DEVELOPMENT AND PROCESS EVALUATION OF IMPROVED FISCHER-TROPSCH SLURRY CATALYSTS

QUARTERLY TECHNICAL PROGRESS REPORT

FOR THE PERIOD 17 OCTOBER 1986 to 31 JANUARY 1987

Submitted to

UNITED STATES DEPARTMENT OF ENERGY

March 23, 1987

by

Howard P. Withers
Air Products and Chemicals, Inc.
Allentown, PA 18105

and

Dragomir B. Bukur and Michael P. Rosynek
Departments of Chemical Engineering and Chemistry
Texas A&M University
College Station, TX 77843

UNDER DOE CONTRACT NO. DE-AC22-85PC80011

DEVELOPMENT AND PROCESS EVALUATION OF IMPROVED FISCHER-TROPSCH SLURRY CATALYSTS

QUARTERLY TECHNICAL PROGRESS REPORT

FOR THE PERIOD 17 OCTOBER 1986 to 31 JANUARY 1987

Submitted to

UNITED STATES DEPARTMENT OF ENERGY

March 23, 1987

by

Howard P. Withers
Air Products and Chemicals, Inc.
Allentown, PA 18105

and

Dragomir B. Bukur and Michael P. Rosynek
Departments of Chemical Engineering and Chemistry
Texas A&M University
College Station, TX 77843

UNDER DOE CONTRACT NO. DE-AC22-85PC80011-1

DISCLAIMER

TABLE OF CONTENTS

I. ABSTRACT

A literature search of precipitated iron/copper/potassium catalyst has been completed. A catalyst precipitation unit has been assembled and tested. A pure precipitated iron catalyst has been synthesized and its BET surface area and temperature-programmed reduction (TPR) behavior have been determined. All equipment supplied by APCI has been made operational. The design of two new reactor systems (slurry and fixed bed) has been completed, and some of the equipment and parts necessary for their construction have arrived. Progress has been made in the areas of chromatograph calibrations and data reduction software.

II. OBJECTIVE AND SCOPE OF WORK

The objective of this contract is to develop a consistent technical data base on the use of iron-based catalysts in Fischer-Tropsch synthesis reactions. This data base will be developed to allow the unambiguous comparison of the performance of these catalysts with each other and with state-of-the-art iron catalyst compositions. Particular attention will be devoted to generating reproducible kinetic and selectivity data and to developing reproducible improved catalyst compositions. To accomplish these objectives, the following specific tasks will be undertaken.

TASK 1 - Project Work Plan

The objective of this task is to establish a detailed project work plan covering the entire period of performance of the contract. This includes estimated costs and manhours expended by month for each task.

TASK 2 - Slurry Catalyst Improvement

The primary purpose of this task is to develop improved iron-based catalysts, both precipitated and supported, that show enhanced activity and selectivity in slurry phase testing. This will be accomplished by gaining systematic understanding of the role of promoters, binders, supports and activation procedures in determining the activity and selectivity of iron-based catalysts. The catalyst development program will incorporate extensive physical and chemical characterization of these materials with the objective to establish correlations between the physical/chemical properties of these catalysts and the corresponding catalytic behavior for synthesis gas conversion.

TASK 3 - Process Evaluation Research

The purpose of this task is to subject the most improved catalysts (based on activity and selectivity) to a thorough process evaluation. This involves long term stability studies, investigation of a wide range of process variables and determination of kinetic parameters. These kinetic parameters will be utilized to simulate catalyst performance under actual bubble column conditions.

TASK 4 - Economic Evaluation

The aim of this task is to develop the relative economic impact for each improved catalyst composition and compare these economics with the economics of using the base case catalyst. Data obtained from Tasks 2 and 3 will be used to generate a product yield structure, Fischer-Tropsch reactor residence time, and key process flow rates. These economic studies will include relative capital costs, operating costs, and required revenues for each catalyst, as well as a sensitivity study of the assigned relative values of the principal products (i.e. diesel and gasoline).

III. SUMMARY OF PROGRESS

During the reporting period, the following accomplishments have been made:

- Task 1 has been completed.
- A literature survey of catalyst compositions (precipitated iron catalysts promoted with copper and potassium) has been conducted.
- A continuous catalyst preparation unit has been assembled and tested.
- A pure precipitated iron catalyst has been synthesized, and its reduction behavior was characterized by temperature-programmed reduction (TPR) technique. The BET surface area of this material was determined before and after the reduction.
- Installation of the APCI slurry reactor system has been completed. This includes all system modifications.
- All slurry reactor system instrument calibrations have been completed.
- The fixed bed reactor system supplied by APCI has been installed and tested. All instruments have been calibrated and the unit is fully operational.
- Designs for the new fixed bed and slurry reactor systems are complete. All items necessary for their construction have been ordered, and the majority of these items have been received.
- All chromatographs have been made fully operational.
- Chromatographic calibrations for gas and aqueous phase compounds are nearly completed.
- A data transfer line has been established between the gas chromatograph integrators and the HP9040 computer system.
- The material balance program and some computer software for data reduction have been developed.

IV. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

TASK 1 - Project Work Plan

The project work plan was completed in November and the detailed work plan was submitted to APCI.

TASK 2 - Slurry Catalyst Improvement

1. Literature Survey of Catalyst Compositions

Since one of the primary goals of this project is to develop improved iron-based catalysts for the Fischer-Tropsch synthesis reaction, it is essential that the ranges of copper and potassium promoter concentrations be explored and those found effective by previous investigators be identified and included within those to be studied. The following summary of pertinent literature references related to precipitated iron catalysts, although not comprehensive, does serve to adequately define the ranges of promoter levels that will be appropriate for inclusion in the present study.

The overall effects of potassium and copper promoters on the behavior of precipitated iron catalysts have been extensively investigated and are well established (1). It is generally believed that potassium introduces electron donating capabilities to the catalyst, thus facilitating chemisorption of carbon monoxide via participation of Fe 3d electrons. The net result is a strengthening of the Fe-C bond and concomitant weakening of the C-O bond. General observations regarding the effect of potassium promotion on iron catalysts for CO hydrogenation include:

1. decrease in methane formation.
2. increase in both olefin and oxygen-containing product formation.

3. increase in average molecular weight (chain length) of hydrocarbon products.
4. increase in carbon deposition, due to dissociative adsorption of carbon monoxide and subsequent formation of various iron carbides.
5. increase in activity for the water-gas-shift reaction.

While the purpose of adding potassium to iron Fischer-Tropsch catalysts is to increase overall activity and modify selectivity, the acknowledged function of the copper promoter is to decrease the temperature required for reduction of the iron component. The addition of copper does not appreciably alter either activity or selectivity. The intimate contact between iron and copper oxide(s) and the facile reduction behavior of the latter are believed to be responsible for the ability of copper to enhance reduction of iron oxide(s).

In the material that follows, all catalytic reaction data, unless specified otherwise, were obtained in fixed-bed, flow-type reactors. Data from slurry-type reactors are specifically identified as such.

1.1 Effect of Potassium Promoter

Previous investigators have added potassium promoter to iron catalysts in a variety of chemical forms, including K_2O, K_2CO_3, KOH, and $KHCO_3$. All of these appear to be equally effective. However, the methods of reporting potassium concentrations have often depended on the chemical identity of the potassium additive, leading to confusion when comparing the results of various workers. In order to prevent ambiguity, all potassium levels summarized in this report have been normalized to g K/100 g Fe, regardless of the potassium salt employed.

Anderson and co-workers were among the first to systematically explore the quantitative effects of potassium promoters on iron catalysts for the Fischer-Tropsch process (2). They observed that potassium levels of 0.1 to 1.0 increased the overall activity of not only precipitated iron, but cemented, sintered, and fused iron catalysts as well. In addition, the increased potassium level caused a shift in selectivity toward higher molecular weight hydrocarbon products at 240°C and 100 psig. Kolbel and co-workers have also made an extensive study of the effects of K_2CO_3 addition on the activity and selectivity of carrier-free iron catalysts used for the Fischer-Tropsch reaction. These authors observed that low levels of potassium (0.1 to 0.3) caused an increase in CO conversion compared to that for an unpromoted catalyst, but that higher potassium levels resulted in a decline in activity (Table 1). Selectivity shifts toward higher molecular weight hydrocarbon products continued to increase, however, even at potassium levels that effected a decrease in overall activity. The change in CO conversion activity was attributed, in part, to changing BET surface areas of the various catalysts, as reported in Table 1. In addition to surface area effects, pore sizes and distributions were also influenced by potassium loading levels in the iron catalysts studied.

Kolbel and Giehring (4) also observed structural changes that occurred during catalyst usage. The general trend was toward increasing surface carbon content and BET surface area and decreasing pore volume and average diameter with increasing reaction time. The increase in surface area with usage was attributed to increased surface carbon concentrations. The surface carbon formed during the synthesis reaction is largely that due to dissociative adsorption of carbon monoxide reactant, rather than hydrocarbon -derived "coke" (CH_x) and leads to ultimate generation of various iron carbide phases. Disproportionation of carbon monoxide ($2 CO \rightarrow C + CO_2$), the so-called Boudouard reaction, may also contribute to surface carbon formation. An additional structural effect observed was that very small additions of potassium (less than 0.1) caused a "structural stabilizing" effect that increased the effective life span of the catalysts. At potassium levels higher than 0.4, on the other hand, larger pores appear to play a role in shifting selectivity toward higher molecular weight hydrocarbon products, an observation that is in accord with the increased pore diameters observed at these potassium levels. When catalytic behavior was tested for long periods (one to four weeks), a gradual increase in methane production and decreases in olefin and "hard paraffins" formation occurred, indicating that the influence of the potassium promoter may eventually become diminished due to accumulation of surface carbon. The general conclusion from the results of Kolbel and Giehring is that potassium levels of ca. 0.1 to 0.2 are most effective in improving the behavior of precipitated iron catalysts for hydrogenation of CO. Although higher potassium levels effect temporary beneficial shifts in reaction selectivity, enhanced rates of formation of surface carbon partially offset these improvements.

Additional studies regarding potassium promotion effects on unsupported, precipitated iron catalysts have been made by several other investigators, including Deckwer and co-workers (5-7). Deckwer and co-workers (5-7) did not make a detailed systematic study of potassium loading levels; however, they noted the enhanced CO conversion activity caused by a potassium level of 1.5. Reproducibility of reaction rates among different runs measured in a bubble column slurry reactor using separate catalyst batches was very good, being within a factor of 2, while that for the same batch was even better, being within 15%. They observed that, although rate constants for catalysts having a potassium level of 1.9 were higher than those for a loading level of 1.5, apparent activation energies were essentially equal for the two promotion levels. Recent results reported by Dry indicate that overall activity for CO conversion passes through a maximum with increasing relative potassium level, while selectivity for higher hydrocarbons continues to increase up to the highest potassium level shown (8,9).

1.2 Effect of Copper Promoter

While several studies have been made of the individual effect of potassium promotion on unsupported iron, relatively few investigations have been reported for copper promotion of precipitated iron catalysts that contain no potassium. Wachs and co-workers (10) recently characterized unpromoted Fe and Fe-Cu catalysts for use in the Fischer-Tropsch synthesis. In this study, an Fe-Cu catalyst containing 1.4 wt% Cu was prepared by impregnation of iron powder with an aqueous solution of copper salt, rather than by co-precipitation of the two metals. Temperature-programmed reduction (TPR) studies confirmed that reduction of the unpromoted catalyst did not commence until a temperature of ca. $300^\circ C$ was attained, while reduction of the Fe-Cu catalyst began to occur as low as $150^\circ C$. The rate of carbon deposition during temperature programming in a 1:1 mixture of H_2:CO was also lower for the bimetallic system than for the unpromoted iron catalyst.

