I. 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 (FT) 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.

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 , FT 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).

II. EXECUTIVE SUMMARY

Slurry phase Fischer-Tropsch processing is considered a potentially economic method to convert coal-derived synthesis gas into liquid fuels. Largely due to its relatively simple reactor design, improved thermal efficiency, and ability to process CO-rich synthesis gas, the slurry process has several potential advantages over conventional vapor phase processes.

While advances have been made in slurry phase Fischer-Tropsch technology, further work is required to more thoroughly evaluate its potential as a viable technology. Therefore, Air Products proposed a program to develop a consistent process/economic data base for a variety of iron-based catalysts. This data base allows unambiguous comparison of the performance of the new catalysts tested, both with each other and with the state-of-the-art catalyst compositions. Particular attention was paid to extracting kinetic and selectivity data, developing improved compositions/process parameters, and to performing process economic comparisons. The effects of activation/reduction procedures, promoters and binders/supports on catalyst activity, selectivity and stability were investigated in a systematic way.

II.1. Summary of Accomplishments

Key accomplishments in individual areas of research are summarized below.

Activation / Reduction Procedure Research

The catalytic behavior of a precipitated promoted iron catalyst (100Fe/3Cu/0.2K) during the Fischer-Tropsch synthesis was studied in a fixed bed reactor following different pretreatments in either CO, H_2, or syngas with $H_2/CO=0.68$. The results show that activation parameters (temperature, pressure, duration and/or the nature of reducing gas) have significant effects on catalyst activity, stability, and selectivity during the synthesis. Activations with CO or syngas minimize production of gaseous hydrocarbons and produce more liquid products and more wax. However, these treatments usually yield catalysts that deactivate fairly rapidly during the synthesis. Good stability can be achieved with the right combination of activation parameters (temperature and duration). Reductions with H_2 resulted in constant or gradually increasing activity over a 120 h period of synthesis. The selectivity of H_2 reduced catalysts is less desirable than that of CO reduced catalysts, as more gaseous and less high molecular weight hydrocarbons are produced. Similar trends were observed in tests with another precipitated iron catalyst (100Fe/3Cu/0.5K).

However, hydrocarbon selectivities in a stirred tank slurry bed reactor test of the 100 Fe/0.3 Cu/0.5 K catalyst were not influenced by the reductant type (H_2 vs CO). Hydrogen activated catalyst displayed no loss in activity during 460 hours of testing under different process conditions. Its hydrocarbon selectivity was very similar to that of the Mobil's I-B catalyst in a high wax mode of operation (low methane and C_2-C_4 gaseous hydrocarbons). Additional slurry reactor tests with this and other precipitated catalysts are needed to confirm these findings.

Promoter Effect Research

The effect of potassium and copper promotion on activity and selectivity of precipitated iron catalysts for the Fischer-Tropsch synthesis were studied in a fixed bed reactor at 200 psig, 235°C to 265°C using synthesis gas with an H_2:CO molar feed ratio of 1:1.

It was found that promotion of iron with potassium in the range 0.2 - 1 wt%, (100Fe/ xK, x=0.2, 0.5 and 1.0) increases activity of the Fischer-Tropsch(FT) and Water-Gas-Shift (WGS) reactions, and the average molecular weight of hydrocarbon and other organic (primarily alcohols) products. It also suppresses olefin hydrogenation and isomerization reactions. Potassium promotion inhibits iron reduction, and as a result, the potassium promoted catalysts require longer times to achieve the steady state activity.

Promotion of iron with copper (100 Fe/3 Cu) also increases the rates of the FT and WGS reactions. Copper is a more effective promoter than potassium in increasing the rate of FT reaction, whereas the opposite applies to WGS activity. Also, promotion with copper facilitates reduction of iron and thus decreases the time required to achieve the steady state activity. In the presence of copper, the hydrocarbon product distribution shifts toward higher molecular weight products, but the magnitude of changes is significantly smaller than that observed with potassium promotion. Copper promotion slightly enhances the secondary reactions (olefin hydrogenation and isomerization).

The FT activity of the two doubly promoted catalysts (100 Fe/3 Cu/0.2 K and 100 Fe/3 Cu/0.5 K) was independent of their potassium content and higher than that of any of the singly promoted catalysts. In tests over a long period of time (up to 460 hours on stream) the catalyst with higher potassium content lost about 9% of its maximum activity, whereas the 100 Fe/3 Cu/0.2 K catalyst lost only 2%. The WGS activity of the doubly promoted catalysts was similar to that of the Fe/K catalysts. Selectivity behavior of the doubly promoted catalysts was strongly influenced by their potassium content. The catalyst containing 0.2 wt% K had selectivities (hydrocarbon product distribution, olefin content) similar to that obtained with the 100 Fe/3 Cu catalyst, whereas the 100 Fe/3 Cu/0.5 K catalyst had selectivities similar to that obtained with the 100 Fe/0.5 K catalyst. This shows that, in the presence of copper, higher potassium loadings are needed to achieve promotional effects on product selectivity.

The optimal promoter levels have not been determined. Obviously higher potassium loadings are needed if the objective is to minimize light gas production, however, the rate of catalyst deactivation increases with potassium addition and it is necessary to achieve a balance between these two conflicting trends. The role of copper is still not completely understood and more detailed studies are required to elucidate its role in Fischer-Tropsch synthesis.

Binder / Support Effect Research

The effect of addition of silica and alumina as binders (promoters) on catalytic behavior of precipitated iron catalyst with composition 100Fe/5Cu/4.2K was studied in a fixed bed reactor. It was found that catalyst activity decreases with addition of either silica or alumina, but its stability increases. Catalysts containing 25 g, or more, of SiO_2 per 100g of Fe had very good stability, whereas the catalysts with smaller amounts of binder (8 parts of SiO_2, or Al_2O_3, per 100 parts of Fe) deactivated during synthesis. The unsupported catalyst (i.e., the catalyst without any binder) had a similar deactivation rate as the two catalysts with small amounts of binder. The water-gas-shift activity decreases with the addition of silica, due to its interaction with potassium, rendering the latter less effective in promoting the WGS reaction.

Hydrocarbon selectivity of all these catalysts was good (low C_1-C_4 fraction) due to their high potassium content. The addition of binder slightly improved the hydrocarbon selectivity of the unsupported catalyst.

Slurry Reactor Kinetic Studies

Kinetic parameters for the Fischer-Tropsch and water-gas-shift reactions were determined from slurry reactor tests with four catalysts (100 Fe/0.3 Cu/0.2 K, 100 Fe/0.3 Cu/0.5 K, 100 Fe/5 Cu/4.2 K/24 SiO_2 and Ruhrchemie LP 33/81). The latter catalyst has a composition similar to the silica containing catalyst synthesized in our laboratory. Only selected mass balances, those made during portions of tests where catalyst activity was fairly stable, were used in the analysis.

