DISCUSSION OF RESULTS

Catalyst Selection

The following nine catalysts were selected for testing:

- BASF K8-11, made by Badische Anilin und Soda-Fabrik AG, which consists of cobalt and molybdenum oxides on a special carrier. It was used in a commercial plant for the production of ammonia from the gasification of heavy fuel oil (Texaco Process). It was specially developed as a shift conversion catalyst for use in systems at pressures higher than 40 atm. The feed gas must contain some hydrogen sulfide to ensure retention of catalyst activity.

- C25-1-01 (formerly C20-6-02), made by Catalysts and Chemicals Inc., is a cobalt-molybdenum catalyst on alumina. It was used in oil desulfurization processes and was tested by CCI in shift conversion prior to submission to IGT for evaluation.

- Catalyst C25-1-02 (formerly C20-6-03), made by Catalysts and Chemicals Inc., is also cobalt-molybdenum. CCI tested it at 1000 psig and over a temperature range of 700° to 990°F with a feed composition of carbon monoxide, carbon dioxide, hydrogen, hydrogen sulfide, and water, but without benzene, ammonia, or phenol. The results were satisfactory, and it was sent to IGT for further evaluation.

- Comox 207, by Laporte Chemical Co., was represented by LDI Catalyst Co., a subsidiary of W.R. Grace and Co. It is a cobalt-molybdenum catalyst used in Lurgi coal gasification plants after water quenching.

- G-3B, made by Girdler Chemicals, Inc., is a chromium-promoted iron-oxide catalyst. It is one of the standard shift catalysts used in hydrogen and ammonia plants.

- Catalyst G51C, made by Girdler Chemicals, Inc., is a low-density cobalt-molybdenum catalyst. It is used principally for hydrodesulfurization of hydrocarbons.

- G-93 (formerly T-2021), made by Girdler Chemicals, Inc., is a cobalt-molybdenum catalyst. It was made to IGT specifications so that it would not require presulfiding and would have some resistance to ammonia and phenol poisoning.

- Catalyst 538, by Shell Oil Company, is a cobalt-molybdenum catalyst that was used in oil gasification plant and has been modified to fulfill our requirements.

- UC-1870-46-1, made by Union Carbide Corp., is a nickel-molybdenum catalyst on zeolite. Prior to submitting this catalyst to IGT for extensive evaluation, Union Carbide had tested it and other shift catalysts, which included UC-1050-56-2, UC-1870-44, UC-1870-50, G-51C, and CCI-5593. Their experimental data showed that the UC-1870-46-1 catalyst had the best performance in the presence of sulfurs and benzene and did not require pretreatment.

Life-Test Results — BASF Catalyst K8-11

This catalyst was one of three selected for preliminary tests. These short-term tests used the major gas components encountered in the raw gasifier product gas at 1000 psi. From the preliminary tests, two catalysts were selected for a life test of 1000+ hours to observe the long-term effect of benzene. During the life test, catalyst activity for destruction or hydrogenation of trace contaminants was also determined.

The BASF catalyst K8-11 was supplied in an oxidized state. After crushing and screening the −6+8 mesh size, the reactor was charged with 30.8 grams of catalyst. It was pretreated in the reactor at 560°F in a flowing atmosphere of nitrogen, followed by a 3 mole % hydrogen sulfide-in-hydrogen mixture at atmospheric pressure to sulfide the catalyst. Sulfur analysis for the feed and product gas streams during the sulfiding of BASF catalyst K8-11 are presented in Figure 9. The temperature never exceeded 600°F. As can be seen from Figure 9, the catalyst reaction with hydrogen sulfide was initially very rapid, but then slowed markedly after 12 hours of operation.

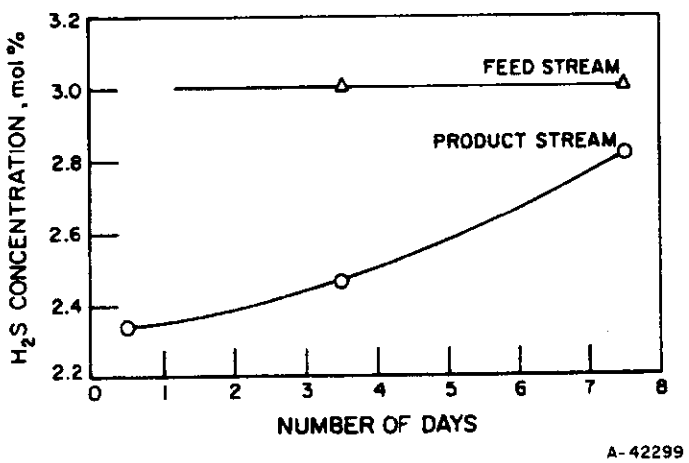


Figure 9. RATE OF SULFIDING BASF CATALYST K8-11

The feed gas composition, as well as the detailed test results, are tabulated in Appendix A, Table A-1. The feed gas stream, sulfur-containing gas stream, steam, and benzene were introduced to the reactor at atmospheric pressure (Run 1). The pressure was slowly increased, and at no time did the temperature of the catalyst bed exceed 650°F. Data were taken at pressures of 200, 425, and 630 psig (Runs 2 to 4). Each run was of at least 2-hours duration, and Run 4 lasted approximately 4 hours. Little conversion occurred

during Runs 1 to 3. In Run 4, the hydrogen/carbon monoxide ratio was shifted from 2:1 to 10:1. Hydrogen concentration increased by 19%, carbon dioxide increased by 42%, and benzene loss was 1.6%. After stopping the benzene feed near the end of Run 4, we noticed no change in gas conversion. The results of this test were sufficiently promising to warrant more testing.

A 20-gram charge of BASF catalyst K8-11 was loaded into the reactor as shown in Figure 10. The catalyst was purged with nitrogen and sulfided as before at 550°F. After two days, the effluent gas-sulfur content equaled the feed concentration. Steam and gas were started at a 1.2 ratio, and the reactor pressure was increased to 1000 psig. Conversion started at 490 psig, as shown in Run 14a of Table A-5. Benzene was added when the pressure reached 1000 psig. Conversion of carbon monoxide remained unchanged after 72 hours of operation (Run 14b). The pressure drop across the reactor increased steadily, and at the end of 96 hours of operation, the run was discontinued because of an excessive pressure drop. When the catalyst was removed, it was wet and pulverized. The outlet temperature of the steam heater had inadvertently dropped, causing the introduction of wet steam into the reactor, leading to pulverization of the catalyst. We also found that a rapid increase in temperature or pressure could also pulverize the catalyst. To avoid this, the steam heater and the start-up procedure were modified.

A fresh charge of 20 grams of BASF catalyst K8-11 was loaded. The pretreatment procedure was the same as the previous one, except that the rate of temperature increase was limited to 150°F/hr, and the pressure was raised at less than 200 psig/hr. The detailed results of this study are presented in Table A-6. In addition to the other major components listed in Table A-6, the feed gas contained 52 ppm carbonyl sulfide and 1.9 ppm ethyl mercaptan on a water-free basis. Steam and dry gas were started at a 1.7 mole ratio, the reactor pressure was increased to 1000 psig over a 52-hour period, and the temperature of the reactor was set at 620°F. Conversion of carbon monoxide began when the pressure reached 40 psig, although the rate and yield were low. Conversion increased with increasing pressure (Run 15a), and all the carbon monoxide in the feed was converted at the end of 51 hours, as the pressure approached 1000 psig (Table A-b, Run 15b).* This condition

* Carbon monoxide concentrations less than 0.1% cannot be detected by the mass spectrometer. Therefore, any carbon monoxide concentration that is less than 0.1% is reported as 0%.