Although most investigators have reported that copper promotion of precipitated iron has only minimal effects on activity and selectivity for CO hydrogenation, some disagreement remains. Wachs observed that product distributions do not change appreciably when copper is incorporated into an iron catalyst. They attributed this to the fact that copper does not wet an iron carbide surface, but forms small agglomerates instead (10). Deckwer, however, indicated that an Fe:Cu catalyst containing 5 wt% Cu is more active than a copper-free catalyst (11). Murata and co-workers made an early study of multi-promoted iron-based catalysts and found that the yield of C_5^+ hydrocarbon products increased with increasing copper content up to ca. 10 wt% Cu, above which no further selectivity changes occurred (12). Kolbel (3) observed that, although very low levels (<0.1%) of copper promotion caused an increase in overall activity for CO conversion at 230°C, further increases in the copper level had no additional effect. Kolbel (3) did not explore the enhanced reduction of iron that is effected by copper and, consequently, may have been studying incompletely reduced catalysts at the lowest copper levels.

It is worth noting that behaviors observed for copper promotion of precipitated iron catalysts must be interpreted with caution, due to pH effects that occur during precipitation. Diffenbach and Fauth, for example, have recently reported that the extent of copper co-precipitation is strongly dependent on solution pH (14). Precipitation pH's that deviate too far in either direction from ca. 7.00 can result in incomplete and, hence, non-quantitative precipitation of copper. Low pH increases the solubility of $Cu(OH)_2$, while high pH causes formation of the soluble complex $Cu(NH_3)_4^{2+}$.

1.3 Combined Effects of Potassium and Copper Promoters

Several investigators have made detailed studies of the behaviors of doubly-promoted Fe/K/Cu catalysts for the Fischer-Tropsch reaction; the following selection of results is representative. Kolbel and Leuteritz (15) have characterized a series of Fe/K/Cu catalysts of varying composition by x-ray diffraction and BET surface area measurements. Their results, summarized in Table 2, reveal the influence of annealing temperature on catalyst crystallite size. For all catalyst compositions studied, an annealing temperature of 400°C yielded the smallest particle size and, in general, the highest overall initial activity for CO conversion. Furthermore, crystallite size generally decreased with decreasing copper content, reaching a minimum at a composition of Fe/K/Cu = 100/0.14/0.2, a combination that also produced the highest surface area material.

A very early study by Fischer and Tropsch indicated that, for a Fe/Cu = 100/25 catalyst, increasing potassium promotion up to a level of 0.73 resulted in correspondingly increasing CO conversion activity in the early stages of reaction ($\leq$ 30 hrs) (16). However, high potassium levels also caused more rapid declines in activity from the high initial values, resulting in eventual steady-state activities that differed little from that of an unpromoted Fe-Cu catalyst. A potassium level of 0.05, on the other hand, although producing a lower initial activity than that for a level of 0.73, resulted in a steady-state activity more than twice that of the unpromoted Fe-Cu material. A potassium level of ca. 0.10 appeared to give the optimal balance between high initial activity and long-term activity maintenance.

A brief study of promoter level effects on precipitated Fe/Cu/K catalysts in a slurry reactor was carried out by workers at Air Products and Chemicals, Inc. (24). From the basecase composition Fe/Cu/K = 100/0.5/0.1, the Cu level was increased to 1.0 and 1.5 while K was kept at 0.1. In a separate experiment, the K was decreased to 0.04 with Cu remaining at 0.5. The relatively small increase in Cu concentration had no effect on the activity but did result in an increase in low molecular weight products. A five-fold increase in activity was observed for the initial test of Fe/Cu/K = 100/1.0/0.1 but this could not be reproduced in a subsequent test. Decreasing the K level to 0.04 dramatically shifted the product distribution toward low molecular weight products while producing no effect on activity.

A detailed study by Anderson (Table 3) indicated that potassium promotion of a precipitated Fe/Cu = 100/9.3 catalyst resulted in enhanced CO conversion activity (2). Potassium contents up to a level of 0.63 also caused decreases in methane production, with concomitant increases in C_5^+ formation and surface carbon deposition.

Several investigators have studied the behavior of a specially-prepared precipitated Fe/K/Cu = 100/0.6/22 catalyst from Harshaw Chemical Co. (18-20). Selected results are summarized in Table 4. Although most available literature references indicate that a copper level of ca. 10 is adequate to provide the necessary enhancement of iron reduction, the fact that several groups have studied this commercial catalyst make it a useful source of comparative data. The results of Bennett (18) and Madon (19), both obtained using similar reaction conditions and reactor types, are quite comparable, in terms of both CO conversion activity and hydrocarbon selectivity behaviors. Satterfield and Stenger (20) employed a stirred tank slurry reactor, which may account for the apparently lower CO conversion activity in comparison to the other two sets of data. Cousins (21) has also reported use of a high-copper level catalyst, having the composition Fe/K/Cu = 100/0.14/20.

1.4 Summary

Based on the reports of previous workers, we feel that the range of copper levels to be investigated in this project should be extended to a lower limit of 0.1 and, in order to obtain results for comparison with users of the Harshaw catalyst, to an upper limit of 20. Specifically, we intend to initially synthesize a series of potassium-free precipitated iron catalysts having copper levels of 0.1, 0.3, 1.0, 3.0, 10.0, and 20.0. The overall influence of the copper level will be assessed by characterizing the reduction behavior of each prepared material by temperature-programmed reduction (TPR). Further characterization will include iron crystallite size measurements obtained by x-ray powder diffraction (XRD) studies. Conventional BET surface area measurements will also be made for each catalyst in both unreduced and reduced states.

In contrast to that of copper, the effect of potassium promotion on both activity and selectivity of iron catalysts for CO hydrogenation is manifested even at very low levels. For this reason, we plan to prepare a series of copper-free precipitated iron catalysts having potassium levels of 0.01, 0.02, 0.05, 0.10, 0.20, 0.50, 1.00, and 2.00. Each material will be characterized by the same array of TPR, XRD, and surface area measurement techniques as those employed for the Fe-Cu catalysts. Based on the characterization results for both series of preparations (Fe-Cu and Fe-K), certain materials will be selected for detailed catalytic testing.

Appropriate compositions of doubly-promoted Fe/K/Cu catalysts to be synthesized will be determined, at least in part, by results obtained for the two series of singly-promoted Fe-Cu and Fe-K materials. Nevertheless, despite the wide ranges of potassium and copper promotion levels that have been reported in the literature, the combined results of a majority of investigators make it appear likely that the most effective potassium level will be in the range 0.05 to 0.50, while that for copper will be optimal at 0.3 to 3.0. An effective initial approach may be to prepare for preliminary screening 100 g. each of nine catalysts having the following

Fe/K/Cu compositions:

100/.05/0.3   100/.05/1.0   100/.05/3.0
100/.20/0.3   100/.20/1.0   100/.20/3.0
100/.50/0.3   100/.50/1.0   100/.50/3.0

In addition, because of the multiple comparative data already available for the Harshaw Fe/K/Cu = 100/0.6/22 catalyst, we plan to either obtain a sample of this material or synthesize a catalyst having the same composition. Additional catalyst compositions may be suggested by the results obtained for those listed above.

2. Catalyst Preparation System

We have completed assembly and testing of the apparatus that will be used for catalyst preparation by continuous precipitation at constant pH. The system is essentially a modified version of that described by Kolbel (22) and Deckwer (11).

The first catalyst synthesized using this apparatus was a pure precipitated iron, which has been prepared to establish the comparative behavior of an unpromoted catalyst. Aqueous solutions of $Fe(NO_3)_3$ (0.75 M) and NH_3 (3.0 M), maintained at 80°C, were separately conveyed at 150 cm^3/min by fluid pumps to a stirred reaction vessel, also thermostatted at 80°C. Precipitation occurred as the two solutions were pumped through the reaction vessel while pH was continuously monitored and controlled by adjusting the flow rate of the NH_3 solution. When a pH of 7.10 ± 0.05 was attained, collection of the precipitate was initiated and continued until consumption of the NH_3 solution was complete. The precipitate was thoroughly washed with distilled, deionized water to remove excess NH_3, and then dried in a vacuum oven for 16 hrs at 60°C, followed by drying for an additional 72 hrs at 120^oC. The BET surface area of the dried, "as prepared" material was 217 m^2/g; after treatment in H_2 for 16 hrs at 400^oC, this value decreased to 20 m^2/g, due to the lack of a stabilizing binder or support. The TPR profile for the material featured two moderately sharp, well resolved peaks at 320 and 400^oC and a broad peak with maximum at ca. 600^oC. These results were obtained using a 12 cm^3/min flow at 5% H_2/N_2 reductant and a program rate of 20°/min. Because water, generated by thermal decomposition of FeOOH and reduction of FeO_x, is not rapidly removed from the catalyst at the low reductant flow rate employed in the TPR measurements, these data must be viewed as a means of comparing the behaviors of various catalysts, rather than as an absolute indication of reduction temperatures required under isothermal conditions.

3. Modifications and Testing of the Existing Reactor Systems

3.1 Slurry Reactor Apparatus

Installation, hardware modifications and instrument calibration of the APCI slurry reactor system are nearly completed. The specific tasks performed are listed below:

- Construction of gas manifolds is complete. The manifolds allow multiple H_2, CO and N_2 cylinders to be shared between the APCI and new slurry reactor systems.
- Product exit lines, vent lines, a feed gas sampling line and cooling lines have been installed.
- Slurry and wax withdrawal lines have been installed in the reactor and tested. Wax accumulation in the reactor during synthesis testing is controlled by removing excess wax through one port.

The use of a filter prevents removal of catalyst. Through a second port, both wax and catalyst may be withdrawn for the purpose of catalyst characterization.

- A cold pressure test has been successfully performed. The system wax pressurized to 600 psi, and a pressure loss of less than 20 psi was observed overnight.
- Calibration of the mass flow meters for CO and H_2 has been completed.
- All pressure transducers and gauges have been calibrated.

Once a blank run and shakedown run have been performed, the system will be fully operational.

3.2 Fixed Bed Reactor Apparatus

The fixed bed reactor system supplied to us by APCI has been installed in our laboratory. Hardware modifications, instrument calibrations and system testing have also been performed. The specific tasks involved the following:

- A gas manifold which allows for H_2 and CO/H_2 mixtures to be shared between the two fixed bed reactor systems has been constructed.
- A product (liquid) collection system has been constructed and installed. This system utilizes two low pressure, 0°C traps, with one trap being used to collect product.
- Product exit lines and emergency vent lines have been installed.
- The temperature indicator has been calibrated.

- The mass flow meter has been calibrated for H_2 and CO/H_2 mixtures.
- Pressure gauges have been calibrated.
- Both a cold and hot leak test have been performed. The system maintained a pressure of 600 psi overnight.
- A blank run has been performed. This run showed the system to be virtually unreactive at Fischer-Tropsch conditions.

The APCI fixed bed reactor system is fully operational at this point in time.

4. Design and Construction of Reactor Systems

4.1 Design of Slurry Reactor Apparatus

A schematic representation of a new 1-*L* autoclave reactor planned for construction is shown in Figure 1. Feed CO and H_2 are supplied to the system after passing through a series of oxygen removal, drying, and carboxyl removal traps, which are shared with an existing 1-*L* autoclave system. 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. The reactor operates in a temperature range of 220-340°C, pressures of 150-700 psig, with gas hourly space velocities (GHSV) up to 1000 h^{-1} (based on the unexpanded slurry volume in the reactor).