Several rate expressions, which included H_2O and/or CO_2 inhibition, were used for each catalyst to model the FT and WGS reaction rates. In all cases, the FT rates were approximately first order with respect to H_2, but better fits were obtained using rate expressions which contain water and/or CO_2 inhibition. The results showed that water inhibits the FT reaction more strongly than does CO_2, and for all catalysts the following rate expression provided a good fit of the data

$$r_{CO-H_2} = k_o P_{CO} P_{H_2} / (P_{CO} + a P_{H_2O})$$

Other models provided a better fit of the data for some of the catalysts (100 Fe/5 Cu/4.2 K/24 SiO_2 and 100 Fe/0.3 Cu/0.5 K), however, even in these cases the above model was quite adequate. The existing data base is insufficient to statistically discriminate among the rival models. Additional experiments would be required to perform such an analysis, however this is difficult to accomplish with catalysts that deactivate fairly rapidly. The underlying causes of the deactivation are not well understood.

The kinetics of the WGS reaction were also studied. A simple first order in CO rate expression provided the best fit to the data obtained with three (100 Fe/0.3 Cu/0.5 K, 100 Fe/5 Cu/4.2 K/24 SiO_2 and Ruhrchemie catalyst), of the four catalyst tested, whereas for the 100 Fe/0.3 Cu/0.2 K catalyst the following rate expression provided the best fit

$$r_{WGS} = k_{w,0}(P_{CO}P_{H_2O} - P_{CO_2}P_{H_2} / K_p) / (P_{CO}P_{H_2} - bP_{H_2O})$$

The first order in CO kinetics provided a good fit of the data with this catalyst as well.

Process Evaluation Studies

Several unsupported (Fe/Cu/K) and silica containing catalysts (Fe/Cu/K/SiO_2) were tested in fixed bed and slurry bed reactors to determine their activity, selectivity and stability with time on stream, and as a function of process conditions. Major highlights from these studies are

- Catalysts containing about 24 parts of SiO_2 per 100 parts of Fe had exhibited very good stability, over 400-500 hours on stream, in both fixed bed and slurry reactor tests, but they were less active than unsupported catalysts. Also, their selectivity toward liquid hydrocarbon products (C_5-) was not as high as that achieved in Mobil's bubble column slurry reactor in high wax mode of operation (70-75% vs. 86%) and methane yields were higher (5-6% vs. 2.7%).
- The 100 Fe/5 Cu/4.2 K/24 SiO_2 catalyst, synthesized at Texas A&M University, had higher activity (~20%) than commercial Ruhrchemie LP 33/81 catalyst (the state-of-the-art catalyst). This catalyst was used initially at SASOL in fixed bed (ARGE) reactors. Both catalysts had similar hydrocarbon selectivities during tests in fixed bed and slurry bed reactors, but the catalyst activity was higher in a fixed bed reactor .

- Catalysts with low silica content (100 Fe/5 Cu/4.2 K/8 SiO_2) or without any silica (100 Fe/3 Cu/0.2 K or 0.5 K, and 100 Fe/1 Cu/0.2 K) had high initial activity, but lacked good stability. Catalyst deactivation was fairly rapid in both fixed bed and slurry bed reactor tests. Hydrocarbon selectivities in some of the tests were better (less CH_4 and gaseous hydrocarbons) than those obtained in tests with the catalysts having about 25 parts of SiO_2 per 100 parts of Fe. However, stability of these catalysts needs to be improved by using different activation procedures and/or by modifications in their composition.

Catalyst Characterization

One of the tasks of this project was to characterize the precipitated iron catalysts prepared, in order to determine the effects of copper and potassium promoters and of SiO_2 and Al_2O_3 supports on reduction behaviors and surface properties. A variety of physical and chemical techniques was used to provide a complete characterization of each catalyst prepared. The elemental composition of each synthesized catalyst was determined by atomic absorption spectroscopy; total surface areas and pore size/volume distributions were obtained from physical adsorption and mercury porosimetry measurements, respectively. Reducibilities of bulk iron and copper were studied by temperature-programmed and isothermal reduction methods, using both H_2 and CO reductants. X-ray photoelectron spectroscopy was used to examine surface oxidation states of catalyst components and the influence of promoters, supports, and reduction conditions on surface iron behaviors. Major conclusions from these studies are

- Temperature-programmed and isothermal reduction measurements showed that the promotional effect of copper on the reduction of iron increased with increasing copper content up to 3 wt% Cu.
- The time required for completion of iron reduction at 300°C in either H_2 or CO decreased with increasing copper content.
- The presence of potassium adversely influenced the reducibility in H_2 of the precipitated iron catalysts, both with and without copper, possibly due to blockage of nucleation sites by surface potassium. By contrast, the time required for completion of iron reduction by CO decreased in the presence of potassium.
- SiO_2 and Al_2O_3 supports exerted an inhibiting effect on the reduction of iron that increased with increasing support content. The inhibition effect was less pronounced for the alumina support than for the silica support.
- X-ray photoelectron spectroscopic results showed that treatments of the precipitated iron

catalysts at 300°C in H_2 resulted in marked differences in surface composition than those resulting from treatment in CO. The surfaces of H_2-reduced samples were largely covered by a layer of unreduced iron oxide; however, the surfaces of the CO-reduced samples possessed substantial amounts of zero-valent iron.

- Water, generated by reduction of Fe/Cu precipitates in H_2, caused extensive migration and surface spreading of potassium promoter, an effect not observed when reduction occurred in CO.

II.2. Recommendations for Future Work

Some promising results in the area of improved catalyst performance were achieved during the course of work on this contract which warrant additional studies.

(1) Our comprehensive studies of the effect of pretreatment conditions (nature of reductant, temperature and duration) on subsequent catalyst performance have shown that pretreatment conditions can be used to alter hydrocarbon selectivity and/or to provide better stability. With CO and/or syngas pretreatment it is difficult to achieve catalyst stability over a long period of time. The optimal activation parameters seem to be dependent upon both catalyst composition and reaction conditions and need to be determined by a trial-and-error procedure. In contrast, catalysts activated with hydrogen have high activity and long term stability. More work should be done in slurry reactors using H_2 activations with both unsupported and silica containing catalysts.

Activation studies in fixed bed and slurry bed reactors should be accompanied by comprehensive catalyst characterization studies in order to gain understanding of the underlying reasons for differences in catalytic behavior following different pretreatments.

(2) Addition of silica to potassium promoted precipitated iron catalysts improves catalyst stability without any adverse effect on product selectivity. Further improvements in catalyst performance (enhanced activity and/or selectivity toward transportation fuels) can be achieved by a judicious choice of silica content and promoter levels. Additional studies are needed to assess the potential for use of these catalysts in slurry reactors.

(3) It is recommended that future studies focus more on thorough evaluation of a few selected catalysts (unsupported and silica containing), rather than on a cursory examination of a large number of catalysts. Also, detailed catalyst characterization studies after the catalyst pretreatment and during the synthesis should play an important role in future studies.