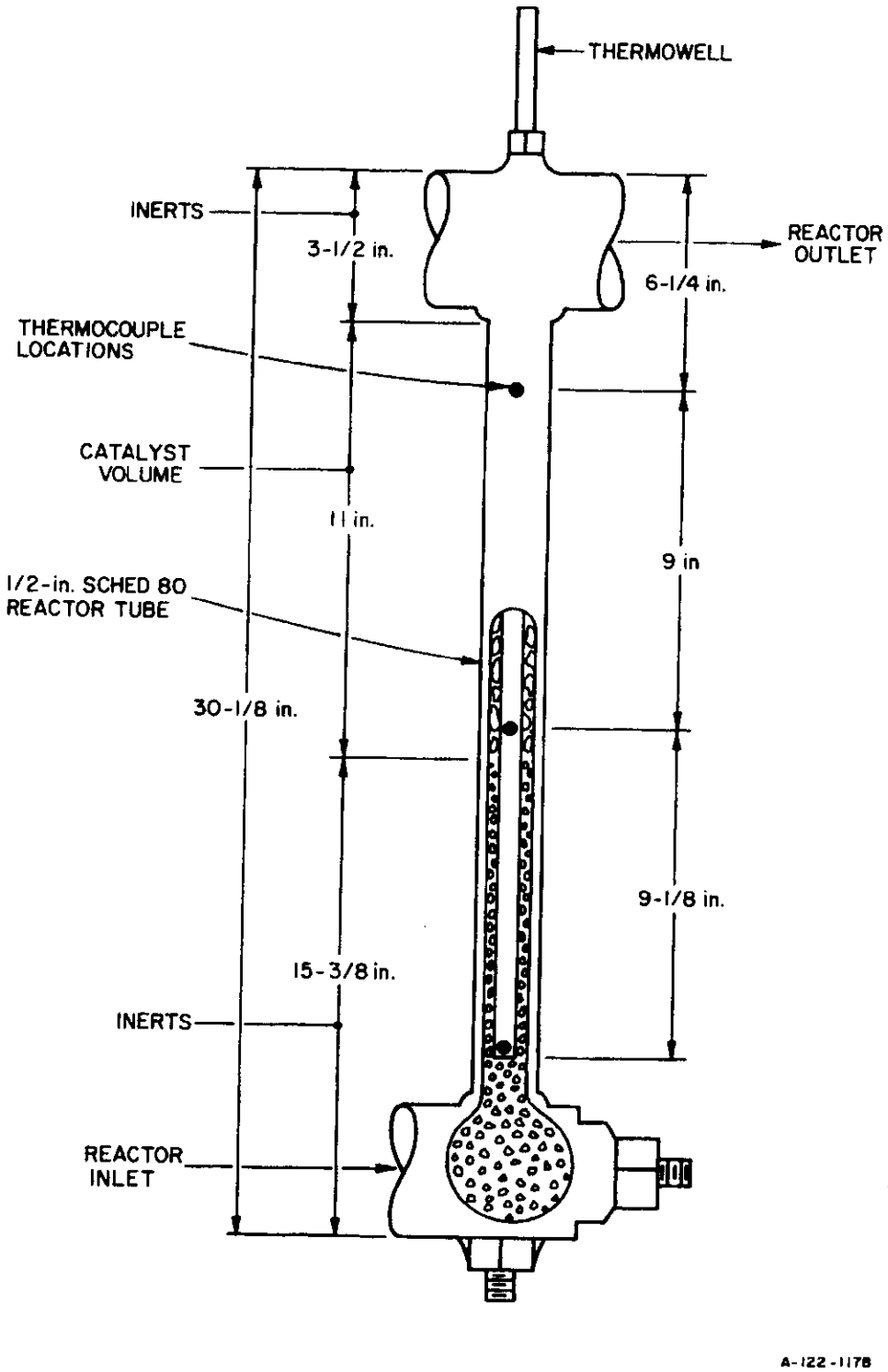


Figure 10. REACTOR LOADING AND THERMOCOUPLE POSITIONS
(Run 14, BASF Catalyst K8-11)

was held for 120 hours, and benzene was fed into the feed stream. Conversion was unchanged after 50 hours (Run 15c). The concentration of carbon monoxide in the product gas increased slightly when the steam/dry gas ratio was decreased to 1.2 (Run 15d), but the reaction went to completion again when the ratio was adjusted to 1.6 (Run 15e). At the end of 118 hours, 0.000018 lb-mole/hr of ammonium hydroxide (0.14 mole %) was added to the feed. The activity of the catalyst decreased continuously after the addition of the ammonium hydroxide, and at the end of 126 hours (8 hours in the presence of 0.14% ammonium hydroxide), carbon monoxide conversion dropped from 100% to 81% (Run 15f). The catalyst was almost totally deactivated after 45 hours in ammonium hydroxide (Run 15g); it was regenerated by stopping the flow of ammonium hydroxide and benzene and by permitting flow of only water and feed gas through the reactor. It took 81 hours of regeneration to return the catalyst to its original activity (Run 15h).

The pressure then was maintained at about 700 psig, and regeneration continued for 192 hours (Run 15i). Benzene was fed into the reactor again, and at the end of 561 hours (Run 15j), the activity of the catalyst remained good. When 0.000017 lb-mole/hr of ammonium hydroxide (0.1 mole %) was added to the feed-gas stream (Run 15k), there was no decrease in catalyst activity. This run was continued for 11 hours (Run 15l), and the activity was not affected. No measurable increase in nitrogen was found in the product gas stream, nor was there any ammonia in the liquid product.

The flow of ammonium hydroxide was discontinued, and the pressure was increased to 1000 psig. When 0.000004 lb-mole/hr of phenol (0.04 mole %) was added to the feed in the absence of benzene after 5 hours, no effect on the reaction (Run 15m) was apparent. Of the phenol fed, 50% was recovered in the liquid-water product. Benzene was added to the feed, and conversion remained the same (Run 15n). This run was continued for 31 hours, and there was a slight increase in carbon monoxide concentration in the product (Run 15o). At the end of 55 hours, the activity decreased a little (Run 15p); however, the conversion remained constant at this level.

The phenol flow was discontinued, which regenerated the catalyst to its original activity. Ammonium hydroxide (0.14 mole %) was again added to the feed gas, and after 6 hours at 1000 psig, the activity decreased (Run 15q).

The conversion of carbon monoxide dropped from 100% to 38%* after 24 hours. When the ammonium hydroxide flow was stopped, the catalyst again was regenerated (Run 15r).

We attempted to inject trace amounts of hydrogen cyanide into the feed without success, but we did manage to feed some potassium cyanide. However, we fear that the potassium cyanide never reached the catalyst bed because conditions favored the precipitation of potassium cyanide as a salt, upstream of the bed. Conversion remained constant after 1243 hours (Run 15s). Space-velocity (dry basis) was doubled, resulting in a decrease in the conversion of carbon monoxide from 100% to 93% (Run 15t). This condition was held through Runs 15u and 15v. When the reactor was disassembled, very slight carbon deposition was observed. Some of the catalyst was pulverized, and its physical strength seemed decreased.

During the life study of the BASF catalyst K8-11, we found that —

1. For the water-gas shift reaction, the catalyst converts at equilibrium conversion in the presence of up to 12% benzene (water-free basis) at the conditions studied, if the steam-to-gas ratio is 1.3 or higher.