Products, together with unreacted synthesis gas, are taken overhead through a heated partial reflux condenser, maintained at a temperature of about 200°C in order to return vaporized slurry oil to the reactor and minimize the carry over of high boiling products. As gases rise in the condenser they become enriched in low boiling point species, while the high boiling species condense. When enough liquid has condensed, the pressure head developed in the condenser allows for a continuous return of liquid to the reactor. An internal thermocouple is situated along the condenser height to monitor temperature changes. This allows for close temperature control to prevent liquid accumulation due to too low a temperature, and oil carry over and cracking due to too high a temperature.

The slurry level in the reactor is controlled by withdrawing accumulated reactor wax at the end of each mass balance period. The reactor wax is removed through a shielded dip tube kept at a fixed level in the reactor. The rise in slurry level is due to the accumulation of high molecular weight products in the reaction during synthesis. By determining the amount of reactor wax 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.

The product stream from the partial reflux condenser flows via a heated line to a back pressure regulator, and then to a C_5/C_6 splitting column, to produce a condensed liquid phase and a gaseous phase. The line between the condenser and the C_5/C_6 splitter is wrapped with heating tape and maintained at a temperature of about 150°C. This prevents condensation of liquid products in this section of the system. The gaseous product 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 a more accurate way of obtaining material balances. A typical mass balance period will last 6-8 hours.

The 1-*L* reactor system has been designed to run continuously and automatically, with a minimum of required operator attendance. An IBM-PC computer will be employed to perform data logging, simple control functions, and provide for an orderly shutdown in the event of an emergency. All major components needed to build the new 1-*L* reactor system have been ordered.

4.2 Design of Fixed Bed Reactor Apparatus

A schematic representation of the fixed bed reactor system to be constructed is shown in Figure 2. A section of the system, including the reactor, exit line, system pressure regulator, and product traps, is assembled in a vertical configuration with flow in a downward direction. Inert (N_2 or He) and process (H_2, CO) gases are delivered to the reactor through a thermal mass flow controller (0-1,000 SCCM) equipped with a digital meter readout. A trap filled with alumina beads is located upstream of the CO flow controller. This trap is electrically heated to 250°C so as to decompose any carbonyls which may be present.

The reactor is made of 0.500 in. O.D. by 0.049 in. wall SS 316 seamless tubing with flange connections welded at either end. It is 10 in. long with an effective bed volume of 20 cc. An aluminum heating block, 2.5 in. O.D. by 0.5 in. I.D. is bolted to the reactor tube and wrapped with a heating tape. A thermocouple is located inside the heating block midway along its length and midway across its radius. This thermocouple serves as the sensor for a temperature controller. Actual bed temperatures are monitored by a multipoint thermocouple located inside the reactor tube. The four thermocouple junctions are spaced at 1 in. intervals to span the entire bed length. A reactor bypass is valved into the system and is used for calibration of feed gas flow and composition. The exit line is wrapped with heating tape from the reactor to the product cold trap. A voltage regulator is used to maintain the line temperature at 150°C.

The product collection system makes use of a high pressure, high temperature trap (hot trap), a low temperature, low pressure trap (cold trap) and a high pressure, low temperature trap (waste trap). The hot trap will be maintained at temperatures between 65 and 100°C while the cold trap will be maintained at 0°C. The waste trap will be at room temperature.

Product is removed from the traps by first diverting the reactor flow to the waste trap. The contents of the hot trap are then drained into the cold trap. The combined product is then drained from the cold trap into a tared vial for future analysis. Traps are constructed of 304 stainless steel and are coated with Teflon. Each trap has a volume of 75 ml. Following the traps, non-condensed gases are directed to a wet test meter. A septum tee is located just before the wet test meter so that gas samples may be taken. Additional components are included in the system for reasons of safety, process control and convenience.

All components necessary for the construction of the new fixed bed reactor system have been ordered. Many items, including valves, controllers, the temperature indicator, tubing and framework material are currently in stock. Fittings are the only major item that has yet to be received.

5. Product Analysis System

5.1 Hardware Description

A versatile analytical and computerized data handling system has been developed for this program. The scheme is illustrated diagramatically in Figure 3, and consists of three separate gas chromatographs linked by a data acquisition system.

Unreacted H_2, CO, and product CO_2 and C_1-C_5 hydrocarbons are analyzed on the Carle AGC-400 chromatograph. Small amounts of C_6 and higher hydrocarbons, and light oxygenates which are not condensed in the cold trap, are analyzed by a Sigma 1B chromatograph equipped with a Porapak Q column. Analyses from the Carle and Sigma 1B will be combined using a number of suitable tie components.

The liquid product will be separated into two parts, an aqueous and organic layer. Each of these layers will be analyzed independently. The aqueous layer will be analyzed on a 0.2% Carbowax 1500 on Carbosieve G (6' x 2 mm glass column) and FID. This column will be contained in the Sigma 1B chromatograph. The aqueous layer will be analyzed for C_1 to C_6 alcohols, C_2 to C_4 aldehydes, C_3-C_6 ketones and C_1-C_3 carboxylic acids. The water content of the sample will be determined using a Karl-Fischer titrator.

The organic layer will be separated on a .32 mm x 30 m fused silica column coated with 0.25μ DB-5 and analyzed on an FID. This column is located within the Sigma 1 chromatograph. Samples of the organic layer will be analyzed for C_5 to C_{30} hydrocarbons, C_4 to C_{11} alcohols, C_3 to C_6 ketones and C_2-C_6 aldehydes.

The wax fraction, dissolved in CS_2, is analyzed in the Sigma 1 chromatograph. Here, a 10 m x 0.53 mm fused silica column coated with 0.25 μ RSL-5 and an FID are employed. The wax fraction will be analyzed for hydrocarbons up to C_{60}.

All work necessary to make the three chromatographs operational has been performed. These tasks involved selecting the appropriate columns, repairing the electronics of the Sigma 1 and modifying this chromatograph for capillary application, and replacing the thermal conductivity bridge of the Carle. Details of these repairs/modifications follow.

A listing of columns which will be used with the various chromatographs are reported in Table 5. These columns provide the separation required to achieve accurate product analyses. All columns have been purchased and are currently located in their respective instruments.

Both the Sigma 1 and Carle chromatographs were defective and required repair. The power supply of the Sigma 1 was defective and was replaced by Perkin-Elmer Service Center, Houston. The thermal conductivity bridge of the Carle was replaced at TAMU. Following these repairs, both instruments were fully operational.

Modifications associated with the Sigma 1 chromatograph consisted of adapting the instrument for capillary application. This involved replacing the standard injectors with on-column injectors and installing detector adaptor kits. These modifications have been completed. The instrument has been tested and has been determined to be functioning properly.

5.2 Response Factors and Retention Times

Response factors and retention times have been determined for all gas and aqueous phase components. The goal associated with the analysis scheme is to provide a high accuracy quantitative product analysis. Analyzed gas mixtures were used as standards for gas phase calibration while aqueous phase calibration standards were prepared by mixing pure components.

Gas phase calibration involved injection of the analyzed gas mixture into the chromatograph using a gas tight syringe. Response factors for these components were determined from the following equations:

$$RF_i' = \frac{AREA_i}{(\text{mole }\%)_i N_i} \qquad (1)$$

$$RF_i = \frac{RF_i'}{RF_{ref}'} \qquad (2)$$

where: RF_i' is the response factor relative to the sample; AREA is the peak area of integration; Mole % is the concentration of component i in the standard; N is the number of carbon atoms in component i (N=1 for H_2); RF_{ref}' in the response factor of a reference component and RF is the calculated, normalized response factor.

For gas phase analyses the standards provided a range of concentration which allowed for check of linearity in the detector signal. It was determined that all responses are linear over the ranges of interest (0.1 to 10 mole percent for hydrocarbons, 1 to 50 percent for CO, H_2).

Response factors and retention times for all gas phase components of interest are reported in Table 6. Also reported in this table are response factors obtained by Dietz (23). As the table shows, the response factors determined in our study compare favorably with those obtained by Dietz. Standard deviation reported in this table provides an indication of calibration reproducibility.

Figure 4A shows a sample GC trace of the hydrocarbon components as detected by the Carle FID. Gas phase components detected by the Carle TDC and by the Sigma 1B are illustrated in Figures 4B and C, respectively. As the figures show, an excellent separation of products is achieved.

Response factors and retention times for aqueous phase components expected in a Fischer-Tropsch product were obtained using a Sigma 1B chromatograph equipped with an FID. Standards were prepared by combining known quantities of pure components. Response factors were calculated using equations 1 and 2. 1-hexanol was used as the reference component, due to its relatively low volatility. Mixtures of selected components were diluted in excess of a factor of 50 with respect to N-hexanol so as to check for response linearity. The detector response was determined to be linear over the range of interest.

Response factors and retention times of aqueous phase components are reported in Table 7. Response factors obtained by Dietz (23) are also reported. Excellent agreement between our response factors and those of Dietz is achieved for the majority of compounds, indicating the accuracy of our analyses.

Figure 5 reports a sample GC trace of the aqueous phase components. The mixture utilized in this trace was prepared so as to simulate a Fischer-Tropsch products. As shown, two separation do not appear, these being acetic acid and 1-butanol, and propanoic acid and 1-pentanol*. Other than these components, an excellent separation of the remaining products is achieved. This will allow us to obtain a high quality aqueous phase analysis.

6. Data Acquisition and Reduction

Progress has been made in the area of data acquisition/analysis. Currently a data link between the chromatograph integrators and Hewlett-Packard 9040 computer system has been established. A complete mass balance/data manipulation routine has been developed and the writing of peak identification software has begun.

---

* Note: Separation of these species may be achieved, but results in loss of separation of other components.

A mass balance program, which will be used to manipulate and store the data obtained from the laboratory reactors and gas chromatographs, has been written and successfully tested. The overall flow of data and results is shown in Figure 6. The program uses pull up templates to prompt the operator to enter the needed information: run designations, catalyst, reactor unit, temperatures, pressure, flow rates, sample time, weight of samples collected, and the locations of peak analysis files from the chromatographs. Compound names, formulas, molecular weights, and calibration data for each chromatograph are stored in data base files. The operator supplied data and peak analysis data along with calculated results are stored on fixed disk. For safe keeping, these files are also stored on removable microdiskettes.

The program is designed to handle up to 50 classes of products, with up to 100 members in each class. At the present time, the program considers paraffins, olefins, alcohols, and their major isomers, certain aromatics, organic acids, aldehydes, ketones, and esters, as well as H_2, H_2O, CO, CO_2, and N_2. Additional individual compounds or entire classes may be easily added if needed in the future.

Five types of streams: feed gas, aqueous liquid product, organic liquid product, reactor tail gas, and reactor wax are considered by the program. The program uses peak area files transferred from the chromatograph integrators and data base GC calibration files to determine the composition of each stream. Using measured sample weights, the program can calculate individual species flow rates and arrive at total inlet and outlet weight and mole flows of all identified compounds. Combination of two different analyses of the same phase, which occurs for the gas product stream, and averaging of multiple analyses, is done automatically.

A sample output of the mass balance program is given in Appendix I. The program logs some general run information, and calculates weight and atomic closures, reactant conversions and reaction rates. The program also calculates and prints tables of yields, product distributions, Schultz-Flory chain growth probabilities (alphas), average carbon numbers and H to C ratio for certain classes of products.

An oxygenate identification routine has been written and tested successfully. Currently, the routine searches for 18 organic compounds typical of an aqueous Fischer-Tropsch product. Peaks are identified based on their retention times relative to either ethanol, 1-propanol or 1-butanol. The relative area of the peak is also taken into account. A user supplied tolerance is incorporated so as to account for change in retention times due to column aging and changes in operating conditions. A sample output is reported in Table 8. All peaks are correctly identified.