III. INTRODUCTION

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

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

In the late 1940s, slurry phase Fischer-Tropsch technology was developed in Germany (Kölbel and Ralek, 1980). Slurry processing provides the ability to more readily remove the heat of reaction, minimizing the temperature rise across the reactor and eliminating localized hot spots. As a result of the improved temperature control, yield losses to methane are reduced and catalyst deactivation due to coking is significantly decreased. This, in turn, allows much higher conversions per pass, minimizing synthesis gas recycle, and offers the potential to operate with CO-rich synthesis gas feeds without the need for prior water-gas shift. Due to the simpler reactor design, capital investment in a slurry phase Fischer-Tropsch reactor is expected to be substantially smaller than in conventional fixed- or fluidized-bed systems. (Gray et al. 1980; Thompson et al., 1981). The slurry process has the ability to produce a variable product slate via changes in catalyst and/or process conditions. One can either maximize the gasoline production or the production of diesel fuels and waxes. This flexibility in the product slate is unique to the slurry phase process.

Economic evaluations of the slurry phase Fischer-Tropsch process have been limited to studies incorporating Kölbel's published data from the Rheinpreussen slurry demonstration plant (Gray, et al., 1980; Thompson et al., 1981) and a techno-economic assessment of Mobil's two-stage slurry Fischer-Tropsch/ZSM-5 process (El Sawy et al., 1984). Sufficient data from processes demonstrated on a large scale are not available to allow an adequate correlation of economic parameters with catalyst activities and selectivities. Furthermore, the relative economic merits of various Fischer-Tropsch product slates have not been adequately quantified. Also, it should be kept in mind that all subsequent attempts to reproduce Kölbel's results (activities and selectivities) were unsuccessful (e.g., Mitra and Roy, 1963; Farley and Ray, 1964; Kuo, 1983, 1985; Zarochak and McDonald, 1987). In all these studies one or more of the following had occurred: (1) catalyst deactivation; (2) catalyst activity was lower than in Kölbel's study; and (3) selectivity was inferior to that reported by Kölbel et al. (1955). The most successful study in a bubble column slurry reactor, other than Kölbel's original work, was made by Mobil (Kuo, 1983, 1985). Even this work was hampered by a variety of operational problems and only a few runs lasted sufficiently long to obtain reliable information on the product distribution and catalyst activity.

III.1. Summary of Previous Work with Iron Catalysts

This summary will focus on results illustrating the current industrial practice (SASOL), the most successful slurry bubble column operation (Rheinpreussen demonstration plant unit) and representative examples of other studies conducted in slurry bed reactors (bubble columns or stirred tank). Process conditions, hydrocarbon product distribution, product yields and information related to catalyst activity, for selected studies, are summarized in Table III-1.

The fixed bed (Arge) reactor at SASOL is used to maximize production of diesel fuel (C_{12}-C_{18}) and heavy hydrocarbon waxes. This gives low yield of methane (2%) and other light hydrocarbons (C_2-C_4 = 11.5%), and high yield of C_{12}— products (68%). The useful lifetime of the catalyst is reported to be between 9 and 12 months. The entrained bed operation in the Synthol reactor is aimed at maximizing gasoline (C_5-C_{11} hydrocarbons) production, and as a consequence of the high operating temperature the yield of methane is high (10.6 %) and the yield of C_{12}— products is low (11.7%). The useful lifetime of the catalyst is about 6 weeks.

The Rheinpreussen demonstration plant performance is regarded as the most successful slurry reactor operation to date (Kölbel et al., 1955). A high single pass conversion was achieved and the catalyst activity was high (STY=0.106 mol/g-cat.h). Results shown in Table III-1 are for the gasoline mode of production, and as can be seen the yield of (C_5-C_{11}) hydrocarbons obtained in the Rheinpreussen demonstration plant is the highest of all. This was also accompanied by low yield of methane + ethane (3.2% only). This product distribution is very unusual and could not be reproduced in any other subsequent studies. In all other studies (regardless of the reactor type) such low methane yields were accompanied by high yields of $C_{12}-$ products. It should be noted that the reported total yield was only 181 g/Nm^3, which indicates some problems with the product collection and/or analysis. If one assumes that the hydrocarbon yield is 200 g/Nm^3, and that all missing hydrocarbons are $C_{12}+$, this gives 21.5% yield of $C_{12}-$ hydrocarbons. However, even the latter value is still much lower than expected based on low yield of $CH_4-C_2H_6$. Kölbel and co-workers have not provided any information on the catalyst aging and deactivation. Based on sketchy information given in the literature, Poutsma (1980) estimated that the catalyst lifetime was about 38 days.

Kunugi, who spent several years working with Kölbel, initiated research on FT synthesis in Japan in the early 60's. Sakai and Kunugi (1974) claimed that they were able to verify Kölbel's results related to the yield of hydrocarbons and product selectivities. However, their results shown in Table III-1, do not reflect this claim. Their product distribution is in agreement with the other studies, i.e., low methane yield gives rise to high yield of $C_{12}-$ products.

Selectivities reported by Mobil workers (Kuo, 1983; 1985) for two modes of operation, low- and high-wax mode, follow the usual trends. In the low-wax mode of operation, which was aimed at maximizing the gasoline fraction, methane selectivity was relatively high (7.9%) and selectivity of $C_{12}-$ was relatively low (26.1%). On the other hand, in the high-wax mode, the selectivity of methane was low (2.7%) and the yield of $C_{12}-$ products was high (68.1%). These trends are qualitatively similar to those obtained in the commercial operation at SASOL. It is interesting to note that the catalyst composition was the same in both modes of operation, and yet significantly different selectivities were obtained. The only major difference between the two catalysts was in the total surface area. The operating conditions and activation procedures were similar in both cases. Some differences in performance were observed in other runs when a new batch of catalyst was used. This shows that subtle differences in preparation and/or activation may have a significant effect on catalyst activity and stability. Although Mobil's study is regarded as the most successful slurry phase operation after the Rheinpreussen demonstration plant, it was hampered by a variety of operational problems and only 2 out of 13 runs had relatively long periods of steady-state operation. In the run designated CT 256-3 (low-wax mode of operation) the process conditions were fairly constant from 8 to 46 days on stream: P=1.48 MPa, $H_2/CO = 0.67 - 0.70$, T=259-261°C, and the (H_2-CO) conversion was

Table III-1. Comparative Catalyst Performance Data

	SASOL (Dry, 1981)		Kölbel et al. (1955)	Sakai and	MOBIL (Kuo, 1985)	
	Arge	Synthol	Rheinpreussen Plant	Kunugi (1974)	CT 256-3	CT 256-13
Catalyst Reactor Type[a]	Pptd. FB	Fused CFB	100Fe/0.1Cu/.05-0.5K_2O BCSR	100Fe/0.3Cu/.6-1.2K_2O BCSR	Fe/Cu/K_2O BCSR	Fe/Cu/K_2O BCSR
Conditions						
Temperature, °C	220	325	268	273	260	258
Pressure, atm	25	25	12	10.8	15	16
SV, Nl/g-Fe/h	-	-	3.4	12.1	2.6	2.4
H_2:CO ratio	1.3-2.0	>2.0	0.67	0.52	0.67	0.67
Activity						
CO+H_2 conv. (%)	-	-	89.0	78.5 (CO)	80.8	82.2
mol/g-cat/h	-	-	.106	-	.070	.061
Nm^3/kg-Fe/h	-	-	3.02	-	2.25	1.97
Selectivity, wt.%						
C_1	2.0	10.6	3.2 (CH_4+C_2H_6)	2.3	7.8	2.7
C_2-C_4	11.2	35.2	31.3	8.2	24.5	11.1
C_5-C_{11}	18.6	42.5	53.6	4.7 (C_5-C_9)	41.5	18.1
C_{12}-C_{18}	14.5	7.5	10.0	12.8 (C_{10}-C_{18})	15.4	10.2
C_{19}+	53.7	4.2	1.9	71.9	10.8	57.9
C_{12}+	68.2	11.7	11.9	84.7 (C_{10}+)	26.2	68.1
Product Yield						
g-HC/Nm^3 converted	-	-	178	151.8	197	206
g-HC/g-Fe/h	-	-	.57	-	.37	.41