2. The conversion decreases as the steam-to-gas ratio decreases.

3. No carbon deposition was found at the conditions studied.

4. Unsaturated steam must be avoided to prevent pulverization of the catalyst.

5. Trace quantities of carbonyl sulfide and ethyl mercaptan do not affect the activity of the catalyst.

6. Ammonium hydroxide (0.14 mole % on a wet basis) does not affect the activity of the catalyst at 700 psig but decreases it at 1000 psig. This aspect was studied further in detail and is discussed below.

7. A phenol concentration up to 0.04 mole % (wet basis) has a slight effect on the activity of the catalyst: It decreases the activity slightly

---

* Based on gas-chromatographic analysis. The composition of the product gas is continuously monitored by gas chromatography, although all these analyses are not reported. Only samples analyzed by both gas chromatography and mass spectrometry are reported. Because gas chromatography can detect only carbon monoxide, carbon dioxide, methane, and ethane, the analysis for hydrogen, helium, nitrogen, and hydroocrabons heavier than ethane is made only by mass spectrometry.

but remains constant at that level for the time studied. The catalyst recovers its original activity by discontinuing the flow of phenol.

8. The physical strength of the catalyst was less at the end of the test.

Effect of Ammonia on BASF Catalyst K8-11 Activity

During life testing of this catalyst, we found that, although 0.14 mole % ammonium hydroxide does not affect catalyst activity at 700 psig, a gradual, continuous decrease in activity occurred at 1000 psig; total deactivation could eventually occur. The catalyst can be regenerated to its original activity by discontinuing the flow of ammonium hydroxide and benzene. Faster regeneration can be achieved by resulfiding the catalyst in a hydrogen sulfide-hydrogen mixture.

There are several possible reasons for deactivation by ammonia:

a. There is a high concentration of carbon monoxide in the feed. Most of the previously published papers or patents dealt with carbon monoxide concentrations of about 2%, whereas we have 20% carbon monoxide. A few of these have as much as 10% carbon monoxide and only three components in the feed, whiel our feed has 12 components. No work was found with benzene in the feed, while ours contained 10%. But the papers and patents did show that the conversion becomes poorer as the carbon monoxide concentration in the feed increases. This can be rationalized by citing an analysis proposed by Powers* which is based on the postulate that 1) ammonia is chemisorbed on preadsorbed carbon monoxide on the catalyst, and 2) the activity of the catalyst is strongly dependent upon the method of catalyst preparation. This fact is accounted for by proposing that a number of active sites (AS) exist on the catalyst, and that this number depends only upon the method of pretreatment. To account for the change in rate with time that occurs following any change in carbon monoxide partial pressure, we propose that the active sites produced in the catalyst's pretreatment do not enter into reaction directly. Instead, an effective site (ES) is visualized that is formed in the presence of carbon monoxide. Therefore, we may write the following for the water-gas shift reaction:

$$AS + CO \overset{k_1}{\rightleftarrows} ES \qquad (2)$$

$$ES + CO \overset{k_2}{\rightleftarrows} ES\text{-}CO \qquad (3)$$

$$ES + H_2O \overset{k_3}{\rightleftarrows} ES\text{-}H_2O \qquad (4)$$

---

* Powers, J. E., "A Reaction Mechanism for the Hydrogenation of Carbon Monoxide Including a Reversible Catalyst Reaction," J. Phys. Chem. 63, No. 8, 1219-23 (1959).

$$ES\text{-}CO + NH_3 \overset{k_4}{\rightleftarrows} X \tag{5}$$

$$ES\text{-}CO + ES\text{-}H_2O \overset{k_5}{\rightleftarrows} 2ES + CO_2 + H_2 \tag{6}$$

where —

AS = active sites

ES = effective sites

X = poisoned sites

Y = mole fraction

P = total pressure

k_i = equilibrium constant.

If equilibrium is assumed for Reactions 2, 3, and 5, then the following relationships results:

$$\begin{aligned} k_4 &= \frac{(X)}{(ES\text{-}CO)\ (NH_3)} \\ &= \frac{(X)}{k_2(ES)\ (CO)\ (NH_3)} \\ &= \frac{(X)}{k_1k_2(AS)\ (CO)^2\ (NH_3)} \end{aligned} \tag{7}$$

Therefore,

$$\begin{aligned} X &= k_1k_2k_4(AS)\ (CO)^2\ (NH_3) \\ &= KY_{CO}^2\ Y_{NH_3}\ P^3 \end{aligned} \tag{8}$$

The analysis indicates that the number of poisoned sites is dependent upon the square of the carbon monoxide concentration and on the cube of the total pressure, which agrees with the observed carbon monoxide concentration and total pressure sensitivity. (If the catalyst were poisoned by the usually assumed reaction, $AS + NH_3 \rightleftarrows X$, the dependency of poisoning on carbon monoxide concentration would not be explained.)

b. The concentration of carbon dioxide in the feed could be higher than expected. From equilibrium considerations, the higher the carbon dioxide concentration, the less the yield of hydrogen:

$$CO + H_2O \overset{K_p}{\rightleftarrows} H_2 + CO_2$$

$$K_p = \frac{(CO_2)(H_2)}{(CO)(H_2O)} \tag{9}$$

We conducted most of this experiment during the winter. The feed-gas supply was stored in high-pressure cylinders in a trailer outdoors. It

was possible that we were operating at a near two-phase region for this mixture, and the feed composition may have fluctuated. The component that would fluctuate the most would be carbon dioxide.

c. Molybdenum nitride may have been present.

$$Mo + N\cdot \rightleftarrows MoN \qquad (10)$$

This formation is only possible when atomic nitrogen, which comes from the cracking of ammonia, is present. This reaction is highly reversible because molybdenum nitride is unstable. The equilibrium of this reaction may be highly pressure dependent. This could cause deactivation at a higher pressure but not at a lower pressure. The catalyst can be regenerated to its original activity.

d. Ammonium monosulfide may be formed. The BASF catalyst K8-11 is a sulfur-active catalyst. At high pressures, equilibrium may favor the formation of ammonium monosulfide, thus stripping the sulfur from the catalyst, causing deactivation. The catalyst would regain its activity when it is resulfided by the feed gas or by a hydrogen sulfide-hydrogen mixture, both of which contain sulfur.

Based on the above considerations, we conducted the following experiment:

1. We presulfided the catalyst with a mixture of 10% hydrogen sulfide in hydrogen, instead of the 3% hydrogen sulfide-hydrogen mixture used before, until the hydrogen sulfide concentration in the product equaled that in the feed.

2. We doubled the hydrogen sulfide content in the feed gas.

3. We used a series of feed mixtures with increasing carbon monoxide and carbon dioxide concentrations.

4. We moved the feed gas cylinders indoors and kept them warm.

These precautions eliminated the possibility of fluctuations in composition and of depleting the sulfur from the catalyst, and permitted study of the effect of carbon monoxide concentration. The only other chance of poisoning is due to metal nitride formation. If the catalyst had been poisoned, we would have analyzed for nitride formation. If the catalyst remained active, we would have gradually decreased the sulfur content in the feed until deactivation occurred. If the high carbon monoxide concentration and low-sulfur feed had no effect on the catalyst's activity, we would know that the catalyst must be thoroughly sulfided during pretreatment and would recommend the pretreatment procedure for future plant use.

