CATALYST AND REACTOR DEVELOPMENT
FOR A LIQUID PHASE FISCHER-TROPSCH PROCESS

Final Report

for

Task 2

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TABLE OF CONTENTS

EXECUTIVE SUMMARY

The preparation, characterization, and performance of a range of metal catalysts for use in slurry phase Fischer-Tropsch technology was investigated with the objective of developing new compositions with improved selectivity for gasoline and diesel fuel range hydrocarbons.

A series of conventional catalysts was identified for testing in both gas and slurry phases. A gas phase screening protocol was set up to allow reasonably rapid determination of each catalyst's synthesis gas conversion characteristic over a range of operating conditions. The catalysts selected represented a range of catalytic metals known to promote conversion of synthesis gas to hydrocarbon liquids. Both precipitated and supported variations of these metals were studied. On the basis of these gas phase studies, a set of conventional catalysts was chosen for further testing in the slurry phase.

Because of the excellent temperature control achievable in the slurry phase, it was anticipated that some of the promising catalysts would show even better selectivity behavior than in the gas phase. However, it was found that while a number of catalysts showed apparent deviations from the normal Schulz-Flory distribution, in general, only low conversions were observed.

A series of catalysts was also prepared by supporting molecular metal cluster compounds on a variety of supports. Clusters were targeted as appropriate precursors based on the premise that supported clusters should decompose at high temperature to controlled particle size fragments. Clusters derived from a variety of catalytic metals were utilized, and a range of supports was studied, providing variation in both surface area and support acidity. In general, ruthenium-based catalysts had a tendency to produce large amounts of methane and oxygenates, while catalysts containing osmium showed poor activity with high methane selectivity. A number of cobalt-derived catalysts were also studied. Cobalt carbonyl supported on zirconia promoted alumina produced substantial amounts of hydrocarbons predominantly above carbon number 10. On

the basis of a preliminary slurry phase test, which showed an apparent deviation from normal Schulz-Flory behavior, a cobalt carbonyl on zirconia promoted alumina catalyst was targeted for further extended testing.

On the basis of initial slurry phase tests of both conventional and supported cluster catalysts, one type from each category was chosen for extended testing. A co-precipitated iron/copper/potassium-derived catalyst gave apparent deviations from the normal Schulz-Flory distribution. A cobalt carbonyl on zirconia promoted alumina composition also gave apparent deviations from the Schulz-Flory distribution. While inconclusive, the extended slurry phase testing of both these materials indicated there is still much to be learned about the influence of catalyst composition on the observed Schulz-Flory distribution.

INTRODUCTION

Several technologies are 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 synthesis, methanol synthesis (fixed-bed and slurry phase), and the Mobil methanol-to-gasoline (MTG) process. Of these technologies, Fischer-Tropsch hydrocarbon synthesis produces the widest slate of products and has been in operation for the longest period. Fischer-Tropsch hydrocarbon synthesis was first developed and practiced in Germany during the 1930s and 1940s. Subsequently, the process was commercialized on a large scale by SASOL in South Africa. The SASOL process includes both fixed-bed and entrained-fluidized-bed operation [1].

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. Representative product distributions from SASOL's fixed-bed (Arge) and entrained-fluidized-bed (Synthol) reactors are summarized in Table 1. Thus, depending upon reactor design, the process can produce both gasoline and diesel range products.

In contrast, the MTG process produces only gasoline range material and may not be as attractive in areas where demand for diesel fuel is high. While Mobil has also been developing a process for converting methanol to both gasoline and diesel [2], the so-called MOGD process (methanol → dimethyl ether → light olefins → gasoline + diesel), many steps are involved and it is difficult to envisage economical competition with the Fischer-Tropsch option.

Table 1

Selectivity of SASOL Commercial Fischer-Tropsch Reactors

Product	Fixed Bed (Arge) at 220°C (%)	Synthol at 325°C (%)
CH_4	2.0	10
C_2H_4	0.1	4
C_2H_6	1.8	4
C_3H_6	2.7	12
C_3H_8	1.7	2
C_4H_8	3.1	9
C_4H_{10}	1.9	2
C_5-C_{11} (gasoline)	18	40
C_{12}-C_{18} (diesel)	14	7
C_{19}-C_{23}	7	
C_{24}-C_{35} (medium wax)	20	4
>C_{35} (hard wax)	25	
Oxygenates	3.2	6

The final processing of gasoline range Fischer-Tropsch products is straightforward, especially if the fraction is olefinic; light olefins can be easily oligomerized to high-quality gasoline. The diesel range Fischer-Tropsch product is of excellent quality and requires minimal upgrading. Diesel yields can be further optimized by a simple hydrocracking of the almost ubiquitous wax produced in the process. Thus, while the Fischer-Tropsch process lacks the selectivity of the MTG process for gasoline production, its versatility may more than compensate in some economic scenarios. Unfortunately, currently available data do not allow an adequate comparison of Fischer-Tropsch synthesis to competing indirect liquefaction technologies in a hypothetical U.S. synthetic fuels industry. Unequivocal comparisons will become possible only when Fischer-Tropsch and competing processes have been demonstrated on a sufficiently large scale. Present research and development efforts need to build confidence in the ability to scale up new indirect liquefaction technologies and indicate the economic incentives for further development and scale-up.

As mentioned above, current Fischer-Tropsch technology involves both fixed- and fluidized-bed variants. Dissipation of the reaction exotherm is a major technical and engineering problem, with the result that a rather large capital investment in reactor equipment is required. In addition, inefficiencies in heat dissipation result in high methane yields and, particularly in the fixed bed, catalyst deactivation resulting from coke deposition. In the late 1940s, slurry phase Fischer-Tropsch technology was developed in Germany [3]. Slurry processing provides the ability to more readily remove the heat of reaction, minimizing 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 from 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. Because of 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. Further economies should be realized from lower recycle compressor requirements and higher conversions per unit volume of reactor.

Improved heat transfer would also be expected to have a major beneficial effect on product selectivity. Higher selectivity through improved temperature control provided the impetus for research to develop a liquid phase process. These efforts began in Germany in 1938 and continued until 1953, culminating with a demonstration plant in Rheinpreussen. Much of this work is summarized by Kolbel and Ackerman (3,4,5). During the period 1944 to 1955, the Bureau of Mines also evaluated liquid phase processes as part of their synthetic liquid fuels program, and a summary of this work appears in a Bureau of Mines report (6). Finally, Hall, Gall, and Smith (7), working at the British fuel research station, Department of Scientific and Industrial Research, compared fixed-bed, liquid phase, and fluidized-bed processes. Iron catalysts were used by all of these workers, and it does not appear that much effort was devoted to catalyst modification for improved activity and selectivity. The results and conclusions reported by these workers are generally but not always in agreement. Liquid phase operations always resulted in improved selectivity to liquid products, usually through lower methane production. However, considerable differences were reported in the space-time yield, catalyst life, and ease of operation of liquid phase reactors.

Despite the utility of the broad product slate obtainable from Fischer-Tropsch processing, product selectivity of the reaction continues to be the focus of extensive research and a prime target for technical innovation. In spite of such extensive efforts, a suitable catalyst has not been developed for producing a narrow-range hydrocarbon product such as gasoline or diesel fuel without the coproduction of lighter and heavier products. Development of a highly selective catalyst certainly has the largest potential impact on the desired product distribution.

The full potential of the liquid phase Fischer-Tropsch process has clearly not yet been realized; in addition to improved product selectivity, liquid phase operation offers the advantages of ease of scale-up and the ability to directly utilize the carbon monoxide-rich synthesis gas produced by coal gasifiers. Thus, its further development is an important part of our country's program to establish viable technology for converting coal to hydrocarbon fuels.

OBJECTIVE

The overall objective of this contract was to evaluate catalysts and slurry reactor systems for the selective conversion of synthesis gas into transportation fuels via a single-stage, liquid phase process.

Task 1 - To establish a detailed Project Work Plan.

Task 2 - To evaluate and test catalysts for their potential to convert synthesis gas to gasoline, diesel fuel, or a mixture of transportation fuels suitable for domestic markets, and to quantify catalyst activity, selectivity, stability, and aging with a target process concept involving a single-stage, liquid phase reactor system.

Task 3 - To evaluate through the use of cold-flow reactor simulators the flow characteristics and behavior of slurry reactors for the production of hydrocarbons from synthesis gas. This includes (1) defining heat, mass, and momentum transfer parameters which affect the design of slurry reactors, (2) establishing operating limits for slurry reactors with respect to system physical parameters, (3) developing or confirming correlations for predicting the flow characteristics and heat/mass transfer of slurry reactors, and (4) defining the necessary requirements for the design of larger scale reactors.

Task 4 - To develop a process design for construction of a bench-scale slurry phase Fischer-Tropsch reactor.

This report summarizes results of the Task 2 program. Tasks 3 and 4 are covered in separate reports.

RESULTS

1. Gas Phase Testing: Conventional Catalysts

A series of conventional catalysts was identified for testing in the gas phase to obtain a preliminary determination of activity for synthesis gas conversion and selectivity to hydrocarbon products. The gas phase screening protocol was set up to allow reasonably rapid determination of each catalyst's synthesis gas conversion characteristics over a range of operating conditions. Further details are available in the appropriate quarterly reports [8-22].

While operating conditions in a gas phase reactor can be changed relatively rapidly, Satterfield [23] has pointed out that catalysts producing reasonable amounts of higher boiling point hydrocarbon products require a substantial period of time to attain equilibrium. The initially observed product distributions are not necessarily representative of the actual distribution in the catalyst pores. The heavier molecular weight materials tend to accumulate in the catalyst pores, and hence, their real concentrations are not initially observed in the reactor effluent stream. Thus, while gas phase testing generally provides a reasonable comparison of conversion activity, selectivity patterns are not generally definitive.

The conventional catalysts selected represent a range of catalytic metals known to promote conversion of synthesis gas to hydrocarbon liquids, particularly iron, ruthenium, cobalt, copper, and manganese. Both precipitated and supported variations of these metals were studied.

Table 2 summarizes the major catalyst categories tested, with a total of 87 gas phase tests being performed during the course of the contract. Each test has already been summarized in detail in the previously published quarterly reports [8-22]; these are referenced in Table 2. In addition, some brief comments on each catalyst family are offered.

