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Slurry Phase Fischer-Tropsch Synthesis: Cobalt Plus a Water-Gas Shift Catalyst

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by

Ian C. Yates

and

Charles N. Satterfield

for

U.S. Department of Energy
Pittsburgh Energy Technology Center
P.O. Box 10940-MS 902-L
Pittsburgh, PA 15236
Attention: William E. McKinstry, Project Manager

MASTER

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Summary

In our last quarterly, we reported on the continuous deactivation of commercially available copper-based water-gas shift catalysts in our slurry reactor system. A detailed literature review and our recent experience both show that activation procedures are critical. Improper reduction procedures and/or incorrect catalyst preparation can explain much of the deactivation observed by us and other researchers working on the problem of finding a water-gas shift catalyst active in a Fischer-Tropsch slurry reactor system.

This report details experiments performed on three different copper-based catalysts: Cu/Cr_2O_3, $Cu/MnO/Cr_2O_3$, and $Cu/ZnO/Al_2O_3$. Of these three catalysts, the $Cu/ZnO/Al_2O_3$ exhibits the greatest stability when slurried in octacosane in our reactor system. Tests lasting more than 1000 hours-on-stream indicate that the activity of this catalyst is not detrimentally affected by high pressure, high H_2/CO ratio, or the presence of alkenes. All of these are necessary stability characteristics for the water-gas shift catalyst, if it is to be used in combination with a cobalt Fischer-Tropsch catalyst.

A review of documented reduction procedures for cobalt-based Fischer-Tropsch catalysts is presented. A reduction procedure is chosen that will allow use of existing equipment, avoiding the need for costly and time-consuming modifications. Once reduced, the cobalt catalyst will be added to the already-activated water-gas shift catalyst and the behavior of the combined catalyst system will be studied.

1. Introduction and Background:

According to patents from Shell a mechanical mixture of a cobalt catalyst and a copper-based water-gas shift catalyst has been used in a fixed-bed reactor to carry out the Fischer-Tropsch synthesis. However, in other fixed-bed studies performed by Union Carbide (February, 1984; May, 1984 and September, 1984) and Tominaga et al. (1987), water-gas shift catalysts have been observed to deactivate rapidly when combined with a cobalt Fischer-Tropsch catalyst in a fixed-bed. In our slurry reactor, we also encountered substantial deactivation with an early $Cu/ZnO/Al_2O_3$ catalyst combined with a cobalt catalyst (Yates and Satterfield, June, 1988).

In an effort to understand the underlying causes of this deactivation, we have performed a number of runs in which a water-gas shift catalyst was the only catalyst present in the slurry reactor. To avoid problems of catalyst instability due to incorrect preparation, we limited these studies to commercially manufactured copper-based catalysts. Great care was taken to remove any potential poisons from our system. Thus, we were able to perform a series of experiments in which we gained insight into the intrinsic behavior of the copper-based catalysts in a slurry reactor system.

Low-temperature, copper-based shift catalysts are typically operated in fixed-bed units (Allen, 1974). As a result, little information is available on the operation of these catalysts in any other type of reactor. Therefore, a challenge for us was to adapt established fixed-bed operating procedures, particularly the reduction procedure, to a slurry reactor system. The first part of this report details our results and conclusions regarding the potential use of these copper-based shift catalysts in a slurry Fischer-Tropsch system. The second part of the report is a literature review of reduction procedures for cobalt-based Fischer-Tropsch catalysts.

2. Cu/Cr_2O_3 (Harshaw Cu 1803-P) Run 4:

The fourth run set of experiments with this catalyst was used to examine the effect of oxidizing gases on the Cu/Cr_2O_3 catalyst (Harshaw catalyst Cu 1803-P). We felt that, if the Cu^+ state was in fact the active phase of copper for water-gas shift, the presence of large amounts of CO_2 might stabilize this active species. The potential effects of oxidizing gases on the activity and stability of copper-based catalysts were discussed in detail in our previous report (Yates and Satterfield, June, 1988).

Oxidizing gases did not appear to stabilize the catalyst. The catalyst continued to deactivate at a rate comparable to that observed in reducing gases. In one sense, this is encouraging because it indicates that the activity of the water-gas shift catalysts in this type of slurry system is not sensitive to the oxidizing or reducing nature of the gases in the reactor, within reasonable limits. This comparable rate of deactivation is additional evidence that the cause of deactivation is likely to be improper reduction, sintering or poisoning.

2.1 Experimental and Results:

The preparation and reductior of this catalyst and important details of the reactor system are reported elsewhere (Huff and Satterfield, 1982; Huff, Satterfield, and Wolf, 1983; Yates and Satterfield, June, 1988). After the 180 hours on-stream in Run 3 (Yates and Satterfield, June, 1988), the activity of the Cu/Cr_2O_3 catalyst had declined to the point where only 70 percent conversion was being observed. At this time, the inlet flow was changed from 60.6 mol% CO, 20.6 mol% H_2, and 19.2 mol% H_2O at 0.033 Nl/min/gcat to 30.1 mol% CO, 52.0 mol% CO_2, and 17.9 mol% H_2O at 0.033 Nl/min/gcat; this was defined to be the beginning of Cu 1803-P Run 4. The temperature and pressure were held constant as before at 220°C and 0.79 MPa.

In all of these experiments, the H_2 used was prepurified grade (MedTech Gases, Inc.), the CO was CP grade (Matheson, Inc.), and the CO_2 was Coleman Grade (MedTech Gases, Inc.). The details of the H_2O purification and feed system have already been reported (Yates and Satterfield, June, 1988).

The catalyst activity was monitored by conversion of H_2, CO, and CO_2. In this and all other sections, the conversion of a given reactant, $-X_r$, i.e. CO or H_2O, is defined by the following equation:

$$-X_r = 100\ [1-(\mu_{out,i} - \mu_{in,i})/(\mu_{eq.react.,i} - \mu_{in,i})] \qquad (1)$$

Similarly for the products, H_2 and CO_2, the conversion, X_p, is defined as:

$$X_p = 100\ [(\mu_{out,i} - \mu_{in,i})/(\mu_{eq.react.,i} - \mu_{in,i})] \qquad (2)$$

where in both equations (1) and (2) for component i:

$\mu_{out,i}$ = measured flow rate at outlet. [Nl/min] (3)

$\mu_{in,i}$ = measured flow rate at inlet. [Nl/min] (4)

$\mu_{eq.react.,i}$ = outlet flow rate at equilibrium. [Nl/min] (5)

Ranging from 0 at no activity to 100 at equilibrium conversion, these definitions of conversion provide a convenient benchmark for comparison of runs with different feed composition and/or flow rate. Material balances were required to close to within 3 percent on carbon and thus in all data reported:

$$97 < 100\ [\mu_{out,CO}+\mu_{out,CO_2}]/[\mu_{in,CO}+\mu_{in,CO_2}] < 103 \qquad (6)$$

Carbon was chosen because, unlike hydrogen or oxygen, it was not condensed out in the form of water in the reactor trapping system.

Table 1 lists the outlet flow rates and concentrations of CO, H_2, and CO_2 and the calculated conversions of the water-gas shift reaction. H_2O was condensed in the trapping system and, because the system was deactivating with time-on-stream, no steady-state data on the concentrations of H_2O were obtainable. Figure 1 shows the conversions during the 214 hours following the switch in feed composition to the more oxidizing mixture. A steady deactivation of the catalyst, apparently linear with time-on-stream, is observed. The rate of deactivation of the catalyst is comparable to the rate of deactivation in the more reducing gas conditions of Cu 1803-P Runs 1 and 3 (Yates and Satterfield, June, 1988). This indicates that the catalyst is not stabilized by oxidizing conditions and that sintering and/or poisoning appears to cause the deactivation.

3. Cu/MnO/Cr_2O_3 (Harshaw 1920-P) Run 1:

According to Harshaw, the Cu/MnO/Cr_2O_3 catalyst possesses greater temperature stability than the Cu/Cr_2O_3 (Harshaw 1803-P) catalyst which was tested previously (Runs 1-4). This enhanced stability is probably due to the MnO, which is stable at the conditions under which we would be operating. The catalyst was tested for more than 300 hours. Despite its alleged stability, the Cu/MnO/Cr_2O_3 catalyst deactivated at approximately the same rate as the previously tested Cu/Cr_2O_3 catalyst.

3.1 Experimental and Results:

The nominal composition of the catalyst is 46 wt% CuO, 46 wt% Cr_2O_3, and 4 wt% MnO. The catalyst has a bulk density of 37 lb/ft^3 and a surface area of 56 m^2/g. Supplied as a powder, the catalyst was sieved to 50 to 90 µm (170 to 270 ASTM Mesh) to remove any fines (particles smaller than 50 µm) that could potentially be carried overhead and subsequently plug the frit of the reactor. 25 grams of the sieved catalyst were loaded to the reactor, which had been previously charged with 400 grams of octacosane (Humphrey Chemical, Inc.). The octacosane had been recrystallized twice in HPLC grade THF (Mallinkrodt, Inc.) to ensure the removal of any potential poisons such as sulfur- or halogen-containing compounds. The catalyst was then reduced in the reactor. Table 2 details the reduction procedure.

Following completion of the reduction, flow of 43.5 mol% CO, 21.7 mol% H_2, and 36.3 mol% H_2O at 0.019 Nl/min/gcat was begun. The temperature and pressure were held constant at 200°C and 0.79 MPa. These are the identical feed composition, flow rate and pressure that were used to examine the behavior of the Cu/Cr_2O_3 catalyst in Runs 1 and 3. To reduce the potential for sintering, the temperature was kept

20°C lower in this run than in those runs. Had the catalyst shown encouraging activity at this lower temperature, we planned to increase the temperature.

Table 3 lists the outlet flow rates and concentrations of CO, H_2, and CO_2 and the calculated conversions of the water-gas shift reaction. The catalyst activity was monitored by conversion of H_2, CO, and CO_2. H_2O was condensed in the trapping system and, because the system was transient, no data on the concentrations of H_2O are presented. Figure 2 shows the deactivation of the catalyst over the over 300 hours that it was on-stream. Although the activity appears to level out somewhat after about 220 hours-on-stream, with conversion near 30 percent, the activity is lower than would be desirable for a water-gas shift catalyst that could be used in conjunction with an industrial Fischer-Tropsch catalyst.

4 Cu/ZnO/Al_2O_3 (Katalco 52-2):

4.1 Run 1:

A Cu/ZnO/Al_2O_3 catalyst supplied by Katalco was run. The catalyst was reduced at a maximum temperature of 200°C, which is lower than that of previous runs with this type of catalyst. Although the catalyst did not exhibit very high initial activity, it was stable over the 150 hours of operation. This encouraging stability prompted another run with a modified reduction procedure. The second run is described below (section 4.2).

4.1.1 Experimental and Results (Run 1):

This catalyst, Katalco 52-2, has a nominal composition of approximately 33 wt% CuO, 33 wt% ZnO, and 33 wt% Al_2O_3. The literature provided by Katalco on the properties of the catalyst and on the reduction procedures for the catalyst have been attached, with the permission of Katalco, as Appendices 1 and 2.

Supplied as a 1/8 inch extrudate, the catalyst was first ground to 50 to 90 µm (170 to 270 ASTM Mesh). This is as small a particle size as can be run without significant entrainment of the catalyst. 25 grams of the catalyst were then loaded to the reactor, which had been previously charged with 400 grams of octacosane (Humphrey Chemical, Inc.). The octacosane had been recrystallized twice in HPLC grade THF (Mallinkrodt, Inc.) to ensure the removal of any potential poisons.

The catalyst was then reduced in the reactor according to the guidelines of the manufacturer (see Appendix 2). Table 2 lists the reduction procedure. It should be remembered, however, that the manufacturer's recommendations are for a fixed-bed reactor and this reduction was carried out in a slurry reactor. As a result of the different reactor residence time distributions, it would be expected that changes in feed composition and flow rate should have different effects on the composition of the gases in each different reactor type. Great care was taken to avoid sintering by ensuring that temperature and hydrogen concentrations in the reactor were carefully controlled during the reduction.

Following reduction, gas with a composition of 43 mol% CO, 21.4 mol% H_2, and 32.6 mol% H_2O was fed at a rate of 0.021 Nl/gcat/min. The temperature and pressure were held constant at 200°C and 0.79 MPa.

The catalyst activity was monitored by conversion of H_2, CO, and CO_2. Table 4 lists the outlet flow rates and concentrations of CO, H_2, and CO_2 and the calculated conversions of the water-gas shift reaction. Figure 3 shows these conversions for the 152 hours following reduction. Although the conversions are not at equilibrium which is close to 100 percent conversion, they do appear to remain reasonably constant after the initial start-up period.

4.2 Run 2:

The stability exhibited by the Katalco 52-2 catalyst in Run 1 was encouraging enough to warrant further experimentation. The reactor feed section was modified to allow for a controlled flow of helium to be passed over the catalyst during the beginning of reduction. Use of a flowing inert during the beginning of the reduction follows the recommendations of Katalco.

4.2.1 Experimental:

The catalyst was ground and loaded to the reactor with octacosane as above (section 4.1.1). The reduction procedure is detailed in Table 5. Comparison of Table 2 and Table 5 shows that the reduction procedure was modified in two important ways: first, by flowing helium during the beginning period of reduction and, second, by reducing the length of time that the catalyst was exposed to the final, most severe reduction conditions.

Following the reduction the catalyst was brought on-stream with a flow of 43 mol% CO, 21.4 mol% H_2, and 35.6 mol% H_2O at 0.019 Nl/min/gcat. Temperature and pressure were held constant at 200°C and 0.79 MPa. These settings are defined as "base case" conditions and are those used to monitor the long-term activity of the catalyst. The rate at which water is fed is approximately three to five times that which would be typically synthesized in our reactor with a cobalt Fischer-Tropsch catalyst. To give an accurate measure of catalyst activity at these conditions, no process changes were made during the first 300 hours-on-stream.

After 300 hours-on-stream, process changes in either the pressure, temperature or feed composition were made. Following a process change conversions were monitored for between 48 and 100 hours. The reactor was then returned to "base case" conditions which would in turn be monitored for between 48 and 100 hours. Thus, we were able to monitor both the effect of the process change on activity (via conversions during the process change) and stability (via conversions after the return to the "base case" following the process change). Table 6 shows the process changes and times at which they were made. The details of the catalyst activity and stability are presented below.

4.2.2 Activity and Stability

Table 7 lists the outlet flow rate, composition, and calculated conversions of H_2, CO, and CO_2 for the "base case" conditions. Extended periods of time-on-stream where no data appear in this table indicate that a different set of process conditions was being studied. The data from these different process conditions are omitted intentionally and will be presented in subsequent sections.