The detailed experimental results are presented in Table A-8. The reactor was purged with nitrogen at atmospheric pressure until all the air was eliminated. We increased the pressure to about 200 psig before switching to a mixture of 10% hydrogen sulfide-hydrogen gas. The temperature was increased to 700°F at a rate of 100°F/hour, and the pressure was increased to 500 psig at 100 psig/hour. The flow rate of the hydrogen sulfide-hydrogen gas was maintained at about 0.1 SCF/hour. The temperature of the bed was controlled carefully, either by adjusting the heat input or the flow of the sulfiding gas. Pretreatment was completed after 4 hours, when the hydrogen sulfide concentration in the product equaled that in the feed. The temperature was decreased to 590°F, and the feed gas was introduced (Run 17a). The steam/gas ratio was adjusted to 1.3 while the pressure was increased to 1000 psig (Run 17b). Benzene was fed in Run 17c after equilibrium conversion was established. We fed 0.2 mole % (wet basis) of ammonium hydroxide (28.2 weight % ammonia) into the reactor after the benzene flow was established (Run 17d). Conversion remained good in Run 17e. The steam/gas ratio was adjusted to 1.6, and equilibrium conversion was still obtained in Runs 17f, 17g, and 17h. We increased the carbon oxides concentration in the feed in Run 17i and increased the ammonia concentration in Run 17j. The conversion remained constant in Runs 17k and 17l. The carbon monoxide concentration in the feed was increased again (Run 17m). There was an increase in nitrogen concentration in the product approximately equal to the amount of nitrogen contained in the ammonia. Although the nitrogen balance varied from 92% to 168%, we can see that the cracking of ammonia did occur. The poor nitrogen balance was the result of the small differences in two big numbers in the wet analysis of ammonia. The steam/gas ratio was decreased from 1.6 to 1.3 (Runs 17n and 17q), and no change in conversion was detected. When the carbon monoxide concentration in the feed was increased again, some carbon monoxide breakthrough was found (Run 17r). This could have been caused by an upset in the equipment, which was repaired quickly, and equilibrium conversion obtained again (Run 17s). Increasing carbon monoxide concentration does not deactivate the catalyst (Runs 17t and 17u). We started to decrease the hydrogen sulfide concentration in the feed to determine the effect of ammonium monosulfide on the catalyst (Run 17v).

The catalyst remained active after 641 hours (Run 17w). We decreased the feed sulfur concentration and increased the feed carbon monoxide concentration (Run 17x) to find the effect of high carbon monoxide concentration and whether or not our pretreatment procedure will prevent the depletion of the sulfur active site on the catalyst. The catalyst was still active after 63 hours in a feed which contained no sulfur (Run 17z). The reactor temperature was lowered to 80°F after Run 17z, and it was purged with nitrogen for 267 hours. The temperature was then raised to 580°F while purging with nitrogen for another 120 hours to remove the sulfur compounds from the piping and the dead volume in the reactor system. A sulfur-free feed gas was again introduced, and after 100 hours, the catalyst remained active (Runs 18a to 18d). At this point, we concluded that deactivation by ammonia is not a problem if the catalyst is thoroughly sulfided.

Life-Test Results — C25-1-01

This catalyst, which was designated as C-20-6-02 in the early phases of its evaluation, was also the subject of preliminary tests. The detailed test results are presented in Appendix A, Table A-2.

The reactor was charged with 25 grams of catalyst which were purged with nitrogen at atmospheric pressure. While purging, the reactor was heated to 700°F at a rate of 150°F/hr. The pressure was increased to 250 psig when the temperature stabilized at 700°F. The catalyst was sulfided by passing 10% hydrogen sulfide in hydrogen through the reactor at 700°F and 250 psig and at a space velocity of 1000 SCF/hr-ft^3.

The reactor was pressurized to 700 psig with the mixture of hydrogen sulfide and hydrogen. Steam was introduced at a temperature of 500°F and was immediately followed by feed gas. Run 5 was performed using no benzene in the feed, and Run 6 followed with benzene introduced into the feed stream. The steam-to-dry gas ratio for Runs 5 and 6 was 0.7. The presence of benzene in the feed did not affect the shift reaction.

Similarly, Runs 7 and 8 were performed at 595 psig with a feed gas containing lower concentrations of carbon oxides and a higher concentration of hydrogen. The steam-to-dry gas ratio for Runs 7 and 8 was 0.6. The effect of benzene in the feed (Run 8) was small compared with Run 7, in which no benzene was fed. A composite sample of liquid condensate from Runs 5 through

8 was analyzed, and the test results are presented in Table 3. Although no visual carbon deposit was apparent, the catalyst was analyzed for carbon.

Table 3. ANALYSIS OF LIQUID PRODUCT FOR RUNS 5 THROUGH 8
(CCI Catalyst C25-1-01, 1/16-in. Extruded Rods)

%	°F	Component	mol %
IBP	167	Unidentified	0.6
5	172	Methyl Naphthalene	0
10	172	Dicyclopentadiene	0
20	172	Naphthalene	0
30	173	Indene	0
40	173	Xylene	0
50	173	Aromatic C9	0
60	173	Toluene	0
70	173	Ethyl Benzene	0
80	173	Styrene	0
90	174	Benzene	99.4
95	175	Cyclopentadiene	0
EP	182	Total	100.0
% Recovery	97.0		
% Residue	0.5		

Sp Gr 60/60°F (distillate) = 0.881

Hydrocarbon Types, vol %

Saturates (F.I.A.)	0
Olefins (diff.)	1
Aromatics (M.S.)	99

Fresh catalyst was loaded into the reactor for a long-term activity test. The reactor was purged with nitrogen and heated at a rate of 150°F/hr to 700°F at a pressure of 250 psig. The catalyst was sulfided using a mixture of 5% hydrogen sulfide in hydrogen for 60 hours, at 700°F and a space velocity of 2000 SCF/hr-ft^3. After sulfiding, steam and dry gas feed were introduced to the reactor. The results, shown in Table A-4 as Run 13, indicate that no conversion took place during the first 8 hours of the run. The flow rate tended to decrease continuously, and readjustments were necessary to maintain it. Finally, the pressure drop increased so much that the run was discontinued.

Upon disassembling the reactor, we found that it was plugged with pulverized catalyst. These catalyst particles, which still retained their original form, shattered easily. Analysis of this catalyst indicated no increase in carbon composition. Screen analyses, whose results are presented in Table 4, clearly showed that the catalyst was pulverized within the reactor, causing the observed high pressure drop.

Table 4. SCREEN ANALYSES OF C25-1-01 CATALYST BEFORE AND AFTER RUN 13

U.S. Standard Mesh Size	Fresh Catalyst	Used Catalyst
	wt %	
10	42.1	14.0
14	57.9	40.8
20	0	19.5
40	0	11.2
60	0	4.7
Pan	0	9.8

This run was repeated again with a fresh sample of catalyst. The reactor was loaded, pretreated, and sulfided as described above. After introduction of dry gas and steam, the reactor once again plugged. The results of the second run are presented in Table A-4 as Run 13a.

We have not yet determined why this problem occurred. Two possibilities are likely: Liquid water may have inadvertently entered the reactor and caused disintegration of the catalyst, or the catalyst may not be sufficiently durable for the moist, high-pressure conditions that exist in shift conversion. This catalyst was designed and has previously been used as an oil hydrogenation catalyst but not as a shift catalyst.

Lift-Test Results — C25-1-02

We asked Catalysts and Chemicals, Inc. (CCI), to do some preliminary work on its second cobalt-molybdenum catalyst for shift reaction. CCI tested it at 1000 psig and over a temperature range of from 700° to 990°F with a feed composed of carbon monoxide, carbon dioxide, hydrogen, hydrogen sulfide, and water. The results were satisfactory, and a sample, originally designated C20-60-03, but later renumbered C25-1-02, was sent to us for further testing.