TASK 3 - Process Evaluation Research

This task is scheduled to begin December 1, 1987.

TASK 4 - Economic Evaluation

This task is scheduled to begin June 1, 1988.

V. FUTURE WORK PLANS

Future work to be completed by the end of the second quarter of the project include the following:

- Begin synthesis of two series of catalysts. These include precipitated iron impregnated at various K_2CO_3 levels and precipitated FeOOH prepared at various copper levels.
- Begin characterization of the two catalysts series. This will involve measuring surface areas before and after reduction and obtaining TPR profiles.
- Complete calibration of the Sigma 1 chromatograph for organic and wax analyses.
- Complete writing and testing of remaining peak identification routines.
- Perform blank run and shakedown run on APCI slurry reactor.
- Determine catalyst compositions and reaction conditions per initial runs.
- Perform initial catalytic reaction studies.
- Construction of a catalyst reduction unit will be completed.
- Start construction of the new reactor systems (fixed bed and slurry).

VI. LITERATURE REFERENCES

1. "New Synthesis with Carbon Monoxide," Falbe, J., ed., Springer-Verlag, Berlin (1981).

2. Anderson, R.B., Seligman, B., Schultz, J.F., Kelly, R., Elliott, M.A., Ind. Eng. Chem. 44, 391 (1952).

3. Kolbel, H., Proc. 2nd Intern. Congr. Catal., Paris, p. 2075 (1960).

4. Kolbel, H. and Giehring, H., Brennstoff-Chemie 44, 343, 369 (1963).

5. Deckwer, W.D., Kokuun, R., Sanders, E., Ledakowicz, S., Ind. Eng. Chem. Proc. Des. Dev. 25, 643 (1986).

6. Sanders, E., Ledakowicz, S., and Deckwer, W.D., Canad. J. Chem. Eng. 64, 133 (1986).

7. Ledakowicz, S., Nettelhoff, H., Kokuun, R., and Deckwer, W.D., Ind. Eng. Chem. Proc. Des. Dev. 24, 1043 (1985).

8. Dry, M.E., in "Catalysis: Science and Technology," Vol. 1, p. 159, Springer-Verlag, Berlin (1981).

9. Dry, M.E., in "Applied Industrial Catalysis," Vol. 2, p. 167, Academic Press, N.Y. (1983).

10. Wachs, I.E., Dwyer, D.J., and Iglesia, E., Appl. Catal. 12, 201 (1984).

11. Deckwer, W.D., Serpemen, Y., Ralek, M., and Schmidt, B., Ind. Eng. Chem. Proc. Des. Dev. 21, 222 (1982).

12. Murata, Y., J. Soc. Chem. Ind. Japan 45, 288, 292 (1942).

13. Kolbel, H., Ackermann, P., Ruschenburg, E., Langheim, R., and Engelhardt, F., Chem. Eng. Technik. 23, 153 (1951).

14. Diffenbach, R.A. and Fauth, D.J., J. Catal. 100, 466 (1986).

15. Kolbel, H.. and Leuteritz, G., Z. Elektrochem. 64, 525 (1960).

16. Fischer, F. and Tropsch, H., Ges. Ab.handl. Kenntis Kohle 10, 333 (1930).

17. Pichler, H. and Hector, A., in "Kirk-Othmer Encyclopedia of Chemistry and Technology," Vol. 4, p. 446 (1964).

18. Borghard, W.G. and Bennett, C.O., Ind. Eng. Chem. Proc. Des. Dev. 18, 18 (1979).

19. Madon, R.J. and Taylor, W.F., J. Catal. 69, 32 (1981).

20. Satterfield, C.N. and Stenger, H.G., Ind. Eng. Chem. Proc. Des. Dev. 23, 849 (1984).

21. Cousins, W.J., N.Z. J. Sci. 27, 15 (1984).

22. Kolbel, H., and Ralek, M., Catal. Rev. Sci. Eng. 21, 225 (1980).

23. Dietz, W.A., J. Gas Chrom. 68, 5 (1967).

24. Carroll et al., "Catalyst and Reactor Development of a Liquid Phase Fischer-Tropsch Process," DOE Quarterly Report January 1 - March 31, 1984, Contract DE-AC22-80PC30021.

Table 1. Effect of Promotion K_2CO_3 on Properties of Precipitated Iron Catalysts [Ref. 3]

K_2CO_3 Content (g K/100 g Fe)	S.A.[1] After Reduction (m^2/g)	Initial Ave. Pore Diam. (nm)	% CO Conv.[2]	Wt% CH_4 in Prods.	Wt% C_{10}^+ in Prods.
0.00	43	18	60	30	2
0.06	-	18	81	23	2
0.11	140	20	72	23	2
0.23	87	20	32	20	3
0.34	123	22	51	15	7
0.46	-	23	18	11	18
0.57	-	25	17	10	22
0.86	-	-	15	-	-
1.14	-	-	16	-	-

[1] Surface Area

[2] $H_2/CO = 1/1$; Rxn. Temp. = 230°C; Space Velocity = 0.1 Nl/g Fe/Hr

Table 2. Effect of Promotion by Potassium and Copper on Physical/Catalytic Properties of Precipitated Iron Catalysts [Ref. 15]

Potassium Content (g K/100 g Fe)	Copper Content (g Cu/100 g Fe)	Annealing Temp. (°C)	S.A.[1] (m^2/g)	Average Cryst. Size (nm)	Relative Act. for CO Conv.
0.00	0.0	100	48	18	1.00
		200	53	18	--
		250	57	17	--
		300	60	--	--
0.11	0.0	100	50	18	1.22
		250	60	17	--
		300	63	--	--
		350	64	15	--
		400	67	15	--
0.14	0.2	100	47	18	--
		250	50	18	--
		300	53	17	--
		350	60	16	--
		400	71	13	--
		450	68	15	--
0.23	0.2	100	49	20	0.61
		250	53	19	--
		300	57	18	--
		350	62	17	--
		400	67	14	--
0.29	0.2	100	48	17	--
		250	54	16	--
		300	63	16	--
		350	67	15	--
		400	--	13	--
		450	66	15	--
0.34	0.2	100	50	16	0.86
		250	61	15	--
		300	64	15	--
		350	68	14	--
		400	72	13	--
		450	71	14	--
		500	60	22	--

[1] Surface Area

Table 2 (cont.)

Potassium Content (g K/100 g Fe)	Copper Content (g Cu/100 g Fe)	Annealing Temp. (°C)	S.A. (m^2/g)	Average Cryst. Size (nm)	Relative Act. for CO Conv.
0.34	1.0	100	50	18	--
		250	52	18	--
		300	52	17	--
		350	65	15	--
		400	66	14	--
		450	65	18	--
		500	59	23	--
0.34	10.0	100	40	--	--
		250	44	--	--
		300	48	24	--
		350	49	22	--
		400	53	20	--
		450	51	21	--
		500	49	24	--

---

[1] Surface Area

Table 3. Effect of Promotion by Potassium on Catalytic Properties of Precipitated Fe/Cu = 100/9.3 for Fischer-Tropsch Reaction [Ref. 2]

	K_2O Content (g K/100 g Fe)		
	0.00	0.43	0.63
Reaction Temp. (°C)	265	261	254
Space Velocity (Nl H_2/CO/g Fe/Hr)	110	112	100
Ave. Activity (Vols. H_2/CO Converted/ g Fe/Hr)	38.6	52.2	59.7
Wt% CH_4 in Products	20	15	13
Wt% C_5+ in Products	35	42	60
C/Fe Atomic Ratio in Used Catalyst	0.05	0.24	0.29

Table 4. Behavior of Harshaw Precipitated Iron Catalyst (Fe:Cu:K = 100:22:0.6) for Fischer-Tropsch Reaction

	Ref. 18	Ref. 19	Ref. 20
GHSV (hr^{-1})	507	244	535
H_2/CO Feed Ratio	1:1	1.5:1	1.4:1
Reaction Temp. (°C)	250	240	240
Reaction Pressure (atm)	14	10	10
% CO Conversion	99	94	41
Wt% CH_4 in Products	4	5	--
Wt% C_5+ in Products	66	75	--

Table 5. G.C. Columns and Chromatographs Utilized in Product Analysis Scheme

Chromatograph	Column	Separation
Sigma 1B	9'x 1/8" Porapack Q	Gas phase, C_2-C_8 hydrocarbons
Sigma 1B	6'x 2mm glass, 0.29 Carbowax 1500 on Carbosieve G	Aqueous phase, C_1-C_6 oxygenates
Sigma 1	30m x 0.32mm, 0.25μ DB-5 Fused Silica	Organic phase C_5-C_{30} hydrocarbons C_3-C_{11} oxygenates
Sigma 1	10m x 0.53mm, 0.25μ RSL-150 Fused Silica	Wax analysis C_{20}-C_{60} hydrocarbons

Table 6. Response Factors and Retention Times of Gas Phase Components

(a) TCD of Carle AGC 400

Compound	Retention Time (min)	Response Factor	
		Present Study	Dietz (23)*
Hydrogen	2.83	0.0676±0.0006	N/R
Carbon Monoxide	15.21	1.23±0.010	1.15
Carbon Dioxide	4.99	1.0	1.0
Methane	14.57	0.88±0.004	0.85
Ethylene	6.48	0.64±0.010	0.57
Ethane	7.72	0.68±0.010	0.61

(b) FID of Carle AGC 400

Compound	Retention Time (min)	Present Study	Dietz (23)*
Methane	5.23	1.05±0.010	1.0
Ethane, Ethylene	6.05	1.00±0.004	1.0, 0.98
Propane	7.82	1.01±0.010	0.99
Propylene	8.65	0.98±0.001	
Isobutane	10.73	1.01±0.001	
n-Butane	12.29	0.98±0.007	1.03
1-Butene	14.22	1.01±0.004	
Isobutene	14.66	--	
t-2-Butene	15.78	1.01±0.007	
c-2-Butene	17.00	--	
Isopentane	19.47	--	
n-Pentane	22.75	0.95±0.001	1.03
1-Pentene	27.02	0.95±0.005	
2-Methyl-2-Butene	30.13	--	
t-2-Pentene	31.68	--	
c-2-Pentene	33.65	--	
C_6+ Backflush	4.74	0.85±0.02	

Table 6 continued.

(c) FID of Sigma 1b

Compound	Retention Time (min)	Present Study	Dietz (23)*
Methane	0.70		
Ethylene	1.11		
Ethane	1.28		
Propylene	2.33		
Propane	2.48	1.01±0.004	0.99
1-Butene	4.11		
n-Butane	4.36	0.99±0.004	1.03
1-Pentene	6.23		
n-Pentane	6.51	1.01±0.002	1.04
1-Hexene	9.56		
n-Hexane	10.04	0.99±0.005	1.05
1-Heptene	15.97		
n-Heptane	16.87	1.01±0.005	1.02
1-Octene	29.02		
n-Octane	30.89	0.93±0.009	0.99

* Dietz's response factor has been converted to a molar basis. See Appendix II.

