<u>Title:</u> **Technology Development for Iron Fischer-Tropsch Catalysts**

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<u>Objective:</u>

The objectives for the catalyst development are, on the one hand, the attainment of the highest possible activity and life, and on the other hand, the highest possible selectivity to the desired products. In the present study the catalyst is to be designed to operate in a slurry phase reactor. Furthermore, the catalyst is to be based on iron and is to be prepared in a continuous process. The continuous preparation is to be designed so that catalysts with a common formulation that are prepared at different times will have the same catalytic properties.

The research program was designed to remove much of the uncertainty regarding the following aspects of catalyst synthesis and testing:

1. The role of promoters and additives.
2. The optimum method of preparation.
3. The reproducibility of large batches of iron catalysts.
4. The pretreatment of the catalysts.

The research to produce data to address the above four issues is outlined below and the progress toward attaining these goals is described.

Task 1 consists of several subtasks. The first, Subtask 1, is to assess the literature concerning the preparation of iron Fischer-Tropsch catalysts and to provide a topical report on previous catalyst improvements. A draft of a technical report is essentially complete at present. STATUS: 90% COMPLETE.

Subtask 1.2 concerns the preparation of the precipitated iron catalyst in a reproducible manner. This has been accomplished. STATUS: COMPLETED.

Subtask 1.2.1 consisted of defining a number of preparative conditions and procedures. The following summarizes the progress made to date:

1. The final pH of the precipitation of the mixture was studied on the basis of the production of a high surface area. Reproducible preparation procedures that yield a solid with a surface area of about 300 m^2/g have been developed when the final pH is in the range of 8-10.5. STATUS: COMPLETED.

2. The maximum iron concentration was primarily determined by the ability to pump the slurry that resulted following the precipitation process. With the equipment that is at hand the maximum iron concentration that could be used was 1.6 molar; however, ease of mixing with the wash water dictated that a more reasonable concentration was 1.2 M iron solution when iron(III) nitrate was used. The base, ammonium hydroxide, was added as a concentrated solution (about 15-16 M 28% ammonia). STATUS: COMPLETED.

3. Several bases were employed in the early studies. Because of the ease of maintaining a steady pH in the precipitation vessel, ammonium hydroxide has been used in the preferred preparation procedure. The use of ammonium hydroxide provides the opportunity to recover and recycle the ammonia when it is used in a large catalyst preparation plant. This is current practice by catalyst manufacturers. Furthermore, it is not necessary to completely remove the base when ammonium hydroxide is used, as it is if sodium hydroxide is used for the precipitation of the iron. The extensive washing required when the alkali metal is used for the base is two-fold: (1) if potassium is used as the promoter it is necessary to remove the sodium to a level below about 0.1 wt% and this requires much washing or (2) even if sodium could be used as the alkali promoter extensive washing would be required to reduce it to the low level needed in the finished catalyst. Ammonium nitrate, the salt produced during catalyst precipitation when ammonium hydroxide is used, volatilizes at about 170-200°C and for this reason does not have to be completely removed. Likewise, if a calcination step is not included, the amount of ammonium nitrate left from the two washings can be eliminated during the carbiding pretreatment step. The use of ammonium hydroxide has one disadvantage in that copper, if it is to be used in the catalyst formulation, cannot be added by coprecipitation with the iron since a soluble copper amine complex is formed when ammonia is present. However, it is possible to incorporate copper even when ammonia is used if it is done by impregnation following the final drying step or it can be added to the slurry prior to the final drying step when spray drying is utilized. STATUS: COMPLETED.

4. Various temperatures of precipitation were utilized from near 0°C to about 90°C for some of the preparations. For the precipitation of the iron oxyhydroxide from an iron nitrate solution, lower surface area materials were produced at the higher temperatures. In our preferred approach, the reagents that are added are at or near room temperature and, because of the heat of reaction, the precipitation is effected at about 35-40°C. STATUS: COMPLETED.

5. Because of mixing considerations, it was found that precipitation in a continuous stirred tank reactor (CSTR) using about 5 minutes of average residence

time led to reproducible catalyst preparations and permitted continuous operations. STATUS: COMPLETED.

6. Aging the precipitate at a high temperature was found to cause a decrease in the surface area; the rate of the loss of area increased with increasing temperature. At about room temperature and a pH of about 8-9, the loss of surface area during a few hours of aging was not noticeable. However, in the continuous mode of precipitation and washing that was used the precipitate was transferred to the wash vessel in less than 10 seconds and there it was diluted with wash water to the same (about 1.2 M iron slurry) concentration as for the precipitation step. STATUS: COMPLETED.

7. In the continuous precipitation mode, the precipitate was collected using a drum filter, and the collection rate was at the rate that the precipitate was produced. STATUS: COMPLETED.

8. The washing was accomplished by precipitate collection followed by re-dispersion and washing cycles. Because of the capacity of the drum filters this operation could not be effected at the same rate as the precipitation. It was found that the filtration rate following the first washing was approximately one-half that of the fresh, un-washed precipitate. Likewise, there was a decrease of about one-half in the rate of the second filtration for the precipitate following the second washing to that of the precipitate following the first washing. Washing the filter cake using vacuum to induce liquid flow was inefficient compared to the re-dispersion and washing cycles unless the filter cake was very thin so that it permits reasonably rapid flows of water. STATUS: COMPLETED.

9. The wet cake, as removed from the drum filter following the second washing, contained about 20 wt.% solids. In addition to the 20 wt.% iron oxide, the slurry contained water and ammonium nitrate. The amount of ammonium nitrate was usually less than about 1-2 wt.%. STATUS: COMPLETED.

10. Drying of small batches of the washed precipitate was effected at several rates and with several slurry bed depths. In addition, spray drying was utilized. Slow drying, from several minutes up to two days, did not have an impact upon the surface area of the dried material. Drying in a bed depth greater than about 1-2 inches produced a heterogeneous solid. Portions of a slurry of a high surface area material were dried in thin layers and in the slurry spray drying; the surface of the completely dried material and the material following calcination at 300°C were the same and did not increase with silica content above 4% SiO_2 (figure 1). The surface area of the calcined material depended upon the calcination temperature (figure 2) and the length of time at the calcination temperature. It did not appear that the rate of heating of the dried precipitate to the calcination temperature had a major impact on the surface area of the calcined material. STATUS: COMPLETED.

Subtask 1.2.2. Alkali was to be added to a series of iron oxide catalysts that had a range of surface areas. To date most of the work has been done with high surface area precipitates. Alkali has been added by impregnation with an aqueous potassium nitrate solution or by the addition of potassium isopropoxide to a slurry of the iron precipitate in the reactor start-up oil. STATUS: COMPLETED FOR HIGH SURFACE PRECIPITATES.

Subtask 1.2.3. A series of catalysts have been prepared that contain increasing amounts of aluminum oxide, silicon dioxide or zirconium dioxide. The zirconia promoted catalyst was less active than either the aluminum or the silica promoted catalyst. For the silica support, it did not appear that loadings higher than about 5.0 wt.% had a detrimental effect on the activity; however, for the alumina support the activity appears to reach a maximum at about 4-5 wt.% alumina and to decrease with increasing alumina content. STATUS: 50% COMPLETED.

Subtask 1.2.4. A process configuration that involves the addition of the iron and aluminum or silica in one stream and the base in the other stream has been defined. The alkali promoter has been added by impregnation when the precipitate was not spray dried. For the spray drying process, the alkali was added to the slurry following the last drying. At the pH used for the present study, it was ascertained that the non-reducible metal oxide was retained essentially quantitatively in the precipitate.

Three methods of solids collection were to be evaluated and two of these have been completed to date. A continuous vacuum filtration technique has been evaluated using a drum filter apparatus that employs vacuum for the collection and water removal from the solid and a positive air pressure to assist in the removal of the solid from the filter. It has been possible to operate the drum filter for collecting the initial precipitate and for washing the precipitate in a continuous operation mode. Spray drying has been effected at the UCI and has been found effective for producing spherical particles in the 60 micron range. STATUS: 90% COMPLETE.

Subtask 1.3. A laser pyrolysis procedure was to be used to prepare small, ultrafine iron carbide particles. This has been accomplished on a small (up to 1 gram) scale for $Fe_{22}C$ and for Fe_7C_3. A large batch (10-12 g.) was prepared using this procedure; however, either isolation of the solid from the collection system or entrained oxygen from the CO used in the preparative procedure led to the formation of about 15% iron oxide when the sample was heated in an inert gas during the pretreatment procedure. A larger collection system has been designed and constructed and this should permit us to place the iron carbide prepared by this technique into the start-up oil without exposure to the atmosphere. STATUS: 80% COMPLETE.