The initial baseline test was performed with a standard catalyst, namely a fused iron oxide-based ammonia synthesis catalyst. A typical hydrocarbon product distribution following a standard Schulz-Flory distribution was obtained.

Of the other catalyst families tested, several were selected for further testing in the slurry phase based on either good activity or apparent deviations from the standard Schulz-Flory distribution in the gas phase test. In particular, a precipitated iron/copper/potassium composition showed significant apparent deviations from the standard distribution, although much of the distribution was wax-like product. The best results were observed with an uncalcined material, which is contrary to the standard practice normally reported in the Fischer/Tropsch literature. In the case of a precipitated iron/manganese/ potassium combination, the calcined catalyst was found to be quite active but nonselective, whereas the uncalcined material showed an apparent deviation from Schulz-Flory behavior.

A ruthenium-on-alumina catalyst prepared with a variety of ruthenium salt precursors generally gave high methane yields. A composition prepared from ruthenium chloride yielded the best hydrocarbon production.

A series of zeolite impregnated catalysts was also studied. In general, these types of materials gave relatively high methane yields often accompanied by bimodal product distributions probably resulting from zeolite-catalyzed hydrocarbon oil cracking. Addition of potassium promoters to the zeolite-based catalysts generally resulted in improved hydrocarbon selectivities.

Several compositions were prepared utilizing zirconium-promoted alumina as a support with iron or ruthenium as a catalytic metal. The ruthenium-based material showed good activity with apparent deviation from Schulz-Flory behavior, whereas the iron-derived material appeared to have a standard Schulz-Flory distribution with a high methane selectivity and also produced large amounts of oxygenates.

Several compositions containing iron, zirconium, and titanium were evaluated. Most of these produced standard Schulz-Flory distributions. In addition, a number of iron/cobalt/potassium compositions were studied, several of which demonstrated excellent activity for synthesis gas conversion. Finally, a novel composition containing iron, niobium, and cesium, was studied. Standard Schulz-Flory distributions were observed.

On the basis of the gas phase studies, a set of conventional catalysts was chosen for further testing in the slurry phase.

2. <u>Gas Phase Testing: Cluster Catalysts</u>

A series of catalysts prepared by supporting molecular metal cluster compounds was tested in the gas phase. Clusters were targeted as appropriate precursors based on the premise that the supported clusters should decompose at high temperature, under testing conditions, to controlled particle size fragments. Clusters derived from catalytic metals such as ruthenium, iron, cobalt, rhodium, platinum, iridium, osmium, and mixtures of some of these metals were utilized. In general, a range of supports was studied, providing variation in both surface area and support acidity. Table 3 summarizes the various catalysts tested by cluster type, and also contains a reference to the appropriate quarterly report, in which each of the tests is discussed in detail. In addition, Table 3 provides a brief comment on each material studied.

Ruthenium carbonyl [$Ru_3 (CO)_{12}$] was studied on a variety of supports. Two of the supports, namely magnesium oxide and cerium oxide, had relatively poor activity, with the magnesia producing predominately methane and methanol, while the cerium oxide-supported material had a high olefin selectivity. Of the supports tested, alumina proved to be the best with barely average activity. An apparent deviation from the standard Schulz-Flory distribution was observed. However, the catalyst deactivated very rapidly during testing.

In general, the ruthenium-based catalyst studied had a tendency to produce large amounts of methane and oxygenates such as methanol and dimethyl ether.

Catalysts containing osmium had generally poor activity with high methane selectivity. This was also true of catalysts derived from mixed clusters of rhodium and platinum.

A number of cobalt-derived catalysts were also studied. Cobalt carbonyl supported on zirconium-promoted alumina produced substantial amounts of hydrocarbons predominately above carbon number 10. An analogous material using a mixture of cobalt and manganese carbonyls on zirconium-promoted alumina showed extremely high activity and again produced a high-molecular-weight product.

Further detail on the above tests can be found in the appropriate quarterly reports [9-15]. On the basis of these gas phase tests, a number of cluster compositions were chosen for further testing in the slurry phase.

3. Slurry Phase Testing: Conventional Catalysts

A series of conventional catalysts that had previously been tested in the gas phase were selected for further testing in the slurry reactors. Because of the excellent temperature control achievable in the slurry phase, it was anticipated that some of the promising catalysts would show even better selectivity behavior than in the gas phase. Various catalysts tested are summarized in Table 4, along with a brief comment and a reference to the appropriate quarterly report [12,13,17-22], wherein extensive details on each test are available.

Sintered Iron Oxide

The slurry testing program was initiated with a commercial, sintered iron oxide catalyst, promoted with alumina, potassium, and calcium. Prior gas phase testing of this catalyst had indicated standard Schulz-Flory behavior.

A major objective of this baseline test was to fully characterize the behavior of the slurry reactors and to perform a test of mass transfer resistance in the Fisher-Tropsch synthesis reaction. The test was initiated by contacting the catalyst with a 2:1 H_2/CO ratio syngas at a pressure of about 450 psig. Stirring speeds were varied from 800 up to 1600 min^{-1}, while temperature was varied from 220 to 300°C. The hydrocarbon product distributions obtained were uniformly approximated by straight-line Schulz-Flory distributions, as expected for this type of catalyst. A number of operational problems were encountered during this initial test, reducing the reliability of some portions of the data.

The data from the run were analyzed to distinguish mass transfer and chemical rate resistance. With constant temperature and space velocity, stirrer speed had little effect on overall conversion. A second test of the same baseline catalyst was carried out, and again stir speed and space velocity were systematically varied over a range of temperatures to give further information about mass transfer limitations, product distribution, and catalyst activity. Unfortunately the mass transfer effects were complicated by concomitant catalyst deactivation. All through the test, a standard Schulz-Flory distribution was observed.

Unfortunately both of these tests were carried out using Edwards No. 16 oil as an initial slurry medium. This oil was subsequently found to contain traces of sulfur-containing compounds, which would be expected to deactivate the catalyst. Thus the reliability of these two tests was significantly reduced.

Fe/Mn/K

Previous gas phase screening tests of a coprecipitated Fe/Mn/K catalyst showed that one of the batches appeared to produce a significant deviation from the standard Schulz-Flory distribution. The particular catalyst batch showing this behavior was not precalcined in air. A slurry test was therefore carried out on this same batch in the slurry reactor. Unfortunately this test also involved in Edwards No. 16 oil, once again raising the potential for sulfur poisoning. Slurry phase activity was

extremely poor, with a synthesis gas conversion of less than 1% at 240°C. At higher temperatures, the conversion could be increased to approach 20%, but no deviations from a standard Schulz-Flory behavior were observed. When a high CO ratio synthesis gas was used, severe deactivation of the catalyst occurred, and it could not be reactivated even with a pure hydrogen atmosphere.

Fe/Cu/K

Previous gas phase testing of a precipitated Fe/Cu/K catalyst indicated that the uncalcined catalyst showed an apparent deviation from the Schulz-Flory distribution. A continuous test of this catalyst over 21 days was carried out in the slurry reactor. Conversions were only moderate all through the test, with a maximum of 15%, and the catalyst deactivated with time above 250°C. Although the data show apparent deviations from the standard Schulz-Flory hydrocarbon distribution, the reliability of the data has to be limited at such a low conversion level because of difficulty in performing adequate mass balances in this conversion range. The catalyst deactivated significantly at higher temperatures and it could not be reactivated. Because of the apparent deviations from the Schulz-Flory distribution in both the gas and slurry phase test and apparent selectivity to liquid hydrocarbon products in the uncalcined catalyst, it was selected for further extended testing in the slurry phase. This test is discussed in a subsequent action of this report.

$RuCl_3/Al_2O_3$

In the gas phase screening tests of catalysts derived from ruthenium chloride supported on alumina, good apparent selectivity to hydrocarbon products was observed. Hence, this catalyst type was chosen for further slurry phase testing. Generally this type exhibited poor conversion levels in the slurry phase, with only 3% conversion observed at approximately 240°C. It is extremely difficult to make conjectures regarding product selectivity at such conversion levels. This catalyst was not studied any further.

Fe/Cu/K/Al$_2$O$_3$

In gas phase testing, this type of catalyst, derived from iron and copper salts successively impregnated on alumina with added potassium as a promoter, enhanced the production of higher molecular weight products. This type of catalyst was therefore chosen for further testing in the slurry phase. Conclusions derived from the slurry phase test are as follows:

a. The catalyst showed significantly lower bulk and specific activities than were measured in the gas phase test.

b. In the slurry phase, the product distribution was of lower molecular weight than was apparent in the gas phase with higher yields of methane.

c. The product distribution was dependent on the CO partial pressure, as is normally observed in slurry catalyst tests.

d. When the CO/H$_2$ ratio was increased from one to two at constant temperature and pressure, the yield of methane increased and the amount of liquid hydrocarbons increased significantly. The methane yield was anomalously high and is not well understood.

e. This catalyst showed a lower bulk activity than the coprecipitated Fe/Cu/K catalyst previously tested.

f. Throughout the test, the observed product selectivity was close to a straight-line Schulz-Flory distribution, again contrasting with the apparent results with the coprecipitated version.

Fe/Zr/Ti/K

This type of precipitated catalyst had been studied in the gas phase. Adding potassium as a promoter showed enhanced olefin selectivity. For slurry phase testing, procedures used in the gas phase test were followed. The main conclusions were as follows:

a. Compared with the previous gas phase test, the activity was reduced in the slurry phase. This phenomenon may be due to prevention of surface exotherms, which are known to occur in a fixed-bed reactor, by the heat transfer properties of the slurry oil.

b. Under analogous conditions (260°C and 300 psig) the bulk activity was 65% lower than in the gas phase.

c. An apparent positive deviation from straight line Schulz-Flory distribution was observed in the liquid hydrocarbon region.

d. Selectivity and activity were found to be dependent on the CO/H_2 ratio.

e. No significant amounts of products greater than C_{26} were observed. However, it should be noted that conversions throughout the tests were very low, with a maximum of 20% at approximately 340°C.