Table 7. Retention Times and Response Factors for Aqueous Phase Compounds

FID of Sigma 1B

Compound	Retention Time (min)	Present Study	Dietz (23)*
Methanol	0.81	0.80	0.58
Ethanol	2.36	0.79	0.84
1-Propanol	4.82	0.95	0.95
1-Butanol	7.65	0.97	0.97
1-Pentanol	10.88	0.99	
1-Hexanol	15.09	1.00	1.00
2-Propanol	3.86	0.95	
2-Butanol	6.36	0.94	
2-Pentanol	9.66	0.99	
3-Pentanol	9.31	0.99	
Acetone	2.72	0.75	0.75
2-Butanone	5.57	0.90	0.87
Acetaldehyde	0.90		
Propionaldehyde	2.56	0.72	
Butyraldehyde	5.98	0.82	0.87
Valeraldehyde	8.85		
Acetic Acid	7.60	0.53	0.57
Propionic Acid	10.81	0.63	0.78
Butyric Acid	12.41		

* Dietz's response factors have been converted to a molar basis. See Appendix II.

Table 8. Sample Output From Peak Identification Routine

```
NUMBER            TIME          AREA        NAME

  1               .8900         .5083       Methanol

  2              2.4500        5.4614       Ethanol

  3              3.9600         .3706       2-Propanol

  4              4.9800        2.4984       Propanol

  5              6.5500         .2406       2-Butanol

  6              7.9400        1.6291       Butanol

  7              9.5600         .2638       3-Pentanol

  8              9.9000         .1798       2-Pentanol

  9             11.1400         .6563       Pentanol

 10             13.6200         .0082       unknown C6

 11             15.5200         .5625       Hexanol

sum of unknown C1:    .0000
sum of unknown C2:    .0000
sum of unknown C3:    .0000
sum of unknown C4:    .0000
sum of unknown C5:    .0000
sum of unknown C6:    .0082
sum of unknown C7:    .0000
```

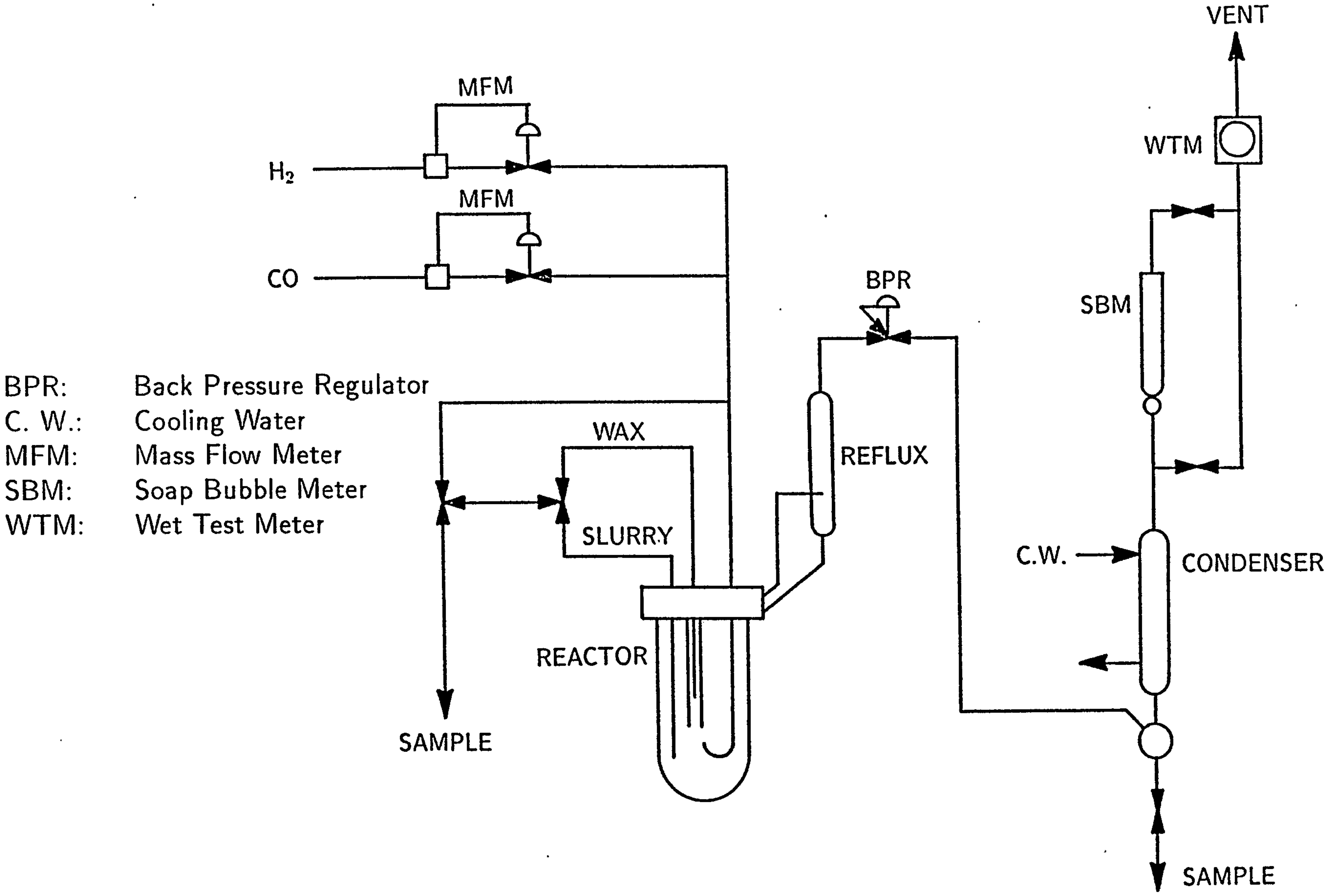

Figure 1. Process schematic of the 1-l slurry reactor system.

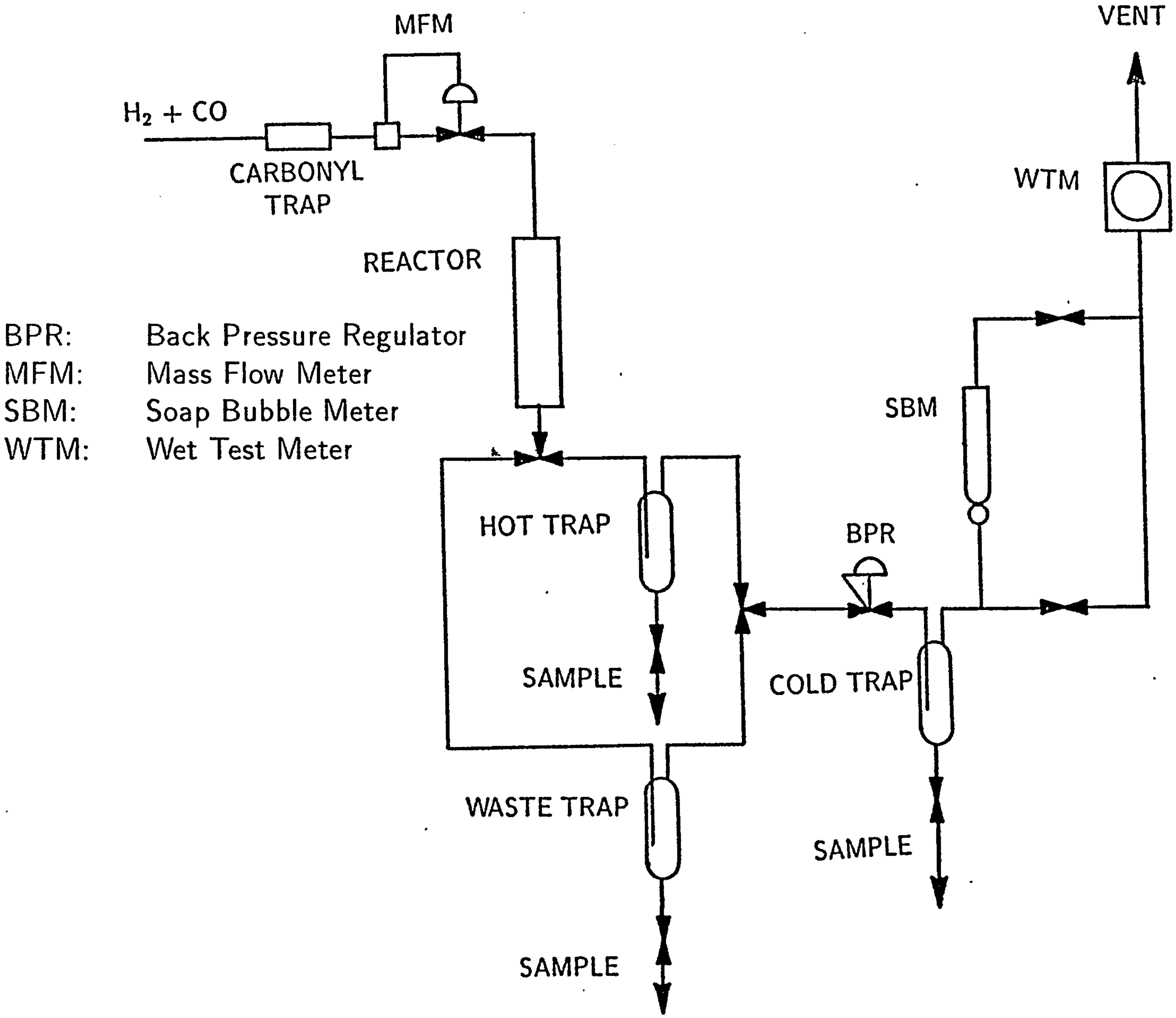

Figure 2. Process schematic of the fixed bed reactor system.

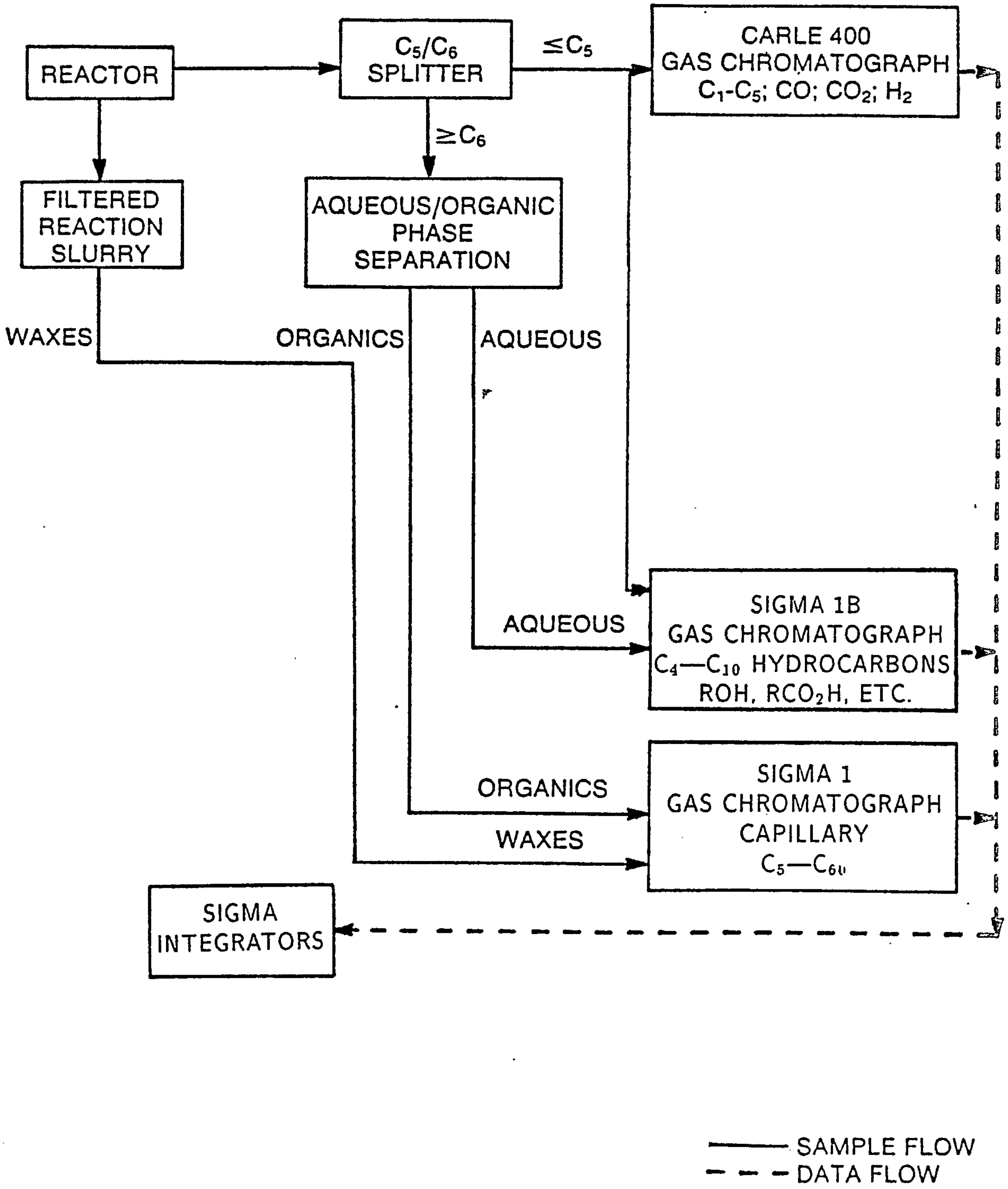

Figure 3. Flow diagram of product analysis system.