Subtask 1.4. The goal of this subtask is to develop a suitable procedure for pretreating iron catalysts. It has been found that the preferred pretreatment for the ultrafine iron catalysts produced by precipitation or the ultrafine iron oxide purchased from a commercial vendor is by heating in CO to and at the reaction temperature for

24 hours. CO is effective for the reduction of the precipitate to Fe_3O_4 so that the sample is comprised of essentially Fe_3O_4 by the time the sample has been heated to 270°C in CO during about five hours (1). It was found that much of the surface area was lost during the reduction in hydrogen to produce about 30% metallic iron with the remainder being Fe_3O_4; during synthesis the metallic iron was quickly converted to a carbide (2). Exposing the catalyst to a H_2/CO mixture without a prior catalyst pretreatment led to a catalyst with lower activity than one first pretreated in CO. Therefore, for these catalysts a pretreatment in CO for about 24 hours is preferred. During the CO pretreatment, about twice as much CO_2 is formed as is required to produce the iron carbide. Apparently some carbon is formed by CO disproportionation; the role or beneficial effect, if any, of this carbon has not been determined to date. Thus, while the preferred pretreatment has been defined as far as this project is concerned, far more is unknown about pretreatment than is known. STATUS: COMPLETED.

Subtask 1.5. Catalyst characterization to determine the bulk and surface composition and structure of the iron catalysts at various stages of the preparation, pretreatment and synthesis has been carried out. Three 300-ml CSTR and one 1-liter CSTR have been constructed and operated so that a catalyst sample can be withdrawn from the reactor at various stages of the pretreatment and FTS synthesis. With the l-liter CSTR accurate mass balances and product selectivities can also be obtained during this operation. Analysis of the off-gas stream permits a calculation of the extent of carbiding of the catalyst.

A typical curve showing the formation of CO_2 during the pretreatment period is shown in figure 3. The activity of the catalyst during one such catalyst withdrawal period of operation is shown in figure 4.

The samples withdrawn from the reactor contain heavy wax after they have been exposed to synthesis conditions. This wax is extracted from the catalyst in a Soxhlet apparatus using toluene for the extraction; during the entire extraction period the catalyst in the extraction apparatus is blanketed with flowing ultrapure nitrogen. However, it appears that this procedure exposes the catalyst to oxygen so that the catalyst is slowly passivated; thus, a catalyst that is withdrawn directly from the reactor is pyrophoric and one that has been subjected to the extraction procedure is not.

The surface area of the catalyst undergoes a dramatic decrease during the 24-hour pretreatment period. Thus, a sample that originally had a surface area of 300 m^2/g rapidly loses area so that at the end of the reduction/carbiding period the area is on the order of 60 m^2/g. Following the 24-hour pretreatment period, there is a gradual loss of surface area; this may be due to changes in the physical properties of the solid catalyst or due to a gradual accumulation of hard wax that becomes more and more difficult to remove from the pores of the catalyst (figure 5).

Mössbauer spectroscopic data indicate that a 24 hour pretreatment in CO at 260°C and 8 atm. in a tetralin solvent almost completely converts ultrafine iron oxide

(about 3 nm) to iron carbide (figure 6). However, pretreatment in hydrogen under the same conditions resulted in reduction of about 33% of the iron to metallic Fe; the remainder was Fe_3O_4. Exposure of the CO pretreated catalyst to a 1:1 H_2/CO synthesis gas resulted in the gradual reoxidation of the carbides to Fe_3O_4. During the first 2 hours of exposure of the H_2 pretreated sample to synthesis gas, the metallic Fe was converted to iron carbides. Further exposure of the H_2 pretreatment sample to synthesis gas did not result in a composition change of the catalyst (figure 7). Therefore, it is concluded that iron carbides with different oxidation characteristics were formed in these two cases. The additional Mössbauer studies will be described in more detail in another presentation at this meeting.

It has been shown that activation of a high surface area Fe_2O_3 catalyst in CO in a CSTR using tetralin as solvent results in an activity that is three times that of the material that is activated in H_2 or directly in the syngas (2). Independent of the catalyst activation, similar methane and CO_2 selectivities are obtained. This suggests that the active catalytic phase is the same for the three pretreatments. Since the particle size estimated by XRD shows a variation within 30%, the difference among the activities of the differently activated catalysts can be attributed to differences in the concentration of active sites on the catalyst surface rather than the extent of the surface. STATUS OF SUBTASK 1.5: 75% COMPLETED.

Subtask 1.6. The CAER PI meets with Dr. Freddie Tungate at least once a month to review the results of the previous month's work.

Task 2. Currently the CAER operates eight 1-liter autoclaves for catalyst testing. These reactor systems were constructed and put into operation to accomplish the studies needed to complete the work for the present contract. These reactors have been operated with 20 wt.% catalyst loading and at flow rates of 3.4 NL/hr/g Fe. This catalyst loading and gas flow rate are higher than have been utilized by most, or all, investigators using CSTR's in the US for Fischer-Tropsch catalyst testing. Many problems were encountered in operating under these severe conditions.

The most serious problem that has been encountered has been the loss of start-up solvent at a more rapid rate than it is replaced by liquid FTS products. This problem does not appear to have been reported for earlier studies with the CSTR's. A recent treatment of FTS reactors to address this issue has been reported (3). These

workers define α/β, where $\beta = \exp[-427.218 \ (\frac{1}{T}-1.029807 \ x \ 10^{-3})]$, where T is

temperature in °C (or $P_i = P_o\beta^i$, where i is the carbon number and P_o is some constant) and α is from the Anderson-Schulz-Flory plot. This parameter defines the fraction of each product of the FTS that remains in the liquid phase in the reactor. Whenever the ratio α/β is greater than one, the FTS products will accumulate in the reactor at a faster rate than gaseous products leave. Under these conditions, the reactor liquid level will increase with time. We have made calculations using our conversion and operating conditions based upon a single alpha value and the

reported hydrocarbon vap.. pressures (4). As shown in figure 8, liquid will not accumulate, but will be lost, during the operation of the CSTR with our low α iron catalyst. Our experimental data agree with this expectation.

During operation with many of our catalysts at the 20 wt.% loading and conversions at the 90% level, we have noted a rapid drop in conversion at 200 to 400 hours of operation. It now appears that the decrease in the liquid level in the reactor, with a corresponding increase in catalyst slurry loading, was the primary cause for this decline in conversion. For some active catalysts we have even observed a completely dry catalyst mass when the reactor was opened following the drop in catalyst activity. The dry catalyst mass was active since it smoldered, or even ignited, when exposed to the air in the laboratory. Thus, it is clear that the rapid decline in conversion was due to physical problems associated with the reactor system, and not the catalyst. It is surprising that this problem has not been encountered and reported in prior studies.

Thus far in the contract, more than 100 catalyst formulations have been tested for periods of 2 to 10 weeks of continuous operation. Mass balances are usually in the 94-105% range. Analyses for products through carbon number 40 are routinely made and are included in the alpha plots. Olefin selectivity data are obtained for carbon numbers 2-40.

The operating conditions specified in the contract include the following:

Process conditions

H_2/CO ratio in the feed	0.7
Synthesis temperature	270°C
Pressure, bar	12
Syngas flow rate(Nm^3/hr/gFe)	3.4

Desired activity and selectivity

CO conversion, %	90
CO + H_2 conversion, %	88
Total CO + H_2 used per kg Fe (Nm^3/hr.)	2.6
Hydrocarbons produced per Nm^3 syngas used:	
Total, g.	178
C_{3+}, g	166
STY of C_{3+} in 24 hr (kg/m^3 of reaction chamber)	900

As shown in figure 9, a catalyst containing 4.4 atomic percent Si and 0.5 wt% K had an activity for the conversion of CO under the above conditions that was at, or

exceeded, 90%. Furthermore, there was sufficient activity for the production of CO_2 so that the combined conversion of CO + H_2 was only about 80%, much less than the 88% that was targeted in the contract. The data plotted in figure 9 is for the actual CO conversion and in figure 10 as the percentage of the targeted conversion of 90%. As can be seen the conversion meets the targeted value.

Because the levels of the alcohols and other oxygenates are low with the silica and potassium promoted iron catalyst, the hydrocarbon yield is produced whenever the targeted CO conversion is obtained. However, the methane production fits the Anderson-Schulz-Flory (ASF) plot so that, even though the C_2 fraction lies below the ASF line, the C_{3+} hydrocarbon yield is below that of the targeted value. STATUS: 80% COMPLETED.