$Fe/ZrO_2/TiO_2$

Prior gas phase testing of this catalyst (see Section 1) had indicated possible deviation from the Schulz-Flory distribution above C_{15}. Hence, further testing was scheduled in the slurry phase. Once again, as compared with the previous gas phase test, this catalyst was considerably less active in the slurry phase. Under similar conditions at 280°C, bulk activity in the slurry phase test was 80% lower, with much higher yields of methane. As temperature and pressure were raised to increase conversion, the yield of methane increased dramatically, approaching 50% at 330°C. It was concluded that this catalyst was not suitable for further development.

$Fe/Zr/Al_2O_3$

Once again the activity in the slurry phase was considerably less than that observed in the gas phase test, with bulk activities approximately 50% lower. The methanation activity was very high, exceeding 40%, while selectivity for liquid range products was significantly decreased.

Fe/Mn/Al$_2$O$_3$

The activity of this catalyst in the slurry phase was also much less than in the gas phase; for example, at 280°C and 300 psig, the activity was as much as 80% lower. Also, yields of methane were much higher, with very little liquid hydrocarbon product. It appears from several of these tests on supported iron catalysts that the precipitated or sintered type are more suitable for use in slurry reactor systems.

Fe-Y

Compared with the previous gas phase test, this catalyst showed significantly more activity in the slurry phase. For example, at 280°C and 300 psig, the bulk activity in the slurry was 42% higher. However, the product selectivity was dissimilar, with higher yields of methane (up to 30 wt % compared to 13 wt % in the gas phase) and lower concentrations of liquid phase hydrocarbons. In this case, the different selectivity observed in the slurry phase may have been due to oil cracking possibly catalyzed by the acidic zeolite surface. Since this catalyst showed no apparent selectivity for fuel range hydrocarbons compared with other iron-based catalysts, no further testing was pursued.

Fe-Offretite

This catalyst was very similar to the Fe-Y zeolite reported on above. Operating temperatures greater than 260°C were required to make the activity comparable to other iron-based catalysts. At low pressure, a bimodal product distribution resulted, indicating some cracking of the slurry oil. Increasing the pressure to 700 psig alleviated this problem, while the product selectivity shifted to the light end. The product distribution was similar to that of Fe/Y at all operating conditions. Methanation activity was high, producing over 20 wt % of the total hydrocarbon yield. Again this test indicated that supported iron catalysts of this type are not particularly suitable for slurry phase processing.

Fe/Co/K

Of the series of Fe/Co/K catalysts tested in the gas phase, a 50-50 wt % Fe/Co composition promoted with 0.1 wt % K was chosen for slurry reactor testing. This catalyst exhibited appreciable activity, comparable to that of Fe/Cu/K at 260°C, but poor selectivity for fuel range products. Selectivity varied strongly with CO/H_2 ratio, but even at high CO ratios, the products were predominantly lower than C_{10}, with methane production at over 20 wt % of the total hydrocarbon yield.

Fe/Nb/Cs

A 50/50 wt % Fe/Nb catalyst promoted with 0.1 wt % Cs was chosen from the series of gas phase screening tests for slurry testing. At 240°C this catalyst was relatively inactive, but the activity increased appreciably when the temperature was raised to 260°, with the bulk activity exceeding that of the standard Fe/Cu/K composition. The selectivity for liquid range hydrocarbons appeared to be most favorable, with CO/H_2 ratios of 1.5 at 260°C. This was accompanied by a relatively low methane yield. As temperature, pressure, and CO/H_2 ratio were raised to improve activity and selectivity, the catalyst performance was most affected by temperature. The bulk activity was as high as 56.5 moles syngas/cat/h at 300°C, but with a shifting of products to the lighter molecular weight end. The results of this test indicated that Fe/Nb/Cs type might be a suitable candidate for further studies.

4. **Slurry Phase Testing: Supported Cluster Catalysts**

Eleven of the supported cluster catalyst compositions examined in the gas phase testing program were chosen for further testing in the slurry phase. The catalysts tested are identified in Table 5, along with a reference to the appropriate quarterly report [13-16], wherein significant detail on the test may be found. Summary statements on each of these cluster slurry tests are as follows:

Ru/Zr(OPr)$_4$/Al$_2$O$_3$
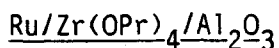
In contrast to the gas phase screening tests of this type of catalyst, the activity measured in the slurry phase was very low, with conversions of only 2 to 6% at comparable conditions in the temperature range of 260 to 350°C. The product distributions obtained showed apparent deviations from a standard Schulz-Flory distribution, with a buildup of C$_{10+}$ hydrocarbons, but also included high yields of methane (a minimum of 21.5%). This combination of low conversion with an observed bimodal product distribution increased significantly the experimental error in obtaining accurate mass balances. Hence, at this low conversion level with poor mass balances, it is very difficult to draw reasonable conclusions relative to observed product distributions.

Ru$_3$(CO)$_{12}$/Al$_2$O$_3$
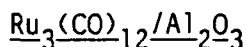
A slurry test of this cluster catalyst was carried out in the liquid phase reactor. Throughout the test, conversions were low, with a maximum of 6.5% at 350°C. For example, at 340°C and 500 psig, slurry phase activity was only 10% of that observed in the gas phase at 224°C and 300 psig. At temperatures up to 300°C, the product was mainly methane. At 350°C, the conversion increased to approach 6%, and the observed hydrocarbon product appeared to show a deviation from the standard Schulz-Flory distribution. Analysis of the Edwards No. 16 oil used in the test showed the presence of 0.14 wt % sulfur, which may have poisoned the supported ruthenium cluster. A second slurry phase test of this supported cluster was therefore carried out using Fisher white paraffin oil. However, use of this sulfur-free oil increased catalyst activity by at most a factor of 2, indicating that this was not the primary cause of the low activity observed previously.

Fe$_3$(CO)$_{12}$/CeO$_2$
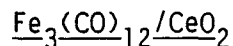
This catalyst was tested in the slurry phase without prior activation, and once again the activity was significantly lower than in the previous gas phase test. While the catalyst was being slurried in oil before reaction,

it was observed that some of the iron complex dissociated from the support and dissolved in the oil, indicating a loss of metal from the catalyst and a possible reason for the low activity. To prevent this occurrence in future tests, it was decided that impregnated cluster catalysts would be activated in the gas phase before slurrying in oil.

$Ru_3(CO)_{12}/Zr(OPr)_4/Al_2O_3$
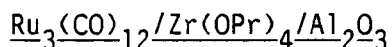
To prevent dissolution of the cluster from the support, as reported above, this supported ruthenium cluster catalyst was activated with synthesis gas in the gas phase before slurrying in oil. This procedure resulted in better conversions and an apparent indication of Schulz-Flory deviations, although the product selectivity reported in the previous gas phase test was not reproduced. A low level of water-gas shift activity was observed for this catalyst, which is consistent with ruthenium-based compositions. This slurry catalyst gave conversions of approximately 20% at 300 psig and 250°C. A significant amount of methane, approaching 30%, was observed in the product distribution.

$Ru_3(CO)_{12}/CeO_2$
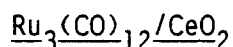
This catalyst was also preactivated in the gas phase before being slurried in oil for slurry phase testing. The specific activity was higher in the slurry phase and at a lower temperature than in the previous gas phase screening test. Deactivation was temperature-dependent: no significant loss in activity occurred at 280°C, but a decrease was noted once the temperature exceeded 300°C. The product selectivity observed in the slurry phase was similar to that in the gas phase test and was notable for a high 1-alkene content and a high propylene selectivity. However, in the slurry phase the methane selectivity was higher and increased with time. Some apparent deviations from the standard Schulz-Flory distribution were observed in the C_{10+} region, and no product was apparently produced above approximately C_{28}.

$Fe_3(CO)_{12}/Zr(OPr)_4/Al_2O_3$
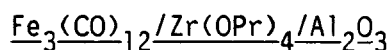
This catalyst was tested using gas phase preactivation. Catalyst bulk activity was very low, leading to conversions in the 2 to 4% range. At this low level of conversion, it is virtually impossible to draw any conclusions relative to the efficacy of the test. There was some evidence that iron carbonyl was desorbed from the catalyst during the test. This may be due to the ease of formation of iron carbonyls and their hydrocarbon solubility.

$Co_2(CO)_8/Zr(OPr)_4/Al_2O_3$
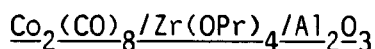
This catalyst was preactivated in the gas phase and again showed much better activity in the slurry phase as a result. A high metal loading was used, and hence, high bulk activities were observed with good conversion levels. Contrary to the gas phase screening test, little water gas shift activity was observed in the slurry phase. Under constant conditions, a slow overall deactivation rate was observed that corresponded to a shift in selectivity to higher molecular weight products. The slurry phase test generally gave lower methane yields and higher apparent liquid hydrocarbon yields than were observed in the gas phase test. Apparent deviations from the Schulz-Flory distribution were observed in the hydrocarbon product, and, as a result, this catalyst was selected for further extended testing in the slurry phase.

$Co_2(CO)_8/TiO_2$
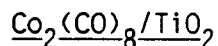
This catalyst was tested in the slurry phase after preactivation in the gas phase. In the middle of the test, after about 156 hours of operation, the behavior and selectivity changed significantly, apparently resulting from experimental problems with wax continually plugging the reactor outlet lines. The activity was considerably less than that observed for the same cluster supported on zirconium-promoted alumina, as reported above. Product selectivity was lower and the methane yield was higher than on the alumina-based catalyst. Product distributions were similar to the related

gas phase test, but displayed higher yields of liquid hydrocarbons. Methane yields were also relatively high, approaching 20 wt %. This catalyst was not considered to be as promising as the alumina-supported version.

5. Extended Slurry Tests

On the basis of the slurry phase tests of both conventional and supported cluster catalysts, one type from each category was chosen for extended testing in the slurry phase. Detailed reports on these extended tests are contained in quarterly reports numbers 9, 10, 11, and 12 [16-19].

Fe/Cu/K Coprecipitated Catalyst: Extended Test

Slurry phase tests indicated that this class of catalyst showed an apparent deviation from the normal Schulz-Flory distribution, and this type was therefore chosen for further testing over an extended period. The actual extended test on this class of catalyst was conducted on three separate batches in three phases. Detailed reports on these extended tests are available in quarterly reports numbers 9, 10, and 11 [16-18]. In this summary, each of the three phases will be reviewed separately. Elemental analyses of the catalyst batches used are listed in Table 6. A summary of process conditions, conversions, activities, product distributions, and the feed and usage ratios for mass balances run during the three test phases is contained in Table 7.