[a] FB - fixed bed, CFB - circulating fluidized bed, BCSR - bubble column slurry reactor

Table III-1. (contd.) Comparative Catalyst Performance Data

	PETC Zarochak & McDonald (1987)		MIT Satterfield (1987)	
Catalyst Reactor Type[a]	100Fe/1Cu/0.5K STSR	100Fe/1Cu/0.5K STSR	Ruhrchemie STSR	C-73 STSR
Conditions				
Time on stream, h	95	359	-	-
Temperature, °C	260	260	263	263
Pressure, atm	15	15	25	8-15
SV, Nl/g-Fe/h	3.7	3.7	2.0	1.0
H_2:CO ratio	1.0	1.0	0.7 (?)	0.7 (?)
Activity				
CO+H_2 conv. (%)	72.6	64.0	33.6	56.0
mol/g-cat/h	.084	.074	.021	.039
Nm^3/kg-Fe/h	2.69	2.37	.67	.59
Selectivity, wt.%				
C_1	5.1	2.7	5.7	11.6
C_2-C_4	20.9	9.9	27.0	39.6
C_5-C_{11}	42.9 (C_5+)	27.0 (C_5+)	40.0 (C_5-C_{12})	39.5 (C_5-C_{12})
C_{12}-C_{18}	-	-	-	-
C_{19}+	31.1 (wax)	60.4 (wax)	-	-
C_{12}+	-	-	27.3 (C_{13}+)	9.3 (C_{13}+)
Product Yield				
g-HC/Nm^3 converted	-	-	172	183
g-HC/g-Fe/h	-	-	.05	.10

[a] STSR - stirred tank slurry reactor

maintained at about 87% by gradually decreasing the gas space velocity from 2.6 to 2.2 Nl/g-Fe/h. After 46 days the loss in activity was compensated by raising the operating temperature (261-266°C) and by decreasing the gas flow rate. Mobil (Kuo, 1983, p. 211) estimates a catalyst life of 60-70 days. The longest period of operation in the high wax mode was 35 days. At 1.48-1.65 MPa, 257°C, $H_2/CO=0.7$ and 2.4 Nl/g-Fe/h the (H_2+CO) conversion was 83% (1.48 MPa) at 9 DOS (days on stream) and it decreased to 79.0% at 28 DOS (P=1.65 MPa), indicating some catalyst deactivation. After that, conversion started to decrease more rapidly reaching 67.9% at 34 DOS, which was followed by catalyst settling and termination of the run.

Results from the most successful run at the US DOE Pittsburgh Energy Technology Center (PETC) are shown in Table III-1. This run is characterized by a relatively low catalyst deactivation rate. However, the hydrocarbon product distribution changed dramatically during the run, and more higher molecular weight hydrocarbons were produced as the catalyst aged. Product distributions at 95 and 359 h on stream exhibit the usual trend, i.e., low methane yield coincides with high yield of heavy hydrocarbons. Different activation (pretreatment) procedures with this and similar catalysts resulted in much higher deactivation rates.

Finally, results obtained by Satterfield and co-workers at MIT with commercial catalysts: C-73 (fused iron catalyst for ammonia synthesis) and the Ruhrchemie catalyst (precipitated iron catalyst that was used initially in the Arge reactors at SASOL), are also included for comparison. Selectivity of the Ruhrchemie catalyst is similar to that of the Mobil catalyst I-B in a low wax mode, whereas selectivity of the C-73 catalyst is similar to that obtained from the Synthol reactor at SASOL. Activities of these two catalysts are significantly lower than those of the other catalysts listed in Table III-1.

III.2. Overview

Results obtained by Kölbel and co-workers on the catalyst productivity and selectivity, have not been achieved in any of the subsequent studies. The catalyst employed in Rheinpreussen demonstration plant produced simultaneously low yields of methane – ethane and $C_{12}-$ products, and high yield of gasoline (C_5-C_{11}). In all other studies, a low yield of methane was accompanied by a high yield of $C_{12}-$ products (mostly wax). The useful lifetime of catalysts with CO rich syngas in slurry bed reactors appears to be 30-60 days. However, there are no data on actual aging rates. In relatively long runs, loss in activity was compensated for by increasing reaction temperature and/or by decreasing gas space velocity. The maximum yield of transportation fuels, C_5-C_{18} hydrocarbons, based on classical Anderson-Schulz-Flory (ASF) distribution, is about 66%, corresponding to α=0.816 (chain growth probability factor). This yield was nearly achieved in Rheinpreussen demonstration plant, and was slightly exceeded in Mobil's low wax operation mode. An alternative way to increase total transportation fuel yield is through maximization of the reactor-wax yield, while simultaneously minimizing the light gas yield. The reactor-wax can be easily upgraded via conventional processes into high quality diesel fuel. The overall goal of our study was to develop improved catalysts which would show enhanced activity and/or better selectivity (low methane and high wax yield) in comparison to the known catalysts for Fischer-Tropsch synthesis.

IV. EXPERIMENTAL

IV.1. Fixed Bed and Slurry Reactor Systems

Fixed Bed Reactor

Two gas phase reactors were used for catalyst testing. A simplified flow diagram of one of these reactors is shown in Figure IV-1.

A section of the system, including the preheater, 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 or premixed synthesis gas) gases are delivered to the reactor through a thermal mass flow controller equipped with a digital meter readout. Flow ranges are 0-500 SCCM. Two purification traps are located upstream of the flow controller. One is filled with copper alumina catalyst and the other is filled with alumina beads, for removing traces of oxygen and for decomposing carbonyls present in the feed gas mixture, respectively.

The reactors are made of 0.500 in OD by 0.049 in wall 316 SS seamless tubing with flange connections welded at either end with an effective bed volume of 30 cc. Two aluminum heating blocks, 2.5 in OD by 0.5 in ID are bolted to the reactor tube and wrapped with a heating tape. A thermocouple is located inside each heating block midway along its length and midway across its radius. This thermocouple serves as the sensor for a temperature programmer, which is capable of multiramp operation at effective heating rates from 0 to about 30°C/min. Actual bed temperatures are monitored by thermocouples installed radially in the reactor tube. The five thermocouples are spaced at 2.5 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, including the body of the system back pressure regulator (BPR), is wrapped with heating tape from the reactor to the product trap. A temperature controller is used to maintain the temperature at about 110°C.