The detailed test results are presented in Table A-9. This catalyst was pretreated the same way as the BASF catalyst. The experiment began with only the feed gas and steam at a steam/gas ratio of about 1.2:1 (Run 19-1). Benzene was added after equilibrium conversion was attained (Run 19-2). The carbon oxides concentrations were increased, and the steam/gas ratio was decreased slightly while benzene was added continuously (Runs 19-3 to 19-4). Equilibrium conversion was still obtained. Ammonia was added, and the activity of the catalyst was decreased slightly (Run 19-5). The activity remained at the same level (Runs 19-6 to 19-8) until the steam/gas ratio was increased to about 1.5:1, whereupon the conversion of carbon monoxide improved (Run 19-9). The steam/gas ratio was adjusted to 1.2:1 again (Run 19-10), and the activity remained the same (Run 19-11).

Phenol was added in place of ammonia (Run 19-12), and at the end of 24 hours, the catalyst activity had decreased. Despite the addition of more hydrogen sulfide and an increased steam/gas ratio, continuous deactivation of the catalyst was observed (Runs 19-13 to 19-17). Both ammonia and phenol were added, and hydroquinone was formed in the liquid feed. The equipment was modified so that the phenol was kept out of the liquid-water solution. The catalyst, which was purged with a 10% hydrogen sulfide-hydrogen mixture for about 90 hours during this period, continued to deactivate (Runs 19-18 to 19-21). The feed lines were partially plugged during Run 19-22. While the feed system was being repaired, the reactor was purged with a 10% hydrogen sulfide-hydrogen mixture in an attempt to regenerate the catalyst. As the life test resumed, the activity decreased sharply (Run 19-23). This condition remained constant for the next 164 hours (Runs 19-23 to 19-27). Although only 40% of the phenol added was recovered in the end because of poor quantitative and qualitative analyses of the liquid products, no additional increase in the amount of the other components was detected in the gas phase. Stepwise deactivation was observed again (Runs 19-28 to 19-34). The space velocity was doubled to accelerate the deactivation and to study the catalyst behavior. The bed temperature increased as expected, and the carbon monoxide breakthrough was increased by 52% (Run 19-35). The activity of the catalyst remained for the next 355 hours (Runs 19-36 to 19-42). The feed space velocity was increased to 3 times that of the original feed. The carbon monoxide breakthrough was increased another 20% (Run 19-43), and the catalyst bed temperature was raised by 10°F. At the end of the 1836-hour test, the

experimental run was voluntarily stopped (Run 19-44). The discharged catalyst was analyzed by the catalyst manufacturer and found to have retained only 16% of its original crush strength; the carbon content had increased by 200%, and the surface area was decreased by 64%.

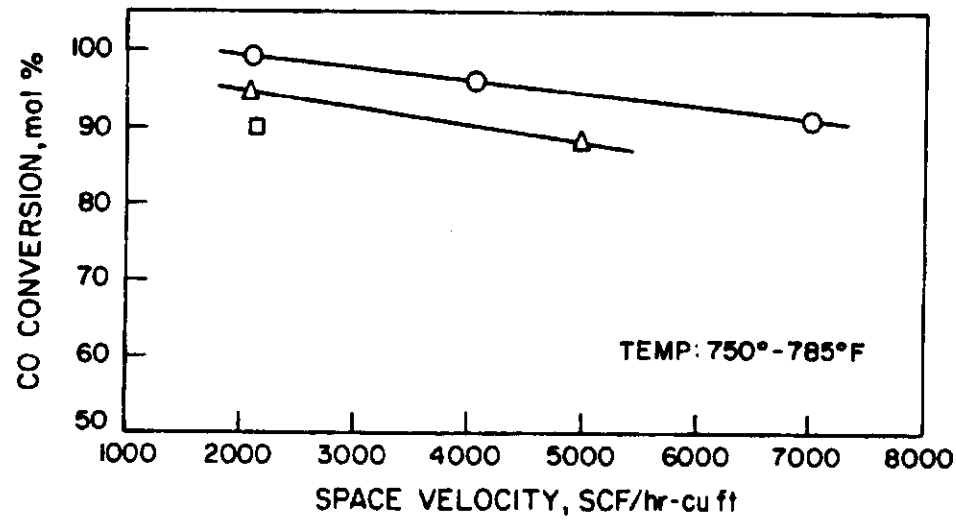
Life-Test Results — Comox 207

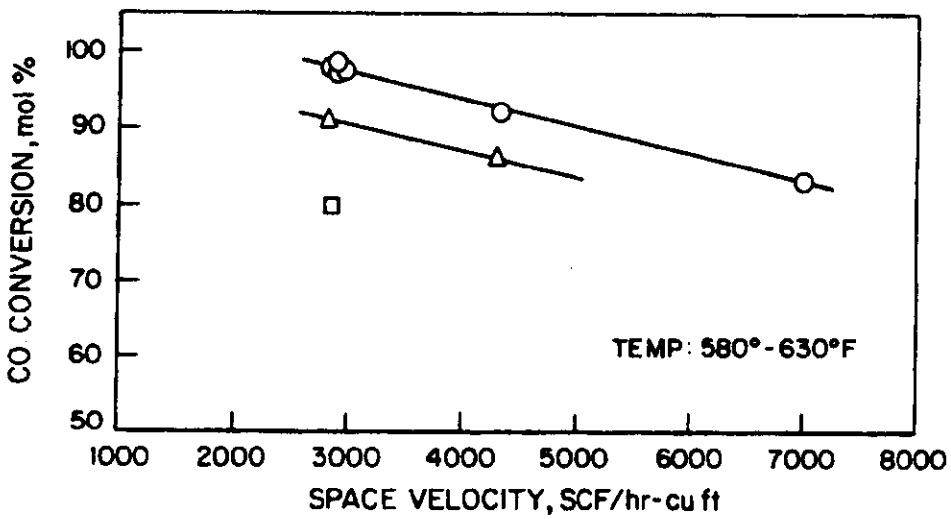
Shift catalyst Comox 207, which was used in a Lurgi coal gasification plant after water quenching, was loaded into our reactor. The three basic methods used for presulfiding this catalyst, in the order of decreasing effectiveness, were —

1. Presulfiding with carbon disulfide in the feedstock
2. Presulfiding with hydrogen sulfide in the treated gas
3. Presulfiding with feedstock.

We selected the third method to activate this catalyst because both the G-93 and the UC-1870-46-1 catalyst were also activated by the feedstock only.

Carbon monoxide conversion was observed as soon as flow was established at 1000 psig, 580°F, and 2200 SCF/hr-ft^3. The detailed results are presented in Table A-12. After 2 hours (Run 22-1), 81% of the carbon monoxide in the feed was converted; after 5 hours (Run 22-2), 95% of it was converted, and equilbrium conversion was obtained at the end of 74 hours (Runs 22-3 to 22-5). Benzene was added in the feed, and no change in reaction or conversion was observed (Runs 22-6 to 22-8). Ammonia was added in the feed, and a slight decrease in conversion was recorded (Runs 22-8 and 22-9). Phenol was added, and a slight stepwise decrease in activity was observed (Runs 22-10 to 22-16). At the end of 570 hours, the carbon monoxide conversion increased from 99.2% to 96.2% (Run 22-17 and Run 22-18). The feed dry-gas space velocity was increased to 4500 SCF/hr-ft^3, and the steam/gas ratio was adjusted to 1.6 (Run 22-19); the carbon monoxide conversion decreased to 92% (Run 22-20). The space velocity was further increased to 6900 SCF/hr-ft^3, and only 86% of the carbon monoxide was converted (Run 22-21). The temperature was increased to 770°F, the conversion improved to 92% (Run 22-22), and the carbon balance was not changed. As the space velocity was decreased to 2500 SCF/hr-ft^3, the carbon monoxide conversion increased to 98% (Run 22-23). Runs 22-24 to 22-30 are summarized in Figure 11.