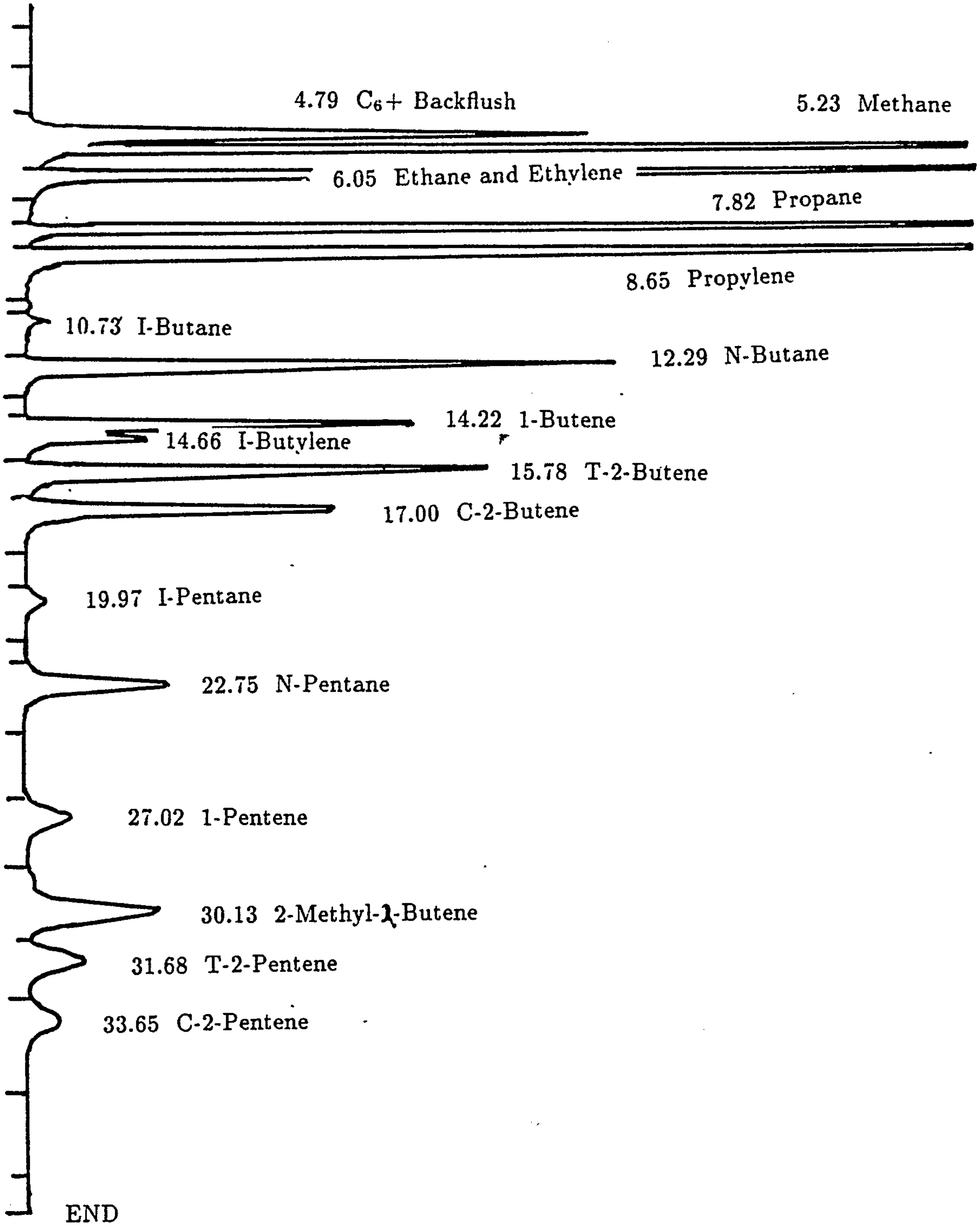

Figure 4A: Sample Chromatograph Showing Peak Identification and Position of Gas Phase Components. Analysis obtained using FID of Carle AGC 400.

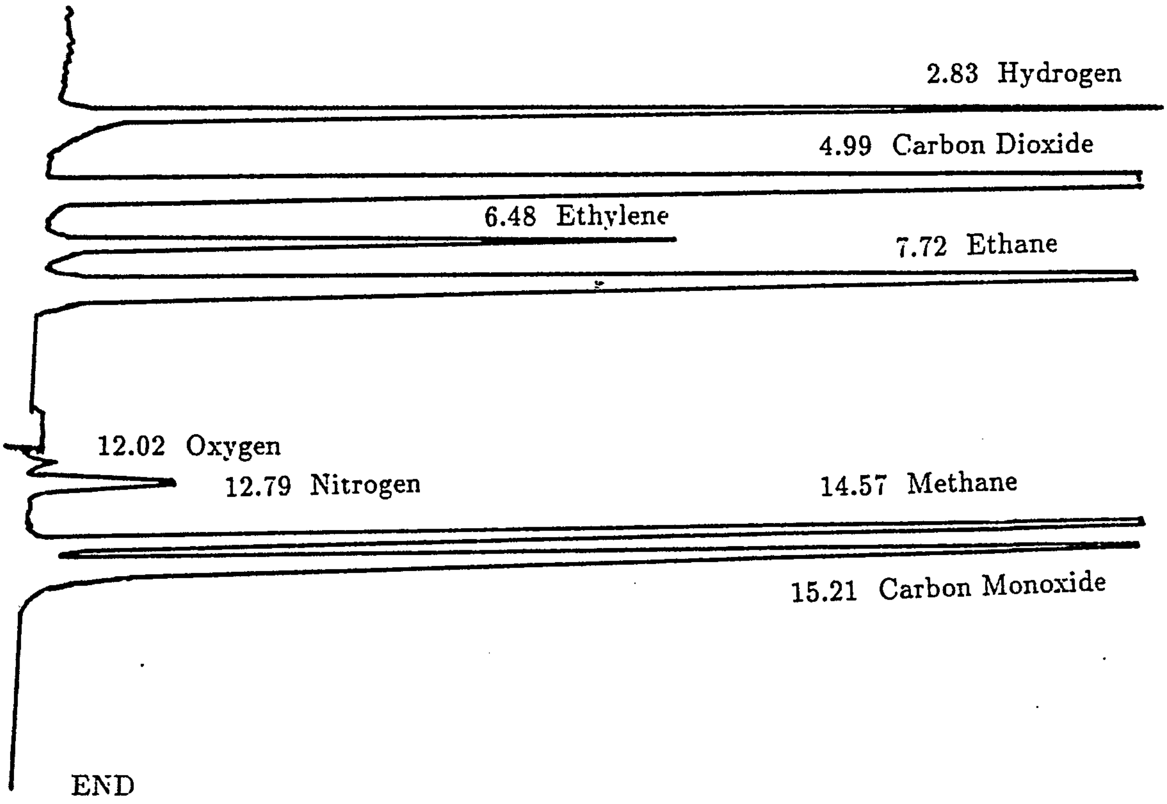

Figure 4B: Sample Chromatograph Showing Peak Identification and Position of Gas Phase Components. Analysis obtained using TCD of Carle AGC 400.

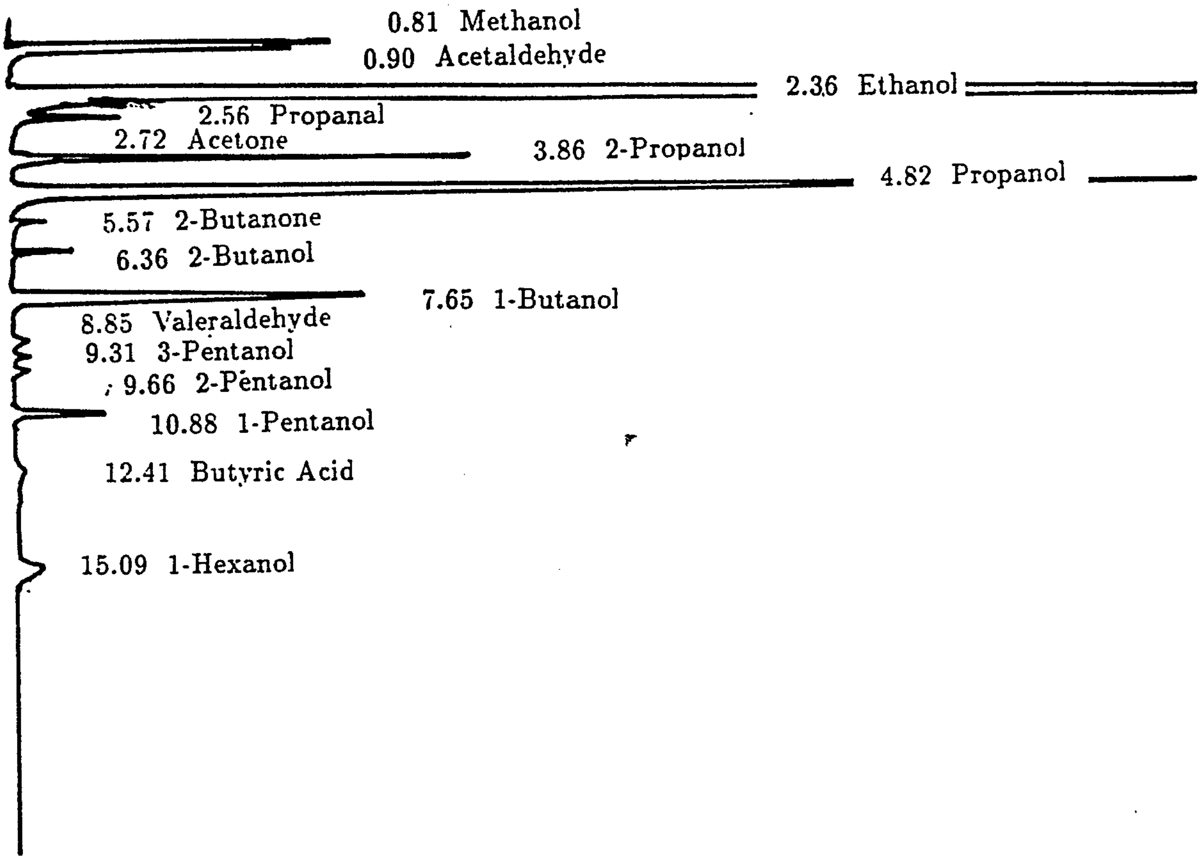

Figure 5: Sample Chromatograph Showing Peak Identification and Position of Aqueous Phase Components. Analysis obtained using FID of Sigma 1B.