Two product collection traps are located downstream of the reactor (high pressure traps) and two low pressure traps are located downstream of the BPR. Product flow may be directed to either trap by turning two 3-way ball valves. In this manner, one trap can serve for product collection during material balance periods (SS trap) while the second trap can serve as a waste trap (USS trap) for collecting products during times when material balances are not necessary (e.g., during changes in reactor conditions). High pressure traps are maintained at 140-210°C to remove high molecular weight products which are solids at room temperature. The low

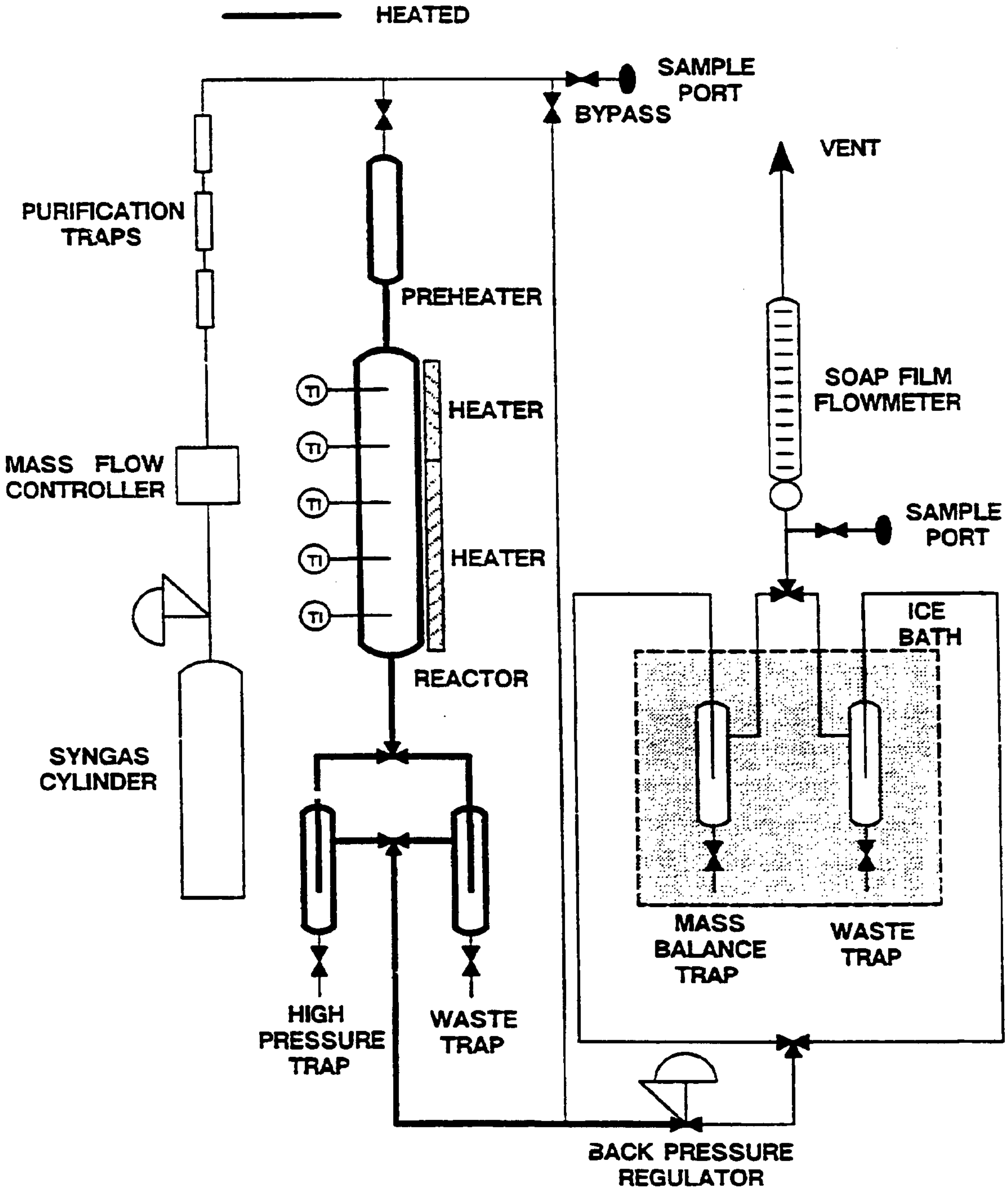

Figure IV-1. Schematic of the fixed bed reactor system pressure traps are immersed in an ice water bath so as to condense out organics. While the low pressure steady state trap is made of glass, the other traps are constructed of 304 stainless steel. Each trap has a volume of approximately 75 ml. Following the ice traps, noncondensed gas is directed to either a wet test meter or a soap bubble 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.

Pressure relief valves and gauges are located on both high and low pressure sides of the system. The pressure switch located on the high pressure side shuts off power and gas flow to the system in the event either a high or low setpoint is exceeded. A low setpoint bypass permits operation at ambient pressures. Each heated zone is protected by a temperature alarm in addition to a controller. Separate thermocouples are used for the alarms, which shut off the system if a high setpoint is exceeded. Solenoid shutoff valves are located on all gas lines supplying the reactor. A multipoint recorder provides a permanent record of system pressure and temperatures during a run.

Slurry Reactor Apparatus

Two slurry reactors were employed for long term catalyst testing and kinetic studies. A schematic representation of one of these 1-liter Autoclave reactors is shown in Figure IV-2. Feed CO and H_2 are supplied to the system after passing through a series of oxygen removal, drying, and carbonyl removal traps. The gas flow rate and H_2 to CO feed ratio are controlled using a mass flow controller for each feed gas. 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 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 either through a 5 μm,