○ P= 1000 psig
△ P= 500 psig
□ P= 200 psig

COMPOSITION OF FEED GAS

COMPONENT	mol %
CO	9.0
CO_2	8.0
CH_4	11.0
C_2H_6	0.3
H_2S	0.4
C_2H_5SH	1.3 ppm
C_4H_4S	0.8 ppm
COS	50 ppm
C_6H_6	4.5
C_6H_5OH	0.03
N_2	0.6
NH_3	0.2
H_2	BALANCE
H_2O	55.0

A-15-60

Figure 11. EFFECT OF SPACE VELOCITY AND PRESSURE ON THE CONVERSION OF CARBON MONOXIDE (Laporte-Davison Shift Catalyst Comox 207)

The weight of the spent catalyst was found to be 21.3 grams. It is being analyzed for its physical properties by Laporte-Davison, Inc.

Life-Test Results — G3B

The Girdler chromium promoted iron-oxide shift catalyst, G3B, has been used for shift conversion for the past 20 years in hydrogen and ammonia plants. The catalyst activity was known to be less when the catalyst was in the sulfided form, but the effect of large amounts of aromatic compounds in the feed gas was not known.

This catalyst was subjected to preliminary lift tests. Forty grams of the G3B catalyst, sized at −6+8 mesh, were loaded into the reactor. The catalyst was presulfided in a flowing stream of 1% hydrogen sulfide in a hydrogen-steam mixture at 500 psig and 620°F.

The fully sulfided catalyst was tested with a mixture of feed gas, steam, and benzene vapor similar to the composition used in previous runs. No conversion was observed at 700°F and 500 psig. The detailed test results are presented in Table A-3 as Run 9. To check this unexpected result, we attempted to reactivate the catalyst by passing 700°F hydrogen containing 1% hydrogen sulfide through the bed for 15 hours. Run 10 was then begun by introducing feed gas containing sulfur but no benzene. Again, essentially no carbon monoxide conversion occurred. When the catalyst was removed from the reactor, no carbon deposition was observed.

Girdler representatives were consulted concerning this performance. In their opinion, the presence of benzene should rapidly deactivate the catalyst. The catalyst could also have been inadvertently deactivated by contamination with an impurity such as inorganic salts, oil, boron, or phosphorous compounds.

A fresh charge of 34 grams of G3B was loaded into the reactor to test catalyst activity with no benzene in the feed gas. Figure 12 shows catalyst and thermocouple locations in the reactor. Girdler's recommended start-up procedure was used. The catalyst was nitrogen-purged and brought to an inlet temperature of 660°F with steam flowing through the catalyst bed. Feed gas flow was started, and when the effluent gas-hydrogen sulfide content equaled the feed hydrogen sulfide content 3 hours later, Run 11 began. The steam/dry gas ratio was 2. Again, we observed no reaction, and the run was then discontinued. After purging with nitrogen, the catalyst was resulfided using

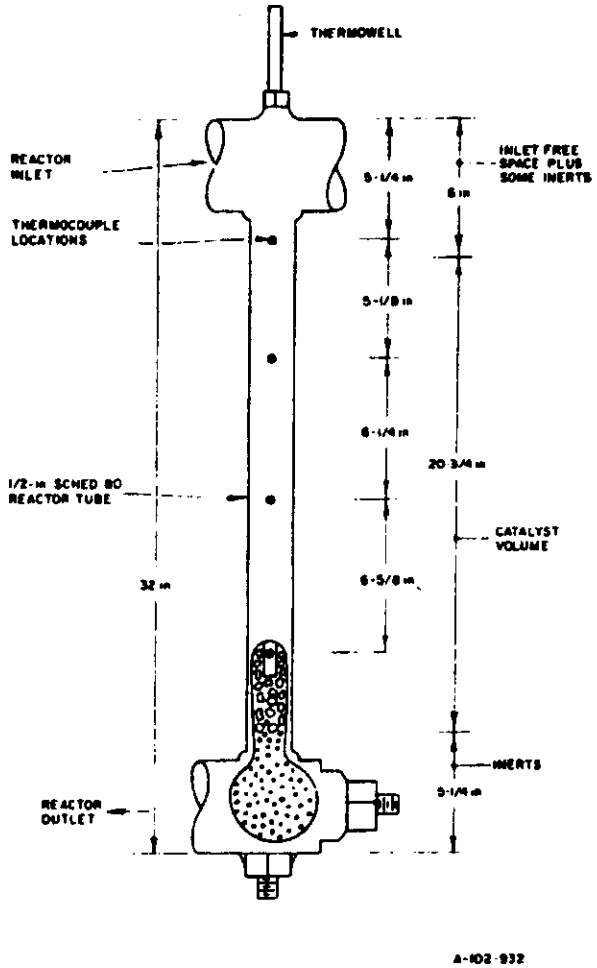


Figure 12. REACTOR LOADING AND THERMOCOUPLE POSITIONS
(Runs 11 and 12, G3B Catalyst)

hydrogen containing 10% hydrogen sulfide at 280 psig and 660°F for 15 hours. Run 12 was started at the same conditions as used for Run 11. The catalyst showed activity for shift conversion. Data for Runs 11 and 12 are also presented in Table A-3.

The results from Runs 11 and 12 seem to indicate that the G3B catalyst was not reduced or sulfided at the start of Run 11, and that its activity is low when it is in the oxide form. However, these results still do not explain the poor catalyst performance in Runs 9 and 10, in which the catalyst was fully presulfided.

Life-Test Results — G51-C

The Girdler G51-C catalyst was also the subject of preliminary tests. Detailed results are presented in Table A-7. This catalyst was not as durable as the other catalysts tested; therefore, it was not tested further.

Life-Test Results — G93

At our request, the Girdler T-2021 (later designated G93) catalyst was tested by the supplier at 1000 psig and at 550°, 650°, and 750°F. The test was started without pretreatment or preactivation. Feed gas of 17% carbon dioxide, 23% carbon monoxide, 23% methane, 26% hydrogen, 10% benzene, and 1% carbonyl sulfide was used at a wet-space velocity of 10,000 SCF/hr-ft^3. The conversion remained constant during the 100-hour test. This catalyst was also pretreated with a hydrogen-hydrogen sulfide mixture at 700°F, and this pretreatment did not appear to affect the final activity.