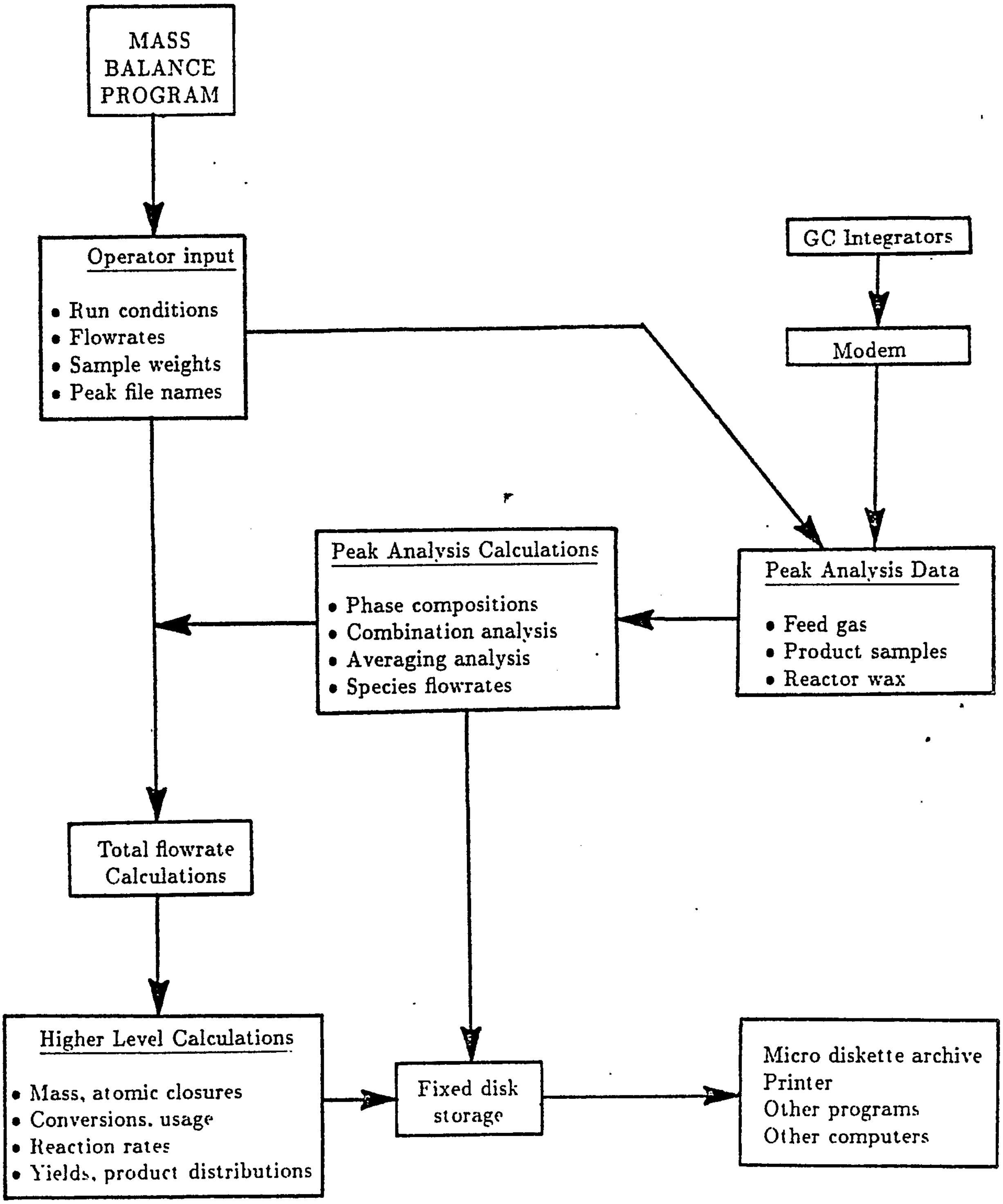

Figure 6. Flow diagram of the mass balance computer program.

Appendix 1

Sample output of mass balance computer program

```
******************************************************************************
                                RUN SUMMARY
******************************************************************************
Run:      EXAMPLE

Sample:   OUTPUT

Date:     00/00/00

Reactor: UNIT S1

Balance Period:      0.00 (hrs)

Time on Stream:      0.00 (hrs)

******************************************************************************
Temperature:                 0. (C)        0. (K)

Pressure:                    0. (psia)     0.00 (MPa)

GHSV:                        0.0000 (Nl/g-Fe*hr)

SV @ RXN T,P:                0.0000 (l/g-Fe*hr)

Inlet Flowrate:              0.0000 (Nl/hr)

H2/CO Feed Ratio:            0.0000 (molar)

Catalyst Type:               EXAMPLE

Catalyst Loading:            0.0 (g - Unreduced)

Fe Concentration:            0.0000 (wt % - Unreduced)

Catalyst Loading:            0.0 (g - Reduced)

Fe Concentration:            0.0000 (wt % - Reduced)

Slurry Liquid Type:          EXAMPLE

Slurry Liquid Loading:       0.0 (g)

Impeller Speed:                0 (rpm)

******************************************************************************
Samples collected during mass balance period -

Syngas Fed:                  0.00000E+00 (Nl)
Tailgas Measured:            0.00000E+00 (Nl)
Aqueous Liquid Collected:    0.00000E+00 (g)
Organic Liquid Collected:    0.00000E+00 (g)
Total Liquid Collected:      0.00000E+00 (g)
Wax Removed from Reactor:    0.00000E+00 (g)
Catalyst Removed from Reactor: 0.00000E+00 (g)

******************************************************************************
```

```
********************************************************************************

Inlet Flowrates -  Total:     0.00000E+00 (g/hr)   0.00000E+00 (mol/hr)
                       C:     0.00000E+00          0.00000E+00
                       H:     0.00000E+00          0.00000E+00
                       O:     0.00000E+00          0.00000E+00

Outlet Flowrates - Total:     0.00000E+00 (g/hr)   0.00000E+00 (mol/hr)
                       C:     0.00000E+00          0.00000E+00
                       H:     0.00000E+00          0.00000E+00
                       O:     0.00000E+00          0.00000E+00

Mass Closures -    Total:     0.00 (%)
                       C:     0.00
                       H:     0.00
                       O:     0.00

********************************************************************************

Conversions -        H2:     0.00 (%)
                     CO:     0.00
                H2 + CO:     0.00
              CO to CH4:     0.00
              CO to CO2:     0.00

% Contraction:               0.00
% CO2-Free Contraction:      0.00

H2/CO Usage Ratio:           0.00000E+00 (molar)

H2/CO Exit Ratio:            0.00000E+00 (molar)

********************************************************************************

Mole Fractions -          H2:  0.00000E+00
                          CO:  0.00000E+00
                         CO2:  0.00000E+00
                         H2O:  0.00000E+00

Partial Pressures -       H2:  0.00000E+00 (psia)   0.00000E+00 (MPa)
                          CO:  0.00000E+00          0.00000E+00
                         CO2:  0.00000E+00          0.00000E+00
                         H2O:  0.00000E+00          0.00000E+00

Liquid Concentrations -   H2:  0.00000E+00 (mol/l-liquid)
                          CO:  0.00000E+00
                         CO2:  0.00000E+00
                         H2O:  0.00000E+00

Reaction Rates -          H2:  0.00000E+00 (mol/g-Fe*hr)
                          CO:  0.00000E+00
                     H2 + CO:  0.00000E+00

[(CO2*H2)/(CO*H2O)]:           0.00000E+00 (Partial Pressures)
WGS KEQ:                       0.00000E+00 (Newsome, 1980)

********************************************************************************
```

```
********************************************************************************

                               Avg C #   H/C      Avg MW    Mol% C  Mol% H  Mol% O

n-Paraffins:                   0.0000   0.0000    0.0000    0.00    0.00    0.00
Total Paraffins:               0.0000   0.0000    0.0000    0.00    0.00    0.00
n-Olefins:                     0.0000   0.0000    0.0000    0.00    0.00    0.00
Total Olefins:                 0.0000   0.0000    0.0000    0.00    0.00    0.00
Total Paraffins + Olefins:     0.0000   0.0000    0.0000    0.00    0.00    0.00
Total Hydrocarbons:            0.0000   0.0000    0.0000    0.00    0.00    0.00
Oxygenates:                    0.0000   0.0000    0.0000    0.00    0.00    0.00
Hydrocarbons + Oxygenates:     0.0000   0.0000    0.0000    0.00    0.00    0.00
Unaccounted Products:                   0.0000              0.00    0.00    0.00

********************************************************************************

Outlet                             Mol %      Wt%     mols/min      g/min

Hydrocarbons:                      0.0000    0.0000  0.00000E+00  0.00000E+00
Oxygenates:                        0.0000    0.0000  0.00000E+00  0.00000E+00
H2:                                0.0000    0.0000  0.00000E+00  0.00000E+00
H2O:                               0.0000    0.0000  0.00000E+00  0.00000E+00
CO:                                0.0000    0.0000  0.00000E+00  0.00000E+00
CO2:                               0.0000    0.0000  0.00000E+00  0.00000E+00
Wax:                               0.0000    0.0000  0.00000E+00  0.00000E+00

Total:                             0.0000    0.0000  0.00000E+00  0.00000E+00

********************************************************************************

Outlet                             Mol %      Wt%     mols/min      g/min
Excluding wax

Hydrocarbons:                      0.0000    0.0000  0.00000E+00  0.00000E+00
Oxygenates:                        0.0000    0.0000  0.00000E+00  0.00000E+00
H2:                                0.0000    0.0000  0.00000E+00  0.00000E+00
H2O:                               0.0000    0.0000  0.00000E+00  0.00000E+00
CO:                                0.0000    0.0000  0.00000E+00  0.00000E+00
CO2:                               0.0000    0.0000  0.00000E+00  0.00000E+00

Total:                             0.0000    0.0000  0.00000E+00  0.00000E+00

********************************************************************************

Products                           Mol %      Wt%     mols/min      g/min

Hydrocarbons:                      0.0000    0.0000  0.00000E+00  0.00000E+00
Oxygenates:                        0.0000    0.0000  0.00000E+00  0.00000E+00
H2O:                               0.0000    0.0000  0.00000E+00  0.00000E+00
CO2:                               0.0000    0.0000  0.00000E+00  0.00000E+00
Wax:                               0.0000    0.0000  0.00000E+00  0.00000E+00

Total:                             0.0000    0.0000  0.00000E+00  0.00000E+00

********************************************************************************
```

```
******************************************************************************

Products                              Wt %      Mol %       g/min        mols/min
Excluding CO2, H2O, Wax


Methane:                             0.0000    0.0000   0.00000E+00   0.00000E+00
Methanol:                            0.0000    0.0000   0.00000E+00   0.00000E+00
Ethane:                              0.0000    0.0000   0.00000E+00   0.00000E+00
Ethene:                              0.0000    0.0000   0.00000E+00   0.00000E+00
Ethanol:                             0.0000    0.0000   0.00000E+00   0.00000E+00
Propane:                             0.0000    0.0000   0.00000E+00   0.00000E+00
Propene:                             0.0000    0.0000   0.00000E+00   0.00000E+00
Propanol:                            0.0000    0.0000   0.00000E+00   0.00000E+00
Butane:                              0.0000    0.0000   0.00000E+00   0.00000E+00
Butene:                              0.0000    0.0000   0.00000E+00   0.00000E+00
Butanol:                             0.0000    0.0000   0.00000E+00   0.00000E+00
C4 Isomers:                          0.0000    0.0000   0.00000E+00   0.00000E+00

C1 Oxygenates:                       0.0000    0.0000   0.00000E+00   0.00000E+00
C2  -  C4 Hydrocarbons:              0.0000    0.0000   0.00000E+00   0.00000E+00
C2  -  C4 Oxygenates:                0.0000    0.0000   0.00000E+00   0.00000E+00
C5  - C11 Hydrocarbons:              0.0000    0.0000   0.00000E+00   0.00000E+00
C5  - C11 Oxygenates:                0.0000    0.0000   0.00000E+00   0.00000E+00
C12 - C17 Hydrocarbons:              0.0000    0.0000   0.00000E+00   0.00000E+00
C12 - C17 Oxygenates:                0.0000    0.0000   0.00000E+00   0.00000E+00
C18 + Hydrocarbons:                  0.0000    0.0000   0.00000E+00   0.00000E+00
C18 + Oxygenates:                    0.0000    0.0000   0.00000E+00   0.00000E+00

******************************************************************************

1 + 2 Olefins/n-Paraffins            Molar      Weight

C2:                                  0.0000     0.0000
C3:                                  0.0000     0.0000
C4:                                  0.0000     0.0000
C5:                                  0.0000     0.0000
C6:                                  0.0000     0.0000
C7:                                  0.0000     0.0000
C8:                                  0.0000     0.0000
C9:                                  0.0000     0.0000
C10:                                 0.0000     0.0000
C11:                                 0.0000     0.0000

C2 +:                                0.0000     0.0000
C2 - C4:                             0.0000     0.0000
C5 - C11:                            0.0000     0.0000
C12 - C17:                           0.0000     0.0000
C18 +:                               0.0000     0.0000

******************************************************************************

% Olefin in Hydrocarbon              Molar     Weight

C2 - C4:                             0.0000     0.0000
C5 - C11:                            0.0000     0.0000
C12 - C17:                           0.0000     0.0000
C18 +:                               0.0000     0.0000
C2 - C30:                            0.0000     0.0000

******************************************************************************
```

```
*******************************************************************************

Mole % Distribution
                         C#          n-Para    1,2-Olef    Isomer      Oxy       Total

                          1          0.0000     0.0000     0.0000     0.0000     0.0000
                          2          0.0000     0.0000     0.0000     0.0000     0.0000
                          3          0.0000     0.0000     0.0000     0.0000     0.0000
                          4          0.0000     0.0000     0.0000     0.0000     0.0000
                          5          0.0000     0.0000     0.0000     0.0000     0.0000
                          6          0.0000     0.0000     0.0000     0.0000     0.0000
                          7          0.0000     0.0000     0.0000     0.0000     0.0000
                          8          0.0000     0.0000     0.0000     0.0000     0.0000
                          9          0.0000     0.0000     0.0000     0.0000     0.0000
                         10          0.0000     0.0000     0.0000     0.0000     0.0000
                         11          0.0000     0.0000     0.0000     0.0000     0.0000
                         12          0.0000     0.0000     0.0000     0.0000     0.0000
                         13          0.0000     0.0000     0.0000     0.0000     0.0000
                         14          0.0000     0.0000     0.0000     0.0000     0.0000
                         15          0.0000     0.0000     0.0000     0.0000     0.0000
                         16          0.0000     0.0000     0.0000     0.0000     0.0000
                         17          0.0000     0.0000     0.0000     0.0000     0.0000
                         18          0.0000     0.0000     0.0000     0.0000     0.0000
                         19          0.0000     0.0000     0.0000     0.0000     0.0000
                         20          0.0000     0.0000     0.0000     0.0000     0.0000
                         21          0.0000     0.0000     0.0000     0.0000     0.0000
                         22          0.0000     0.0000     0.0000     0.0000     0.0000
                         23          0.0000     0.0000     0.0000     0.0000     0.0000
                         24          0.0000     0.0000     0.0000     0.0000     0.0000
                         25          0.0000     0.0000     0.0000     0.0000     0.0000
                         26          0.0000     0.0000     0.0000     0.0000     0.0000
                         27          0.0000     0.0000     0.0000     0.0000     0.0000
                         28          0.0000     0.0000     0.0000     0.0000     0.0000
                         29          0.0000     0.0000     0.0000     0.0000     0.0000
                         30          0.0000     0.0000     0.0000     0.0000     0.0000

                        2-4          0.0000     0.0000     0.0000     0.0000     0.0000

                        5-11         0.0000     0.0000     0.0000     0.0000     0.0000

                       12-17         0.0000     0.0000     0.0000     0.0000     0.0000

                        18+          0.0000     0.0000     0.0000     0.0000     0.0000

                       Total         0.0000     0.0000     0.0000     0.0000     0.0000
*******************************************************************************

Alpha from First Ten Carbon Numbers

Alpha from Slope:                    0.0000     0.0000     0.0000     0.0000     0.0000
Alpha from Intercept:                0.0000     0.0000     0.0000     0.0000     0.0000
R Correlation:                       0.0000     0.0000     0.0000     0.0000     0.0000


*******************************************************************************

Alpha from Entire Distribution

Alpha from Slope:                    0.0000     0.0000     0.0000     0.0000     0.0000
Alpha from Intercept:                0.0000     0.0000     0.0000     0.0000     0.0000
R Correlation:                       0.0000     0.0000     0.0000     0.0000     0.0000

*******************************************************************************
```

```
******************************************************************************

                          TOTAL FLOWRATE RESULTS


                                  INLET


        Compound Name              Wt %         Mol %         g/min       mols/min


Hydrogen                      0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00
Carbon Monoxide               0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00


Total:                        0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00

******************************************************************************

                                 OUTLET


        Compound Name              Wt %         Mol %         g/min       mols/min


Hydrogen                      0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00
Water                         0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00
Carbon Monoxide               0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00
Carbon Dioxide                0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00
Methane                       0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00
Methanol                      0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00
Methanal                      0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00
Methanoic Acid                0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00
Etnane                        0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00
Ethylene                      0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00
Ethanol                       0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00
Ethanal                       0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00
Ethanoic Acid                 0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00
Methoxymethane                0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00
Propane                       0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00
Propene                       0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00
1-Propanol                    0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00
2-Propanone                   0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00
Propanal                      0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00
Propanoic Acid                0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00
Methoxyethane                 0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00
n-Butane                      0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00
2-Methylpropane               0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00
1-Butene                      0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00
cis-2-Butene                  0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00
trans-2-Butene                0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00
1-Butanol                     0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00
2-Butanone                    0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00
Butanal                       0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00
Butanoic Acid                 0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00
Methoxypropane                0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00
n-Pentane                     0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00
Pentane Isomers               0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00
1-Pentene                     0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00
1-Pentanol                    0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00
2-Pentanone                   0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00
Pentanal                      0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00
Pentanoic Acid                0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00
Methoxybutane                 0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00
```