Task 3. The aging studies have been complicated because of the decrease of the liquid level in the reactor during operation. Thus, we have been able to operate during a one month (30 days) period with a decline in activity of 1.5 % CO conversion per week; however, there have been many runs where this was not accomplished. The data in figure 11 is typical of many reactor runs. Initially the CO conversion is approximately 90%. However at about 100-200 hours there begins a rapid decline in CO conversion followed in nearly all instances in a recovery of part of the initial CO conversion. Following the decline and recovery of about 80% of the initial CO conversion, the activity declined only at a rate of 0.12% per day (0.85% per week). Two attempts have been made to obtain catalyst samples during the period of activity decline; however, in both of these runs the activity remained essentially constant for four weeks of continuous operation.

In summary, the 4.4 or 5 atomic % silica promoted iron catalyst that contains 0.5 wt.% K appears to have the required stability so that the activity decline will be equal to or less than the targeted 1 % CO conversion per week; however, operating problems during the two months of continuous running has prevented us from attaining this level of activity for two months on a consistent basis. STATUS: 50% COMPLETED.

Task 4. A design basis has been presented to United Catalyst, Inc. personnel who will develop the plant design, specify equipment, and make a cost estimate for a plant that will have a capacity of 100 pounds of catalyst per week. UCI personnel are currently working on the design for this plant. Iron catalysts have been prepared at the design rate at the CAER laboratory, and in quantities up to 50 pounds during 16 hours of continuous operation. Thus, no scale-up will be involved in the plant design. The plant will utilize ammonium hydroxide as the base and iron nitrate as the iron source. Silica will be added together with the iron nitrate solution and will be derived either from sodium water glass or from the hydrolysis of silicon n-butoxide, which is the preferred silica source. Precipitation and two washings will be accomplished on a continuous basis using drum filters to collect the solid at each stage. When the silica is added as a sodium waterglass additional washing will be required to reduce the sodium level to less than 0.1 wt.%. Potassium will be added to the iron slurry prior to

884

spray drying. Catalyst calcination, when used, shall be in a rotating drum with countercurrent flow of solid and drying air.

TESTING UCI CATALYSTS FOR LA PORTE OPERATION

About 50% of the effort during the past year has been in testing of catalysts prepared by UCI. The goal of this testing is to obtain a catalyst for the upcoming run at La Porte. Initially four catalysts were tested at CAER, and portions of one or more of these catalysts were tested by other organizations. From the four catalysts, two were selected for further testing at CAER, and results of this testing is described below. The runs made with two formulations of these two catalysts are summarized below:

Run	Catalyst[a]	Pretreat	Solvent	Temp.	Pressure	Flow Rate
75	1185-61	1	DRAKEOL 265	200	200	1.25
76	1185-57	1	DRAKEOL 265	200	200	1.25
83	1185-61	2	DRAKEOL 265	200	200	2.5
84	1185-57	2	DRAKEOL 265	200	200	2.5
90	1185-61	3	C-28	270	175	2.4
91	1185-57	3	C-28	270	175	2.4
100	1185-78	3	C-28	270	175	2.4
101	1185-75	3	C-28	270	175	2.4
104	1185-78	3	WAX[b]	270	175	2.4
105	1185-75	3	WAX[b]	270	175	2.4

Pretreat 1: 280°C; to 200°C in nitrogen; heat-up at 7°/min in 150 psig H_2/CO = 0.7 (25% Nitrogen) at 1.0 Nl/hr.g(Fe); stirrer = 750 rpm.

Pretreat 2: 265°C; 150 psig CO (25% nitrogen); heat to 200°C at 2°/min. Then at 7°/hr; 2.0 Nl/hr.gFe; 12 hours at 265°C; stirrer at 750 rpm.

Pretreat 3: 270°C; 175 psig CO at 1.4 Nl/hr.gFe; heat to 270°C at 2°/min. And hold at 270 for 24 hours; stirrer speed 750 rpm.

a. Catalyst 1185-57 contained about 30 wt.% Kaolin and catalyst 1185-61 was an unsupported iron catalyst containing only 0.1 Wt% k_2o; catalyst 1185-75 was prepared to duplicate 1185-57 and 1185-78 was to duplicate 1185-61.

b. Polyethylene wax.

The catalysts produced following the pretreatments used for runs 75 and 76 were not very active; for run 75 the CO conversion started at about 35% and declined to about 10% after 24 hours and remained at this level for 140 hours and for run 76 the CO conversion started at about 58%, declined to 30% after 24 hours and then gradually increased during the next 175 hours of operation to about 45%. The pretreatment for these two runs followed the temperature ramp and pressure used during the last run at LaPorte with a gas mixture containing 25% nitrogen and 75% of a H_2/CO = 0.7 mixture.

Runs 83 and 84 were to repeat runs 75 and 76 except that a different pretreatment was used. Instead of using the H_2/CO gas mixture, only CO was used to make up 75% of the pretreatment gas with the remainder being nitrogen. The unsupported catalyst (UCI 1185-61) initially converted about 90% of the CO; at about 200 hours a decline in activity occurred so that the conversion at about 300 hours was about 70%. The initial activity for the kaolin containing catalyst was about 90% CO conversion; however, for this run the activity began to decline at about 100 hours.

Runs 90 and 91 were intended to reproduce runs 83 and 84 with two major exceptions: (1) the start-up oil was pure octacosane (a C_{28}-alkane) so that the measured alpha value would not be impacted by the start-up oil as it was when Drakeol was used and (2) the pretreatment gas was pure CO undiluted by nitrogen. The CO conversion of the unsupported catalyst remained at 90% for 350 hours (about 15 days); following this period there was a decline in activity. Likewise, about 5 grams of the start-up oil distilled from the reactor and condensed in the hot trap per day so that there was a gradual loss in liquid level in the reactor. The activity of the kaolin containing catalyst was similar to that of the unsupported catalyst at about 90% for more than 300 hours, and then the conversion declined. The data in figures 12 and 13 show that the unsupported catalyst has lower water-gas-shift activity since the H_2 conversion is only slightly less than that of the CO whereas for the kaolin containing catalyst the H_2 conversion is 10-12% lower than that of the CO.

Runs 100 and 101 were to reproduce runs 90 and 91 to demonstrate that the second catalyst preparation resulted in a catalyst with activity and selectivity properties that were the same as those of the earlier preparation used for runs 90 and 91. As shown by comparing the data in figures 14 and 15 with those in figures 12 and 13 it is evident that both catalysts have a similar activity. In both runs the CO conversion declined following about 300 hours of operation; this is most likely due to the loss of the C_{28} oil during operation. After about 23 days of operation, additional C_{28} oil was pumped into the reactor; however, this did not restore the CO conversion, and the conversion continued to decline.

In an effort to reduce the rate of loss of the start-up oil, a polyethylene wax was obtained from Allied-Signal. This wax was supposed to have a molecular weight corresponding to C_{50} and therefore should have a much higher boiling range than either the Drakeol or the C_{28} alkane. While the highest weight % alkane occurred at about C_{50}, the wax contained a wide range of alkane numbers, and showed significant concentrations of alkanes from below C_{20} to about C_{90}. The purpose of this run was to learn of the productivity of the two catalysts at higher pressures and flow rates. Using the lower boiling solvents would lead to such a rapid loss of solvent under these higher flow and temperature conditions that reliable data could not be obtained. The initial operation using this solvent produced CO conversions that were similar to those obtained in the lower boiling solvents; however, this material contained sufficient low boiling material so that start-up oil was lost from the reactor nearly as rapidly as with the other solvents. The data from this run are only of qualitative value. It does not appear that an increase in the total pressure caused a significant alteration of the

conversion when using the same inlet flow rate of synthesis gas. However, the general conversion curve was continued when the inlet gas flow rate was increased from 2.4 to 4.8 NL/hr.-g.Fe only if the temperature was increased from 270° to 300°C.

A sample of hydrogenated hard Fischer-Tropsch wax has been obtained from the U.S. distributor of SASOL wax. This material will be analyzed and used for further studies if it indeed has the higher molecular weight distribution that is expected.

Similar alpha values are obtained with the two catalysts and for the various solvents. However, there are deviations from the alpha plots at higher (above about C_{15}) carbon numbers when the Drakeol was used (figures 14 and 15). ASF plots that are typical of the two catalysts obtained using the C_{28} alkane solvent are shown in figures 16 and 17. While one can conclude that the plot shows a two-alpha plot, the data do not deviate greatly from that required for a one-alpha plot. Considering the data to produce a two-alpha plot yields values of about 0.63 and 0.75 for the alpha values. Methane production at the 90% CO conversion period is about 8-10 wt.% of the hydrocarbon products. The light gases have a lower alkene fraction than is expected for catalysts containing higher potassium content. Thus, the C_2 fraction is comprised of 90% or greater of ethane and the C_4 fraction is only about 60% alkenes.

