APPENDIX

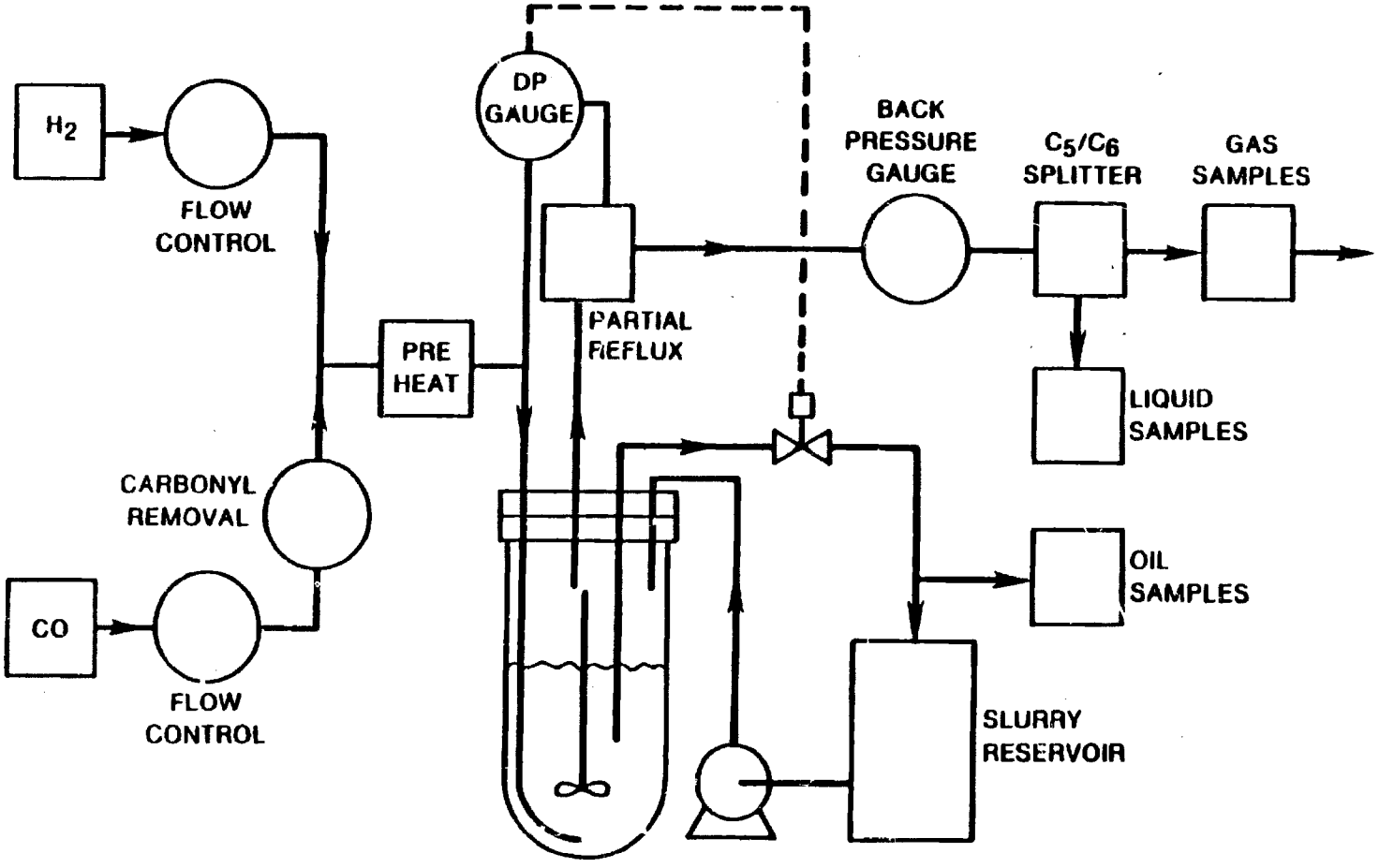
FISCHER-TROPSCH SLURRY REACTORS

The continuous, stirred, slurry phase reactors used for the Fischer-Tropsch synthesis have a volume of either 300 ml or 1 liter. Figure 1 is a schematic representation of one of these units. Inlet CO and H_2 streams are passed through separate oxygen removal and drying stages, and for the CO stream, an additional iron carbonyl removal stage using a heated alumina trap, before being mixed and preheated. Any desired ratio of CO to H_2 can be fed to the stirred reactor system with the help of mass flow controllers. The reactor is fully baffled, and the gas inlet point is directly beneath the flat-bladed impeller to maximize gas shear. The reactor operates in a temperature range of 220-330°C, pressures of 160-510 psi, and gas hourly space velocities (GHSV) up to 1000 h^{-1}. Products, together with unreacted syngas, are taken overhead through a heated partial reflux condenser, and maintained at a top temperature of about 200°C to return vaporized slurry oil to the reactor.

The level of slurry in the reactor is continuously monitored by determining the differential pressure between the gas inlet and outlet streams to detect any buildup of higher molecular weight products in the reactor. When this occurs, hydrocarbon product can be removed from the reactor directly via a heated sidestream, filtered through a 5-μm stainless steel sinter, and analyzed. Automatic slurry level control is possible via feedback from the differential pressure gauge, and a pump enables fresh or regenerated slurry catalyst to be recycled back into the reactor. By a determination of the amount of slurry oil withdrawn to maintain a constant level at a particular set of process conditions, the higher molecular weight hydrocarbons that do not distill with the gas phase product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 of the system. This procedure is essential to obtain an overall product selectivity.

FIGURE

CONTINUOUS, AUTOMATED FISCHER-TROPSCH SLURRY REACTOR SYSTEM



The product stream from the partial reflux condenser flows via a heated line to a pressure reduction stage, and then to a C_5/C_6 splitting column, to produce a condensed liquid phase and a gaseous phase. The gaseous stream consists of unreacted syngas, CO_2, and products with carbon numbers from C_1 to C_5. The condensed liquid product consists of hydrocarbons with carbon numbers C_6 and above, and an aqueous phase containing dissolved oxygenates. This method of product collection avoids the use of high-pressure traps, is more suited to continuous operation, and, by reducing the number of product fractions, is more accurate in obtaining material balances.

The whole system is designed to run continuously and automatically when unattended, with automatic sampling of the split gas phase stream and collection of liquid samples. After any change in process parameters, the reactor system is allowed to equilibrate for 14 to 16 hours before carbon and hydrogen material balances are obtained over an additional 8-hour period.