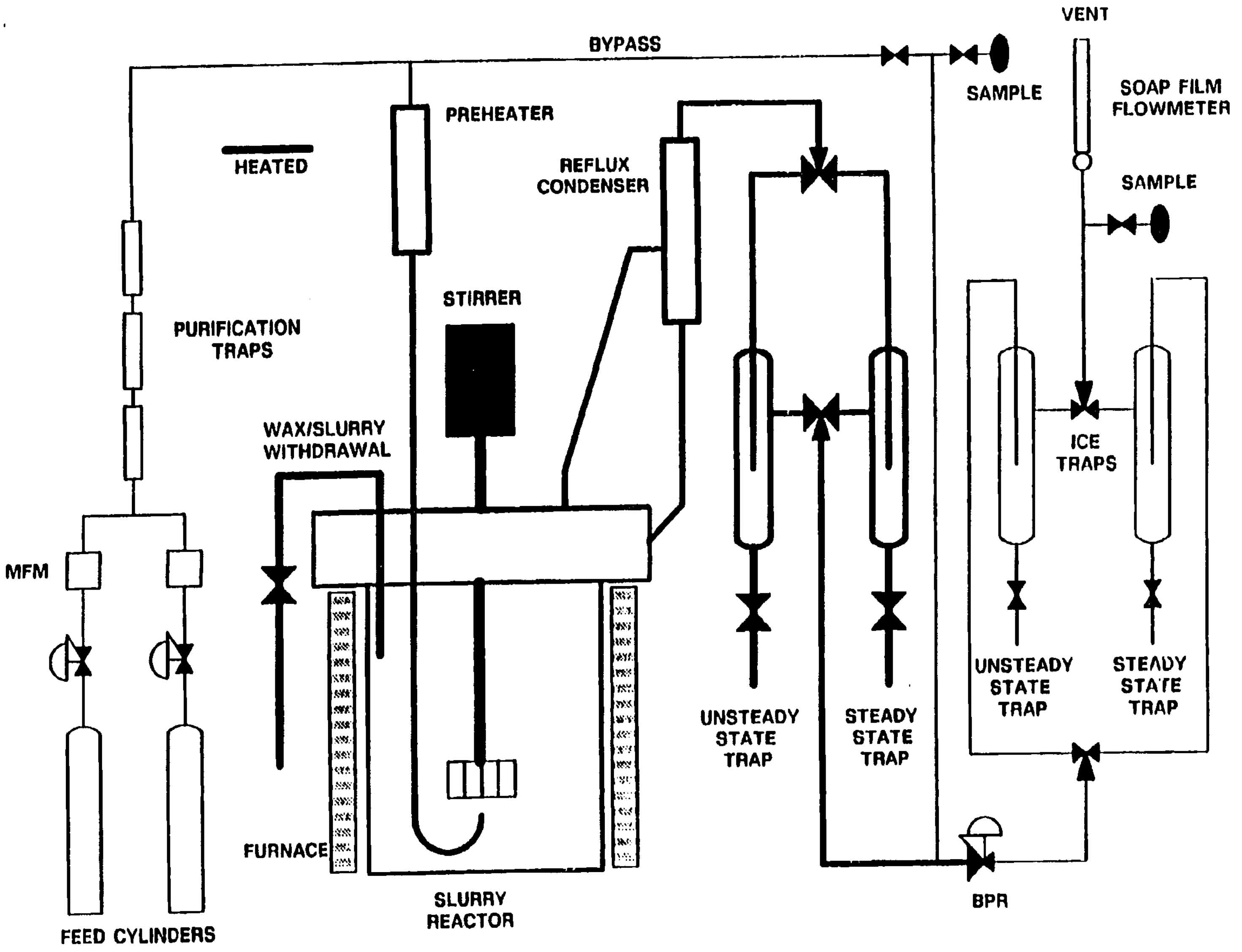

Figure IV-2. Schematic of the slurry bed reactor system

0.5" OD metal filter located internal to the reactor, or through a dip tube into an external settling tank, which is located vertically at the top of 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 heated lines to either a SS or an USS high pressure trap, back pressure regulator, and then to either a SS or an USS low pressure trap. The high pressure traps are maintained at a temperature of about 90°C with heating tapes, while the low pressure traps are placed in an ice bath. During a mass balance period, flow is diverted to the SS traps, and during USS and change over periods the product gases flow through the USS traps. The uncondensable gas is directed to either a wet test meter or a soap bubble meter.

Both of the 1-liter reactor systems are designed to run continuously and automatically, with a minimum of required operator attendance. The reactor head and reactor furnace temperature are controlled from separate, independent controllers; other heaters for the preheater, reflux condenser, high pressure traps and outlet lines are controlled by separate variacs. All system temperatures are monitored by type J or type E thermocouples. System pressure is monitored with a pressure transducer on the reactor inlet line, and the feed flowrate is obtained as a 0–5 V signal from the mass flow controller.

The slurry reactor A utilizes a multipoint recorder for recording the system temperatures and pressures during a run. The slurry reactor B utilizes an IBM–PC based data acquisition/control system to monitor process variables, implement alarms, and provide simple temperature control. All computer interface hardware was purchased from Interactive Microware, Inc. (State College, PA). An ADALAB–PC board provides for the interface between the computer and reactor system. Additional 16–channel and 32–channel multiplexer boards provide up to 48 channels of analog input, 8 bits of digital input, and 8 bits of digital output. An additional 8 bits of digital output are available directly from the ADALAB–PC board. A 16–channel relay board, using the 16 bits of digital output, is used to drive relays for alarms and temperature control. In the event of an excessively high reactor temperature, or abnormally high or low system pressure, the computer initiates a controlled shutdown by cutting all power to heaters and turns off the reactor stirrer.

IV.2. Experimental Procedure and Product Collection

IV.2.1. Fixed Bed Operating Procedure

Prior to loading, the catalyst is crushed and sieved to 30/60 mesh. A 3 to 5 cc sample of catalyst and 24 cc of glass beads of the same mesh size range are mixed and loaded into the reactor using glass wool plugs to fix and contain the catalyst bed. In order to minimize axial temperature gradient, catalyst loading is varied along the length of the reactor, with dilute catalyst concentrations at the inlet region of the bed. The system is then pressurized to 600 psig and leak tested. Following depressurization, the reactor is heated to 150°C and purged with helium for 2 hours. Depending upon the activation procedure being used, the appropriate gas is introduced and the temperature raised to the desired value. Following activation (reduction), the flow is switched to helium and the bed is cooled down to 190°C. The system is then pressurized to a desired operating pressure, the helium flow is cut off, and synthesis gas is introduced at a desired gas space velocity. The bed temperature is gradually increased to the desired value and then the reactor is allowed to run uninterrupted for at least 40 h before making the first mass balance.

To begin the material balance, the gas flow is diverted to tared sample (SS) traps. Material balance periods are typically 6-8 hours in length. During this time, two exit gas samples are analyzed by GC. The product flow rate is periodically measured and recorded. At the completion of the balance, product flow is diverted to the waste traps. The low pressure steady state product trap is removed from the system and is allowed to equilibrate to room temperature. The external surface of the trap is wiped clean and the weight of the trap is recorded. The contents of the trap are then drained and separated into an aqueous and organic layer. The trap is then washed with hot toluene and purged with N_2, and is then tared and replaced into the system. The contents of the high pressure SS trap are drained and weighed. These products are generally solid at ambient temperature. The liquid and solid products collected are analyzed by gas chromatography.

IV.2.2. Slurry Reactor Operating Procedure

The catalyst is generally ground to less than 325 mesh, and is loaded into the reactor with an excess of n-octacosane (or FT-300 paraffin wax). n-octacosane is purified with tetrahydrofuran and air dried prior to use. The system is then pressurized to 600 psig and leak tested. Following depressurization, the reactor is heated to 150°C and purged with helium for 2 hours.

Depending on the activation procedure being used, appropriate gas is introduced and the reactor temperature raised to the desired value. Following activation, excess wax is withdrawn from the reactor. The flow is switched to helium and the bed is cooled down to less than 220°C. The system is then pressurized to the desired operating pressure, the helium flow is cut off, and the synthesis gas feed is introduced at desired flow rate. Then, the reactor temperature is increased to the desired value.

The reactor is allowed to run uninterrupted for at least 40 h before initiating the first mass balance. The tasks related to products collection are similar to those described for fixed bed reactor. At the end of mass balance period, the excess wax is withdrawn from the reactor to estimate the wax production.