One of the objectives of the study was to learn whether the spherical shaped catalyst particles with an average size of 60 microns survived during the pretreatment and use. In the first test of this at the CAER, the catalyst was pretreated for 24 hours and then used for 24 hours of synthesis. The material was withdrawn from the reactor, extracted to remove the wax and then examined by SEM. The pictures clearly showed that essentially all of the 60 micron spheres had been broken up so that all of the catalyst was now present in the individual 1-2 micron particles that make up the 60 micron spheres. In an effort to learn whether this breakup of the spheres was due to carbiding or to the agitation in the CSTR, a run was made in which the material was dispersed in the C_{30} oil, heated to the pretreatment temperature under nitrogen pressure and then held at this temperature for 24 hours with stirring. This sample was treated as the carbided sample and then examined by SEM. The pictures showed that agitation alone was adequate to break up the catalyst spheres to the individual particles that make up the spheres.

A carbiding run was attempted in the CAER six-foot long, two-inch inside diameter reactor. In the first attempt, a solid deposited in the bottom 6-12 inches of the reactor so that the carbided sample could not be collected. The solid withdrawn from the reactor ignited in air so it is apparent that it was carbided. A sample of the solid from the bottom of the reactor was withdrawn without exposure and then treated to remove the wax. Examination of this sample in the SEM indicated that the spherical particles had been retained. Likewise, a sample withdrawn from the liquid at the upper portion of the reactor contained spherical particles. The results of this unsuccessful attempt to prepare a pound of carbided catalyst suggest that carbiding alone does not cause the spherical particles to disintegrate during a 24 hour pretreatment in flowing CO.

Accomplishments & Conclusions:

1. Catalysts (up to 50 lb.) have been prepared on a continuous basis at a rate that exceeds the design rate for the 100 lb.catalyst/day rate. The data given to UCI for the plant design will therefore not have to be scaled up. It has been demonstrated that the catalysts can be prepared on a large scale (10-50 pounds) in a manner that provides high (300 m^2/g) surface area and reproducible activity.

2. The optimum level (about 5 wt.%) of silica has been determined for producing the maximum surface area; however, the ultimate conversion, based upon gram of iron in the catalyst, does not depend upon the amount of silica in the catalyst.

3. A level of 0.5 to 1.0 wt.% K appears to produce the maximum activity for the catalyst activated by carbiding with CO at the reaction conditions.

4. It appear that there is an optimum level for alumina concentration for maximum catalyst activity; this level is about 5 wt.%.

5. Zirconia added to the iron catalyst produces a material with lower activity than either alumina or zirconia.

6. Catalysts have been prepared that have the targeted activity, 90% CO conversion at a flow rate of 3.4 NL/g. Fe-hr., for both silica and alumina promoters.

7. Because of the small amount of oxygenates in the products, the catalysts that attain the targeted activity of 90% CO conversion attain the targeted hydrocarbon production rate. However, because the amount of methane and ethane follow, or are slightly below, the values required to fit the Anderson-Schulz-Flory plot, the targeted C_{3+} hydrocarbon yield is not attained.

8. Catalyst activity stability corresponding to 1.5 % CO conversion decline per week (1 % CO conversion decline per week targeted) has been obtained during a 30 day period; however, due to loss of liquid level in the reactor during the run it has not been possible to attain the slow rate of activity loss for 60 days.

Thus, all of the targeted performance levels have been attained except for the C_{3+} hydrocarbon production and the catalyst activity maintenance. It is anticipated that the use of a higher boiling point start-up solvent will permit us to attain the targeted activity maintenance.

Plans:

In the remaining period of the contract it is anticipated that we will:

1. Complete the plant design and catalyst manufacturing cost estimate.

2. Continue testing UCI catalysts that have been prepared for use for the La Porte, Texas plant run early in 1994.
3. Complete the definition of the optimum alumina level in the catalyst to produce the maximum CO conversion.
4. Complete the definition of the optimum potassium level for the silica containing catalyst.
5. Complete runs in a higher boiling start-up solvent to better define the activity maintenance of the promoted catalysts.