Figure 4 presents these "base case" data graphically. It can be seen that the catalyst deactivate slowly for the over 1000 hours which it was on-stream. After an initial period of levelling-off, conversions were almost constant at around 70 percent, although a small fall-off to around 60 percent is seen over the 1000 hours. Some scatter in the data is observed. The scatter in the data is explained by experimental error.

4.2.3 Effect of Pressure

Because total pressure does not affect the equilibrium of the water-gas shift reaction (Moe, 1962), increasing pressure is expected to change conversion only by changing the concentrations of the components in the reactor.

After 303 hours-on-stream, the pressure was increased from 0.79 MPa to 1.48 MPa (100 to 200 psig). Temperature, space velocity, and feed composition were held constant. The reactor was held at this higher pressure for 55 hours until 358 hours-on-stream. At this time, the reactor was returned to the "base case" conditions and held there for 67 hours.

Table 8 shows the conversions and time-on-stream for the first 425 hours-on-stream which includes this pressure change and the subsequent return to the "base case" conditions. Figure 5 shows these data for the time period before, during, and after the pressure change. Comparing the data before and during the increase in pressure, it can be seen that the pressure change did not affect the rate of water-gas shift markedly. Further, it can be seen that the catalyst activity remains at its previous level following the pressure increase. This indicates that the increase in pressure did not have a measurable effect on the long-term stability of the catalyst.

4.2.4 Effect of Inlet H_2/CO Ratio

The ratio of H_2/CO in the inlet gas is an important parameter to consider when evaluating the stability of a water-gas shift catalyst for the Fischer-Tropsch synthesis. The H_2/CO ratio which had been chosen for the "base case" provided an *in situ* H_2/CO ratio of approximately 2 which is close to the usage ratio reported for cobalt catalysts (Storch, et al., 1951). The water-gas shift catalyst had shown stability at this reactor H_2/CO ratio which makes the catalyst a viable candidate for operation in combined catalyst system.

To examine the kinetics and selectivity, it is expected that the ratio will be varied in order to determine the independent effects of both hydrogen and carbon monoxide. Thus, it is necessary to establish the stability of the water-gas shift catalyst at a variety of conditions. To elucidate the effect of H_2/CO, two different feed ratios were studied: 0.7 and 1.0. These produced *in situ* H_2/CO ratios near 2.5 and 3 respectively. Higher H_2/CO ratios were examined because it was felt that higher hydrogen partial pressures would increase the likelihood of sintering. Higher CO partial pressures are not reported to have deleterious effects on the water-gas shift catalysts (Moe, 1962; Newsome, 1980).

Table 9 shows the outlet and conversion data for 425 to 925 hours-on-stream. The data between 637 and 693 hours-on-stream have been omitted intentionally as these were the data collected at 220°C (see section 4.2.5 for discussion of these data). Figure 6 shows the time-on-stream dependence of overall conversion during this period. The component conversions which are usually plotted are not displayed in order to make the plot less complicated. It can be seen that the overall conversion drops somewhat with increased inlet (and reactor) H_2/CO; at both the increased H_2/CO ratios conversions fell about 3 to 5 percent. This drop in reaction rate is consistent with a simple equilibrium-limited expression presented by Moe (1962) which has the form:

$$R_{WGS} = k \, [\, P_{CO} P_{H_2O} - P_{H_2} P_{CO_2} / K_p \,] \qquad (7)$$

because increasing the hydrogen partial pressure in the reactor decreases the "driving force" for reaction.

4.2.5 Effect of Temperature

Copper melts at 1356 K. Bulk mobility becomes significant at the Tammann temperature, approximately 0.5 $T_{m.p.}$; surface mobility at the Hüttig temperature, approximately 0.3 $T_{m.p.}$. Thus, temperature may be the single most important cause of sintering for copper-based shift catalysts. As a result, the catalyst manufacturer, Katalco, recommends that the catalyst not be used at temperatures above 250°C.

For most of the run, the reactor was operated at 200°C, which is the lowest temperature at which $Cu/ZnO/Al_2O_3$ catalysts are reported to have appreciable activity (Newsome, 1980). Figure 4, which presents the "base case" data, indicates that at 200°C the catalyst converted approximately 70% of the H_2O and CO fed. With the equilibrium constant Kp equal to 228 at 200°C (Newsome, 1980), equilibrium conversion at this temperature should be essentially 100. Thus, it appears that conversion is reaction limited rather than equilibrium limited. Unless the catalyst deactivated at the higher temperature, increasing reactor temperature would therefore be expected to increase the conversion.

After 637 hours-on-stream, the reactor temperature was increased from 200 to 220°C at 693 hours-on-stream the temperature was dropped back to 200°C. Table 10 shows the outlet flow rate, concentrations and calculated conversions between 500 and 770 hours-on-stream. Figure 7 presents these conversion data graphically.

Figure 8 shows an Arrhenius plot for the rate of water-gas shift reaction (i.e. the log of the rate is plotted versus reciprocal absolute temperature). It can be seen that the rate of reaction did not increase drastically with increasing temperature. The apparent activation energy for the reaction is around 15 kJ/mol (3.6 kcal/mol). It should be observed, however, that increasing the temperature increased the reactor H_2/CO ratio from 2 to around 2.5. It was seen in section 4.2.4 that this increase would be expected to decrease the conversion as it decreases the "driving force" for reaction (see equation 7).

A low activation energy of this magnitude is known be indicative of mass transfer limitations (Satterfield, 1970). In order to examine the potential for intra-particle mass transfer limitations, the Thiele modulus and effectiveness factor were estimated. Appendix 3 outlines these calculations. At 200°C with the particle sized used, the effectiveness factor is estimated to be around 0.7, confirming that some mass transfer limitations may exist. It is certainly encouraging that the catalyst is active enough to convert 70 percent of the feed, even when some mass transfer limitations may exist. As the calculations indicate, use of a smaller size fraction (270 to 325 ASTM Mesh) could alleviate some of these mass transfer problems. This will be done in future runs with this catalyst.

4.2.6 Effect of 1-Butene:

In discussing the potential causes of the deactivation of water-gas shift catalysts in combination with cobalt-based Fischer-Tropsch catalysts Union Carbide (February, 1984; May, 1984 and September, 1984) speculated that alkenes may adsorb on the surface of shift catalysts, inhibiting its reactivity. Since it is well known that alkenes adsorb strongly on reduced metal surfaces (Satterfield, 1980), it is reasonable to postulate that alkenes could inhibit the rate of water-gas shift reaction. The two effects that we wanted to examine were: the inhibition of the rate of water-gas shift reaction by alkenes and the reactions, if any, the added alkene underwent.

To examine the effects of alkenes, 1-butene was added to the feed at 924 hours-on-stream. The 1-butene was in an analyzed mixture of 2 mol% 1-butene in 98 mol% prepurified hydrogen supplied by Matheson Gases, Inc.. 1-Butene was chosen because it is representative of alkenes of the Fischer-Tropsch synthesis and, from an experimental point-of-view, it is easy to add because it is a gas a room temperature. Ethene was not used because it is reportedly more reactive than is typical of 1-alkenes.

Table 11 shows the outlet compositions, flows and calculated conversions of H_2, CO, and CO_2 for the period before and during the 1-butene addition. The data after the 1-butene addition are currently being collected. Figure 9 presents these data and shows that conversion remains essentially unchanged by the addition of the 1-butene to the feed. The lack of observed inhibition may have resulted from the fact that the alkenes are at too low a concentration to have an effect, although a slight inhibition may be observed by detailed examination of the data of Table 11 which indicate that the CO_2 conversion falls somewhat upon the addition of the 1-butene to the feed. It should be noted that some hydrogen, a product of the shift reaction, is being consumed in the hydrogenation of 1-butene which may changing the relative rates of reaction of the components in the shift reaction. The definitive test of the existence of alkene inhibition will be the combination of the water-gas shift catalyst with the cobalt catalyst, but it appears that the effect of alkenes on the water-gas shift activity is small.

Although in this low concentration the 1-butene may not inhibit the water-gas shift reaction, it did undergo reaction. As indicated by Figure 10a, the 1-alkene was hydrogenated to butane and isomerized to both *cis*-2-butene and *trans*-2-butene. Figure 10b is presented to verify the validity of the identification of the gas chromatographic peaks. Typically, over 95 percent of the 1-butene was reacted. Essentially all of this consumed 1-butene reacted to form C_4 hydrocarbons and no significant amount was cracked to smaller hydrocarbons.

Figure 11 shows the time-on-stream dependence of the selectivity of the added 1-butene. No changes in selectivity of the catalyst are seen for the 50 hours that 1-butene was present in the feed. As can be seen, the primary product is butane which is approximately 55 percent of the total C_4 compounds. It is postulated that the hydrogenation occurs on the reduced copper, a known hydrogenation catalyst (p.20, Satterfield, 1980,). As can also be seen, *cis*-2-butene and *trans*-2-butene are synthesized in almost equilibrium ratios. This alkene isomerization presumably takes place on the acidic Si-Al sites almost certainly present in the Al_2O_3 support.

The results presented here on the behavior of the Katalco 52-2 $Cu/ZnO/Al_2O_3$ water-gas shift catalyst in the presence of alkenes and alkanes are preliminary. Certainly, to characterize fully the reaction pathways of 1-alkenes in this system would require further experimentation.

5. Conclusions about water-gas shift catalysts:

1. Oxidizing conditions do not appear to stabilize the Cu/Cr_2O_3 catalyst and they do not appear to significantly change the activity of copper-based catalysts in our reactor system.

2. The Katalco 52-2 $Cu/ZnO/Al_2O_3$ catalyst shows reasonably stable activity for water-gas shift in our octacosane slurry reactor system.

3. The stability of the catalyst is not noticeably changed by pressure or the presence of 1-alkenes. Increasing H_2/CO ratio appears to decrease the conversion of the water-gas shift reaction. Increasing temperature at a fixed feed rate and composition increases the rate of reaction, but the system appears to be somewhat mass-transfer limited.

4. 1-Butene, when added to the system, is almost completely reacted. The primary product is butane and the 2-butenes are produced in close to equilibrium amounts.

5. Smaller particles (270 to 325 ASTM Mesh) of the Katalco 52-2 should be used to minimize intra-particle mass transfer limitations. This will be done in future work with the catalyst.

6. From experience with the 1000 hours-on-stream with the Katalco 52-2 catalyst, it is worth noting that at least 24 hours should be allowed between set point changes for the outlet compositions to be at steady-state.

6. Reduction of Cobalt-Based Fischer-Tropsch Catalyst.

In order to develop a reduction procedure that will provide repeatable activity and selectivity for the cobalt catalyst that we have, a review of the available literature on cobalt catalysts has been performed. This includes reduction procedures used in large plants as well as in research facilities.

6.1 Literature Review of Reduction Procedures:

Table 12 summarizes the reduction procedures that are in the literature. Particular attention is given to the composition of the reducing gas and to the temperature profile used during reduction. Generally, the catalysts are reduced in hydrogen and temperature is increased from ambient to between 350°C and 400°C over 4 to 6 h. The catalyst is then held at this maximum temperature for between 2 and 16 h.

The most useful information on the effects of various different reduction procedures is provided in literature published in the 1950s. Cobalt-based catalysts were developed and used in Germany from 1936 to 1945 (Anderson, 1984). Therefore, a good deal of the literature which describes the reduction of cobalt Fischer-Tropsch catalysts comes from data collected in Germany by Ruhrchemie. These data are summarized and analyzed by Storch, et al. (1951) and Storch, et al. (1959). As can be seen from Table 12, most of the recent procedures for the reduction of cobalt catalysts are similar to those outlined by Storch and co-workers. Deviations from the "standard" reduction procedures are generally not explained. As a result, very little can be gained from examining recent work.

On the basis of their own work at the Bureau of Mines and review of work done in Germany, Storch, et al. (1951, 1959) make four important conclusions about the reduction of Co/ThO_2/kieselguhr and $Co/ThO_2/MgO$/kieselguhr catalysts.

1. Sintering must be avoided during reduction. Hence, reduction should be performed in a short bed, with a high space velocity of hydrogen, at the lowest temperature possible, and in the shortest time possible.

2. The most active catalysts were obtained by ending the reduction before all the cobalt was reduced to metal. The most active catalysts had between 55 and 70 percent of available Co reduced. It was speculated that unreduced CoO prevented sintering of the catalyst.

3. When cobalt-based catalysts were reduced and then subsequently carbided with carbon monoxide, the activity of the catalyst was markedly less. A completely carbided sample, presumed to have 100 percent of the cobalt as Co_2C, was shown to be inactive for the Fischer-Tropsch synthesis.

4. It was found that when MgO was present the catalyst was harder to reduce, and thus a maximum reduction temperature of 400°C is recommended for $Co/ThO_2/MgO$/kieselguhr as compared to 360°C for Co/ThO_2/kieselguhr.

6.2 Recommended Preparation and Reduction Procedure:

1. The catalyst is ground to the desired particle size (50 to 90 µm) and calcined overnight at 100°C in a vacuum oven to remove any water from the catalyst sample. This is particularly important as the unreduced catalyst is reported to have a high moisture content.

2. The catalyst is reduced in 3000 V/V/h pre-purified hydrogen at

atmospheric pressure. For the purpose of the space velocity calculations, a catalyst density of 0.65 g/cm^3 will be used.

3. On the basis of the above literature, the following temperature profile is recommended:

A. 100°C for ½ to 1 hour.

B. 200°C for ½ to 1 hour.

C. 300°C for ½ to 1 hour.

D. Heating in 10°C increments from 300°C to 365°C. The temperature should be allowed to level off at each increment for at least ½ hour.

E. Holding at 365°C for 16 hours.

7. Conclusions about Reduction of Co-Based Fischer-Tropsch Catalysts:

Because of the temperatures used during the reduction, it is best to reduce the catalyst in the external reduction unit that has been used to reduce the C-73 fused magnetite catalyst. Reducing the catalyst in the external reduction tube will allow us to monitor the weight of oxygen removed during reduction. Because of the high temperature of the final stage of reduction, it is undesirable to perform the reduction in the slurry reactor. At a temperature of 365°C, a significant amount of octacosane (N.B.P. 432°C) would inevitably be carried over into down-stream sections of the system.

The required reduction conditions are achievable in our external reduction unit without any costly or time-consuming modifications to our current equipment.

8. Future Work.

We now have what we consider to be a viable catalyst for the water-gas shift reaction. It remains, therefore, to add a cobalt Fischer-Tropsch catalyst to the system which already contains the shift catalyst. This will verify the stability of the dual catalyst system. Having reduced the cobalt catalyst as described above, the two catalysts will be combined. The effects of a number of operating parameters will then be examined.