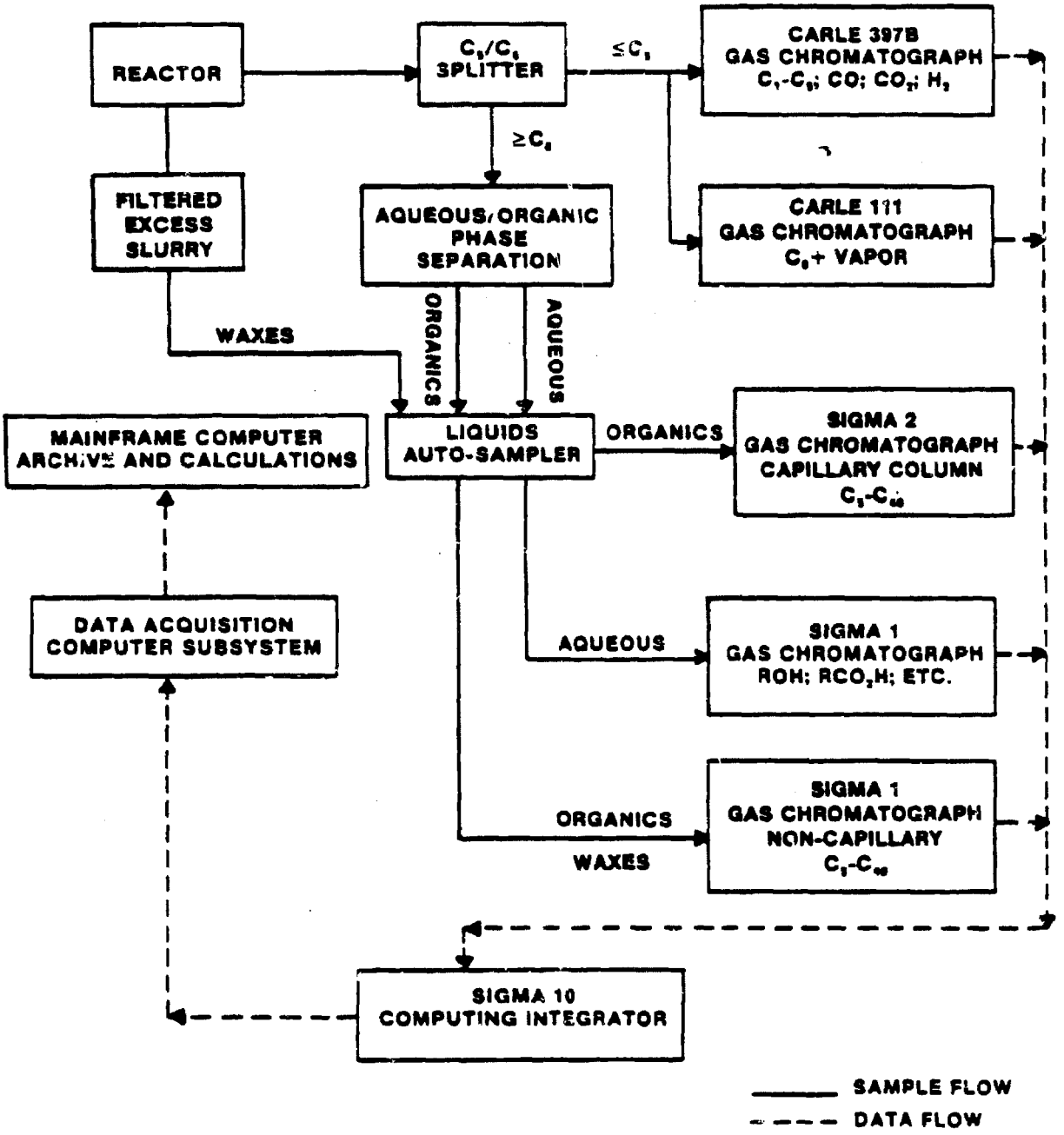
Because of the complexity of the Fischer-Tropsch product, equilibration of the reactor and the product collection systems and a flexible, quantitative analysis scheme incorporating all products including waxes, are required to produce good carbon and hydrogen material balances and prevent misleading results.

A versatile analytical and computerized data handling system has been developed for this program. The scheme is illustrated diagramatically in Figure 2, and consists of five separate gas chromatographs linked, via a Sigma 10 computing integrator, to a Tektronix 4052 microcomputer equipped with a 1.8-megabyte disk system.

Unreacted syngas, CO_2, and C_1 to C_5 isomers are analyzed by a Carle 397B process gas chromatograph (GC). Low concentrations of C_6 and higher hydrocarbons that appear in the gas phase product because of inefficiencies in the C_5/C_6 splitting column are analyzed by a Carle 111 GC with a Porapak QS column. After the condensed liquid phases are weighed and separated,

FIGURE 2

PRODUCT ANALYSIS AND DATA ACQUISITION SCHEME



aqueous phase samples are analyzed for C_1-C_6 alcohols, aldehydes, ketones, and acids using a 3-mm x 3-m 10% SP1200/1% H_3PO_4 on Chromosorb/WAW column. Samples of the separated organic phase are analyzed for C_5-C_{40} hydrocarbons using a 3-mm x 3-m SP2100/Supelcoport column, or for additional resolution, an OV-1001 WC 46-m x 0.25-mm capillary column. Filtered wax samples removed directly from the reactor are also analyzed on the 3-mm SP2100 column for C_5-C_{40} hydrocarbons, and any contribution from the initial slurry oil is subtracted from the analysis.

The analytical data are collected and temporarily stored in the Sigma 10 integrator before direct transfer to the Tektronix disk system. After compilation into matrix format, the six data files for each sample point are assembled by the computer into an overall product matrix, and weight percent, mole percent, and Schulz-Flory distributions, selectivity and conversion fractions, and C and H material balances are calculated. The Tektronix graphics routines provide immediate plots of the hydrocarbon weight and Schulz-Flory product distributions.