Compound Name	Wt %	Mol %	g/min	mols/min
n-Hexane	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
Hexane Isomers	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
1-Hexene	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
2-Hexenes	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
1-Hexanol	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
2-Hexanone	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
Hexanal	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
Hexanoic Acid	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
Methoxypentane	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
n-Heptane	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
Heptane Isomers	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
1-Heptene	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
2-Heptenes	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
1-Heptanol	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
2-Heptanone	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
Heptanal	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
Heptanoic Acid	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
Methoxyhexane	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
n-Octane	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
Octane Isomers	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
1-Octene	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
2-Octenes	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
1-Octanol	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
2-Octanone	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
Octanal	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
Octanoic Acid	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
Methoxyheptane	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
n-Nonane	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
Nonane Isomers	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
1-Nonene	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
2-Nonenes	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
1-Nonanol	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
2-Nonanone	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
Nonanal	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
Nonanoic Acid	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
Methoxyoctane	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
n-Decane	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
Decane Isomers	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
1-Decene	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
2-Decenes	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
1-Decanol	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
n-Undecane	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
Undecane Isomers	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
1-Undecene	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
2-Undecenes	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
n-Dodecane	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
Dodecane Isomers	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
1-Dodecene	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
2-Dodecenes	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
n-Tridecane	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
Tridecane Isomers	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
1-Tridecene	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
2-Tridecenes	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
n-Tetradecane	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
Tetradecane Isomers	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
1-Tetradecene	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
2-Tetradecenes	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
n-Pentadecane	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
Pentadecane Isomers	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
1-Pentadecene	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
2-Pentadecenes	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00

Compound Name	Wt %	Mol %	g/min	mols/min
n-Hexadecane	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
Hexadecane Isomers	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
1-Hexadecene	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
2-Hexadecenes	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
n-Heptadecane	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
Heptadecane Isomers	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
1-Heptadecene	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
2-Heptadecenes	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
n-Octadecane	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
Octadecane Isomers	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
1-Octadecene	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
2-Octadecenes	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
n-Nonadecane	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
Nonadecane Isomers	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
1-Nonadecene	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
2-Nonadecenes	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
n-Eicosane	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
Eicosane Isomers	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
1-Eicosene	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
2-Eicosenes	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
n-Heneicosane	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
Heneicosane Isomers	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
1-Heneicosene	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
2-Henesicosenes	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
n-Docosane	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
Docosane Isomers	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
1-Docosene	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
2-Docosenes	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
n-Tricosane	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
Tricosane Isomers	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
n-Tetracosane	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
Tetracosane Isomers	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
n-Pentacosane	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
Pentacosane Isomers	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
n-Hexacosane	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
Hexacosane Isomers	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
n-Heptacosane	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
Heptacosane Isomers	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
n-Octacosane	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
n-Nonacosane	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
n-Nonacosane	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
n-Pentacontane	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
n-Triacontane	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
Total:	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00

****

Appendix II: Response Factor Comparison

For Dietz's response factor utilization:

$$T_i = A_i/D_i \tag{1}$$

where: T_i is the true area; A_i is the actual area of integration and D_i is the weight response factor as determined by Dietz.

The true area, T, divided by the sum of the true areas yields the weight percent:

$$(\text{Weight } \%)_i = T_i/\Sigma T_n \tag{2}$$

The mole percent of component i is then:

$$(\text{mole } \%)_i = (T_i/M_i)\ \Sigma\ \frac{T_n}{M_n} \tag{3}$$

where M is the molecular weight.

In this study, response factors were determined so as to yield mole percents of the components.

$$T_i' = \frac{A_i}{N_i{*}R_i} \tag{4}$$

where: T' is the true area ($T' \neq T$), N is the hydrocarbon chain length and R is the response factor determined by this study.

The mole percent of component i is calculated as:

$$(\text{mole } \%)_i = T_i'/\Sigma T_n \tag{5}$$

Equating equations (3) and (5), followed by rearrangement, yields:

$$D_i\ M_i \sum \frac{A_n}{D_n M_n} = R_i\ N_i \sum \frac{A_n}{R_n N_n} \tag{6}$$

The solution to equation (4) is

$$D_i M_i = C_i R_i N_i \tag{7}$$

The constant, C_i, is solved for using a common component*.

For gas phase hydrocarbons, C_2 - C_4 hydrocarbons were chosen as common components. This resulted in $C_i = 14$. 1-Hexanol was chosen as the common component for aqueous analysis, and C_i was calculated to be 12.58.

---

* By common components, we refer to components whose response factors have been determined by Dietz and in this laboratory.