Phase 1 - Previous 21-day slurry tests of this class of catalyst showed an apparent enhancement in product selectivity around the C_{10} region, when the catalyst was not calcined in air before reduction. For this reason, coprecipitated Fe/Cu/K prepared without air calcination was selected for an extended slurry phase test. Slurry phase activation was carried out in situ with a 1:1 CO/H_2 mixture by first slowly increasing the temperature and then the pressure to the operating conditions. Large apparent deviations from a Schulz-Flory distribution were observed subsequently, but at a higher carbon number range than before, with product peaking at approximately C_{25}.

In the initial phases of the test, activity appeared to be about 66% higher than in the initial 21-day test. Most of the observed product was in the C_{18}-C_{35} region, with low methane yields of about 6%. This product distribution resulted in a comparatively rapid increase in slurry level in the reactor because of the production of relatively involatile hydrocarbon wax. This wax was regularly withdrawn through a 5-micron filter to maintain a constant slurry level that enabled continuous operation. In all cases the filtered wax samples were weighed and analyzed and included in the material balance to give an overall hydrocarbon product analysis.

After about 250 hours onstream, the operating pressure was reduced to 150 psig at constant temperature in an attempt to move the hydrocarbon distribution to a lower molecular weight range. The apparent deviation from the Schulz-Flory distribution in the C_{18} - C_{35} region remained, with low yields of methane. No significant deactivation was observed in this phase of the test. Overall conversions never exceeded 20% based on the synthesis gas supplied. Because of the difference in the product selectivity from the initial 21-day test, this first phase of the extended test was halted after 476 hours onstream and subsequently restarted with a fresh catalyst batch.

Phase 2 - A new batch of coprecipitated catalyst was prepared, and after the standard activation procedure, a second phase of the extended test was run for 478 hours at 240°C and 300 psig. Although the product distribution initially contained more methane and a higher amount of C_5-C_{11} hydrocarbon, the methane yield decreased with time, and the yield of high-molecular-weight material appeared to increase, giving an apparent significant deviation from straight-line Schulz/Flory distribution. The bulk activity was consistently higher than the prior phase, and little evidence of deactivation was observed over the 478-hour period.

Toward the end of this period of operation, the filter on the slurry withdrawal line became partially blocked; this resulted in a progressively longer period for wax withdrawal to maintain a constant slurry level, and on day 52, a carry-over of slurry into the gas phase product outlet line

occurred. For this reason the reactor was maintained under nitrogen purge for several days while the system was cleaned up. Following restart of the test, an initial effort was made to reestablish the selectivity and activity observed before the nitrogen purge. Comparable yields of the main product fractions were again produced, and after an initial decrease, the bulk activity level was regained. Following this restart, the CO/H_2 ratio was increased to 1.5:1 at 240°C and 300 psig. Initially this led to decreased amounts of C_5-C_{11} and increased yields of C_9-C_{25} hydrocarbons. The distribution appeared to move to higher molecular weight products, and the buildup of product in the $C_{18}-C_{35}$ region became more marked. This higher amount of $C_{26}+$ hydrocarbons was reflected in a greater amount of accumulated high-molecular-weight material withdrawn from the reactor via the filter.

However, further problems resulting from clogging of the filter and a leak in an alternative open pipe slurry withdrawal line led to outlet blockages and the loss of 236 grams of slurry from the reactor on day 84. The reactor was shut down under nitrogen while the blockage was cleared, and the slurry lost through leakage was returned to the reactor (this slurry was deposited on the floor of the reactor cell and was at least partially exposed to air oxidation).

Subsequently, an effort was made to reestablish the selectivity and activity observed before loss of catalyst. At this stage the initial methane level was high with an anomalously high $C_5 - C_{11}$ fraction. The bulk activity observed before the spill was not regained and was 30% less.

The operating temperature was then increased to 260°C at the same pressure and synthesis gas ratio. During this period, higher molecular weight hydrocarbons were removed from the reactor using an open pipe to avoid removal via the clogged filter. Although this higher temperature resulted in consistently higher bulk activity, the overall conversion remained in the range of 20%. The net effect of operating at this higher temperature was to increase the product fraction in the C_2-C_4 range, while the apparent deviations from Schulz-Flory distributions were maintained. As

slurry was withdrawn from the reactor through an open pipe, some catalyst was also inadvertently removed, reducing the catalyst loading in the reactor.

On day 130, the total amount of withdrawn catalyst was dewaxed by hot toluene extraction under nitrogen and was returned to the reactor as a dry powder. The testing was continued with a higher hydrogen to carbon monoxide ratio, and the product moved to a higher molecular weight range. On day 156 the reactor was shut down to begin the third phase of the extended test.

Phase 3 - Because of the probable effects of air exposure on the catalyst in Phase 2, a third phase of the extended test was carried out with a fresh catalyst batch in which the reactor was heated directly to 260°C after activation.

Initially with 1:1 CO/H_2 at 260°C and 300 psig, the activity increased gradually over a period of almost 200 hours with an increase in conversion from 27 to 45%. Associated with this increase in activity was an apparent increase in product selectivity for C_9-C_{25} hydrocarbons. The yield of methane remained relatively constant at about 7%, and the selectivity for C_5-C_{11} hydrocarbons increased during the period. All product profiles obtained showed some apparent deviation from the Schulz-Flory distribution. When the CO:H_2 ratio, was increased to 1.5, conversion and activity increased further. With this higher ratio the methane decreased to approximately 5%, and the C_9-C_{25} fractions also increased. At this stage there was an apparent substantial deviation from the Schulz-Flory distribution.

Throughout this period of operation, the level of slurry was maintained constant by withdrawal of wax through the internal filter. However, toward the end of this period, the filter became blocked and carry-over of slurry into the gas phase product line occurred. At this stage the reactor was accidentally left under a carbon monoxide and nitrogen atmosphere for

approximately 24 hours. After cleanup of the reactor, the test was continued at the same operating conditions, namely 1.5:1 CO/H_2 at 260°C and 300 psig.

Following the accidental CO exposure, bulk activity decreased by 45% with a decrease in overall conversion to about 25%. Product selectivities also varied during this period. However, the yield of methane continued to be very low at about 4%, while the yield of waxy material increased, making a greater rate of withdrawal of higher molecular weight hydrocarbons necessary.

Because of the carbon monoxide exposure and resulting change in activity and selectivity, the reactor was shut down after about 500 hours of operation in Phase 3.

Extended Test: $Co_2(CO)_8/Zr(OPr)_4/Al_2O_3$

Phase 1 - Following the behavior observed in the 21-day slurry test, a new batch of this type of catalyst was prepared for testing in an extended slurry phase test. The catalyst was treated in the same manner as in the previous short test, with preactivation in a gas phase reactor. Table 8 contains a summary of the elemental analyses of the various batches of this form of catalyst screened in the gas and slurry phase reactions. It can be readily seen from the data that all the batches had different cobalt and zirconium contents.

A summary of process conditions, conversions, activities, product distributions, and the feed and usage ratios for the mass balances run during the 1950 hours on stream are given in Table 9. While the results at 250°C with CO/H_2 ratios of 1.5 and pressures of 300 psig indicated good catalyst stability, the current batch was not as active or selective as the batch used in the prior slurry test.

In terms of product selectivity, the distribution obtained at 250°C, under steady-state conditions, was approximately intermediate between those obtained in the prior slurry test at varying synthesis gas ratios, except for a higher methane yield.

The differences observed in activity between this batch and the prior one could be attributable to the zirconium content, which was significantly lower in this particular batch.

During this extended test, attempts were made to increase both activity and selectivity for fuel range hydrocarbons by raising temperature and pressure and increasing the CO/H_2 ratio. When the CO/H_2 ratio was changed to two while temperature was maintained at 250°C and pressure at 300 psig, the net result was an increase in the C_9-C_{25} hydrocarbons, a small increase in the amount of wax, and a small decrease in methanation activity. When the operating pressure was raised to 600 psig while the temperature was maintained at 250°C and the CO/H_2 ratio at two, the bulk activity was lower and a pronounced reduction occurred in the C_9-C_{25} fraction, while methanation activity remained high at 18 wt % of the total product. Finally, temperature was raised to 280°C in an attempt to improve activity. The bulk activity increased, but there was an accompanying increase in methane yield to 26%.

As all attempts at improving activity and selectivity failed, a decision was made to stop the run at 1950 hours on-stream and to begin a second phase of testing with a new catalyst batch.

Phase 2 - Table 10 contains the data on this second phase of the extended slurry test. For Phase 2, a considerable improvement in activity was observed, making this batch nearly twice as active as in the prior tests. However, the product selectivity was not altered. This phase of the test was terminated after a total of 618 hours on-stream. Wax production was generally observed to be low throughout the run.

6. Contract Modification: Tasks 5, 6, 7

Following the apparent observation of significant deviations from the Schulz-Flory distribution in the iron/copper/potassium coprecipitated catalysts, a contract modification was made, adding tasks to search for an optimum catalyst of this type with both good activity and further enhanced selectivity to liquid fuels.   To this end, coprecipitated iron/copper/potassium catalysts were prepared utilizing varying levels of copper and potassium.   Detailed results of this phase of the contract are contained in quarterly reports numbers 14 and 15 [21,22].   Initially, anomalously good results were obtained with some compositions showing very high apparent activity.   However, this was later traced to problems in the slurry reactor operation, and the results of this phase of the contract are not adequate to allow any definitive conclusions to be drawn on the effects of promoter levels on coprecipitated iron catalyst behavior.   However, this is a topic that definitely merits significant further study, since an understanding of both surface chemistry and activity effects related to the levels of promoters should be very useful in enhancing fundamental understanding of this type of catalyst.