The information that these experiments may provide is expected to be limited, primarily because the run will probably be short. The length of this run may be short for at least two reasons. First, we know very little about the behavior of the cobalt catalyst on its own. We cannot, therefore, expect these series of experiments to provide us with a complete characterization of the combined catalyst system, as we will not necessarily know what kinds of experiments to run. Second, from a more practical standpoint, the reactor has been on-stream for over 1000 hours without shutdown for cleaning or maintenance. To ensure that we are collecting reliable data, cleaning and/or repair may be advisable soon after the addition of the cobalt catalyst to the reactor.

Following the brief combined catalyst run, we plan to examine the kinetics and selectivity of the cobalt Fischer-Tropsch catalyst. Particular attention will be given to understand ways to maximize the selectivity to specified hydrocarbon product cuts, such as gasoline or diesel fuel. Although the development of a complete understanding of the behavior of cobalt-based Fischer-Tropsch catalysts in a slurry reactor will take a good deal of time, preliminary results are expected by the next quarterly.

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Table 1

Outlet Compositions and Flows for Cu 1803-P Run 4

CU 1803P - RUN 4

OXIDIZING CONDITIONS FEED = 0.281 L/MIN CO, 0.486 L/MIN CO2, 0.167 L/MIN H2O

DATE	TIME	TOS	FLOW	%H2	%CO	%CO2	XH2	-XCO	XCO2
JUN 21	08:30	0	0.824	6.740	23.784	69.399	33.254	50.905	51.405
JUN 21	10:30	2.0	0.819	6.772	24.101	69.019	33.211	50.065	47.464
JUN 21	12:30	4.0	0.823	6.735	24.036	69.137	33.191	49.511	49.699
JUN 21	17:30	9.0	0.821	6.597	23.955	69.322	32.432	50.497	49.791
JUN 21	19:00	25.5	0.826	6.544	24.224	69.172	32.365	48.449	51.114
JUN 23	06:00	47.5	0.816	5.976	25.204	68.748	29.199	45.109	44.599
JUN 23	10:00	22.0	0.822	6.317	24.982	68.617	31.093	45.295	46.726
JUN 23	18:00	30.0	0.822	6.233	25.124	68.450	30.650	44.599	45.904
JUN 29	11:00	167.0	0.753	5.431	27.199	67.287	25.463	40.739	24.463
JUL 01	11:30	214.0	0.767	4.690	28.502	66.745	21.541	37.359	15.529

Table 2

Reduction Procedure for Cu 1920-P Run 1 and Katalco 52-2 Run 1

P_r = 100 psig.
Impeller = 800 RPM.
400 g of octacosane.
25 g of Katalco 52-2 (nominal composition 33%CuO/33%ZnO/33%Al_2O_3)

TOS (h)	T (°C)/(°F)	CH1[1] (SLPM/mA)	CH2[2] (SLPM/%)	COMMENTS
0.00	70 / 158	0	0	Under He. Leak test:200 psig. Tr -> 178.
0.50	78 / 172	0	0	Vent He & reload to 100 psig. Tr -> 192.
0.75	89 / 192	0	0	Vent He & reload tc 100 psig. Tr -> 208.
1.00	98 / 208	0	0	Vent He & reload to 100 psig. Tr -> 226.
1.25	108/ 226	0	0	Vent He & reload to 100 psig. Tr -> 248.
1.50	120/ 248	0	0	Vent He & reload to 100 psig.
2.00	120/ 248	0	0	0.1%H_2/N_2 flow -> 0.1 l/min.
2.25	120/ 248	0.1/4.78	0	0.1%H_2/N_2 flow -> 0.3 l/min.
2.50	120/ 248	0.3/6.40	0	0.1%H_2/N_2 flow -> 0.6 l/min.
3.70	120/ 248	0.6/8.79	0	T_r -> 135 / 275.
4.50	135/ 275	0.6/8.79	0	T_r -> 150 / 302.
5.00	150/ 302	0.6/8.79	0	T_r -> 165 / 329.
5.50	165/ 329	0.6/8.79	0	T_r -> 180 / 356.
6.00	180/ 356	0.6/8.79	0	T_r -> 200 / 392.
7.00	200/ 392	0.6/8.79	0	H_2 flow -> 0.02 l/min (01.0 % CH2).
20.00	200/ 392	0.6/8.79	0.02/01.0	Bring onstream.

Notes:

[1] 1000 ppm H_2 in N_2 both prepurified supplied by Specialty Gas Products Inc.

[2] Prepurified H_2 supplied by Med Tech Gases Inc.

Table 3

Outlet Compositions, Flows and Conversions for Cu 1920-P Run 1

TOS (H)	Q (SLPM)	%H2	%CO	%CO2	X H2	-X CO	X CO2
3.500	0.418	46.122	33.676	20.136	51.970	57.625	50.400
5.000	0.416	46.243	33.661	20.043	51.719	58.066	49.927
7.000	0.418	46.458	33.759	19.720	52.811	57.418	49.359
52.500	0.418	44.638	37.794	17.505	48.256	47.318	43.815
54.000	0.424	44.540	37.961	17.444	49.611	45.536	44.289
56.000	0.413	44.043	38.324	17.565	45.448	47.139	43.439
73.000	0.397	42.675	39.801	17.457	37.976	47.299	41.500
75.000	0.395	43.407	39.394	17.130	39.196	48.739	40.517
77.500	0.406	43.636	39.337	16.962	42.612	46.283	41.237
97.500	0.407	42.351	40.802	16.784	39.742	42.477	40.905
103.000	0.405	42.544	40.800	16.597	39.703	42.970	40.250
117.500	0.398	41.815	41.967	16.159	36.182	41.899	38.511
120.000	0.406	42.575	41.276	16.083	40.033	41.569	39.100
122.500	0.403	42.741	41.571	15.634	39.668	41.598	37.728
124.500	0.400	42.753	41.424	15.761	38.929	42.697	37.751
126.250	0.398	42.860	41.322	15.766	38.672	43.436	37.574
142.000	0.401	41.344	42.992	15.587	35.802	38.684	37.427
143.500	0.400	42.333	42.149	15.440	37.923	40.960	36.982
145.000	0.403	42.595	41.992	15.425	39.316	40.582	37.223
167.500	0.403	42.197	42.638	15.107	38.356	39.023	36.456
169.000	0.395	42.171	42.812	14.953	36.273	40.654	35.368
173.500	0.388	42.240	43.042	14.665	34.665	41.914	34.072
190.000	0.390	41.016	44.065	14.856	32.313	39.010	34.694
195.500	0.401	41.607	43.845	14.492	36.434	36.636	34.798
197.000	0.399	41.805	43.727	14.386	36.408	37.443	34.371
215.000	0.386	40.314	45.481	14.157	29.708	36.792	32.722
217.500	0.388	41.023	44.731	14.194	31.838	37.990	32.978
265.500	0.389	39.480	46.386	14.060	28.489	33.867	32.751
286.000	0.389	39.201	46.496	14.242	27.839	33.611	33.174

Table 4

Outlet Compositions, Flows and Conversions for Katalco 52-2 Run 1

KATALCO 52-2 FEED = 0.110437 L/MIN H2 0.236626 L/MIN CO 0.167 L/MIN H2O

RUN1

DATE	TIME	TOS	FLOW	%H2	%CO	%CO2	XH2	-XCO	XCO2
JUL 14	08:30	2.5	0.430	40.330	31.530	28.140	37.714	60.507	72.456
JUL 14	10:00	4.0	0.435	43.576	30.580	25.844	47.376	62.038	67.318
JUL 14	12:00	6.0	0.441	47.029	28.597	24.293	58.060	66.176	64.151
JUL 14	14:00	8.0	0.444	47.416	28.362	24.132	59.934	66.257	64.159
JUL 14	16:00	10.0	0.444	47.814	28.286	23.912	60.992	66.499	63.309
JUL 14	17:30	11.5	0.446	48.268	27.919	23.739	62.777	67.130	63.396
JUL 15	08:00	22.0	0.443	47.527	28.263	24.159	59.945	66.718	64.056
JUL 15	09:30	23.5	0.447	48.094	27.975	23.955	62.601	66.913	63.951
JUL 15	12:45	26.8	0.447	47.900	28.129	23.958	61.914	66.401	64.127
JUL 15	14:30	28.5	0.449	47.956	28.531	23.448	62.518	65.154	62.902
JUL 15	17:00	31.0	0.446	47.965	28.300	23.823	61.976	66.113	63.089
JUL 16	11:30	49.5	0.442	47.445	28.601	23.954	59.452	65.993	63.215
JUL 18	09:00	95.0	0.429	45.292	33.299	21.342	50.219	56.152	54.925
JUL 18	11:00	97.0	0.436	46.987	31.645	21.313	56.543	59.075	55.644
JUL 18	15:00	101.0	0.437	46.243	33.133	20.529	54.977	54.991	53.720
JUL 18	16:30	103.5	0.438	45.903	33.835	20.187	54.262	52.951	52.946
JUL 19	08:00	119.0	0.431	44.785	34.808	20.339	49.453	51.959	52.491
JUL 19	10:00	120.0	0.427	46.149	32.624	21.124	51.968	55.276	54.012
JUL 20 OFFSTREAM UNDER HELIUM FOR 21.5 HOURS.									
JUL 21	07:30	144.0	0.435	45.920	32.523	21.557	52.441	56.152	56.152
JUL 21	09:30	145.5	0.423	46.722	31.479	21.707	52.214	61.958	54.952
JUL 21	11:00	147.0	0.422	46.949	31.385	21.677	52.255	62.354	54.777
JUL 21	16:00	152.0	0.404	47.302	31.240	21.366	48.301	66.115	51.688

Table 5

Reduction Procedure for Katalco 52-2 Run 2

P_r = 100 psig.
Impeller = 800 RPM.
400 g of octacosane.
25 g of Katalco 52-2 (nominal composition 33%CuO/33%ZnO/33%Al_2O_3)

TOS (h)	T (°C)/(°F)	CH1[1] (SLPM/mA)	CH2[2] (SLPM/%)	COMMENTS
0.00	70 / 158	0	0	Helium flow = 0.4 SLPM
16.00	78 / 172	0	0	Helium flow = 0.4 SLPM Tr -> 226.
17.50	108/ 226	0	0	Helium flow = 0.4 SLPM Tr -> 248.
18.00	120/ 248	0	0	Helium flow -> Off; 0.1%H_2/N_2 -> 0.1 l/min.
18.50	120/ 248	0.1/4.83	0	0.1%H_2/N_2 flow -> 0.2 l/min.
19.00	120/ 248	0.2/5.64	0	0.1%H_2/N_2 flow -> 0.4 l/min.
19.50	120/ 248	0.4/7.29	0	T_r -> 135 / 275.
20.00	134/ 274	0.4/7.29	0	T_r -> 150 / 302.
20.50	153/ 308	0.4/7.29	0	T_r -> 165 / 329.
21.00	168/ 334	0.4/7.29	0	T_r -> 180 / 356.
21.50	180/ 356	0.4/7.29	0	T_r -> 200 / 392.
22.50	200/ 392	0.4/7.29	0	0.1%H_2/N_2 ->0.3 l/min; 3%H_2/N_2 -> 0.1 l/min.
23.00	200/ 392	0.3/6.46	0.10/05.0	0.1%H_2/N_2 ->0.2 l/min; 3%H_2/N_2 -> 0.2 l/min.
23.50	200/ 392	0.2/5.64	0.20/10.0	0.1%H_2/N_2 ->0.1 l/min; 3%H_2/N_2 -> 0.3 l/min.
24.00	200/ 392	0.1/4.83	0.30/15.0	0.1%H_2/N_2 ->Off; 3%H_2/N_2 -> 0.4 l/min.
25.00	200/ 392	0	0.40/20.0	Bring onstream.

Notes:

[1] 1000 ppm H_2 in N_2 both prepurified supplied by Specialty Gas Products, Inc.

[2] 3.0 mol% prepurified H_2 in prepurified N_2 supplied by Matheson Gases, Inc.

SLPM is standard liters per minute.

Table 6

Process Changes and Times-on-stream for Katalco 52-2 Run 2 (see note below)

TOS (h)	Process Change
0.0	Bring on-stream with "base case" conditions
303.0	Pressure raised to 1.48 MPa
358.0	Return to "base case" conditions
425.0	H2/CO raised to 1.0. Synthesis gas space velocity held constant
473.0	Return to "base case" conditions
637.0	Temperature raised to 220 C
693.0	Return to "base case" conditions
783.5	H2/CO raised to 0.7. Synthesis gas space velocity held constant
830.0	Return to "base case" conditions
924.5	Added 2 mol% 1-Butene to hydrogen feed.
1030.0	Return to "base case" conditions

Note: "Base case" conditions: T=200 C; P=0.79 MPa; Inlet Flow= 43 mol% CO, 21.4 mol% H2, 35.6 mol% H2O at 0.019 Nl/min/gcat, Impeller speed= 800 RPM.

Table 7

Outlet Composistions, Flows and Calculated Conversions for Katalco 52-2 Run2 "base case" conditions (see text for details)

TOS (h)	Q (SLPM)	%H2	%CO	% CO2	X H2	-X CO	X CO2
0.000	----	----	----	----	----	----	----
18.750	0.468	50.909	21.713	27.312	79.793	76.876	76.539
22.000	0.467	50.674	22.453	26.808	78.831	74.937	74.966
45.000	0.469	49.474	22.421	28.029	76.068	74.758	78.716
92.500	0.469	49.730	23.481	26.723	76.787	71.781	75.048
112.500	0.466	48.109	24.615	27.203	71.370	69.038	75.908
121.000	0.461	50.045	22.083	27.819	75.274	76.765	76.794
136.500	0.454	48.470	23.786	27.666	68.894	73.061	75.212
140.000	0.452	48.903	23.676	27.335	69.486	73.643	73.985
184.500	0.456	47.585	23.996	28.332	67.058	72.203	77.362
192.000	0.456	47.636	24.204	28.096	67.198	71.635	76.717
207.500	0.453	46.713	25.537	27.671	63.838	68.454	75.060
256.500	0.456	46.469	25.295	28.146	64.011	68.656	76.854
260.000	0.457	47.393	24.684	27.815	66.818	70.176	76.116
280.500	0.461	47.486	24.547	27.884	68.210	69.963	76.973
287.000	0.462	47.802	23.561	28.559	69.368	72.544	79.008
303.000	0.463	46.723	25.050	28.151	66.663	68.275	78.047
303.000	P REACTOR TO 200 PSIG						
358.000	P REACTOR BACK TO 100 PSIG						
361.000	0.457	49.230	23.834	26.864	71.845	72.502	73.514
404.000	0.465	49.949	22.660	27.310	76.205	74.629	76.043
423.500	0.461	51.020	23.224	25.691	77.965	73.615	70.919
425.000	0.459	51.134	22.959	25.829	77.668	74.622	70.991
425.000	FLOW CHANGE TO:~ 0.15 L/MIN CO; ~ 0.15 L/MIN H2; ~0.167 L/MIN H2O						
473.000	FLOW CHANGE BACK TO: 0.2 L/MIN CO; 0.1 L/MIN H2; 0.167 L/MIN H2O						
493.500	0.456	49.315	25.206	25.404	71.782	68.899	69.367
499.667	0.450	49.947	24.323	25.660	71.713	72.184	69.144
548.000	0.452	49.857	24.738	25.331	72.068	70.769	68.561
612.500	0.455	47.484	27.286	25.141	66.498	63.382	68.498
615.000	0.451	48.514	26.586	24.816	68.143	65.926	67.018
637.000	0.455	47.738	27.376	24.886	67.191	63.138	67.803
637.000	T REACTOR TO 220 C						
693.000	T REACTOR BACK TO 200 C						
757.500	0.453	47.289	27.495	24.130	65.401	63.142	65.454
762.000	0.450	48.285	27.449	24.178	67.235	63.760	65.150
764.500	0.453	48.038	27.740	24.141	67.432	62.478	65.484
780.500	0.456	48.042	28.138	23.745	68.306	60.893	64.837
782.000	0.455	47.782	28.361	23.799	67.310	60.454	64.842
783.500	FLOW CHANGE TO: CO ~ 0.176 L/MIN; H2 ~ 0.124 L/MIN; H2O ~ 0.167 L/MIN						
830.000	FLOW CHANGE BACK TO: 0.2 L/MIN CO; 0.1 L/MIN H2; 0.167 L/MIN H2O						
853.000	0.458	46.509	30.217	23.165	64.677	54.854	63.530
854.500	0.452	46.702	30.097	23.108	63.529	56.264	62.544
883.500	0.456	48.091	29.110	22.716	68.440	58.239	62.027
924.000	0.453	48.508	28.771	22.639	68.707	59.681	61.410
924.500	FLOW CHANGE TO: 0.2 L/MIN CO; 0.1 L/MIN 2% 1-BUTENE IN 98% H2; 0.167 L/MIN H2O						

Table 8

Outlet Conversions for Katalco 52-2 Run 2: Effect of pressure: 0 to 425 hours-on-stream.