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SURFACE AREA AS A FUNCTION OF CALCINATION TEMPERATURE
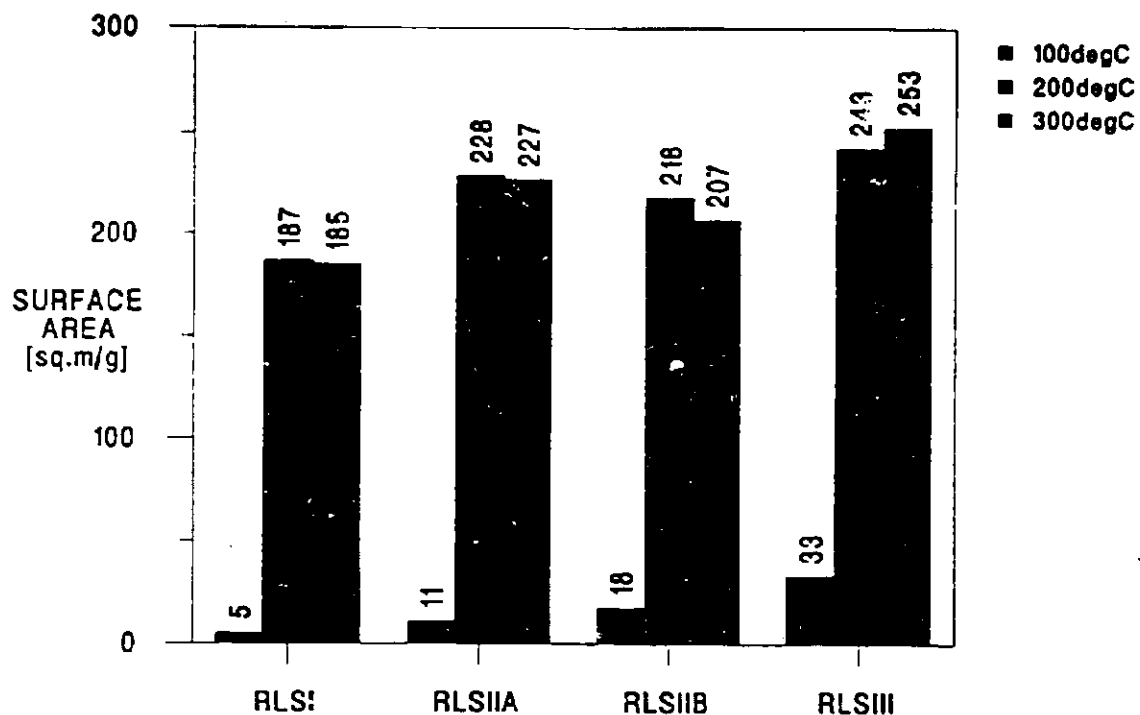
Figure 1. Surface area of iron catalysts containing increasing amounts of silica (RLS I = 5.0 atomic%; RLS II = 9 wt.%; RLS III = 14 wt.% silica) following drying at 100°C and calcination at 200° or 300°C.
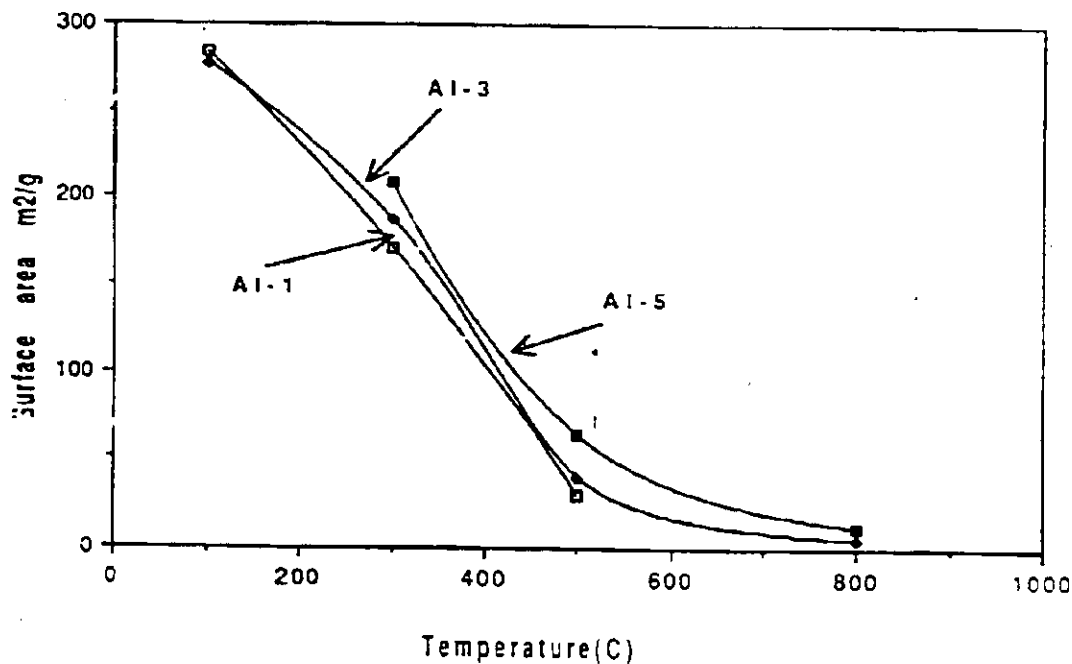
Figure 2. Role of calcination temperature on the surface area of FeOOH containing 1, 3 or 5 wt.% alumina.
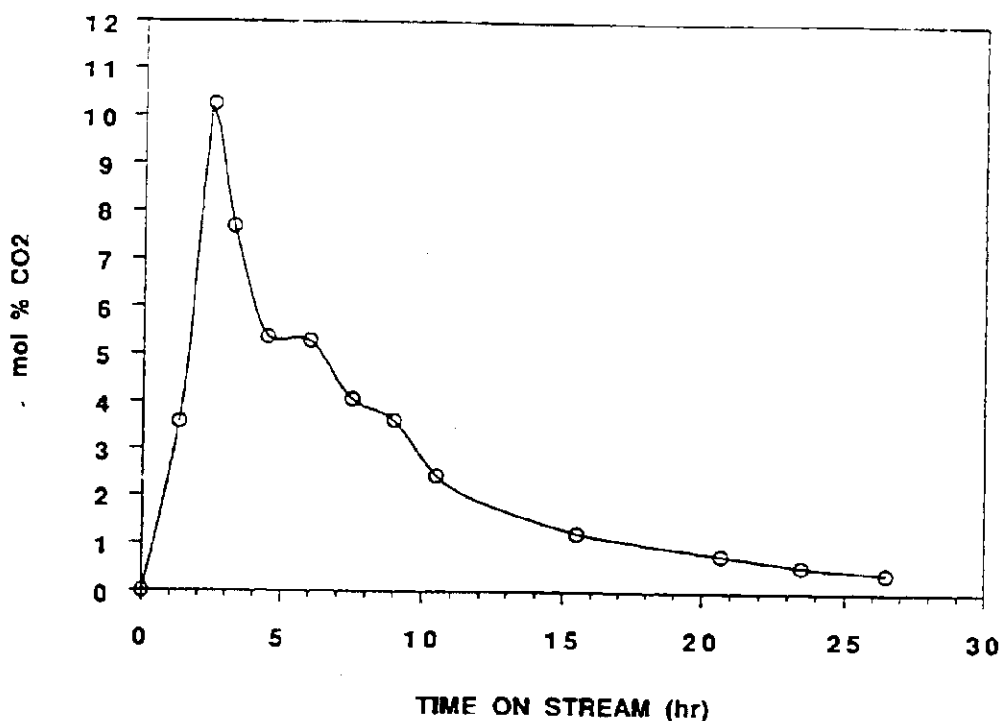
Figure 3.   Amount of CO_2 in the exit gas when pretreating UCI 1185-57 catalyst while heating to 270°C during 3 hours at 170 psig CO and holding at that temperature for an additional 21 hours.
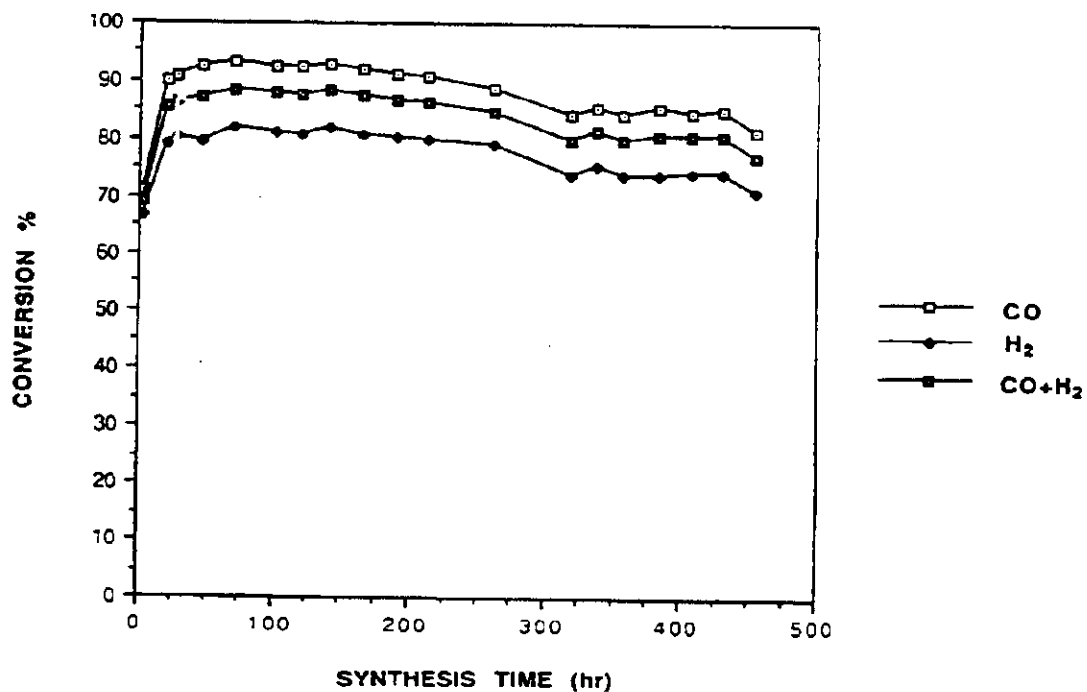
Figure 4.   CO and H_2 conversion following the pretreatment shown in figure 3 (reaction temperature 270°C, 170 psig, H_2/CO = 0.67, gas flow 3.4 NL/hr.-g.Fe.
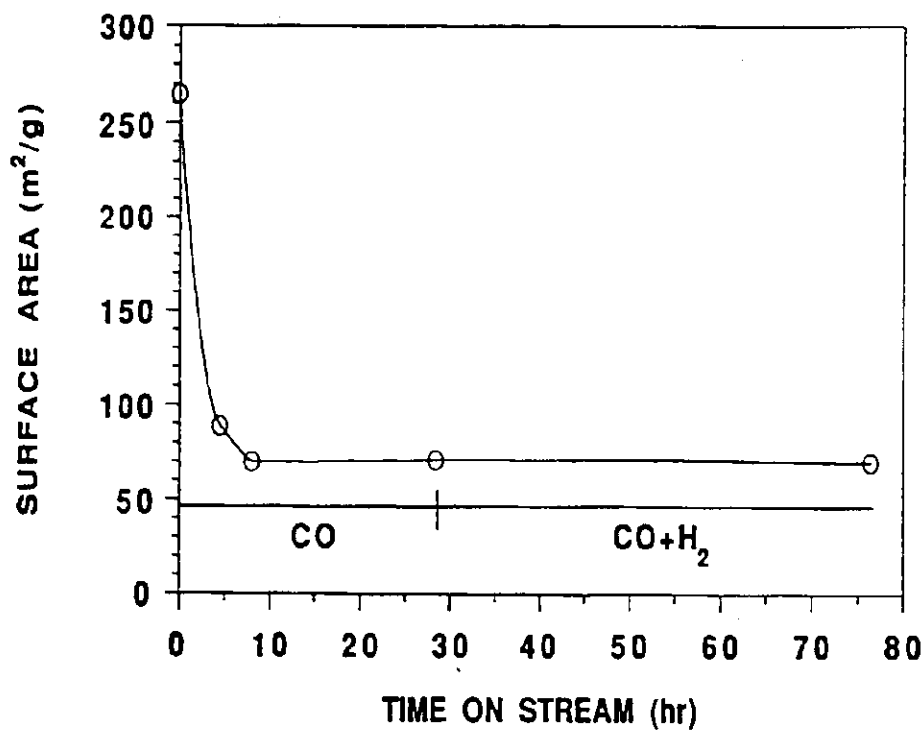
Figure 5.   Change in surface area during carbiding during 24 hours in CO and during synthesis at the conditions given in figure 4 legend.
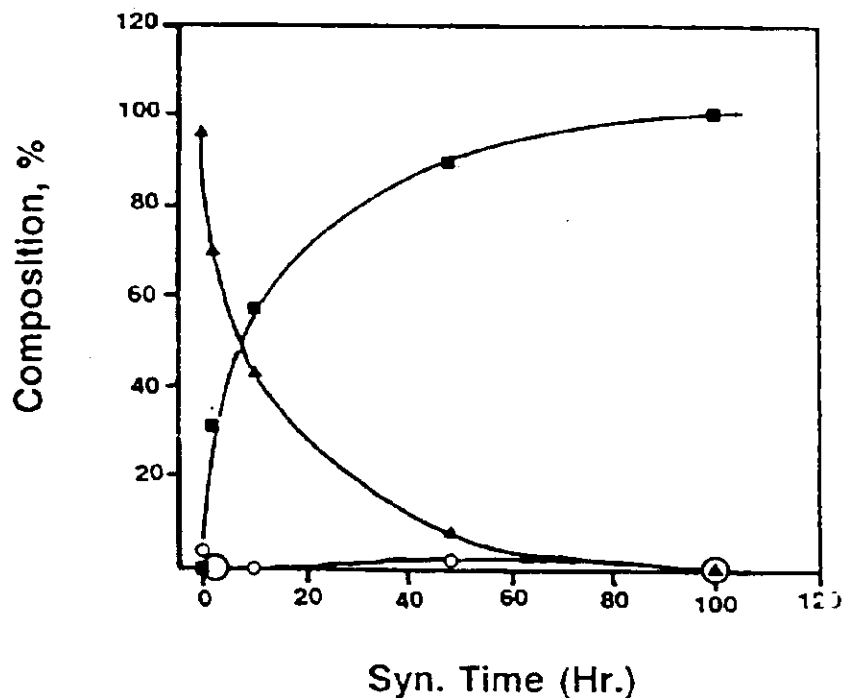
Figure 6.   The change with exposure time in synthesis gas of the iron chemical state following 24 hours of pretreatment in CO (Fe_3O_4, ■: Fe_2O_3, ○: Fe carbines, ▲).