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TABLE 2

GAS PHASE TESTING: CONVENTIONAL CATALYSTS

Catalyst	Comment	Quarterly Report No.	Ref.
Fused Fe_2O_3	Baseline catalyst; standard Schulz-Flory.	2	9
Fe/Cu/K	Precipitated catalysts; best uncalcined; deviation from Schulz-Flory noted.	2,3	9,10
Fe/Mn/K	Precipitated catalysts; calcined: very active, nonselective; uncalcined: deviation from Schulz-Flory.	3,4	10,11
Fe/Aluminosilicate	Fe exchanged aluminosilicate, impregnated with Fe; very high methane yields.	4,5	11,12
Ru/Al_2O_3	Supported catalysts; generally high methane yields; $RuCl_3$ precursor gave best hydrocarbon production.	4,6,7,8	11,13, 14,15
Ru/NaY	Series of zeolite (NaY)-impregnated catalysts; all produced large amounts of methane.	5	12
Ru/CeY		5	12
Fe/Mn/NaY		5	12
Fe/Ru/NaY		6	13
$FeCu/Al_2O_3$	Alumina impregnated with mixed Fe and Cu salts; poor activity; high methane selectivities.	3,5,8	9,11,15
$Ru/Zr(OPr)_4/$ Al_2O_3	Ru salt supported on Zr-promoted Al_2O_3; good activity, apparent deviation from Schulz-Flory distribution.	5	11
Fe/Zr/Ti (K)	Precipitated catalysts from co-precipitation of Fe, Zr and Ti salts; standard distributions; added potassium enhanced olefin selectivity.	8,9	15,16
$Fe/ZrO_2.TiO_2$	$ZrO_2.TiO_2$ impregnated with iron salt; possible deviation from Schulz-Flory distribution above C_{15}.	9,10	16,17
$Fe/Cu/Al_2O_3$ (K)	Cu and Fe salts successively impregnated on Al_2O_3, largely light products; K added as promoter; K enhanced higher molecular weight products.	9	16

29

1320G-IA

TABLE 2
(continued)

GAS PHASE TESTING: CONVENTIONAL CATALYSTS

Catalyst	Comment	Quarterly Report No.	Ref.
Fe/Zr (OPr)$_4$/ Al$_2$O$_3$	Fe salt supported on Zr-promoted Al$_2$O$_3$; Schulz-Flory distributions with low ; high CH$_4$ selectivity; high oxygenate selectivity.	10	17
Fe/Mn/Al$_2$O$_3$	Alumina impregnated with Fe and Mn salts; standard Schulz-Flory distributions.	10,11	17,18
Fe/Offretite	Fe exchanged and impregnated ammonium offretite; K promotion enhanced selectivity to hydrocarbons.	11,12	18,19
Fe-Y	Iron-exchanged Y zeolite; high Fe loading detrimental; K promotion gave apparent non-Schulz-Flory behavior.	12	19
Ru-Y	Ru-exchanged and impregnated Y-zeolite; high CH$_4$ selectivity; hydrocarbon oil cracking under some conditions; RuCl$_3$-derived catalyst had apparent Schulz-Flory deviation.	12,13	19,20
Fe/Co/K	Series of coprecipitated Fe/Co catalysts with K promoters; very good activity; standard Schulz-Flory distributions.	12,13,14	19,20, 21
Fe/Nb/Cs	Coprecipitated catalysts; standard Schulz-Flory distribution.	13,15	20,22

30

TABLE 3

GAS PHASE TESTING: SUPPORTED CLUSTER CATALYSTS

Cluster	Support	Comment	Quarterly Report No.	Ref.
$Ru_3(CO)_{12}$	MgO	Low activity; Schulz-Flory distribution; predominantly CH_4 and CH_3OH.	2	9
	Al_2O_3	Average to poor activity; apparent deviation from Schulz-Flory distribution; deactivated rapidly; high methanation activity.	2	9
	CeO_2	High olefin selectivity; Schulz-Flory distribution.	3	10
	$Zr(OPr)_4/Al_2O_3$	Poor activity.	3	10
	Poly(styrene)	Inactive.	4	11
	TiO_2	Inactive below 300°C.	7	14
$Na[HRu_3(CO)_{11}]$	MgO	Low activity; Schulz-Flory distribution.	2	9
$HCoRu_3(CO)_{13}$	MgO	Low activity.	3	10
	Al_2O_3	High CH_4 selectivity.	3	10
	CeO_2	Good activity; >35% CH_4.	5	12
$H_4Ru_4(CO)_{12}$	Al_2O_3	Poor activity; major product was dimethyl ether.	3	10
	MgO	Good activity; Schulz-Flory distributions.	3	10
	$Zr(OPr)_4/Al_2O_3$	CH_4 and CH_3OCH_3 predominant products.	4	11

31

1320G-IA

TABLE 3

GAS PHASE TESTING: SUPPORTED CLUSTER CATALYSTS

(continued)

Cluster	Support	Comment	Quarterly Report No.	Ref.
	Poly(styrene)	Inactive.	4	11
	TiO_2	Predominantly CH_4 produced.	7	14
$H_2FeRu_3(CO)_{13}$	Al_2O_3	Low activity; high CH_4 selectivity.	3	10
	$Zr(OPr)_4/Al_2O_3$	Low activity; good selectivities to methane and dimethyl ether.	4	11
	CeO_2	High yields of methane and oxygenates.	4	11
	MgO	Inactive up to 290°C.	5	12
$Ru_6C(CO)_{17}$	MgO	Hydrocarbon products; moderate activity; apparent Schulz-Flory deviation; deactivated rapidly.	4	11
	Al_2O_3	Low activity; high CH_4 selectivity.	4	11
$H_2FeOs_3(CO)_{13}$	MgO	Inactive.	4	11
	Al_2O_3	Low activity; produced only light hydrocarbons.	4	11
$Fe_3(CO)_{12}$	CeO_2	Good activity; apparent deviation from Schulz-Flory distribution; deactivated with time on-stream.	4	11
	$Zr(OPr)_4/Al_2O_3$	Low activity; high dimethyl ether selectivity.	5	12
$HOs_3(CO)_{11}$	Al_2O_3	High methane selectivity (>60%).	5	12
	MgO	High methane selectivity (>50%).	5	12

TABLE 3

(continued)

Cluster	Support	Comment	Quarterly Report No.	Ref.
$Ir_2Cu_4(C=CPh)_8(PPh_3)_2$	Al_2O_3	>50% methane.	5	12
$[Rh_2Pt(CO)x]_n$	CeO_2	Low activity, high methane selectivity.	5	12
	$Zr(OPr)_4/Al_2O_3$	Low activity.	5	12
	Al_2O_3	Primary product methane.	6	13
	MgO	CH_4 and CH_3OH predominant products.	6	13
$K[MnFe_2(CO)_{12}]$	MgO	Inactive.	6,7	13,14
	Al_2O_3	High methane selectivity.	6	13
$Co_2(CO)_8$	$Zr(OPr)_4/Al_2O_3$	Saturated hydrocarbons, predominantly C_{10+}.	6	13
	MgO	Schulz-Flory distribution.	6	13
$Co_2(CO)_8/Mn_2(CO)_{10}$	Al_2O_3	Schulz-Flory distribution; high CH_4.	8	15
	MgO	Predominantly oxygenates.	8	15
	$Zr(OPr)_4/Al_2O_3$	Very active; high molecular weight product.	8	15

33

TABLE 4

SLURRY PHASE TESTING: CONVENTIONAL CATALYSTS

Catalyst	Comment	Quarterly Report No.	Ref.
Fused Fe_2O_3	Baseline tests; Schulz-Flory distribution; conversion not significantly affected by mass transfer; potential S poisoning of catalyst.	5	12
Fe/Mn/K	Apparent Schulz-Flory deviation in gas phase; poor slurry activation; standard Schulz-Flory distribution; severe deactivation at high CO ratios.	5	12
Fe/Cu/K	Maximum conversion of 15%; apparent deviation from Schulz-Flory distribution; deactivation as temperature increased above 260°C.	6	13
Ru/Al_2O_3	Very low conversions.	6	13
$Fe/Cu/K/Al_2O_3$	Lower activity than in gas phase; standard Schulz-Flory distribution.	10	17
Fe/Zr/Ti/K	Lower activity than in gas phase; apparent deviation from Schulz-Flory distribution.	10	17
$Fe/ZrO_2/TiO_2$	Much lower activity than gas phase; high methane selectivity.	11	18
$Fe/Zr/Al_2O_3$	Poor activity; high methane selectivity.	11	18
$Fe/Mn/Al_2O_3$	Extremely low activity.	11	18
Fe-Y	More active than in gas phase; high methane selectivity; low selectivity to liquid hydrocarbons.	12	19
Fe-Offretite	Moderate activity; poor selectivity.	13	20
Fe/Co/K	Good activity; poor selectivity; high CH_4 yield.	14	21
Fe/Nb/Cs	Low activity at 240°C; good activity at 300°C, but produces light products.	15	22

34

1320G-IA

TABLE 5

SLURRY PHASE TESTING: SUPPORTED CLUSTER CATALYSTS

Catalyst	Comment	Quarterly Report No.	Ref.
$Ru_3(CO)_{12}/Zr(OPr)_4/Al_2O_3$	Very low conversions (2-6 wt %); apparent Schulz-Flory deviation.	6	13
$Ru_3(CO)_{12}/Al_2O_3$	Low activity; maximum 6.5% conversion.	7	14
$Fe_3(CO)_{12}/CeO_2$	Loss of metal to slurry oil; low activity.	7	14
$Ru_3(CO)_{12}/Zr(OPr)_4/Al_2O_3$	Gas phase activated; improved activity; CH_4 selectivity approaching 30%.	8	15
$Ru_3(CO)_{12}/CeO_2$	Activity comparable to gas phase; high selectivity to methane and 1-alkenes.	8	15
$Fe_3(CO)_{12}/Zr(OPr)_4/Al_2O_3$	Very low activity; Fe loss from support.	8	15
$Co_2(CO)_8/Zr(OPr)_4/Al_2O_3$	Good activity; low methane; apparent Schulz-Flory deviation.	8	15
$Co_2(CO)_8/TiO_2$	Catalyst loss from reactor; poor selectivity.	9	16

35

1320G-IA

TABLE 6

ANALYSIS OF UNREDUCED COPRECIPITATED Fe/Cu/K

Run No.	Wt. Fraction	Batch No.	Wt%		
			Fe	Cu	K
7165-66-1.2	1.00	5868-32-1.2	66.20	0.47	0.18
7002-1-1.2	1.00	5868-6-1.2	67.2 ±1.3	0.1 ±0.1	0.08 ±0.01
7165-30-1.2	0.626	5868-25-1.2	69.11	0.43	0.09
	0.374	5868-28-1.2	65.02	0.43	0.14