	P = 100 PSIG.			P = 200 PSIG.		
TOS(H)	X H2	-X CO	X CO2	X H2	-X CO	X CO2
0.000	79.793	76.876	76.539			
18.750	78.831	74.937	74.966			
22.000	76.068	74.758	78.716			
45.000	76.787	71.781	75.048			
92.500	71.370	69.038	75.908			
112.500	75.274	76.765	76.794			
121.000	68.894	73.061	75.212			
136.500	69.486	73.643	73.985			
140.000	67.058	72.203	77.362			
184.500	67.198	71.635	76.717			
192.000	63.838	68.454	75.060			
207.500	64.011	68.656	76.854			
256.500	66.818	70.176	76.116			
260.000	68.210	69.963	76.973			
280.500	69.368	72.544	79.008			
287.000	66.663	68.275	78.047			
303.000						
303.000				69.217	73.018	80.265
309.500				72.275	74.162	78.952
311.000				66.149	73.104	81.635
326.500				66.259	71.011	81.239
330.500				71.502	72.426	77.966
334.000				74.432	76.200	79.376
350.000				76.017	79.520	79.913
351.500				73.195	73.425	75.510
356.500				75.014	73.937	75.932
358.000						
358.000	71.845	72.502	73.514			
361.000	76.205	74.629	76.043			
404.000	77.965	73.615	70.919			
423.500	77.668	74.622	70.991			
425.000						

Table 9

Outlet Conversions for Katalco 52-2 Run 2: Effect of H_2/CO inlet ratio: 425 to 924 hours-on-stream.

TOS (h)	H2/CO in	Q (SLPM)	%H2	%CO	% CO2	X H2	-X CO	X CO2	X FLOW
358.000		P REACTOR BACK TO 100 PSIG							
361.000	0.5	0.457	49.230	23.834	26.864	71.845	72.502	73.514	0.701
404.000	0.5	0.465	49.949	22.660	27.310	76.205	74.629	76.043	0.749
423.500	0.5	0.461	51.020	23.224	25.691	77.965	73.615	70.919	0.725
425.000	0.5	0.459	51.134	22.959	25.829	77.668	74.622	70.991	0.713
425.000		FLOW CHANGE TO:~ 0.15 L/MIN CO; ~ 0.15 L/MIN H2; ~0.167 L/MIN H2O							
428.500	1	0.452	61.487	16.016	22.429	67.618	60.843	60.706	0.677
446.500	1	0.459	60.768	16.297	22.862	68.219	59.399	62.836	0.713
448.500	1	0.452	60.517	16.596	22.307	64.992	59.273	61.729	0.671
452.500	1	0.449	60.644	16.247	23.029	64.246	60.510	61.916	0.653
471.000	1	0.450	60.247	16.411	23.246	63.540	59.970	62.639	0.659
473.000	1	0.450	60.163	17.022	22.73	63.313	58.324	61.249	0.659
473.000		FLOW CHANGE BACK TO: 0.2 L/MIN CO; 0.1 L/MIN H2; 0.167 L/MIN H2O							
493.500	0.5	0.456	49.315	25.206	25.404	71.782	68.399	69.367	0.695
499.667	0.5	0.450	49.947	24.323	25.660	71.713	72.184	69.144	0.659
548.000	0.5	0.452	49.857	24.738	25.331	72.068	70.769	68.561	0.671
612.500	0.5	0.455	47.484	27.286	25.141	66.498	63.382	68.496	0.689
615.000	0.5	0.451	48.514	26.586	24.816	68.143	65.926	67.018	0.665
637.000	0.5	0.455	47.738	27.376	24.886	67.191	63.138	67.803	0.689
637.000		T REACTOR TO 220 C							
693.000		T REACTOR BACK TO 200 C							
757.500	0.5	0.453	47.289	27.495	24.130	65.401	63.142	65.454	0.677
762.000	0.5	0.450	48.285	27.449	24.178	67.235	63.760	65.150	0.659
764.500	0.5	0.453	48.038	27.740	24.141	67.432	62.478	65.484	0.677
780.500	0.5	0.456	48.042	28.139	23.745	68.306	60.893	64.337	0.695
782.000	0.5	0.455	47.782	28.361	23.799	67.310	60.454	64.842	0.689
783.500		FLOW CHANGE TO: CO ~ 0.176 L/MIN; H2 ~ 0.124 L/MIN; H2O ~ 0.167 L/MIN							
786.500	0.7	0.447	53.531	23.963	22.439	65.439	59.312	60.061	0.641
790.500	0.7	0.449	53.866	23.320	22.743	66.981	61.253	61.147	0.653
804.000	0.7	0.447	52.865	24.044	23.088	63.657	59.595	61.798	0.641
808.500	0.7	0.448	53.086	24.248	22.589	64.566	58.904	60.599	0.647
829.500	0.7	0.449	53.147	24.072	22.707	65.048	59.232	61.051	0.653
830.000		FLOW CHANGE BACK TO: 0.2 L/MIN CO; 0.1 L/MIN H2; 0.167 L/MIN H2O							
853.000	0.5	0.458	46.509	30.217	23.165	64.677	54.854	63.530	0.707
854.500	0.5	0.452	46.702	30.097	23.108	63.529	56.264	62.544	0.671
883.500	0.5	0.456	48.091	29.110	22.716	68.440	58.239	62.027	0.695
924.000	0.5	0.455	48.500	28.271	22.639	66.272	59.336	61.681	0.689

Table 10

Outlet Conversions for Katalco 52-2 Run 2:
Effect of Temperature: 499 to 703 hours-on-stream.

	T = 200 C			T = 220 C		
TOS(H)	X H2	-X CO	X CO2	X H2	-X CO	X CO2
493.500	71.782	68.899	69.367			
499.667	71.713	72.184	69.144			
548.000	72.068	70.769	68.561			
612.500	66.498	63.382	68.498			
615.000	68.143	65.926	67.018			
637.000	67.191	63.138	67.803			
637.000	T REACTOR TO 220 C					
640.000				80.023	77.071	78.505
661.000				80.139	76.031	77.736
665.000				81.311	78.421	78.293
685.000				81.696	79.205	79.350
688.000				81.911	77.803	77.747
691.500				81.852	78.337	77.792
693.000	T REACTOR BACK TO 200 C					
737.500	65.401	63.142	65.454			
762.000	67.235	63.760	65.150			
764.500	67.432	62.478	65.484			
780.500	68.306	60.893	64.837			
782.000	67.310	60.454	64.842			

Table 11

Outlet Compositions, Flows and Calculated Conversions: The Effect of 1-Butene Addition: 800 to 1000 hours on-stream.

TOS (h)	Q (SLPM)	%H2	%CO	% CO2	X H2	-X CO	X CO2
830.000	FLOW CHANGE BACK TO: 0.2 L/MIN CO; 0.1 L/MIN H2; 0.167 L/MIN H2						
853.000	0.458	46.509	30.217	23.165	64.677	54.854	63.530
854.500	0.452	46.702	30.097	23.108	63.529	56.264	62.544
883.500	0.456	48.091	29.110	22.716	68.440	58.239	62.027
924.000	0.453	48.508	28.771	22.639	68.707	59.681	61.410
924.500	FLOW CHANGE TO: 0.2 L/MIN CO; 0.1 L/MIN 2% 1-BUTENE IN 98% H2;						
925.500	0.433	49.323	28.031	22.569	64.982	65.062	58.504
930.500	0.434	49.689	27.140	23.106	66.258	67.193	60.048
948.000	0.435	49.395	28.156	22.379	65.789	64.384	58.293
949.500	0.436	49.092	28.407	22.437	65.294	63.560	58.578
951.000	0.436	48.782	28.890	22.277	64.485	62.299	58.160
954.000	0.435	47.844	29.744	22.355	61.749	60.248	58.230
958.500	0.435	47.970	29.426	22.532	62.078	61.076	58.691
973.000	0.434	47.622	30.253	22.070	60.886	59.103	57.356
974.500	0.434	47.642	29.810	22.461	60.938	60.254	58.372
983.000	0.435	47.926	29.232	22.769	61.963	61.581	59.308
996.000	0.435	47.293	29.526	22.421	60.314	60.816	58.402

TABLE 12

REDUCTION OF COBALT-BASED FISCHER-TROPSCH CATALYSTS

CATALYST	GAS	SPACE VELOCITY (v/v/h)	P (psig)	T. HISTORY (°C)	REFERENCE
Co/ThO_2/MgO kieselguhr (used by Ruhrchemie in plant)	75 H_2/ N_2	10000	Not Given	1 h at 400°C	Storch, et al., 1951.
Co/ThO_2/MgO/ kieselguhr	N_2 H_2	No flow 3000	0	2 h to 400°C 2 h at 400°C	Storch, et al., 1951.
Co/ThO_2/ kieselguhr	H_2	250 to 3000	0	1 h at 250°C 2 h at 280°C 2 h at 300°C 2 h at 330°C 5 h at 360°C	Storch, et al., 1951.
Co/ThO_2/MgO/ kieselguhr	H_2	250 to 3000	0	1 h at 250°C 2 h at 280°C 2 h at 300°C 2 h at 350°C 5 h at 400°C	Storch, et al., 1951.
Co/Cu/Al_2O_3	H_2	Not given	5	1 h at 250°C 4 h at 510°C	Yang, et al., 1979.
Co/M/Al_2O_3 Co/M/kies. M=Cr,Cu,Mn w	H_2	900	33	16 h at 400°C	Dent and Lin, 1979.
Co/Fe	H_2 10 vol% CO in helium	4000	0	1 h at 300°C 2 h at 450°C 16 h at 350°C	Nakamura, et al. 1979.
Co/Ru/ThO_2/ Al_2O_3	5% H_2/N_2 H_2 2% Air/N_2	1000	Not Given	1 h at 100°C 2 h at 200°C 16 h at 360°C 16 h at 200°C	Beutner, et al., 1983.
Co/Al_2O_3 Co/ThO_2	H_2	Not given	0	16 h at 400°C 1 h at 300°C	Reuel and Bartholomew, 1984.
Co/Al_2O_3	H_2	1000	140	4 h at 400°C	Lu, 1985.
Co/SiO_2	H_2	Not given	0	12 h at 350°C	Zhang, 1986.
Co Co/B	H_2	Not given	0	16 h at 400°C	Wang, 1987.

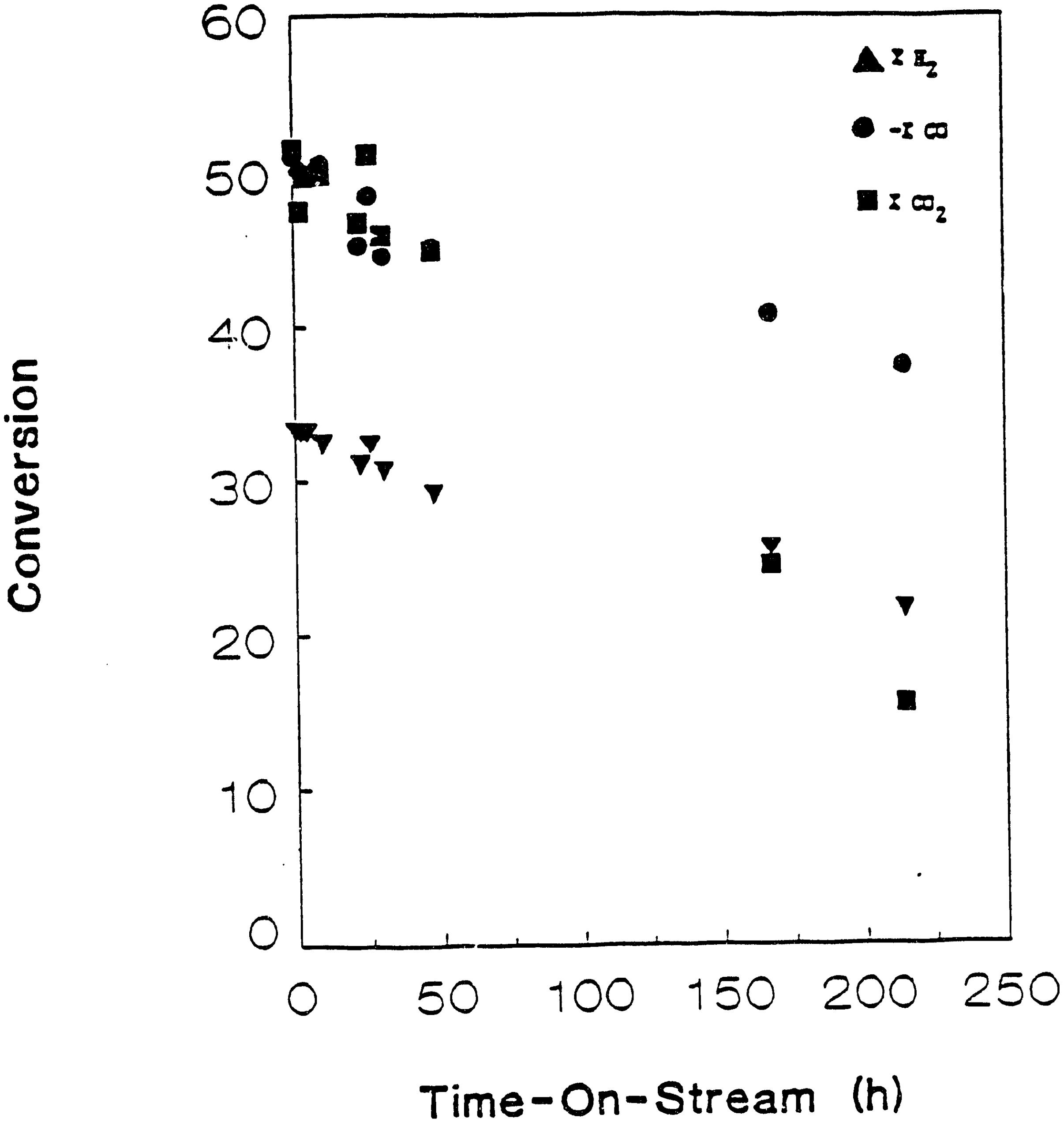


Figure 1. Time-on-stream Dependence of Conversion of H_2, CO, and CO_2 for Cu 1803-P Run 4.