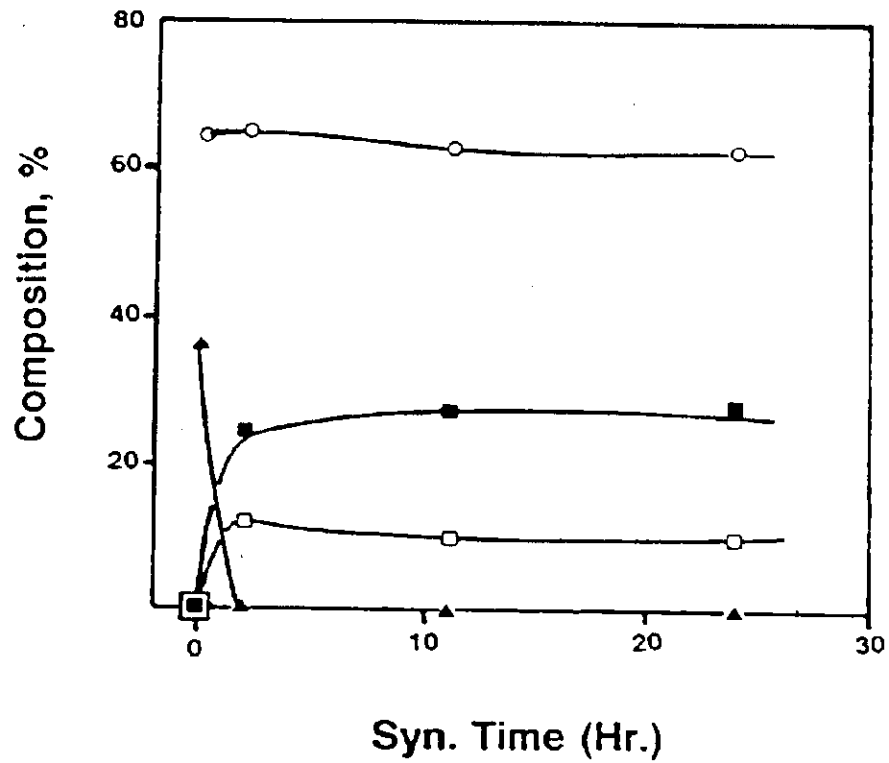
Figure 7. The change with exposure time in synthesis gas of the iron chemical state following 24 hours of pretreatment in hydrogen (Fe, ▲; $Fe_{2.2}$, ■; Fe_3C, ☐; Fe_3O_4, o).
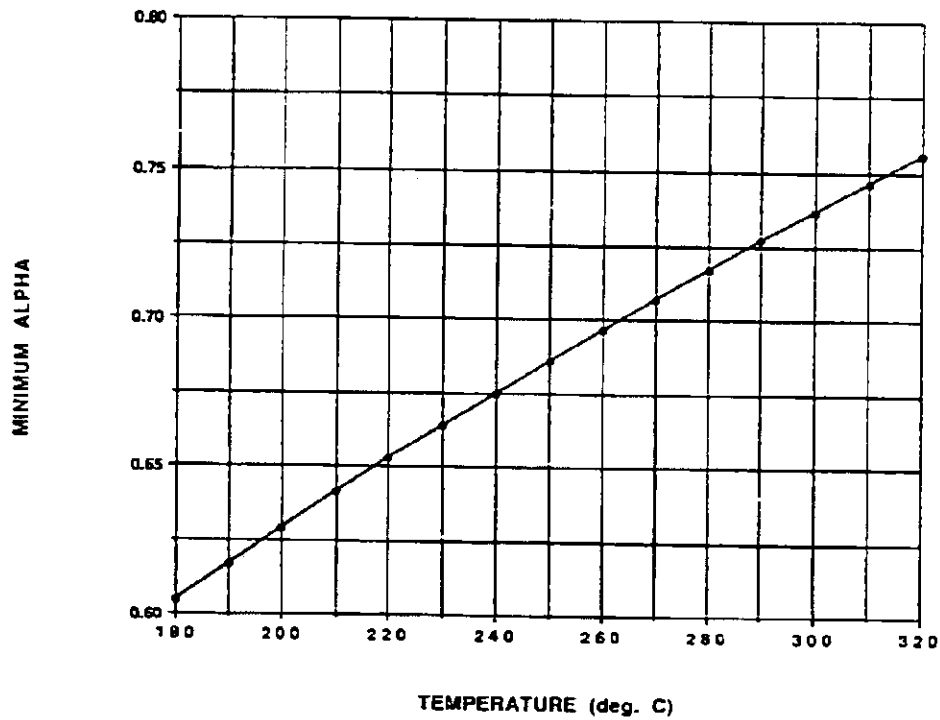
Figure 8. Minimum value of alpha required to accumulate liquid product in the reactor during Fischer-Tropsch synthesis.
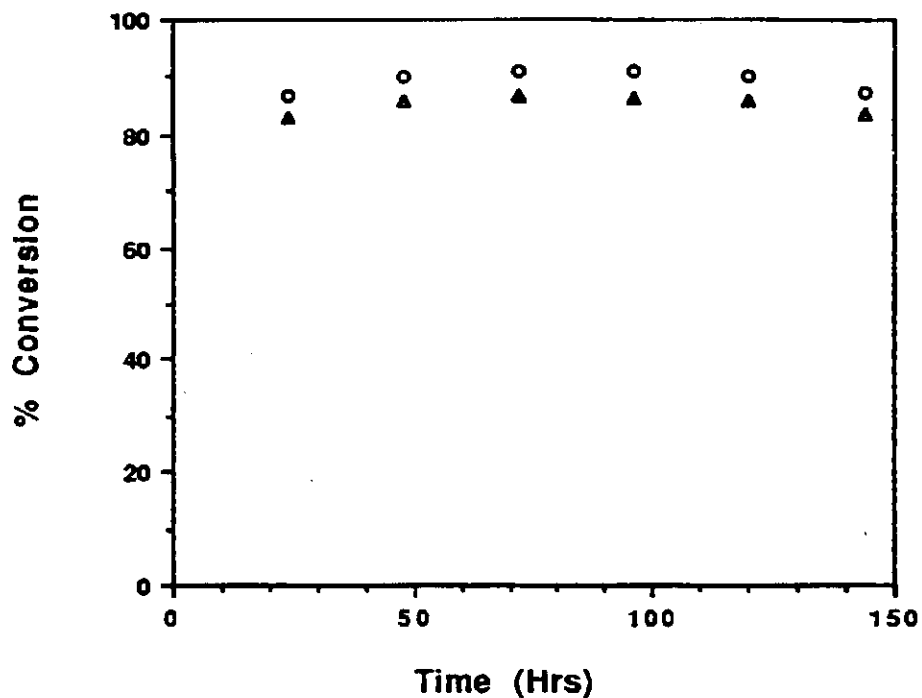
Figure 9.   Activity for conversion of CO (○) and H_2 (△) of a catalyst based upon α-FeOOH containing 4.4 atomic % Si and 0.5 wt.% K following CO pretreatment at 270°C and synthesis at 270°C, 3.4 NL/g.Fe-hr., H_2/CO = 0.67 and 170 psig).
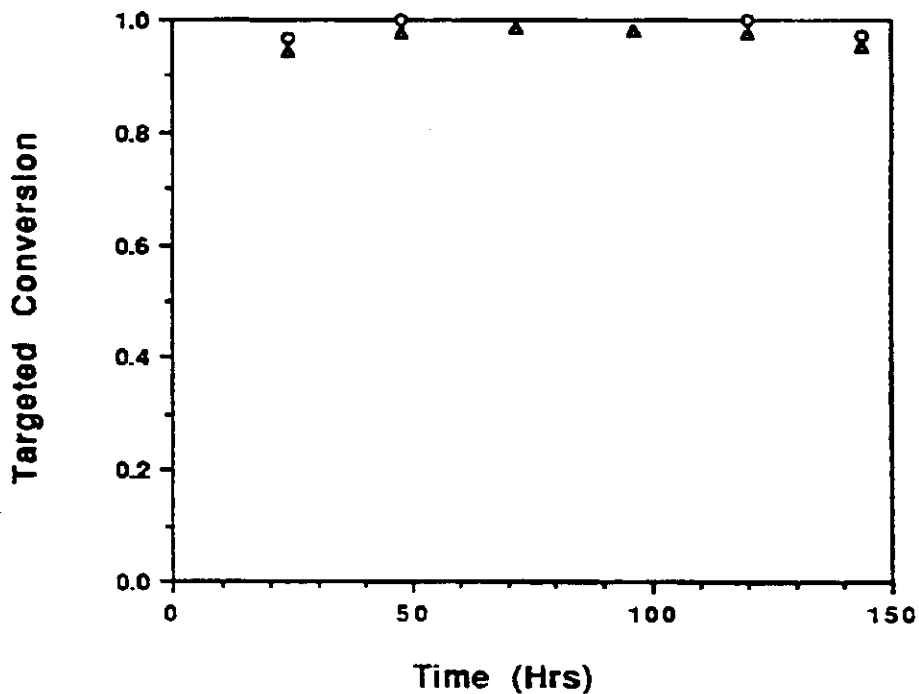
Figure 10.   Fraction of targeted conversion of CO (○) and H_2 (△) during the run describer in figure 9.
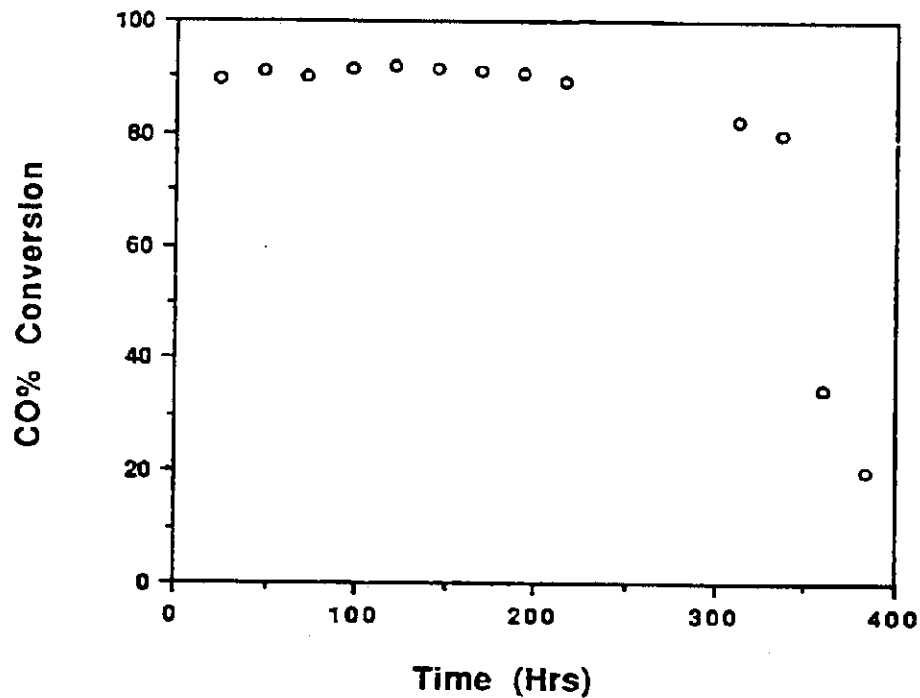
Figure 11. CO conversion with reaction time (conditions as shown in figure 9 legend).
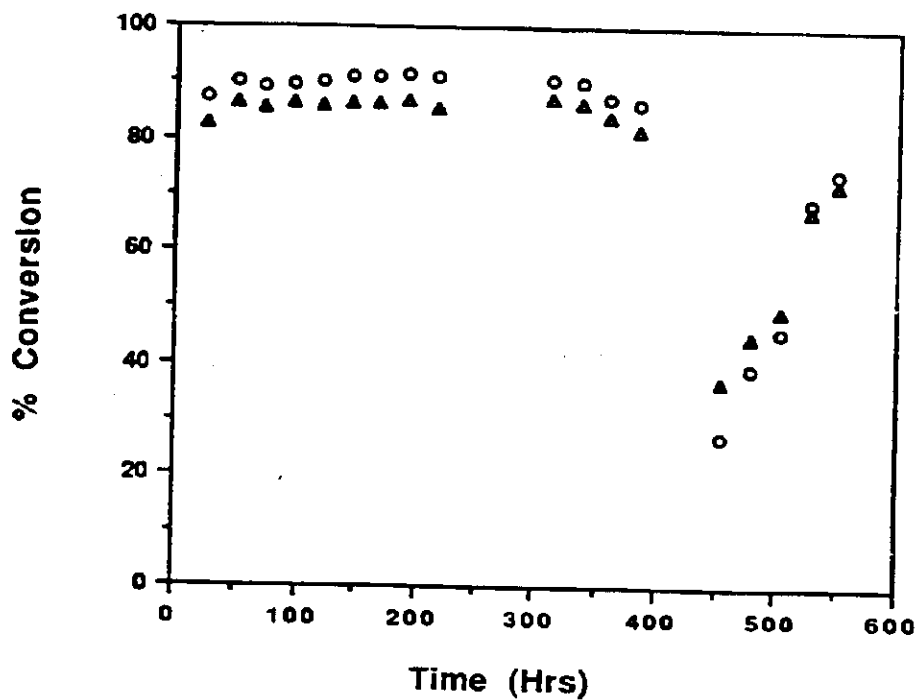
Figure 12. CO conversion for an unsupported catalyst (UCI 1185-61) using conditions shown in figure legend 9.
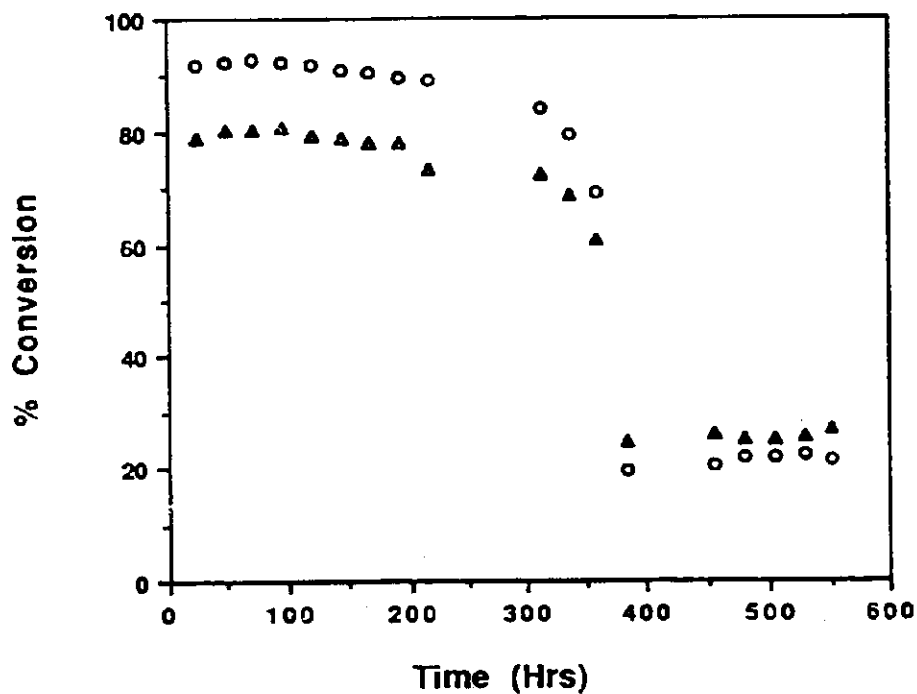
Figure 13. CO conversion for an iron catalyst containing 30 wt.% kaolin (UCI 1185-57) using conditions shown in figure legend 9.
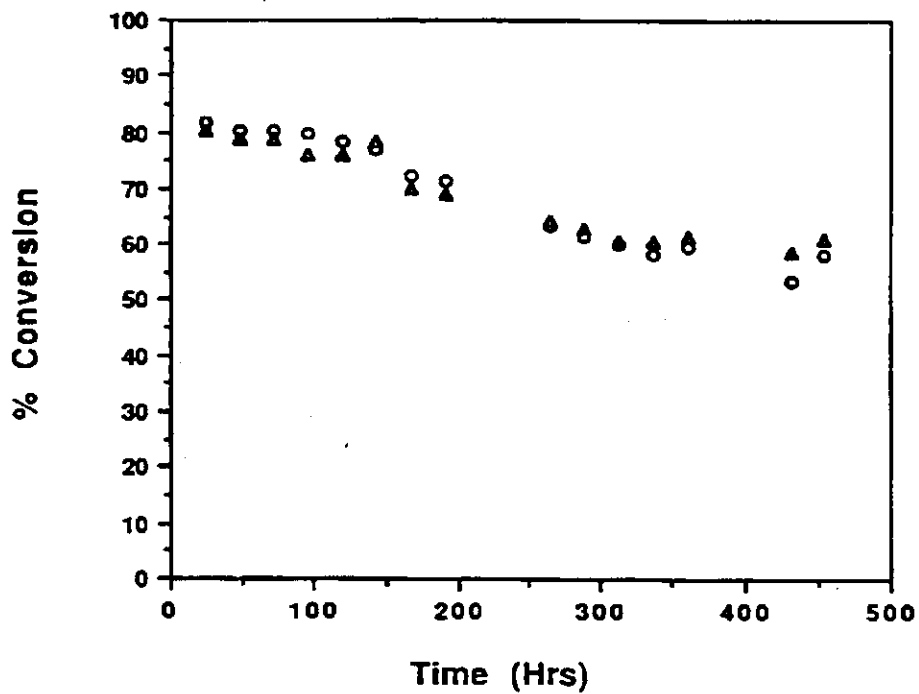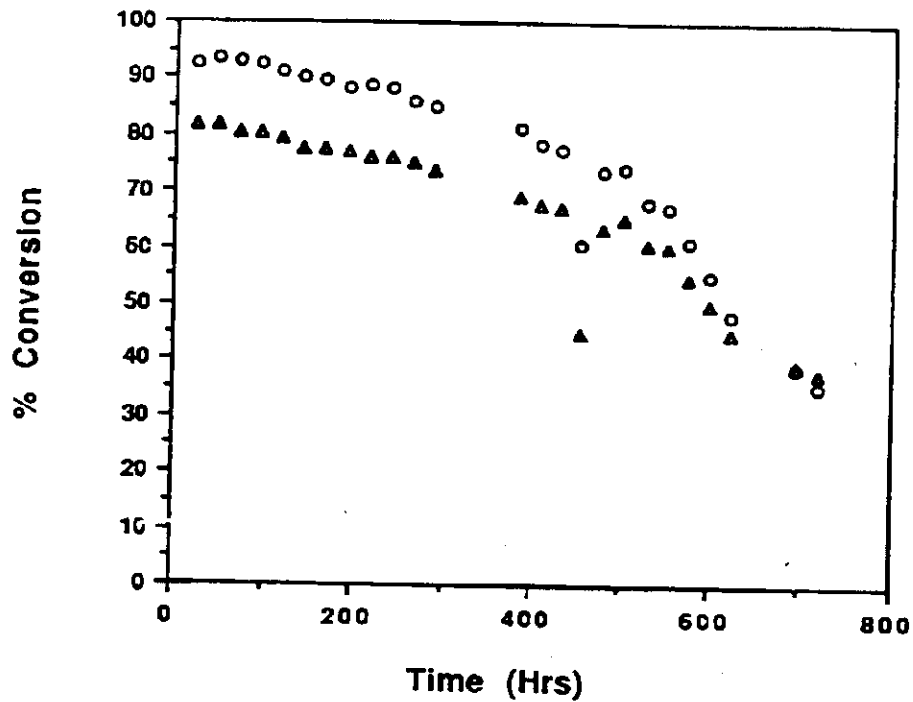