IV.3. Product Analysis System

A versatile analytical and computerized data handling system has been developed for this program. The system consists of four separate gas chromatographs linked to a data acquisition system (Figure IV-3).

(a) Product Gas

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 are combined using suitable tie components

(b) Aqueous Phase

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

(c) Organic Phase

The organic sample dissolved in CS_2 is separated on a .20 mm x 30 m fused silica column coated with 0.1 μm DB-5 (J&W Scientific) and analyzed on an FID, located within the Sigma 1 chromatograph. The organic sample is 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.

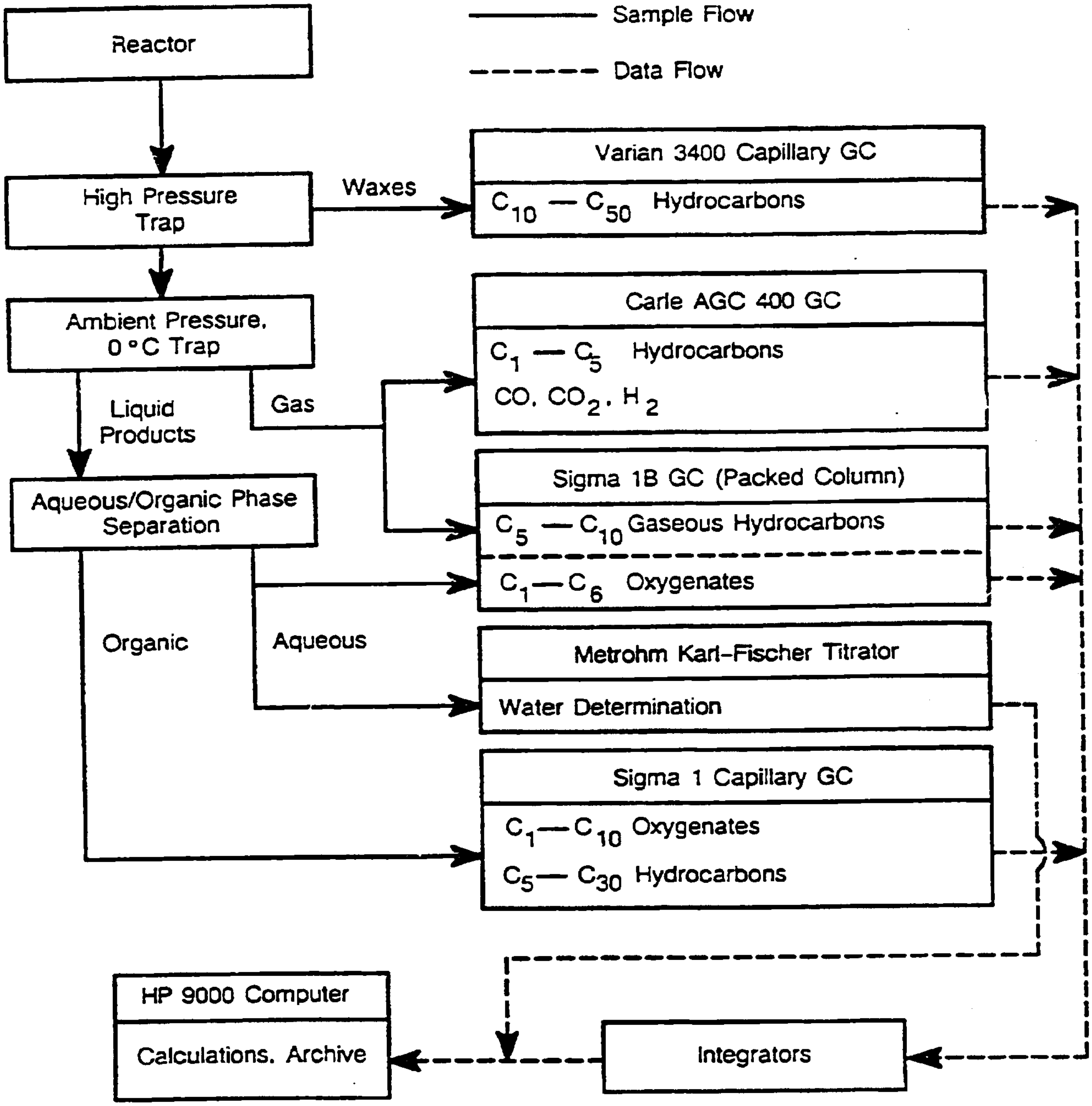

Figure IV-3. G. C. analysis scheme

(d) Wax Fraction

The wax fraction, dissolved in CS_2 or other organic solvent is analyzed on the Varian 3400 chromatograph. Here, a 10 m x 0.53 mm fused silica column coated with 0.25 μm RSL-150 (Alltech) and an FID are employed. The wax fraction is analyzed for hydrocarbons up to C_{60}.

For all samples, components were initially identified by mass spectrometry, peak spiking, and/or retention time comparisons to known standards.

IV.3.1. Response Factors and Retention Times

Response factors and retention times were determined for a large number of gas and aqueous phase components. Analyzed gas mixtures were used as standards for gas phase calibration while aqueous phase calibration standards were prepared from mixtures of 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:

$$RF'_i = AREA_i / (Mole\%)_i N_i \qquad (IV-1)$$

$$RF_i = RF'_i / RF'_{ref} \qquad (IV-2)$$

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

For gas phase analyses, the standards provided a range of concentrations which allowed for check of linearity in the detector signal. It was determined that all responses were 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 aqueous phase components expected in 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 IV-1 and IV-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 for organic phase components of interest expected in Fischer-Tropsch product were obtained using a Sigma 1 chromatograph equipped with an FID. These components include C_6-C_{30} n-paraffins, C_6-C_{20} α-olefins, C_4-C_{10} n-alcohols and C_6-C_8 aromatics. Response factors for these components were determined from equations VI-1 and VI-2. Typically all n-paraffins and 1-olefins present in the calibration sample whose RF'_1 value was 10% of the average were used in calculation of RF'_{ref}.

Response factors for hydrocarbons from C_7 up to C_{20} were found to be approximately equal to 1.0. Response factors for C_6 to C_8 aromatics were determined relative to n-paraffins. Response factors for these components were found to be 1.0. Response factors for C_4 to C_{10} n-alcohols were determined relative to n-paraffins.

Response factors and retention times for the wax phase components of interest expected in a Fischer-Tropsch product were obtained using a Varian 3400 GC equipped with an FID. The wax standard used contained selected C_{16}-C_{44} n-paraffins and 1-eicosene (C_{20}) in approximately equal weight fractions dissolved in CS_2 to about 6 mg/ml. An internal standard (n-hexadecane) was used to calculate absolute weight fractions of wax samples. The wax, with approximately 10 wt% n-hexadecane, was dissolved in CS_2. The presence of the internal standard permits absolute weight fractions to be calculated directly from the peak areas and response factors of a given sample.

