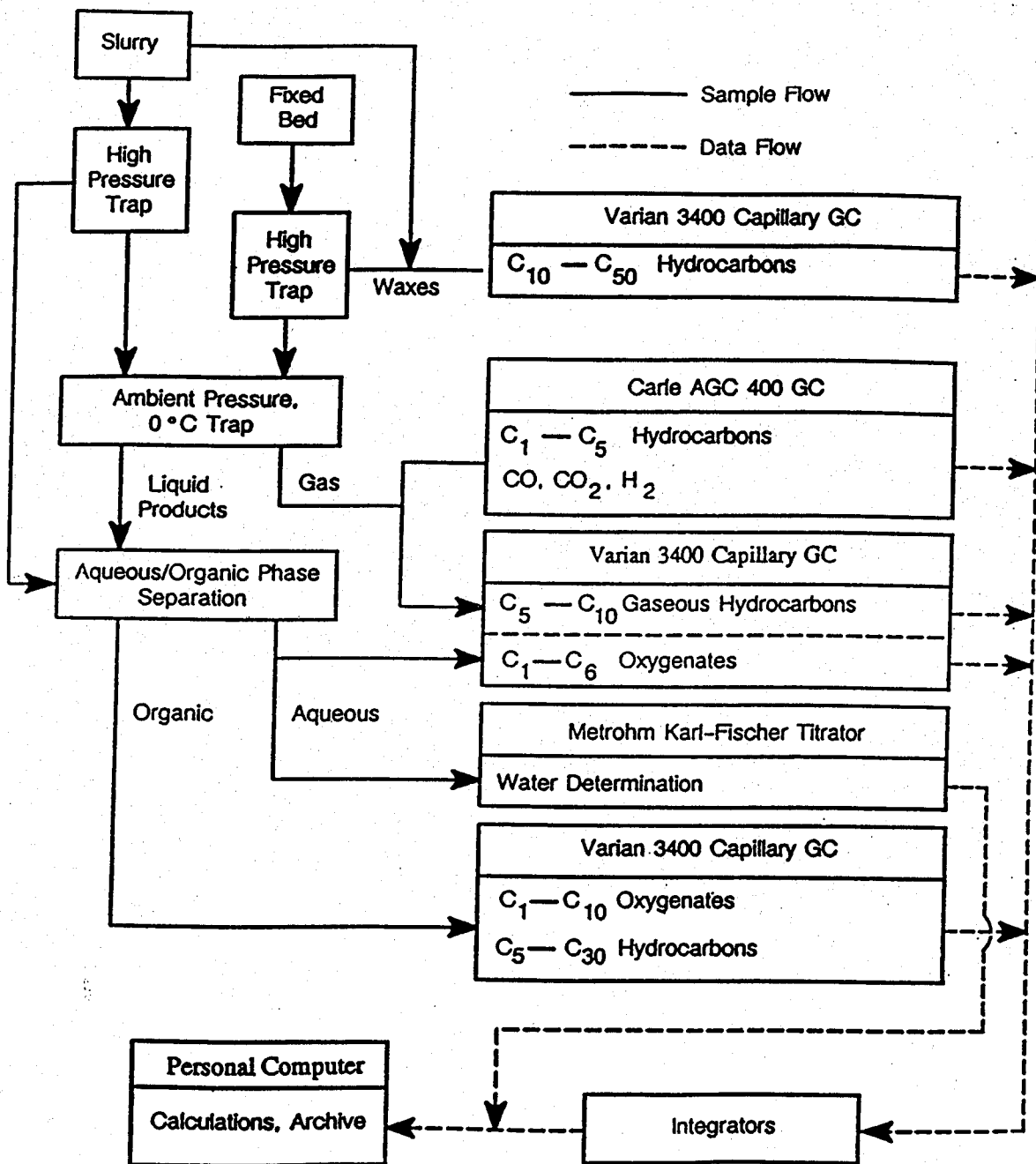


Figure A3-3 Analysis of Fischer-Tropsch synthesis products with automated data acquisition and reduction system.

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 products according to carbon numbers. The mass balance program also calculates Schulz-Flory chain growth parameters and produces Schulz-Flory plots.