Figure 1₄. CO conversion for an unsupported catalyst (UCI 1185-78) using conditions shown in figure legend 9.

Figure 15. CO conversion for an supported catalyst containing 30 wt.% kaolin (UCI 1185-75) using conditions shown in figure legend 9.
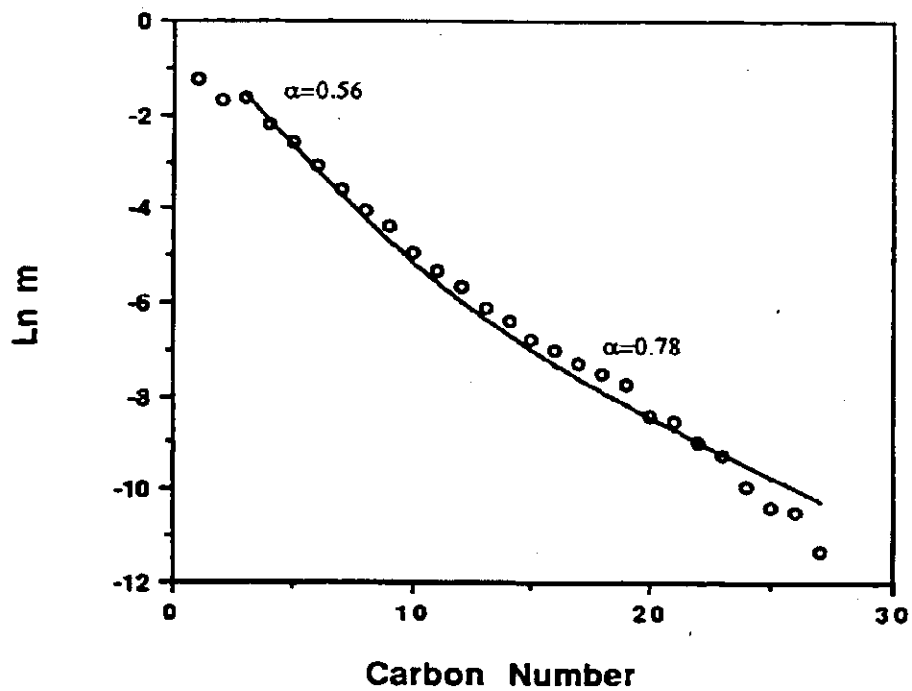