Table 7

EXTENDED SLURRY TEST SUMMARY

Fe/Cu/K

Phases 1 and 2

Total Run Time Days	Sample #	Time on Stream h	P psig	T °C	GHSV h⁻¹	ν min⁻¹	X_{CO+H_2}	X_{CO}	X_{H_2}	S	U	Bulk Activity mol syngas/kg cat/h	Selectivity wt%			
													C_1	C_5-C_{11}	C_9-C_{25}	$C_{26}+$
7165-30-1.2 - 19.2 wt% of Fe/Cu/K (batch nos. 5868-25-1.2, 5868-28-1.2)																
9	23	173.9	320	237.2	307.3	1200	0.194	0.154	0.235	0.968	1.48	13.85	6.2	9.8	46.1	26.8
16	40	308.9	162	237.9	303.2	1200	0.191	0.185	0.198	0.998	1.07	13.58	4.3	14.0	33.1	37.0
17	43	331.9	160	240.7	302.7	1200	0.160	0.156	0.164	0.996	1.05	11.34	4.0	25.1	35.9	27.8
20	51	403.3	167	238.7	298.4	1200	0.130	0.137	0.123	1.032	0.928	9.07	4.0	18.5	43.6	29.5
21	54	427.3	168	241.2	297.1	1200	0.148	0.175	0.121	1.043	0.722	10.26	6.4	25.1	43.9	18.4
22	60	451.4	162	240.6	297.2	1200	0.159	0.166	0.153	1.043	0.958	11.08	4.3	23.7	44.5	23.4
23	64	475.9	165	240.5	297.6	1200	0.162	0.174	0.150	1.042	0.895	11.26	5.1	23.0	46.2	24.8
24-30	7165-66-1.2 - 16.9 wt% slurry of Fe/Cu/K (batch no. 5868-32-1.2) Reactor dismantled to change slurry															
37	12	141.8	300	240.1	295.7	1200	0.197	0.166	0.228	1.00	1.37	16.43	12.2	15.1	37.6	27.3
38	15	165.6	300	241.8	296.3	1200	0.200	0.188	0.212	1.00	1.11	16.73	10.6	21.6	42.8	22.4
39	19	189.8	300	242.0	296.1	1200	0.186	0.160	0.212	1.00	1.26	15.53	8.4	25.1	43.7	19.1
42	25	260.7	300	241.7	294.4	1200	0.190	0.165	0.215	1.00	1.24	15.74	5.7	11.0	47.5	26.5
43	28	285.6	300	239.5	297.3	1200	0.189	0.174	0.204	1.00	1.15	15.86	3.3	21.4	43.4	25.8
44	32	311.1	297	238.3	297.4	1200	0.196	0.167	0.224	1.00	1.29	16.40	4.1	17.5	42.6	27.3
46	36	357.7	297	240.6	300.1	1200	0.228	0.217	0.239	1.01	1.11	19.32	6.8	15.7	45.1	23.3
49	38	428.1	300	233.0	298.8	1200	0.186	0.174	0.199	1.01	1.13	15.68	2.9	11.5	49.8	30.5
50	42	451.0	300	237.0	299.1	1200	0.183	0.176	0.190	1.00	1.08	15.44	4.1	8.5	47.8	30.2
52-60	N₂ purge	478.2	300	237.8	12.0	1200	reactor under N₂ purge after wax blockage in outlet line									

Table 7 (Cont'd.)

EXTENDED SLURRY TEST SUMMARY
Fe/Cu/K
Phases 1 and 2

Total Run Time Days	Sample #	Time on Stream h	P psig	T °C	GHSV h⁻¹	v min⁻¹	X_{CO+H_2}	X_{CO}	X_{H_2}	S	U	Bulk Activity mol syngas/kg cat/h	Selectivity wt%			
													C_1	C_5-C_{11}	C_9-C_{23}	$C_{26}+$
66	49	506.6	303	240.2	284.8	1200	0.173	0.189	0.158	1.00	0.84	13.93	2.5	13.0	43.2	34.1
67	52	529.4	302	239.3	284.7	1200	0.168	0.176	0.161	1.00	0.92	13.52	2.5	14.5	47.2	30.9
71	62	625.8	300	242.5	285.4	1200	0.183	0.191	0.176	1.00	0.93	14.75	4.6	19.1	50.3	21.2
73	66	659.6	305	239.0	298.2	1200	0.187	0.203	0.162	0.64	0.51	15.72	3.1	9.5	55.4	29.4
74	70	683.8	303	240.0	297.9	1200	0.188	0.201	0.169	0.64	0.54	15.83	4.9	10.3	56.1	25.6
79	75	803.6	308	237.4	298.7	1200	0.187	0.204	0.162	0.65	0.51	15.79	2.5	12.3	45.1	37.1
80	79	839.0	307	238.1	299.1	1200	0.176	0.187	0.150	0.65	0.54	14.83	2.6	7.5	50.5	30.3
84-100	N₂ purge	925.6	305	227.1	24.0	1200	reactor under N₂ purge after wax blockage in product outlet line and leak in slurry removal line									
101	85	958.0	320	240.7	419.2	1200	0.270	0.229	0.333	0.65	0.94	22.74	11.5	41.1	34.1	5.2
106	91	1000.1	310	238.2	422.5	1200	0.098	0.080	0.126	0.65	1.02	8.35	5.9	25.0	37.6	16.6
107	95	1023.9	310	240.2	421.2	1200	0.118	0.104	0.139	0.65	0.87	9.97	3.6	22.8	48.7	15.2
108	99	1047.8	302	242.5	423.0	1200	0.129	0.105	0.167	0.65	1.03	10.99	6.3	22.6	49.3	13.6
109	102	1071.3	307	240.9	423.3	1200	0.118	0.095	0.154	0.65	1.05	10.08	4.2	23.6	48.5	15.0
113	113	1122.7	300	261.2	652.4	1200	0.216	0.193	0.251	0.66	0.86	25.24	6.0	20.2	42.2	21.0
114	117	1146.1	300	261.8	653.6	1200	0.192	0.162	0.238	0.66	0.97	22.51	5.5	29.2	44.2	15.9
115	121	1170.4	292	260.7	653.4	1200	0.200	0.172	0.243	0.66	0.94	23.43	5.6	32.7	38.2	17.3
116	125	1194.4	295	262.0	653.7	1200	0.208	0.188	0.240	0.66	0.85	24.40	4.1	34.6	37.5	16.4
118-119	N₂ purge	1238.3	295	253.5	24.0	1200	reactor under N₂ purge after gas in line plugged									

Table 7 (Cont'd.)

EXTENDED SLURRY TEST SUMMARY
Fe/Cu/K
Phases 1 and 2

Total Run Time Days	Sample #	Time on Stream h	P psig	T °C	GHSV h⁻¹	v min⁻¹	X_{CO+H_2}	X_{CO}	X_{H_2}	S	U	Bulk Activity mol/syngas/kg cat/h	Selectivity wt%			
													C_1	C_3-C_{11}	C_5-C_{23}	$C_{26}+$
121	135	1285.8	307	261.0	647.8	1200	0.203	0.178	0.241	0.65	0.88	24.95	8.6	32.3	38.1	7.2
122	138	1308.9	313	260.3	649.2	1200	0.227	0.171	0.230	0.65	0.83	27.99	10.6	25.7	32.9	8.4
123	142	1332.0	313	261.1	650.2	1200	0.231	0.208	0.267	0.65	0.83	28.54	9.5	27.6	36.3	6.8
126	150	1405.9	320	261.1	653.8	1200	0.243	0.222	0.277	0.65	0.81	33.30	9.6	32.3	34.4	5.7
127	155	1429.6	299	261.7	652.9	1200	0.236	0.213	0.273	0.65	0.83	32.26	9.2	30.4	36.3	5.4
128	159	1453.7	297	261.6	652.1	1200	0.257	0.236	0.290	0.65	0.79	35.09	9.5	32.1	33.3	4.9
129	163	1477.9	300	259.7	652.8	1200	0.276	0.258	0.304	0.65	0.76	37.70	9.1	32.2	34.3	4.9
133	172	1548.8	298	255.9	332.3	1200	0.335	0.324	0.353	0.64	0.70	28.53	6.8	22.3	43.6	11.9
134	176	1572.4	303	254.7	331.9	1200	0.312	0.293	0.341	0.65	0.75	26.49	6.0	25.7	48.6	10.0
135	179	1596.2	303	260.2	331.9	1200	0.335	0.326	0.349	0.64	0.69	28.43	6.7	31.5	43.4	7.8
142	187	1661.1	310	260.1	371.1	1200	0.381	0.376	0.390	0.65	0.67	32.51	6.9	30.9	47.4	7.8
143	191	1685.3	307	259.4	371.9	1200	0.334	0.315	0.363	0.65	0.75	28.48	7.7	34.4	39.0	8.2
148	193	1710.4	310	259.4	183.4	1200	0.421	0.428	0.469	0.54	0.51	17.74	7.6	31.4	37.4	13.0
150	198	1758.3	305	257.4	184.5	1200	0.513	0.505	0.536	0.55	0.57	21.75	6.9	40.0	37.5	10.5
156	210	1866.5	313	257.1	185.0	1200	Reactor Shutdown									

39

Table 7 (Cont'd.)