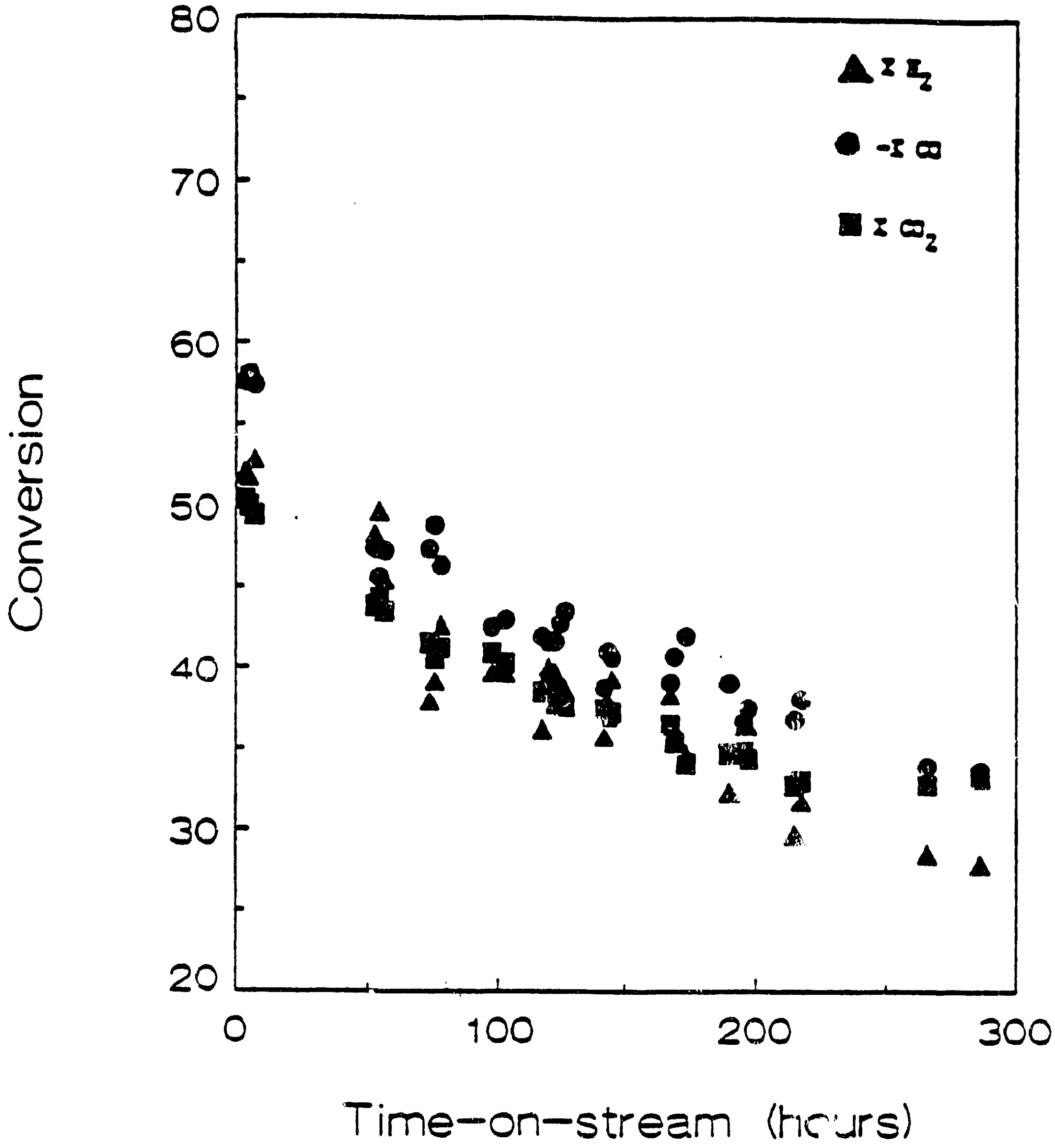


Figure 2. Time-on-stream Dependence of Conversion of H_2, CO, and CO_2 for Cu 1920-P Run 1.

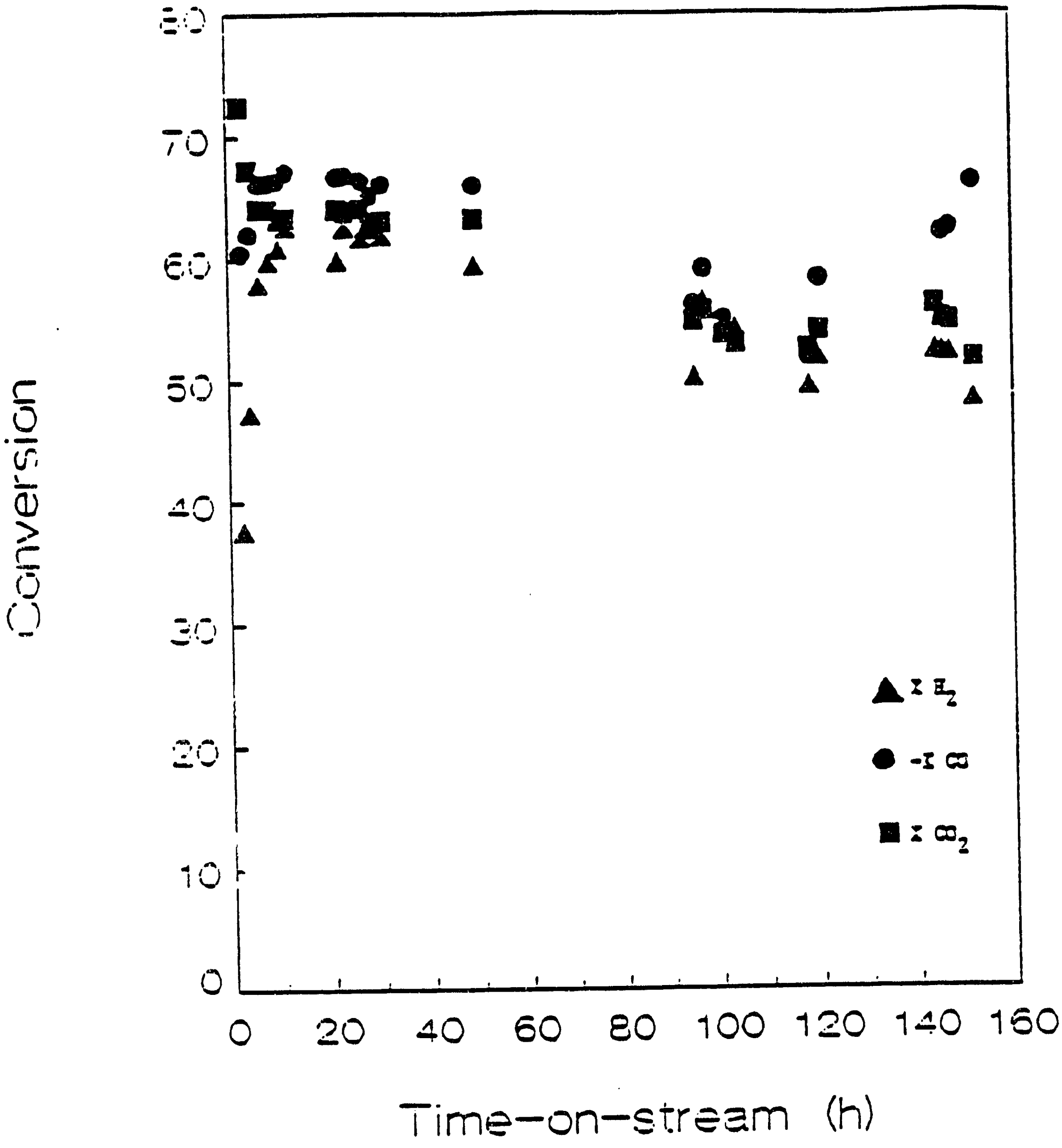


Figure 3. Time-on-stream Dependence of Conversion of H_2, CO, and CO_2 for Katalco 52-2 Run 1.

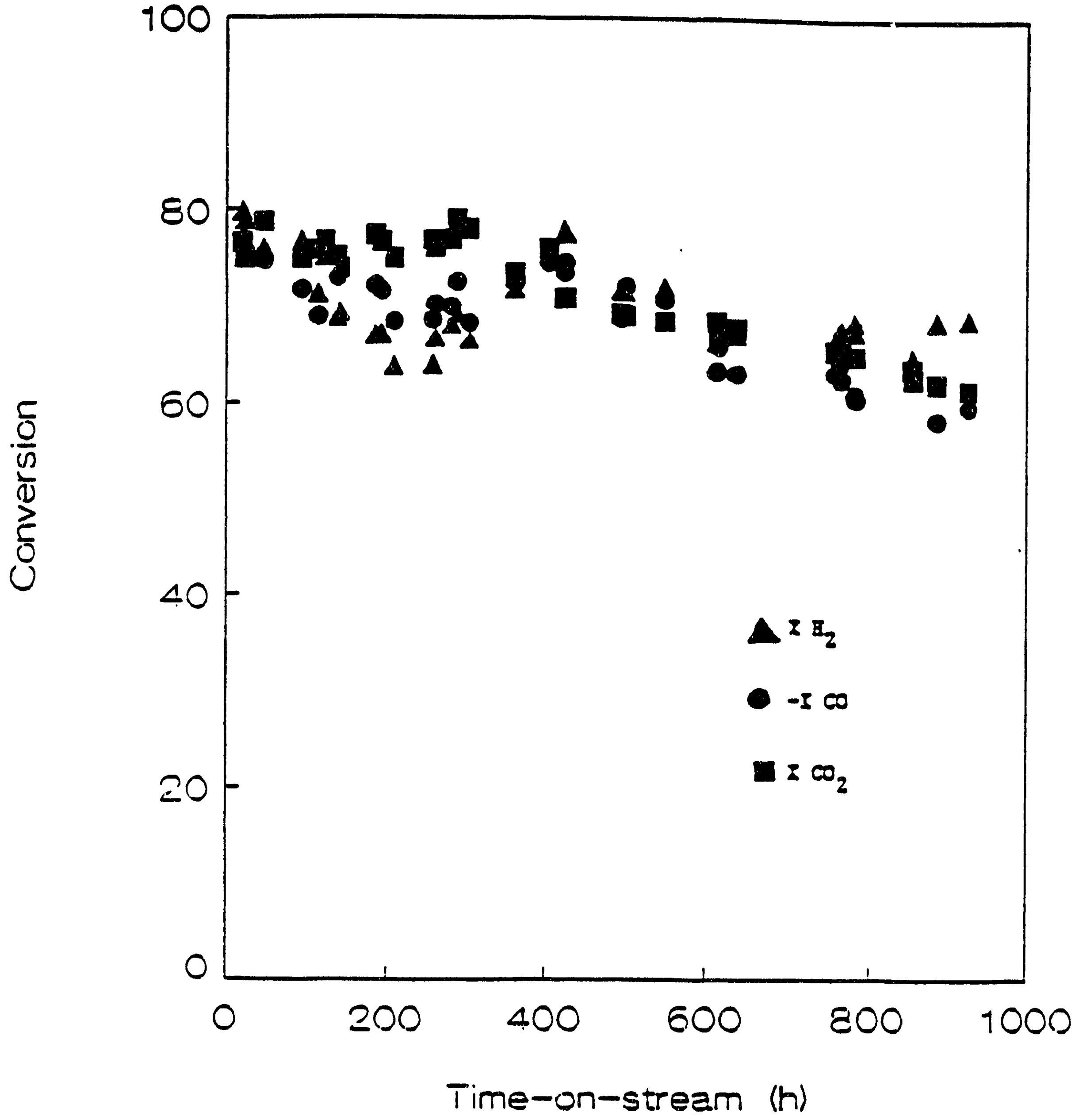


Figure 4. Time-on-stream Dependence of Conversion of H_2, CO, and CO_2 for Katalco 52-2 Run 2. Temperature=200°C, Pressure =0.79 MPa, Inlet Flow= 43 mol% CO, 21.4 mol% H_2, 35.6 mol% H_2O at 0.013 Nl/min/gcat.