We tested the catalyst for 1583 hours. A 20.2-gram charge was loaded into the reactor and was heated to 580°F while purging with nitrogen. The catalyst was sulfided with a mixture of 10% hydrogen-hydrogen sulfide for 48 hours, at a space velocity of 370 SCF/hr-ft^3. The temperature of the catalyst bed pretreatment, which was conducted to prevent depletion of the sulfur-active sites by ammonia, is mild when compared with the standard pretreatment of other catalysts, in which the catalyst is sulfided with a 10% hydrogen sulfide-hydrogen mixture at 700°F and 1000 SCF/ft^3-hr until the sulfur content in the exit stream equals that in the inlet stream or until the temperature in the reactor becomes constant. Steam and gas mixtures were introduced to the reactor; the detailed results are presented in Table A-10. One-half of the carbon monoxide in the feed was converted within 1/2 hour, 80% of it was converted after 1 hour, and 99% of it was converted at the end of 2 hours. Equilibrium conversion was obtained at 9 hours (Run 20-1), and this condition was held for the next 147 hours (Runs 20-2 to 20-5). The temperature at the entrance of the catalyst bed was also constant at 645°F during this period. Benzene was introduced to the reactor (Run 20-6), and the conversion of carbon monoxide remained constant for the next 322 hours (Runs 20-7 to 20-14). Ammonia was added (Run 20-15), and slight deactivation was observed. However, the activity remained constant for 258 hours after the initial decrease (Runs 20-16 to 20-21). Phenol was added, and ammonia was discontinued (Run 20-22). The conversion was not affected after 98 hours

(Runs 20-23 to 20-25). The transferring lines then became plugged by foreign materials in the feed and the experiment was temporarily stopped. The reactor was purged with a hydrogen sulfide-hydrogen mixture and maintained at 580°F. Both ammonia and phenol were added to the feed (Run 20-26), and only slight deactivation was observed during the next 430 hours (Runs 20-27 to 20-36). The space velocity (dry basis) was increased from 2900 to 5600 SCF/hr-ft^3, while the feed composition was kept constant (Run 20-37). The space velocity was further increased to 7500 SCF/hr-ft^3 (Run 20-41), which decreased the conversion of carbon monoxide and increased the bed temperature (Runs 20-38 to 20-43). These runs at increased space velocity were conducted to determine the performance of the catalyst at conditions other than equilibrium. The conversion remained constant during this test period of 242 hours. The temperature of the furnace was increased until the catalyst bed temperature reached 817°F. The activity decreased slightly (Runs 20-44 and 20-45), and the carbon balance became poorer. Although carbon deposition had occurred at temperatures between 600° and 700°F, it was negligible, but it became appreciable at 800°F. The space velocity was decreased, and the conversion improved (Runs 20-46 and 20-47). The experimental run was terminated voluntarily, and the catalyst was removed and examined. There was an increase of 4% in catalyst weight, an increase of 1500% in carbon content, and a decrease of 63% in surface area.

The overall performance of the Girdler G93 shift catalyst can be summarized as follows:

- The activity is high. Near-equilibrium conversion was obtained at a space velocity of 7000 SCF/hr-ft^3 (dry basis).
- Its resistance to benzene is high.
- The lower temperature limit appears to be about 530°F, based on the data supplied by Girdler Chemical, Inc. The upper temperature limit appears to be less than 900°F. The problem at high temperatures is not the loss of activity but the deposition of carbon, which seems to occur with all the catalysts.
- No pretreatment was required to activate this catalyst when sulfur was present in the feed gas.
- The steam requirement for the shift reaction when using this catalyst was about the same as that for other catalysts. We found that a steam/dry-gas mole ratio of 1.2 or more was best for this reaction, although a steam/gas ratio of 1.0 was used in the data obtained by Girdler.

Life-Test Results — Shell Oil 538

At our request, this catalyst was tested by Shell Oil Co. at 1000 psig, 600°F, 3000 SCF/hr-ft^3, and a steam/gas ratio of 1.2 with a 7-component feed mixture containing 10% benzene and 0.2% ammonia. Equilibrium conversion was obtained.

We then tested this catalyst, using the procedure that was used for the other catalysts. The detailed results are presented in Table A-13. The effect of varying space velocity on carbon monoxide conversion is shown in Figure 13.

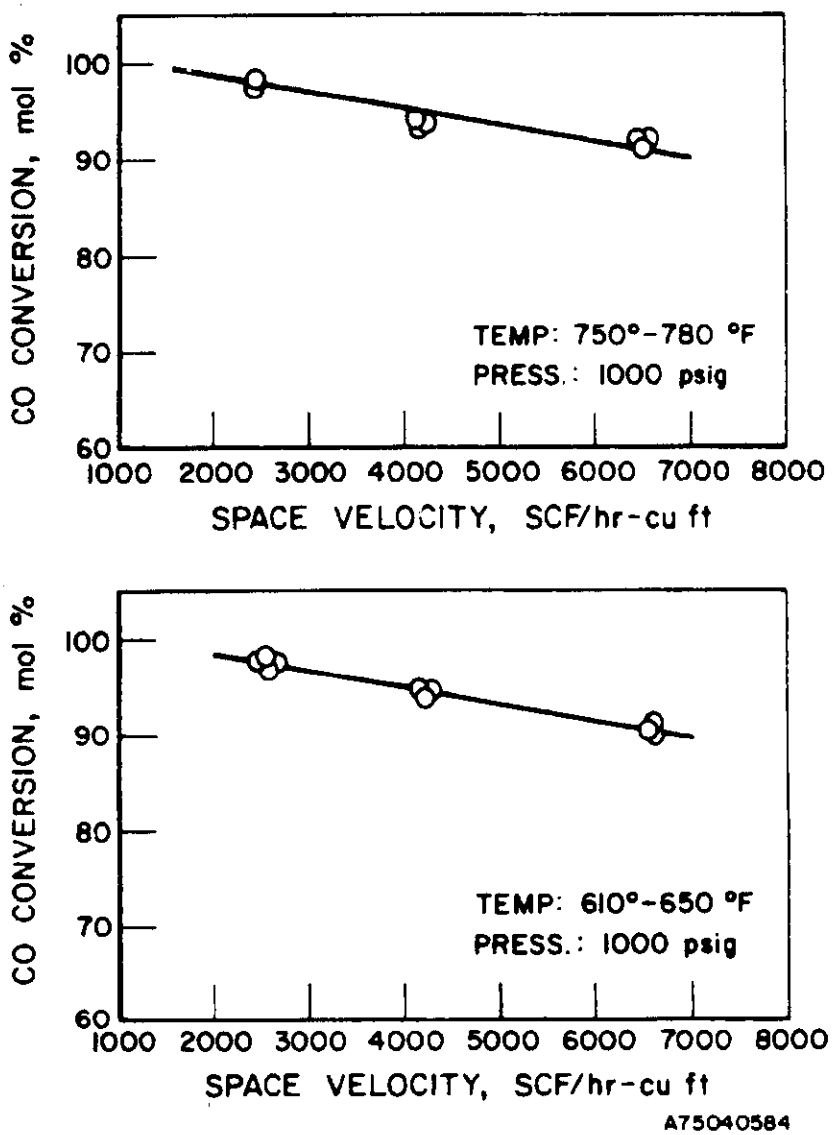
The performance of this catalyst with our standard 14- to 17-component feed mixture may be summarized as follows:

- It is a sulfur-active catalyst. Deactivation may occur in a sulfur-free feed mixture.
- Equilibrium conversion was obtained in the presence of benzene and ammonia at 1000 psig at 2300 SCF/hr-ft^3.
- Conversion of carbon monoxide decreased when phenol was added.
- The carbon content in the catalyst increased after high-temperature runs, and carbon was found in the reactor after the runs.
- It has high crush strength.