EXTENDED SLURRY TEST SUMMARY
Fe/Cu/K

Phase 3

Total Run Time Days	Sample #	Time on Stream h	P psig	T °C	GHSV h⁻¹	v min⁻¹	X_{CO+H_2}	X_{CO}	X_{H_2}	S	U	Bulk Activity mol/syngas/kg cat/h	C_1	C_5-C_{11}	C_9-C_{23}	$C_{26}+$
157-172		7516-30-1.2 - 19.8 wt% slurry of Fe/Cu/K (batch 5868-37-1.2). Reactor dismantled to change slurry.														
178	8	77.9	300	260.2	282.9	1200	0.269	0.303	0.289	1.01	0.97	19.21	7.3	21.0	35.6	19.9
179	12	100.7	298	259.2	282.6	1200	0.326	0.326	0.325	1.01	1.01	21.13	7.2	22.4	39.6	16.6
183	21	197.4	303	259.6	281.9	1200	0.449	0.500	0.400	1.01	0.81	29.11	6.8	26.3	41.9	15.4
184	25	221.3	303	259.3	294.5	1200	0.448	0.445	0.448	0.65	0.65	30.30	5.0	25.4	48.1	16.0
185	30	245.9	308	260.0	294.8	1200	0.460	0.455	0.467	0.65	0.66	31.15	4.3	22.0	47.5	20.6
186-191	N₂ purge	272.2	305	260.0	150.0	1200	Reactor exposed to excess CO after wax blockage in outlet line.									
192	39	295.8	305	261.0	295.9	1200	0.252	0.218	0.303	0.65	0.90	17.11	3.9	12.7	31.0	3C.8
193	43	320.3	298	259.9	295.2	1200	0.296	0.269	0.338	0.65	0.81	20.11	3.5	17.4	37.8	32.2
197-206	N₂ purge	400.5	305	260.0	150.0	1200	Reactor under N₂ purge after wax blockage in outlet line. Exposed to excess CO for 8 hours.									
210	57	503.4	290	261.6	128.2	1200	0.325	0.334	0.310	0.65	0.60	9.66	4.5	16.4	39.7	26.8
210		Reactor shutdown														

40

Table 8

ELEMENTAL ANALYSIS OF $(CO_2(CO)_8)/Zr/Al_2O_3$

Run Description	Run No.	Catalyst No.	Batch No.	Before Reaction Wt%		*After Reaction Wt%			
				Co	Zr	Co	Zr	C	H
Fixed bed reactor screening	6930-34-48.2	1	7045-11-48.3	1.99	13.0				
Slurry 21 day test	7077-75-C48.4	2	7045-43-48.4	6.22	11.9	6.53 ±0.07	5.3 ±0.2	9.72	1.68
Extended slurry test	7516-72-C48.4	3	7054-78-48.4	6.72	4.51				

*Slurry extracted under N_2 with (a) toluene for 72 h, (b) hexane for 24 h

Table 9

EXTENDED SLURRY TEST SUMMARY
13.14 Wt% Slurry of $(CO_2(CO)_8)/Zr(OPr)_4/Al_2O_3$

Total Run Time Days	Sample #	Time on Stream h	P psig	T °C	GHSV h⁻¹	v min⁻¹	X_{CO+H_2}	X_{CO}	X_{H_2}	S	U	Bulk Activity mol/syngas/kg cat/h	Selectivity wt% C_1	C_3-C_{11}	C_3-C_{23}	$C_{26}+$
9	18	174.3	300	219.9	300.5	1200	0.115	0.076	0.173	0.68	1.56	13.13	9.3	42.9	36.9	2.9
13	27	270.5	305	219.0	301.4	1200	0.081	0.050	0.127	0.68	1.72	9.27	9.9	46.4	31.8	3.2
14	31	294.5	303	220.6	301.1	1200	0.122	0.081	0.182	0.68	1.53	13.94	6.2	45.6	36.9	3.5
16	38	340.8	297	220.4	301.4	1200	0.056	0.019	0.110	0.68	3.92	6.41	11.0	44.6	33.3	3.5
21	52	458.6	305	220.6	301.4	1200	0.065	0.014	0.141	0.68	7.08	7.48	11.4	44.3	33.1	3.1
24	57	507.3	300	240.4	300.6	1200	0.206	0.103	0.356	0.68	2.35	23.48	12.2	36.3	44.0	4.8
28	64	578.2	308	239.7	300.9	1200	0.133	0.042	0.267	0.68	4.32	15.19	9.2	40.2	46.9	5.2
30	69	609.8	302	251.8	298.4	1200	0.151	0.041	0.316	0.67	5.14	17.09	17.3	39.6	38.0	3.1
31	73	633.5	303	251.7	297.3	1200	0.157	0.053	0.312	0.67	3.95	17.64	18.3	32.5	40.6	3.4
35	83	727.6	317	251.7	298.5	1200	0.209	0.101	0.369	0.67	2.45	23.62	19.9	34.1	38.9	3.5
36	87	749.6	310	249.4	298.7	1200	0.202	0.091	0.367	0.67	2.69	22.84	17.6	35.7	44.2	2.8
37	91	773.3	320	248.5	298.5	1200	0.195	0.089	0.352	0.67	2.61	22.04	16.9	37.5	44.8	2.0
38	95	796.5	320	248.3	298.4	1200	0.220	0.121	0.368	0.67	2.04	24.87	18.8	32.7	44.5	3.6

Table 9 (Cont'd.)

EXTENDED SLURRY TEST SUMMARY

13.14 Wt% Slurry of $(CO_2(CO)_8)/Zr(OPr)_4/Al_2O_3$

Total Run Time Days	Sample #	Time on Stream h	P psig	T °C	GHSV h⁻¹	v min⁻¹	X_{CO+H_2}	X_{CO}	X_{H_2}	S	U	Bulk Activity mol/syngas/kg cat/h	Selectivity wt%			
													C_1	C_5-C_{11}	C_9-C_{25}	$C_{26}+$
42	106	893.2	310	249.1	299.3	1200	0.162	0.052	0.328	0.67	4.23	18.38	17.7	31.7	45.1	5.1
43	110	917.1	315	246.3	298.2	1200	0.138	0.048	0.274	0.67	3.82	15.65	16.7	33.4	46.8	5.2
44	114	940.6	293	250.6	298.9	1200	0.176	0.067	0.339	0.67	3.39	19.90	17.7	33.6	43.9	5.1
45	119	966.4	295	251.2	299.2	1200	0.159	0.087	0.303	0.51	1.76	18.06	16.6	30.0	43.9	6.6
48	126	1037.3	293	248.9	300.5	1200	0.130	0.055	0.279	0.51	2.58	14.81	14.4	31.2	50.3	6.9
49	131	1061.2	292	250.3	301.3	1200	0.135	0.064	0.273	0.51	2.15	15.39	14.9	34.0	45.8	7.1
50	133	1086.4	295	252.2	300.5	1200	0.151	0.088	0.277	0.51	1.60	17.24	19.3	33.8	39.6	5.5
51	134	1134.2	290	251.9	305.0	1200	0.117	0.033	0.283	0.51	4.41	13.53	19.3	26.2	43.6	7.6
56	145	1230.1	290	251.9	300.2	1200	0.107	0.023	0.271	0.51	5.92	12.14	20.5	36.9	34.7	4.1
58	146	1277.9	290	251.9	300.4	1200	0.103	0.017	0.273	0.51	8.33	11.73	14.1	31.8	50.8	6.1
59	150	1301.6	290	251.8	300.2	1200	0.137	0.060	0.287	0.51	2.40	15.55	16.3	31.8	49.4	5.3
62	151	1373.6	290	252.8	300.3	1200	0.113	0.028	0.281	0.51	5.12	12.86	14.7	25.3	49.3	9.3

43

Table 9 (Cont'd.)

EXTENDED SLURRY TEST SUMMARY

13.14 Wt% Slurry of $(CO_2(CO)_8)/Zr(OPr)_4/Al_2O_3$

Total Run Time Days	Sample #	Time on Stream h	P psig	T °C	GHSV h⁻¹	v min⁻¹	X_{CO+H_2}	X_{CO}	X_{H_2}	S	U	Bulk Activity mol/syngas/kg cat/h	Selectivity wt%			
													C_1	C_5-C_{11}	C_9-C_{25}	C_{26}^+
63	154	1398.3	600	250.4	301.9	1200	0.149	0.063	0.322	0.49	2.50	17.04	19.5	26.9	36.7	10.1
64	155	1421.5	600	250.0	300.4	1200	0.155	0.073	0.318	0.51	2.19	17.72	17.9	26.9	38.2	10.6
66	162	1469.5	603	250.8	299.6	1200	0.118	0.041	0.268	0.51	3.32	13.36	18.1	30.2	37.8	7.7
70	168	1566.1	610	248.3	300.6	1200	0.100	0.040	0.218	0.51	2.75	11.39	20.3	38.7	28.9	7.6
71	171	1588.8	613	248.9	300.6	1200	0.089	0.019	0.225	0.51	5.78	10.12	15.7	24.6	48.0	11.7
79	181	1759.1	623	280.1	299.8	1200	0.281	0.179	0.484	0.50	1.36	32.00	25.8	33.0	31.3	2.8
80	184	1782.7	613	280.5	299.9	1200	0.265	0.135	0.522	0.50	1.94	30.11	28.3	32.3	28.0	2.7
83	193	1854.3	620	281.3	300.2	1200	0.293	0.191	0.496	0.50	1.31	33.38	24.7	34.1	30.1	5.1
84	196	1878.0	617	279.5	300.3	1200	0.271	0.174	0.463	0.50	1.34	30.83	24.3	34.8	30.2	5.4
85	197	1900.8	610	278.5	300.1	1200	0.270	0.172	0.463	0.50	1.36	30.68	26.3	30.4	29.7	6.2
87	203	1948.6	620	277.6	300.4	1200	0.245	0.149	0.435	0.50	1.47	27.89	28.2	27.6	27.5	7.3