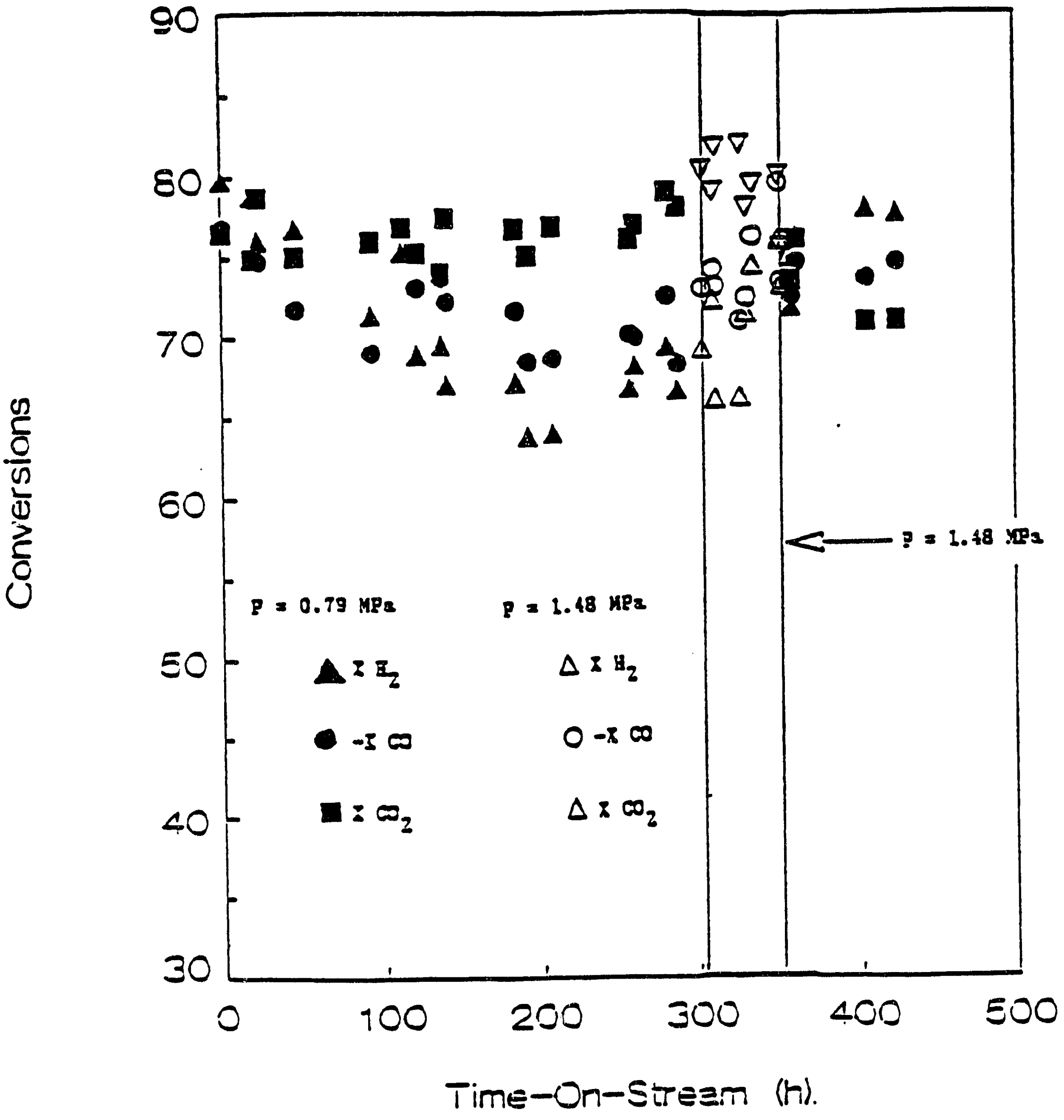


Figure 5. The Pressure Dependence of Conversion of H_2, CO, and CO_2 for Katalco 52-2 Run 2. Temperature=200°C, Inlet Flow=43 mol% CO, 21.4 mol% H_2, 35.6 mol% H_2O at 0.019 Nl/min/gcat.

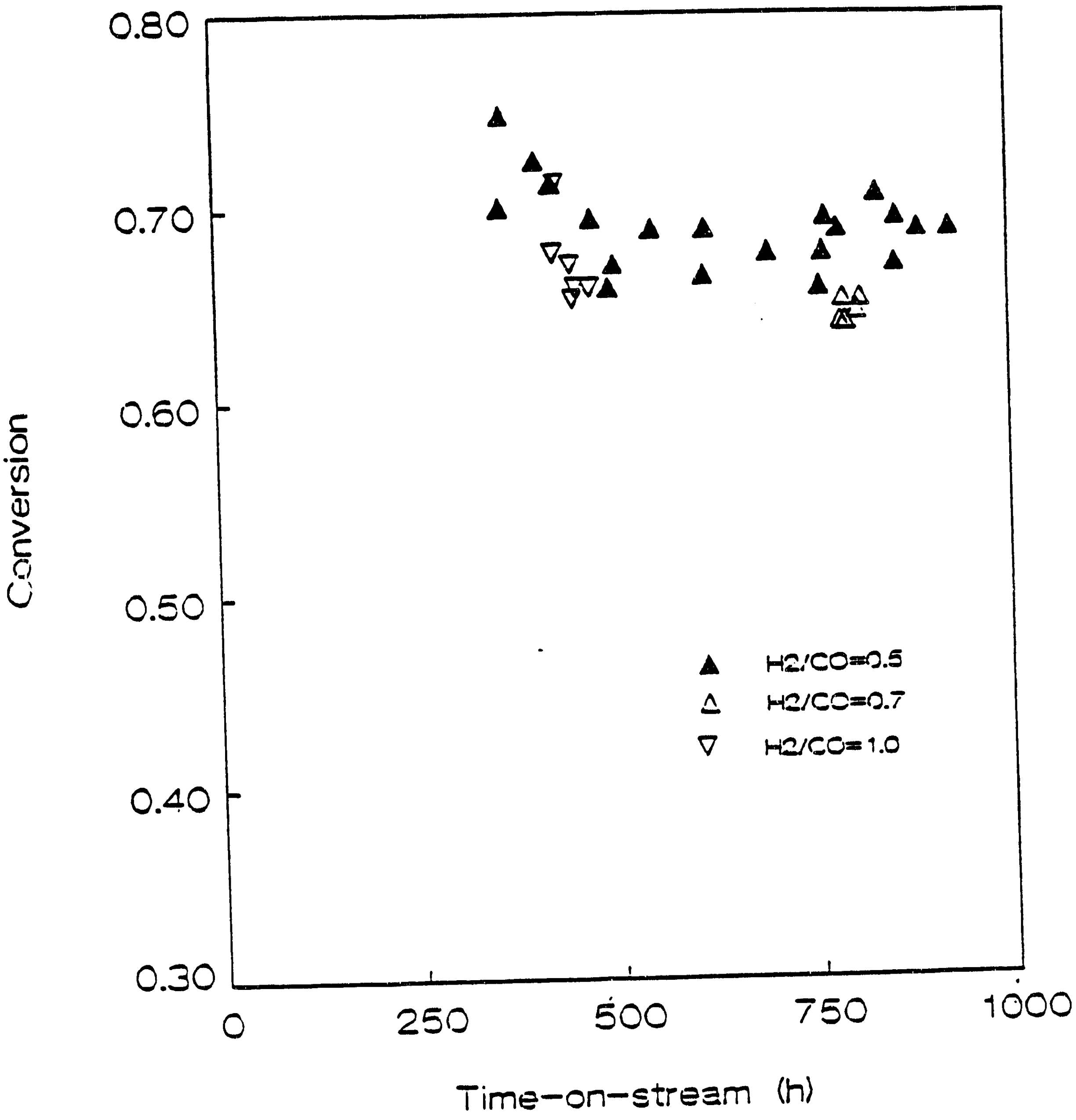


Figure 6. The Dependence of Conversion of H_2, CO, and CO_2 on inlet H_2/CO ratio for Katalco 52-2 Run 2. Temperature=200°C, P=0.79 MPa, Inlet Flow = 0.019 Nl/min/gcat.

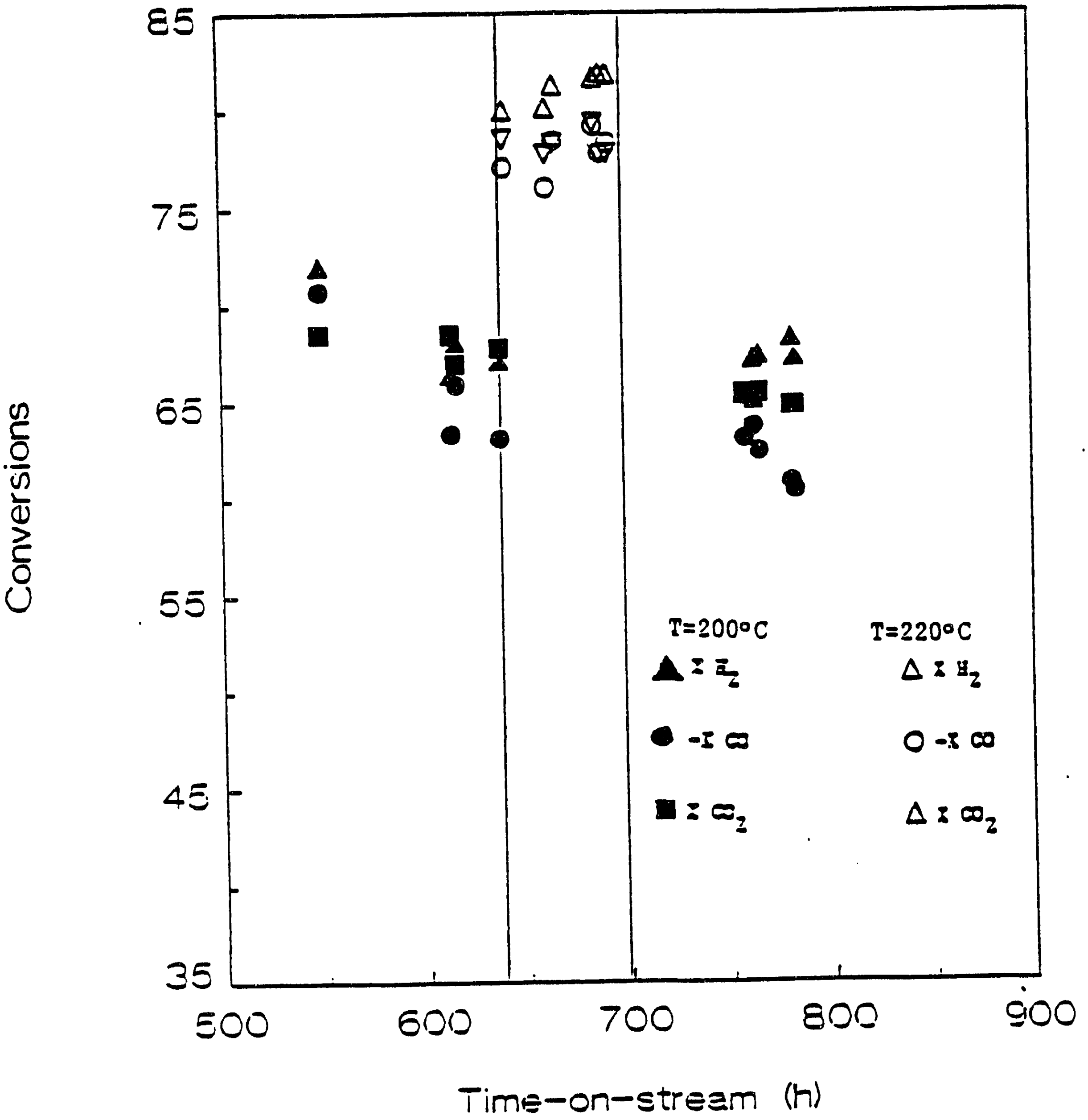


Figure 7. Temperature Dependence of Conversion of H_2, CO, and CO_2 for Katalco 52-2 Run 2. P=0.79 MPa, Inlet Flow=43 mol% CO, 21.4 mol% H_2, 35.6 mol% H_2O at 0.019 Nl/min/gcat.

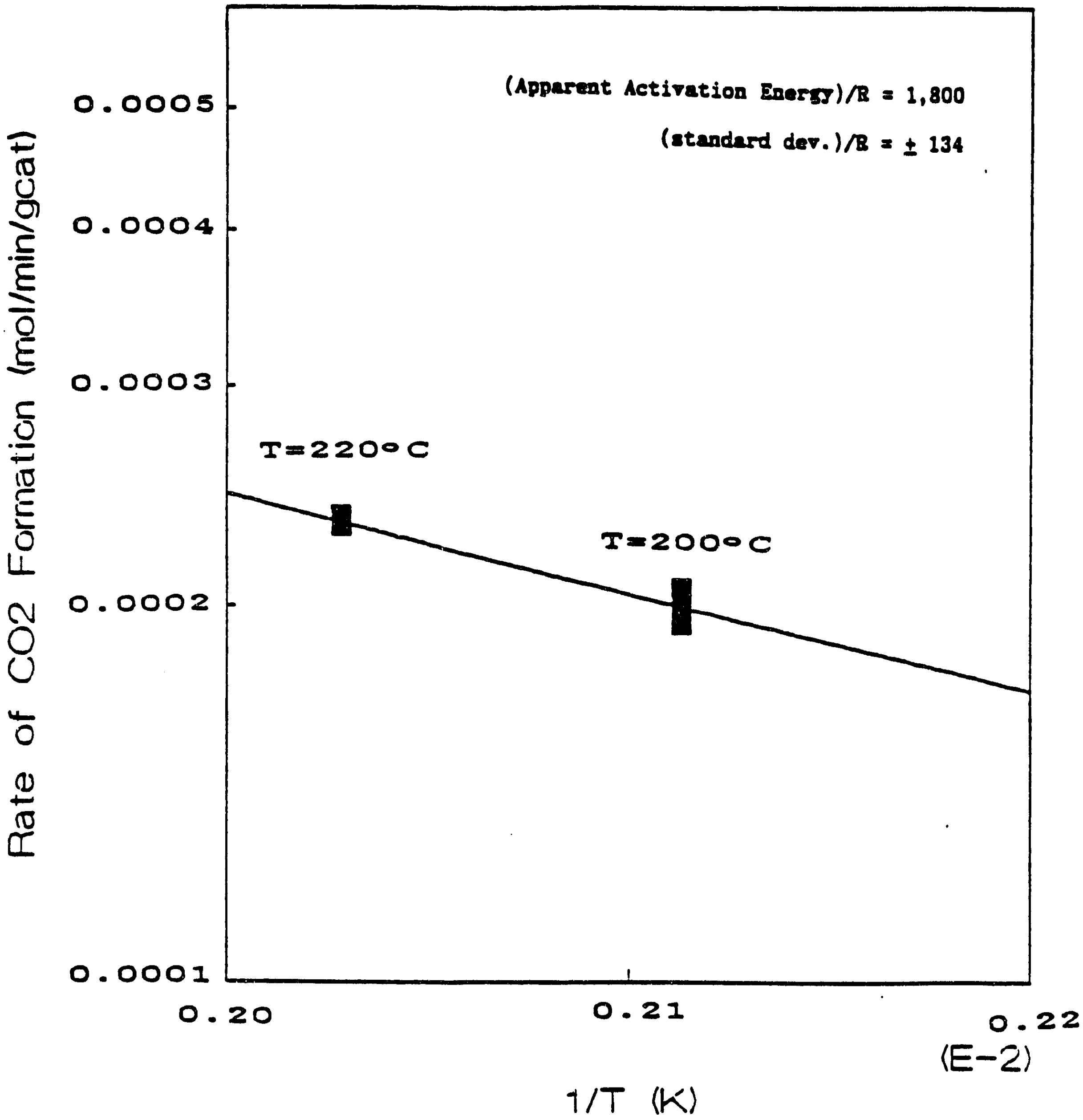


Figure 8. Arrhenius Plot for Katalco Run 2. P=0.79 MPa, Inlet Flow=43 mol% CO, 21.4 mol% H_2, 35.6 mol% H_2O at 0.019 Nl/min/gcat.