IV.4. Data Reduction System

Perkin Elmer Sigma 1B, Sigma 15 and Hewlett-Packard 3390 integrators are used to collect and integrate the data obtained from the gas chromatographs. The results are then transferred to a Hewlett-Packard (HP) 9000 series mini computer for further analysis and reduction. The overall flow of data and results is shown in Figure IV-4. The data reduction system consists of peak identification routines and mass balance programs.

Peak identification programs identify gas and liquid phase Fischer-Tropsch product composition on the basis of the retention times of the components. By using the software, the product analysis is done automatically. After data processing, the output is checked for possible errors in identification.

The mass balance program uses 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

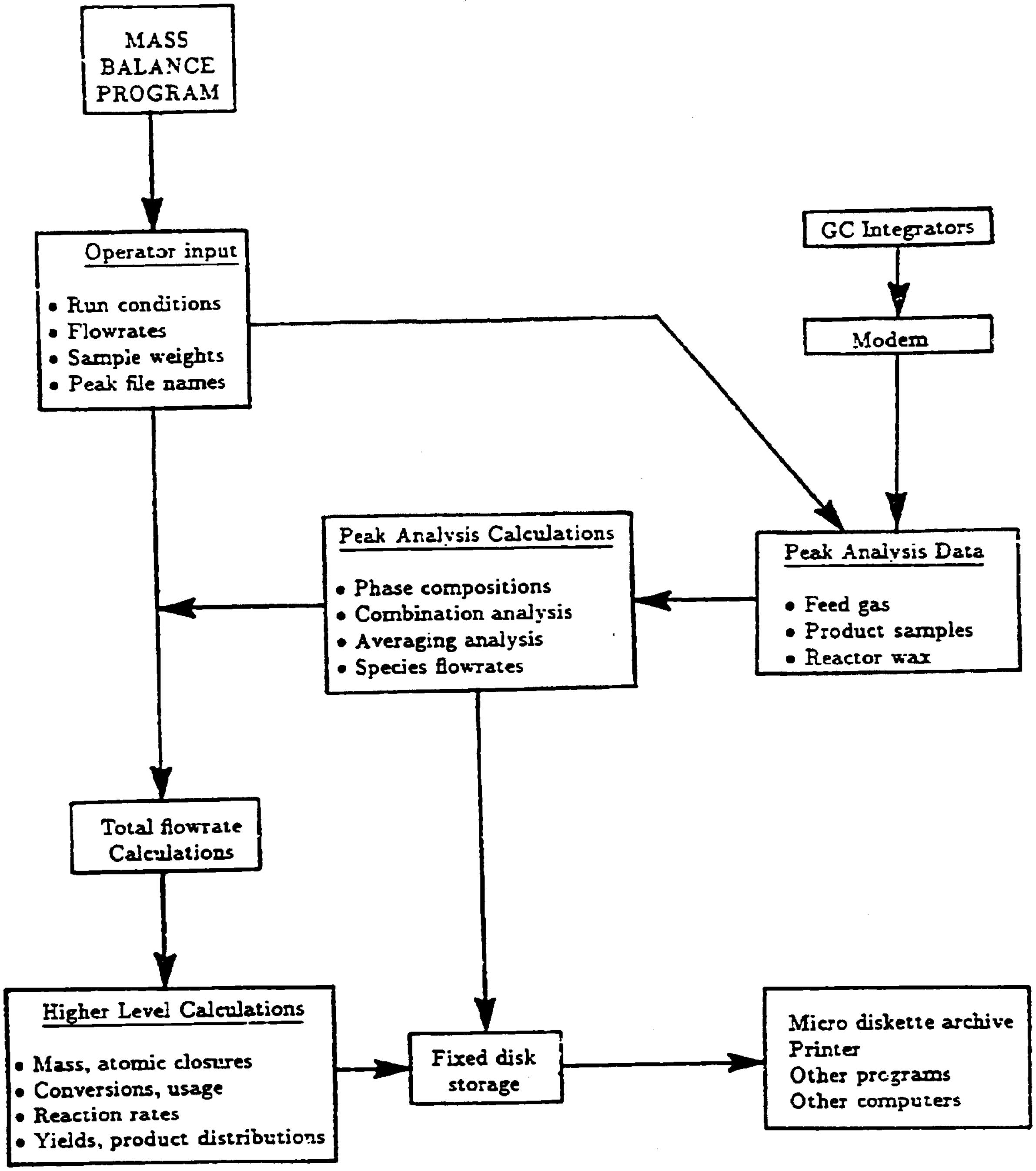

Figure IV-4. Flow diagram of the mass balance computer program chromatograph are stored in data base files. The operator supplied data and peak analysis data along with calculated results are stored on fixed disk. For safe keeping, these files are also stored on removable microdiskettes.

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.

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 mass 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. The material balance program calculates mass and atomic balance closures, yields and selectivities of products, and lumps products according to carbon numbers. These data are useful for comparison of results obtained under different process conditions and are presented in the form of tables. The program also calculates the Anderson-Schulz-Flory (ASF) chain growth parameter and produce ASF plots from which deviations from the ASF distribution can be observed.

IV.5. Coding System for Runs

All run numbers have the following format:

(Reactor Unit)-(Catalyst)-(Date)(Year)

(Reactor Unit) refers to the reactor system used during the run: FA or FB for fixed bed reactors A or B , respectively; SA or SB for slurry reactors A or B respectively. (Catalyst) is a two digit code used to reference each catalyst. This code is suffixed with a '.2' when catalyst from a second batch is used. The codes for the commercial, promoter effect series and binder/support precipitated catalysts are given in Table IV.1. (Date) refers to the day of the year corresponding to the start data of the run. Finally (Year) corresponds to the last digit in the year of the start date, (e.g., 7 for 1987, 8 for 1988, etc.). For example, a run using United Catalyst C-73 fused iron in fixed bed reactor A, beginning March 22, 1987 would be designated as: FA-01-0817.

Table IV-5. Catalyst Codes for Run Designations

Nominal Compositions				
Fe	Cu	K	Support	Code
United Catalyst C-73				01
100	0.0	0.00		00
100	0.0	0.01		41
100	0.0	0.02		42
100	0.0	0.05		43
105	0.0	0.10		44
100	0.0	0.20		45
100	0.0	0.50		46
100	0.0	1.00		47
100	0.0	2.00		48
100	0.3	0.00		32
100	0.3	0.05		03
100	0.3	0.20		05
100	0.3	0.50		07
100	1.0	0.00		33
100	1.0	0.05		13
100	1.0	0.20		15
100	1.0	0.50		17

Table IV-5. (cont'd) Catalyst Codes for Run Designations

Nominal Compositions				
Fe	Cu	K	Support	Code
100	3.0	0.00		34
100	3.0	0.05		23
100	3.0	0.20		25
100	3.0	0.50		27
100	10.	0.00		35
100	20.	0.00		36
100	5.0	4.20		31
100	5.0	4.20	8 SiO_2	63
100	5.0	4.20	25 SiO_2	66
100	5.0	4.20	100 SiO_2	69
100	5.0	4.20	8 Al_2O_3	73
100	5.0	4.20	20 Al_2O_3	76
Ruhrchemie Catalyst LP 33/81				99