Table 10

EXTENDED SLURRY TEST SUMMARY

11.22 Wt% Slurry of $(CO_2(CO)_8)/Zr(OPr)_4/Al_2O_3$

Phase 2

| Total Run Time Days	Sample #	Time on Stream h	P psig	T °C	GHSV h⁻¹	v min⁻¹	X_{CO+H_2}	X_{CO}	X_{H_2}	S	U	Bulk Activity mol/syngas/kg cat/h	Selectivity wt%			
													C_1	C_5-C_{11}	C_3-C_{23}	C_{24}
3	7	31.2	303	221.2	303.9	1200	0.107	0.057	0.154	1.06	2.83	14.72	18.5	29.5	23.7	3.4
6	11	102.2	307	220.9	302.0	1200	0.064	0.033	0.109	0.67	2.18	8.72	16.6	21.6	25.9	7.9
7	14	126.1	317	249.9	302.7	1200	0.285	0.170	0.455	0.67	1.79	39.08	13.7	33.8	45.8	0.6
9	17	149.9	320	248.9	304.0	1200	0.262	0.143	0.436	0.68	2.07	36.06	12.3	35.7	47.3	1.6
10	20	175.4	313	249.4	303.6	1200	0.245	0.134	0.409	0.67	2.05	33.68	14.6	29.3	43.8	5.2
11	23	230.5	313	249.2	303.2	1200	0.238	0.141	0.382	0.67	1.82	32.69	14.3	27.8	45.8	5.7
14	31	256.5	317	249.4	302.9	1200	0.244	0.157	0.374	0.67	1.61	33.56	14.7	34.2	39.2	4.3
15	34	281.1	293	250.4	303.7	1200	0.236	0.155	0.355	0.68	1.55	32.43	14.7	29.6	44.5	4.5
16	38	305.7	297	251.4	304.1	1200	0.263	0.182	0.383	0.68	1.42	36.27	15.4	33.3	38.7	4.7
17	41	330.5	303	250.2	303.9	1200	0.250	0.176	0.361	0.68	1.39	34.47	15.1	34.8	37.9	4.5
18	43	354.5	303	251.7	303.8	1200	0.292	0.225	0.392	0.68	1.18	40.26	18.5	30.2	34.9	4.1
23	54	474.2	300	248.7	306.2	1200	0.215	0.162	0.319	0.51	1.01	29.84	19.7	28.2	32.7	3.3
24	56	497.5	300	249.4	306.8	1200	0.189	0.121	0.323	0.51	1.37	26.31	23.1	19.4	27.1	4.9
29	62	618.5	300	249.0	306.9	1200	0.228	0.175	0.331	0.51	0.97	31.67	20.3	18.5	21.5	4.2

FISCHER-TROPSCH SLURRY REACTORS

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

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

FIGURE 1

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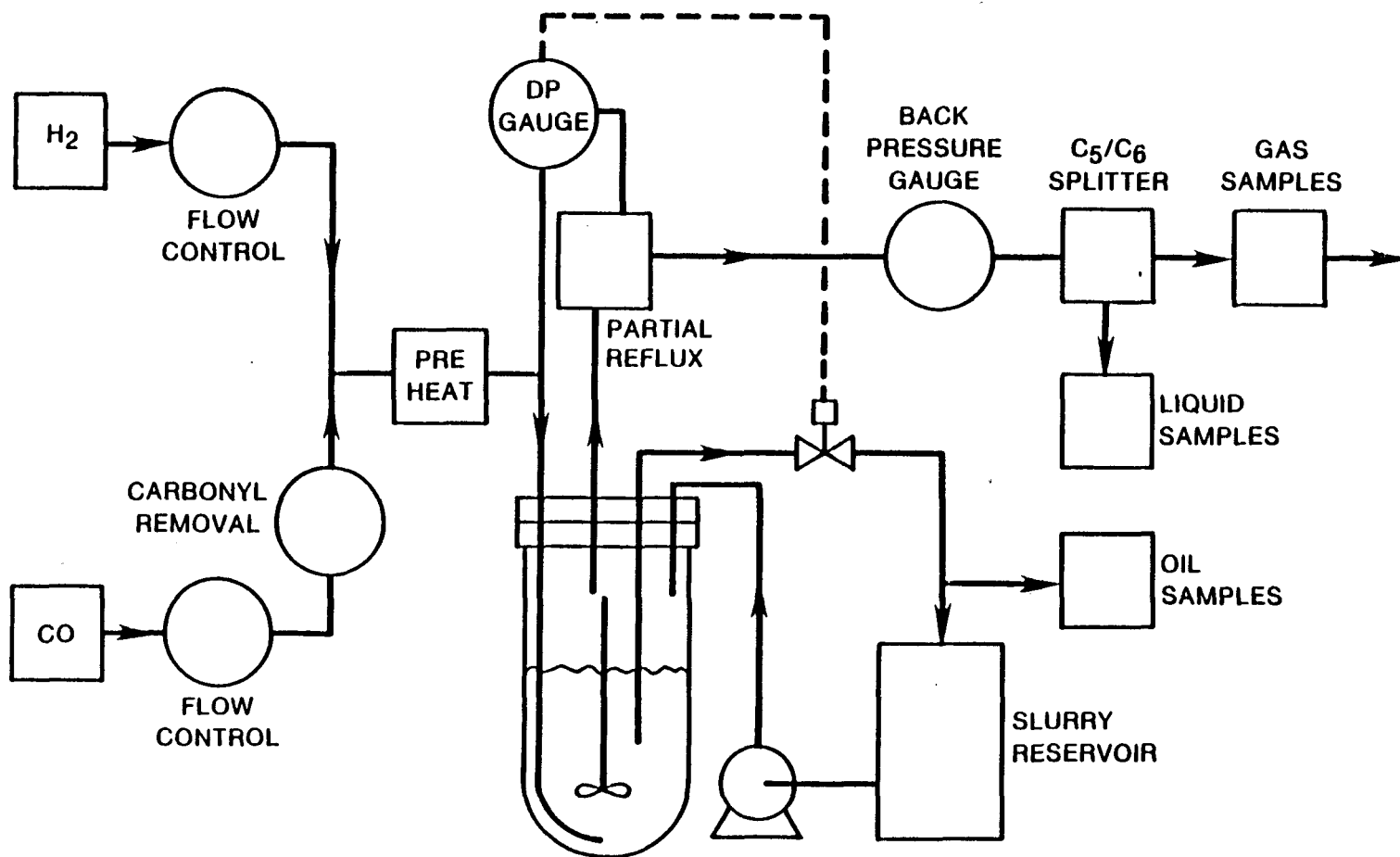
The product stream from the partial reflux condenser flows via a heated line to a pressure reduction stage, and then to a C_5/C_6 splitting column, to produce a condensed liquid phase and a gaseous phase. The gaseous stream consists of unreacted syngas, CO_2, and products with carbon numbers from C_1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

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

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

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

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

FIGURE 2

PRODUCT ANALYSIS AND DATA ACQUISITION SCHEME

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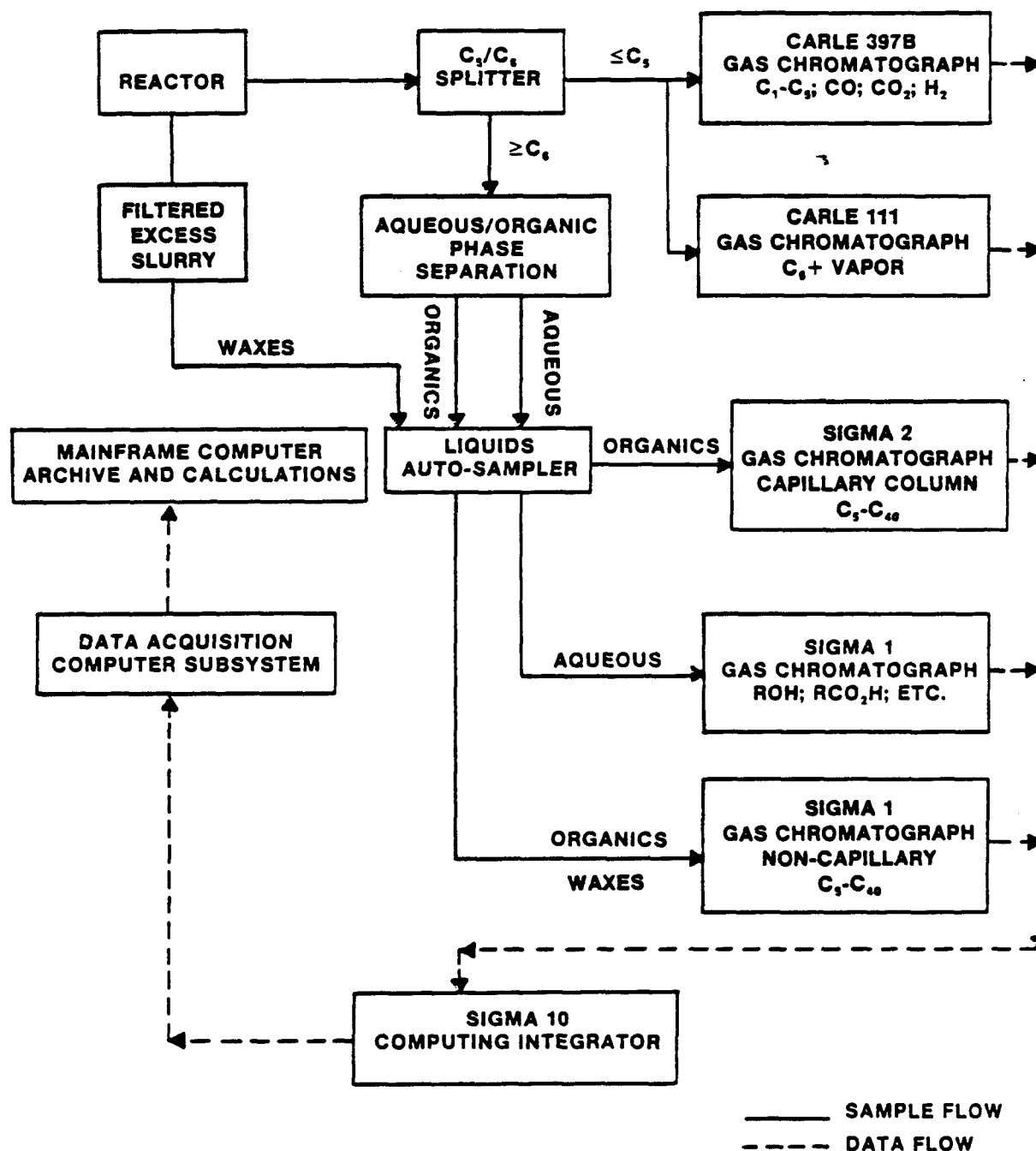
aqueous phase samples are analyzed for C_1-C_6 alcohols, aldehydes, ketones, and acids using a 3-mm x 3-m 10% SP1200/1% H_3PO_4 on Chromosorb/WAW column. Samples of the separated organic phase are analyzed for C_5-C_{40} hydrocarbons using a 3-mm x 3-m SP2100/Supelcoport column, or for additional resolution,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

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