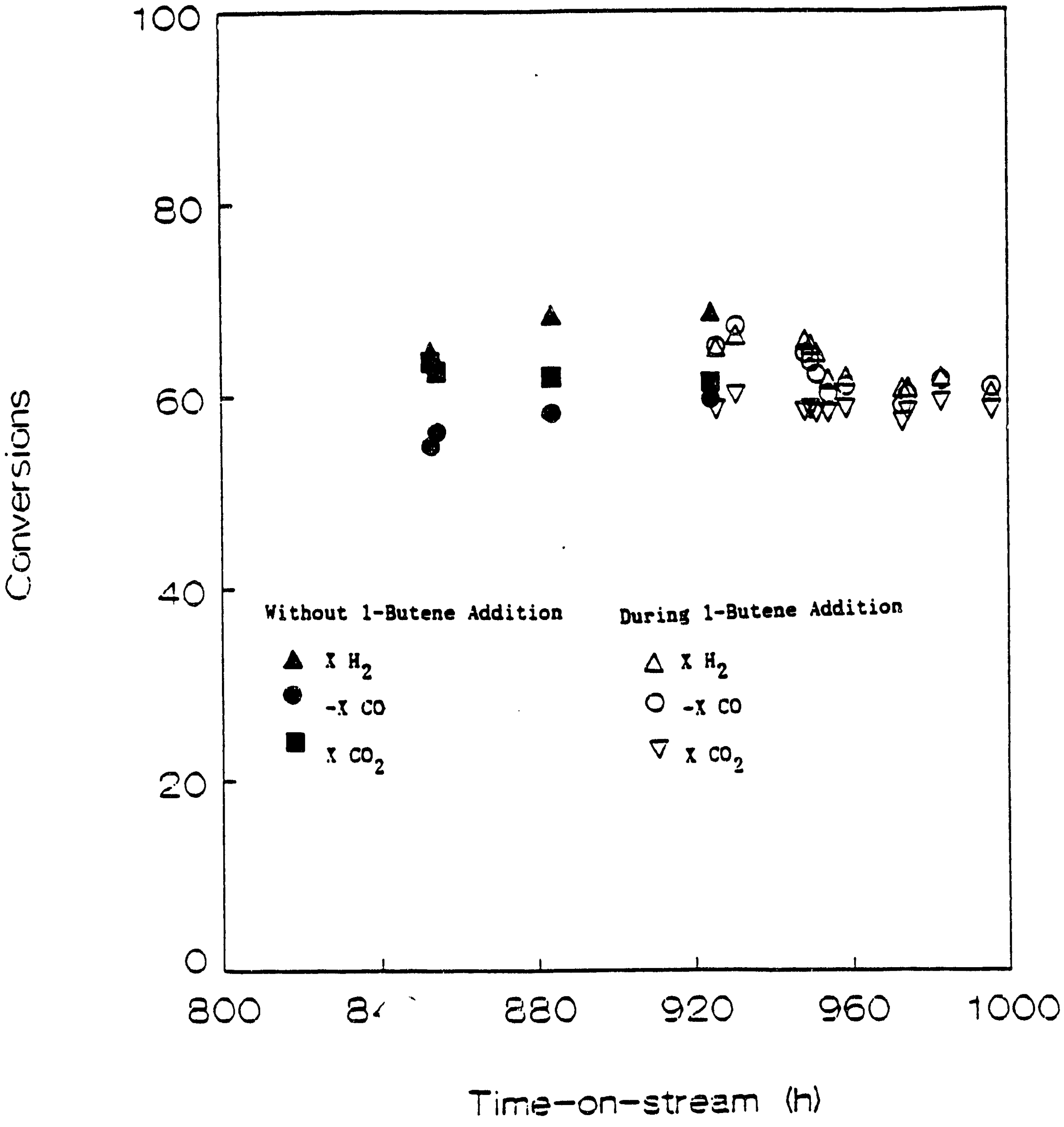


Figure 9. The effect of 1-butene on the conversions of the water-gas shift reaction for Katalco 52-2 Run 2. T=200°C, P=0.79 MPa, Inlet Flow = 42 mol% CO, 20.4 mol% H_2, 35.6 mol% H_2O, and 2 mol% 1-butene at 0.019 Nl/min/gcat.

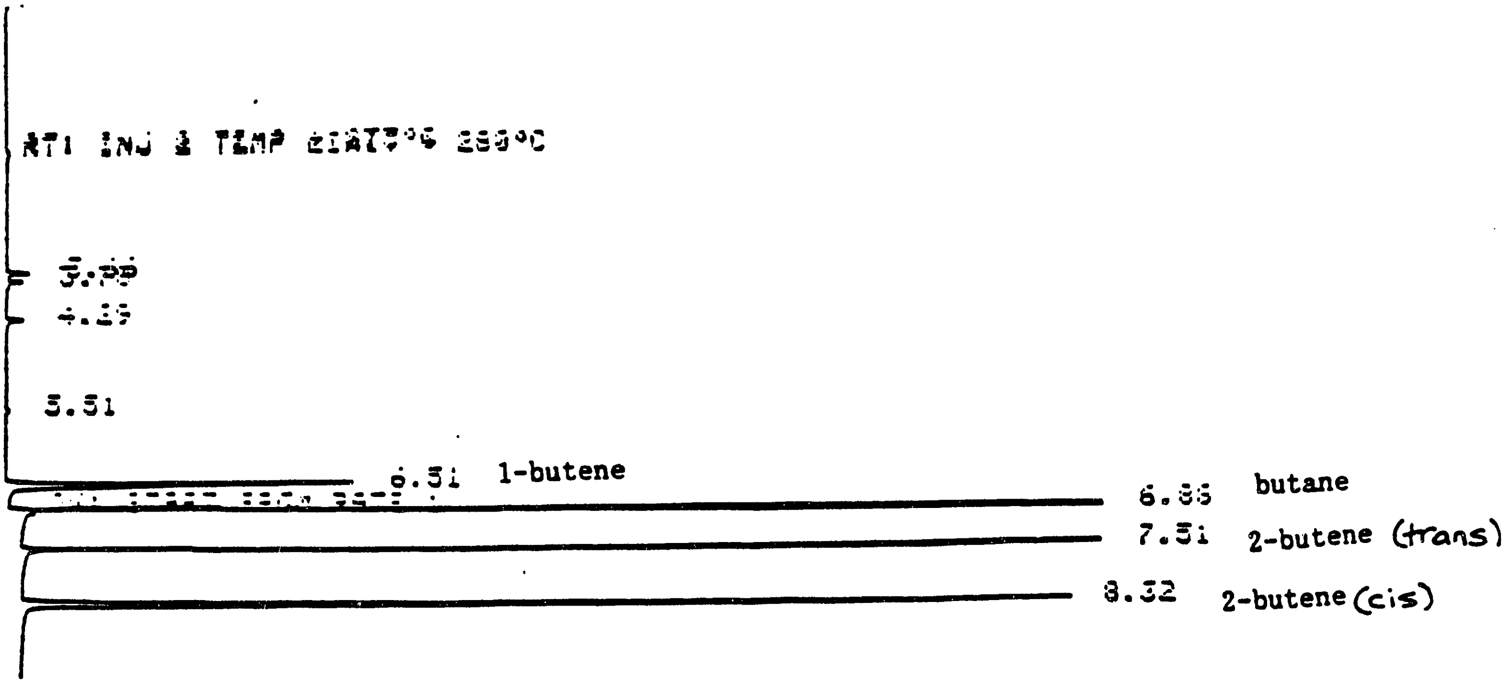


Figure 10 a

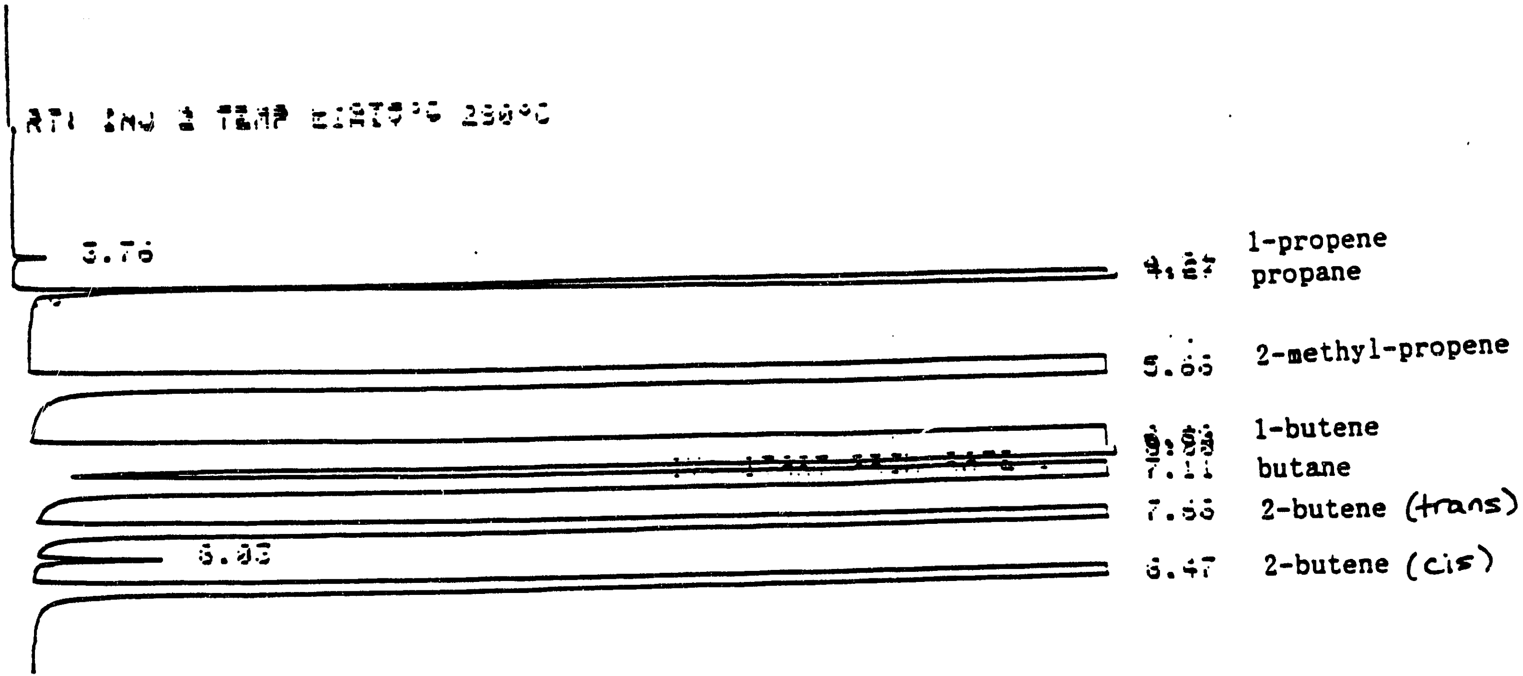


Figure 10 b

Figure 10: a). Typical hydrocarbon gas chromatagraph for 1-butene addition experiments with components assigned to peaks.

b). Hydrocarbon gas chromatagraph for ASTM Section L, Blend 6 mixture. Peaks labelled to verify above analysis.

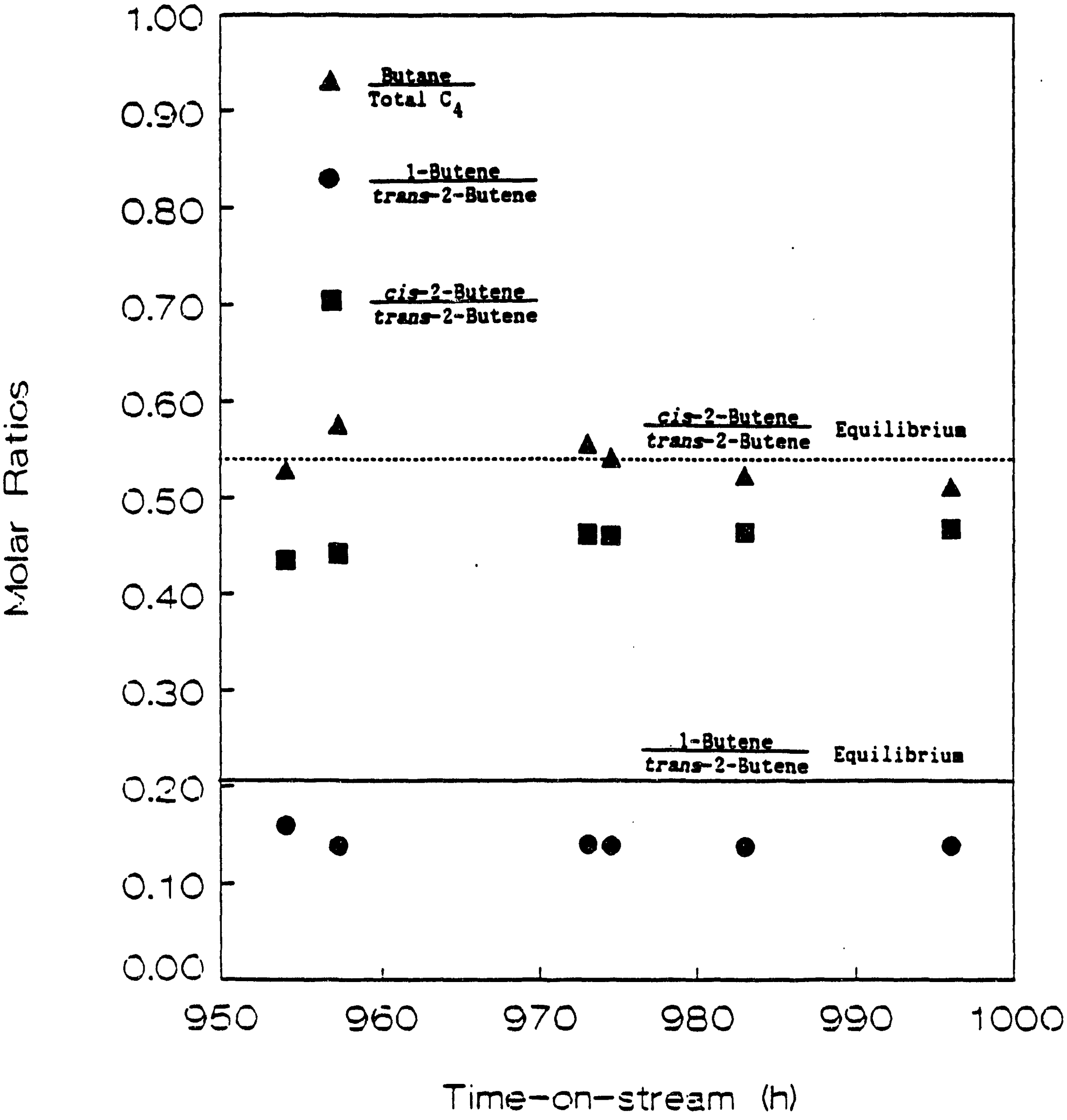


Figure 11. Time-on-stream dependence of selectivties of added C_4 compounds for Katalco 52-2 Run 2. T=200°C, P=0.79 MPa, Inlet Flow = 42 mol% CO, 20.4 mol% H_2, 35.6 mol% H_2O, and 2 mol% 1-butene at 0.019 Nl/min/gcat.