Life-Test Results — UC-1870-46-1

A new reactor was assembled, tested, and loaded with the Union Carbide UC-1870-46-1 nickel-molybdenum shift catalyst. Prior to submitting this catalyst to IGT for extensive testing, Union Carbide had tested it and their other shift catalyst. Included in these tests were UC-1050-56-2, a cobalt-molybdenum catalyst; nickel-molybdenum catalysts UC-1870-44 and UC-1870-50; and catalysts G-51C and CCI 5593. Their experimental data showed that the UC-1870-46-1 catalyst had the best performance in the presence of sulfurs and benzene and did not require pretreatment.

The reactor was purged with nitrogen while it was heated to 580°F at a rate of 50°F/hr. After being stabilized at 580°F, the reactor was pressurized with nitrogen to 100 psig at a rate of 50 psi/hr. Steam was introduced first to the catalyst bed followed by introduction of the feed gas. Detailed results are presented in Table A-11. Conversion of carbon monoxide was detected



COMPOSITION OF FEED GAS

COMPONENT	mol %
CO	7.0
CO_2	8.0
CH_4	10.0
C_2H_6	0.2
H_2S	0.6
C_2H_5SH	1.3 ppm
C_4H_4S	0.8 ppm
COS	50.0 ppm
C_6H_6	4.5
C_6H_5OH	0.03
N_2	0.5
NH_3	0.2
H_2	BALANCE
H_2O	55.0

Figure 13. EFFECT OF SPACE VELOCITY AND TEMPERATURE ON CARBON MONOXIDE CONVERSION (Shell Oil 538)

within the first hour (Run 21-1), and equilibrium conversion was obtained after 30 hours (Runs 21-1 to 21-5). Nitrogen was introduced in place of the feed gas, and the pressure was lowered to 50 psig. Feed gas was introduced again in place of nitrogen, and heavy conversion was observed by the time the pressure reached 170 psig (Run 21-6). The conversion improved as the pressure was increased (Runs 21-7 to 21-11), and equilibrium converison was obtained when the pressure reached 1000 psig (Runs 21-12 to 21-16). Benzene was added, and no adverse effect was observed (Runs 21-17 to 21-21). Ammonia was added to the feed (Run 21-22), and the activity remained unchanged after 30 hours (Run 21-23). Although material balance calculations showed a 5% (weight) loss of ammonia, there was no apparent increase in either nitrogen or hydrogen; the loss probably occurred in handling of the liquid samples. Phenol was added in place of ammonia (Run 21-24), and after 94 hours, the activity had not changed (Runs 21-25 and 21-26). Both ammonia and phenol were added (Run 21-27), and no change in activity was detected after 48 hours (Run 21-28).

After the 14-component feed flow was established, the effects of pressure, temperature, and space velocity on the catalyst activity were studied. The method used was to keep the feed composition constant and change the other variables, one at a time. The pressure was changed from 200 to 1000 psig, the temperature was changed from 475° to 802°F, and the dry-gas space velocity was changed from 2300 to 6300 SCF/hr-ft^3. The catalyst was repeatedly tested at the initial conditions of 1000 psig, 580°F, and 2300 SCF/hr-ft^3 (dry) to check its activity after each change was made. At the end of this 2221-hour test, the carbon monoxide conversion was decreased by 0.6 mole % at the initial conditions. The steam/dry gas ratio varied from 1.0 to about 1.4 during these tests. Carbon deposition and a decrease in activity were observed when the steam/dry gas ratio used was less than 1.1, especially at temperatures higher than 750°F. The weight of the catalyst increased 8% by the end of this test. The experimental data presented in Table A-11 are summarized in Figure 14. The effect of pressure on the catalyst activity is significant.

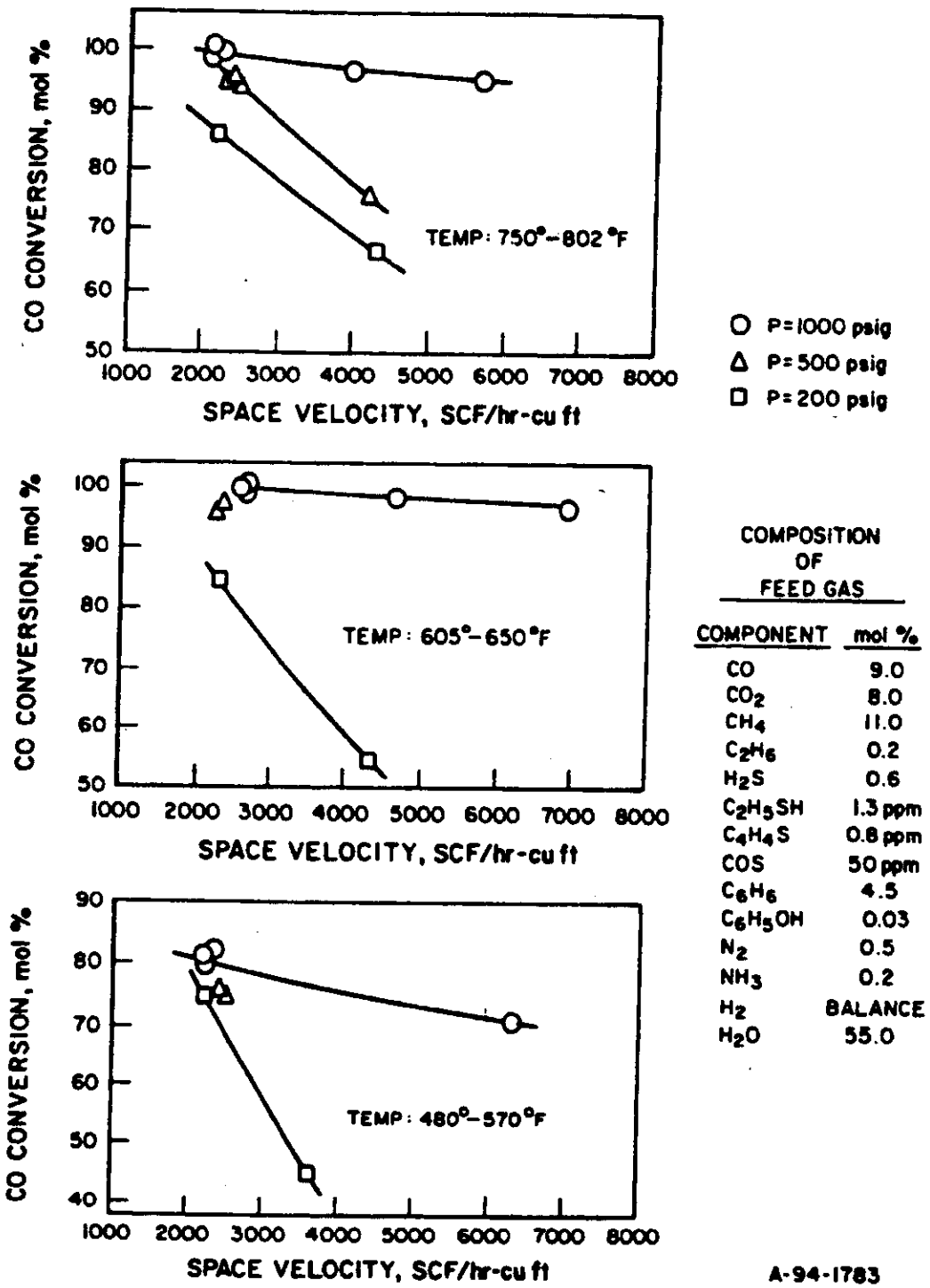


Figure 14. EFFECT OF SPACE VELOCITY, TEMPERATURE, AND PRESSURE ON THE CONVERSION OF CARBON MONOXIDE (Catalyst UC-1870-46-1)