Figure 16. Typical Anderson-Schulz-Flory plot for the hydrocarbon products produced during run 100.
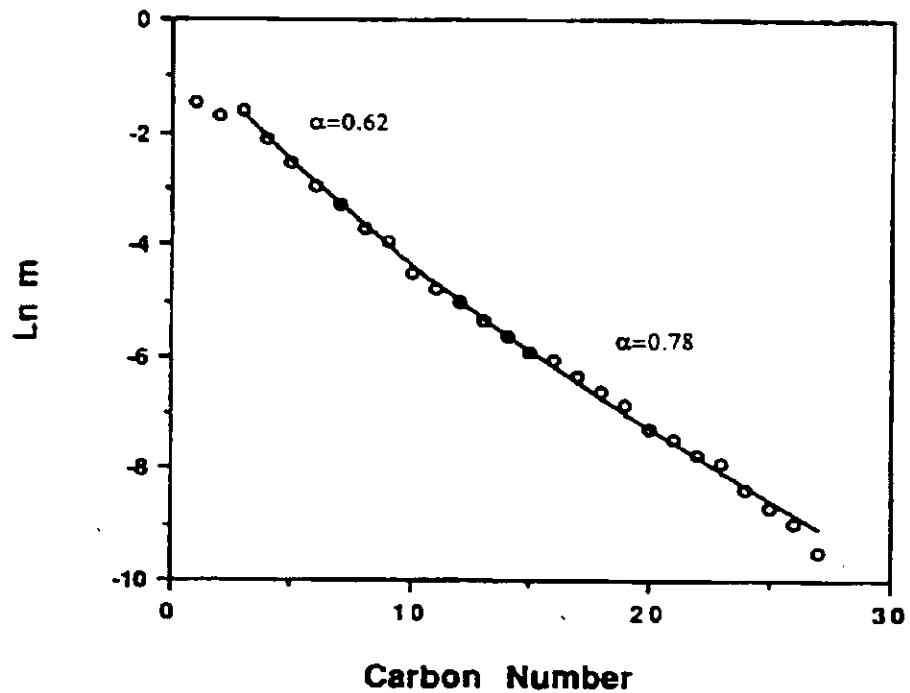
Figure 17. Typical Anderson-Schulz-Flory plot for the hydrocarbon products produced during run 101.