Appendix 1

Product Information: Katalco 52-2 Low Temperature Shift Catalyst

KATALCO

52-2

Product Bulletin KAT-52-2

A strong, active low temperature shift catalyst —

- ***High thermal stability***
- ***Good poison resistance***
- ***Fast reducing***

USE

Low temperature CO conversion by the reaction:

$$CO + H_2O = CO_2 + H_2$$

KATALCO 52-2 requires initial reduction of the copper oxide to copper, after which it normally operates in the temperature range of 380 – 482°F. The normal operating pressure range is up to 50 atmospheres. Normal wet gas space velocities are in the range of 2000 – 5000 volumes of gas at STP per hour per volume of catalyst. Your Katalco Sales and Service Representative will provide detailed recommendations on request.

DESCRIPTION

KATALCO 52-2 is a strong, poison-resistant low temperature shift catalyst. It exhibits a slower rate of die-off than KATALCO 52-1, while maintaining high activity.

KATALCO 52-2 is manufactured as a 5.4 x 3.6 mm pellet with the following typical composition:

CuO	30 – 35% weight loss free
ZnO	29 – 36% weight loss free
Al_2O_3	Balance
Bulk Density	62 ± 5 lb/cu ft
Vertical Crush Strength	195 ± 25 lb

POISON RESISTANCE PROVIDES LONGER LIFE

Sulfur and chlorine are the two most lethal poisons of low temperature shift catalysts. For maximum LTS catalyst life, meticulous attention should be paid to steam purity and feedstock contamination. KATALCO 52-2 has a high surface area of free zinc oxide available for sulfur pickup.

Catalyst	% ZnO	Free ZnO Surface area, m^2/g
52-2	33.[illegible]	36
X	45.[illegible]	29
Y	32.3	15

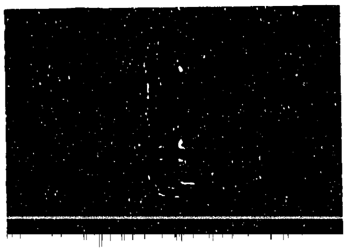
Grab samples from the top of a 1000-tpd Kellogg ammonia plant (Figure 1) at 2 years gave the following analyses:

Contaminant	Sample 1	Sample 2
Sulfur	0.45%	0.85%
Chlorine	0.21%	0.36%

These results show excellent retention of both sulfur and chlorine at the top of the bed to allow good performance under adverse conditions.

(Continued on Reverse Side)

KATALCO CORPORATION
2901 BUTTERFIELD ROAD □ OAK BROOK, ILLINOIS 60521



[illegible] of Katalco Corporation □ Printed in U.S.A. 9-81

ONG LIFE AND LOW PRESSURE ROP

y using KATALCO 52-2 low temperature shift catalyst, plant can achieve a long low temperature shift life ithout the pressure drop penalty associated with maller pellets. Pressure drop can be costly; your atalco Sales and Service Representative can help ou determine your potential cost savings.

AST REDUCTION TIME RODUCES MORE H_2 OR NH_3 AND ASTES LESS GAS

ATALCO 52-2 is reduced at temperatures between 00 and 480°F using 2% hydrogen for most of the eduction (6–14% at the end). This allows a fast eduction with minimal plant downtime and carrier gas wastage.

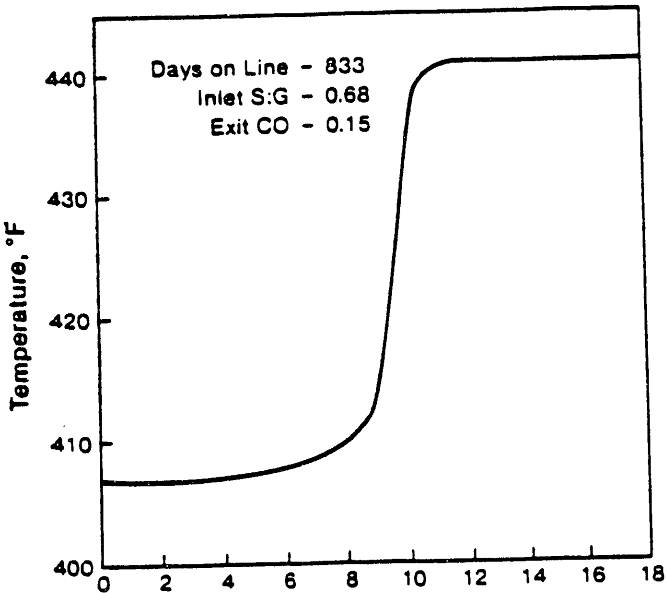


FIGURE 1 — *KATALCO 52-2 in a 1000-tpd Kellogg ammonia plant*

TWO PLANT RECORDS

A mixed charge of KATALCO 52-2 and KATALCO 52-1M produced a record low CO slip of 0.17% (equilibrium at an inlet S:G of 0.585) after 760 days of service at 120% rate in one 600-tpd ammonia plant. KATALCO 52-2 had a record 28-month run in a problem LTS vessel, which previously had never exceeded a 14-month acceptable life.

SHIPPING

KATALCO 52-2 is shipped in steel drums (7.5 cu ft per drum). A substantial inventory is maintained at our Chicago warehouse.

FOR FURTHER INFORMATION

If you would like to know more about KATALCO 52-2, contact your local Katalco Sales and Service Representative, or phone 312–887-1120.

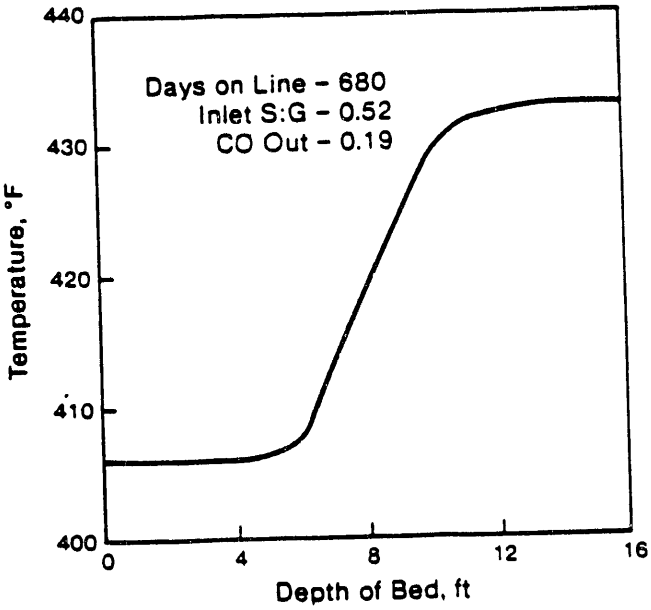


FIGURE 2 — *KATALCO 52-2 in a 1000-tpd ammonia plant*

Appendix 2

Recommended Reduction Procedure for Katalco 52-2

Katalco

Process Catalysts

KATALCO 52 SERIES

REDUCTION PROCEDURE

Katalco 52 Series as supplied contains copper oxide, it is activated for the Low temperature shift duty by reducing the copper oxide component to metallic copper with hydrogen. The reaction is highly exothermic. In order to achieve maximum activity, good performance and long life, it is essential that the reduction is conducted under correctly controlled conditions. Great care must be taken to avoid thermal damage during this critical operation.

RECOMMENDED PROCEDURE

1. Purge the converter free of oxygen with an inert gas. If natural gas is to be used as the carrier gas, then normal safety procedures for gas/air systems should be followed.

2. Check all associated pipework is free of water, then establish a flow of carrier gas (nitrogen or natural gas) at a space velocity of 150-800 hrs^{-1}. The reduction is more quickly completed at higher space velocities.

3. On most plants the reduction may be carried out at any convenient pressure. To ensure adequate flow distribution, it is recommended that the pressure be such that the superficial linear velocity is at least 0.2 ft/sec.

4. Heat the catalyst at a rate of not greater than 150°F/hour. During the heat up, while the bed temperatures are below 250°F, the hydrogen injection valve should be checked and calculated over the range 0.5 - 2% hydrogen inlet the converter. This should be done as swiftly as possible and the valve isolated between injections.

5. When at least one-third of the bed is at 330-350°F establish a hydrogen flow, aiming for not greater than 1% H_2 at this stage. When gas analysis confirms the hydrogen concentration and the exotherm is stable, the hydrogen concentration may be raised to approximately 2% in stages. THIS MUST BE DONE WITH CAUTION AND ONLY IF THE CATALYST TEMPERATURES ARE AT A SAFE LEVEL AND THE ENTIRE SYSTEM IS STABLE.

   With Katalco 52 Series the maximum bed temperature during reduction should be limited to 470°F. In any situation, if a bed temperature reaches 480°F then the inlet hydrogen should be reduced to less than 1%.

6. When an elevated hydrogen concentration consistent with a safe temperature is established, the reduction should be allowed to continue until the exit gas analysis indicates a rising hydrogen concentration. When the inlet and exit hydrogen concentrations differ by less than 0.5%, the inlet hydrogen should be raised above 5% in stages. The bed temperatures should be watched closely after each hydrogen adjustment.

7. The entire bed should be raised to 400-420°F.

8. The reduction can be considered complete when the entire bed is at 400°F or greater and the inlet and exit hydrogen concentrations differ by no more than 0.2%.

9. The catalyst can now be put into service.

POINTS TO NOTE

A) EQUIPMENT/UTILITIES

I) Carrier Gas

Desulfurized natural gas and nitrogen are acceptable. Ideally the carrier gas is hydrogen and oxygen free. In the event of contamination, levels should be

Hydrogen	not greater than 0.5%
Oxygen	not greater than 0.1%

(Note 0.1% oxygen consumes 0.2% hydrogen and produced an exotherm of 30°F in nitrogen).

II) Hydrogen Source

The hydrogen should be free of sulfur and chlorides. Carbon monoxide in the hydrogen is acceptable but the additional associated temperature rise must be allowed for.

III) Temperature Control

There must be an adequate mechanism for inlet gas temperature control and as an absolute minimum. thermocouples at the inlet and exit of the bed.

IV) Sample Points

Gas sample points must be available inlet and exit

V) Pressure Control

The system must have an adequate mechanism for pressure control. Wild pressure fluctuations might otherwise result in unacceptable surges of hydrogen flow to the catalyst.

VI) Cooling/Condensing/Catchpot

Recirculating systems must have a mechanism for controlled removal of the water of reduction.

B) CONTINGENCIES

I) With natural gas as the carrier in the event of an excessively high temperature (above 550°C), additional hydrogen can be produced by the thermal cracking of the gas. Should, for whatever reason, an excessive temperature rise occur, the natural gas must be isolated and the contents of the reactor purged and cooled with nitrogen.

II) In the event of a temperature runaway, the vessel pressure should be reduced to minimize any chance of vessel damage.

III) Again, in the event of thermal runaway, if posssible the heat should be vented by reverse flow to avoid damage to hitherto unaffected catalyst.

APPENDIX 3

Calculation of Effectiveness Factor for Katalco 52-2

Page numbers given in parentheses are for

Satterfield, C.N., Mass Transfer in Heterogeneous Catalysis, Robert E. Krieger Publishing Company, Malabar, Florida, 1970.

from which the outline of the analysis in taken.

Without definitive knowledge of the kinetics, the following Φ_s analysis is used, as recommended.

$$\Phi_s = \frac{R^2}{D_{eff}} \left[\frac{-1}{V_c} \frac{dn}{dt} \right] \frac{1}{C_s} \qquad (p.142) \qquad (1)$$

where: R = radius of catalyst particle (if spherical) [cm]

D_{eff} = effective diffusivity [cm^{2}/s]†

$\frac{-1}{V_c}\frac{dn}{dt}$ = observed rate of reaction unit volume of catalyst [mol/s·cm^{3}of cat.]†

C_s = concentration [mol/cm^3]†

$\dagger$ denotes that this refers to the "key" species.

This leaves us to chose the key species for the forward water-gas shift reaction and then to estimate all the parameters in equation (1):

$$CO + H_2O \Longleftrightarrow H_2 + CO_2 \qquad (2)$$

Therfore, the choice is between CO and H_2O. In the current system,

$P_{CO} > P_{H_2O}$ and

$D_{CO} < D_{H_2O}$

therefore, we would expect Φ_s to be similar were it calculated on either basis. However we will choose H_2O because C_s should be lower because its Henry's law constant for octacosane would be lower.

Calculation of R:

R = D/2 where D is the diameter determined from the size fraction which lies between 50 and 90 µm (170 to 270 ASTM Mesh).

$$R = \frac{70 \times 10^{-4}}{2} \text{ cm} = 3.5 \times 10^{-3} \text{ cm}$$

Estimation of D_{eff}:

$D_{eff} \approx 10^{-5}$ cm^2/s for dilute liquids diffusing through liquids.

Calculation of V_c:

$V_c = 25$ gcat/[(70lb/ft³)(ft³/28,316cm³)(1000g/2.21b)]

$= 22.25$ cm^3

Calculation of $-\frac{dn}{dt}$:

$$-\frac{dn}{dt} = \frac{(0.167 \text{ Nl/min } H_2O \text{ in})(0.7 \text{ conversion})}{(22.4 \text{ Nl/mol})(60 \text{ s/min})}$$

$= 8.33 \times 10^{-5}$ mol/s

Estimation of C_s:

$C_s =$ H.P where: H is the Henry's law constant

$H \approx 40$ mol/m^3MPa for H_2 and CO in C_{28}
(Matsumoto and Satterfield, 1985)

Assume it's about the same for H_2O.

$= (40\ mol/m^3MPa)(1\ m^3/1{,}000{,}000\ cm^3)(0.1\ MPa)$

$= 3 \times 10^{-6}$ mol/cm^3

Plug into equation (1)

$$\Phi_s = \frac{R^2}{D_{eff}} \left[\frac{-1}{V_c} \frac{dn}{dt} \right] \frac{1}{C_s} \qquad \text{(p.142)}$$

≈ 1.513

Assume isothermal catalyst pellet (ß=0). Then, from Figure 3.6 (p. 145), the effectiveness factor is in around 0.7 to 0.8.

Note: for 270 to 325 ASTM Mesh the average particle radius would decrease from 3.5×10^{-3} cm to 2.3×10^{-3} cm which would lower the Φ_s to 0.65 and raise the effectiveness factor to around 0.9 to 0.95.

END

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