

## CONCLUSIONS

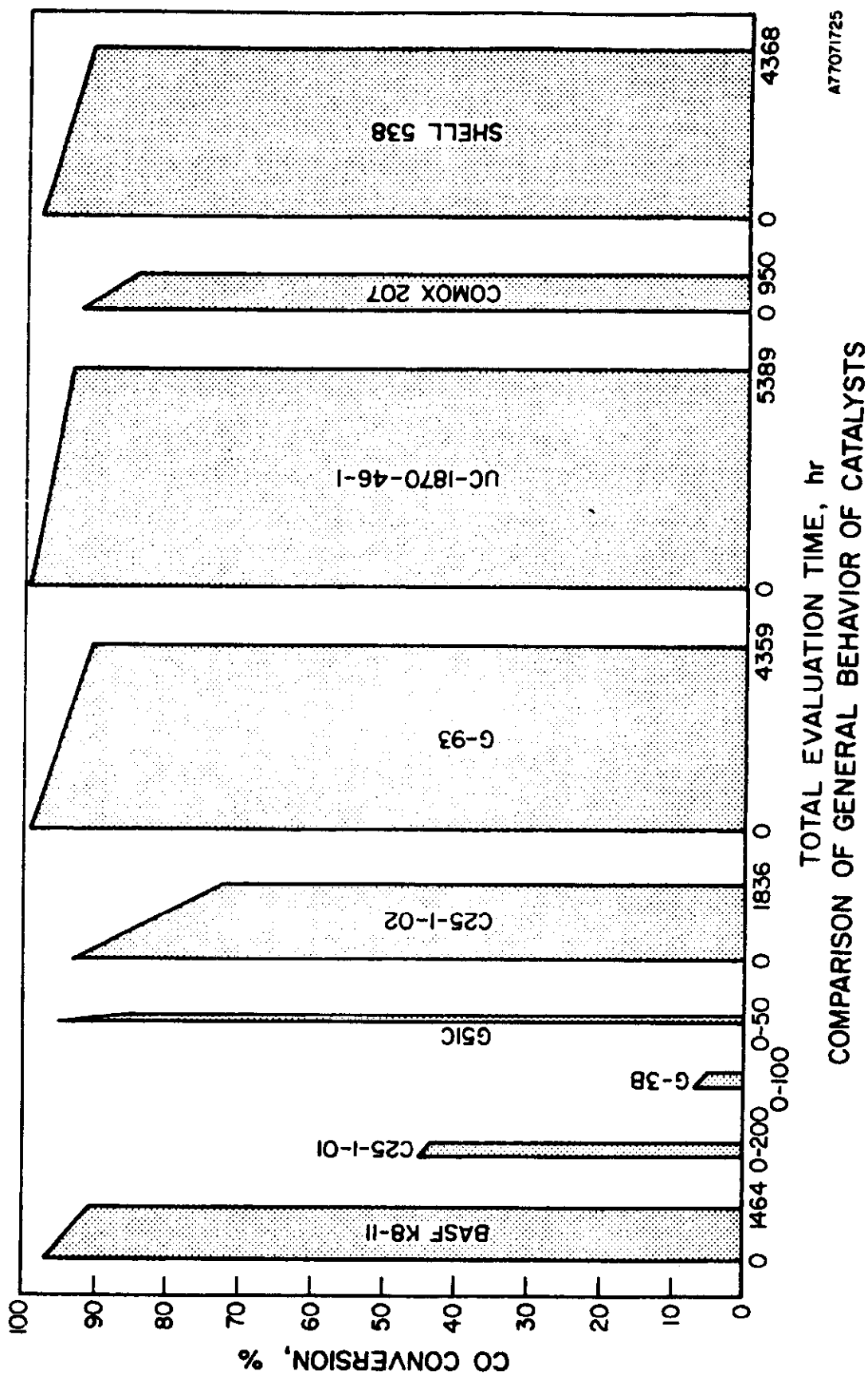
Comparison of Catalysts

The experimental data of the screen-life tests and that of the kinetics studies for all the catalysts studied were analyzed. The process variables that we have investigated are temperature, pressure, space velocity, steam/gas ratio, benzene concentration, ammonia concentration, phenol concentration, and the carbon deposition conditions. For comparison purposes, the effects of these variables on the conversion of carbon monoxide to hydrogen by the water-gas shift reaction are presented in Figures 85 through 91. Often, one set of operating conditions is presented in one figure. Although the results varied nonlinearly with operating conditions, the relative differences between catalysts remain about the same.

Figure 85 presents the change in relative carbon monoxide conversion with time during which the operating conditions were changed many times from one extreme to the other. Of necessity, the test conditions were not identical for all catalysts. For example, the BASF catalyst K8-11 was not tested for phenol concentrations higher than 0.04%, whereas the UC-1870-46-1 and Shell Oil 538 catalysts were tested for phenol concentrations up to 1.0%. The data obtained with the CSTR for kinetics studies were included in this figure for G-93, UC-1870-46-1, and Shell Oil 538 catalysts. The CSTR space velocity has the unit of SCF/hr-g, which is not the same as that for the packed-bed reactor used in the life test studies. The CSTR space velocity was converted to the volumetric basis used in the life tests by employing the bulk density of the catalysts. Therefore, the curves presented in Figure 85 are not exact in nature, but serve adequately for comparison.

The following conclusions are drawn:

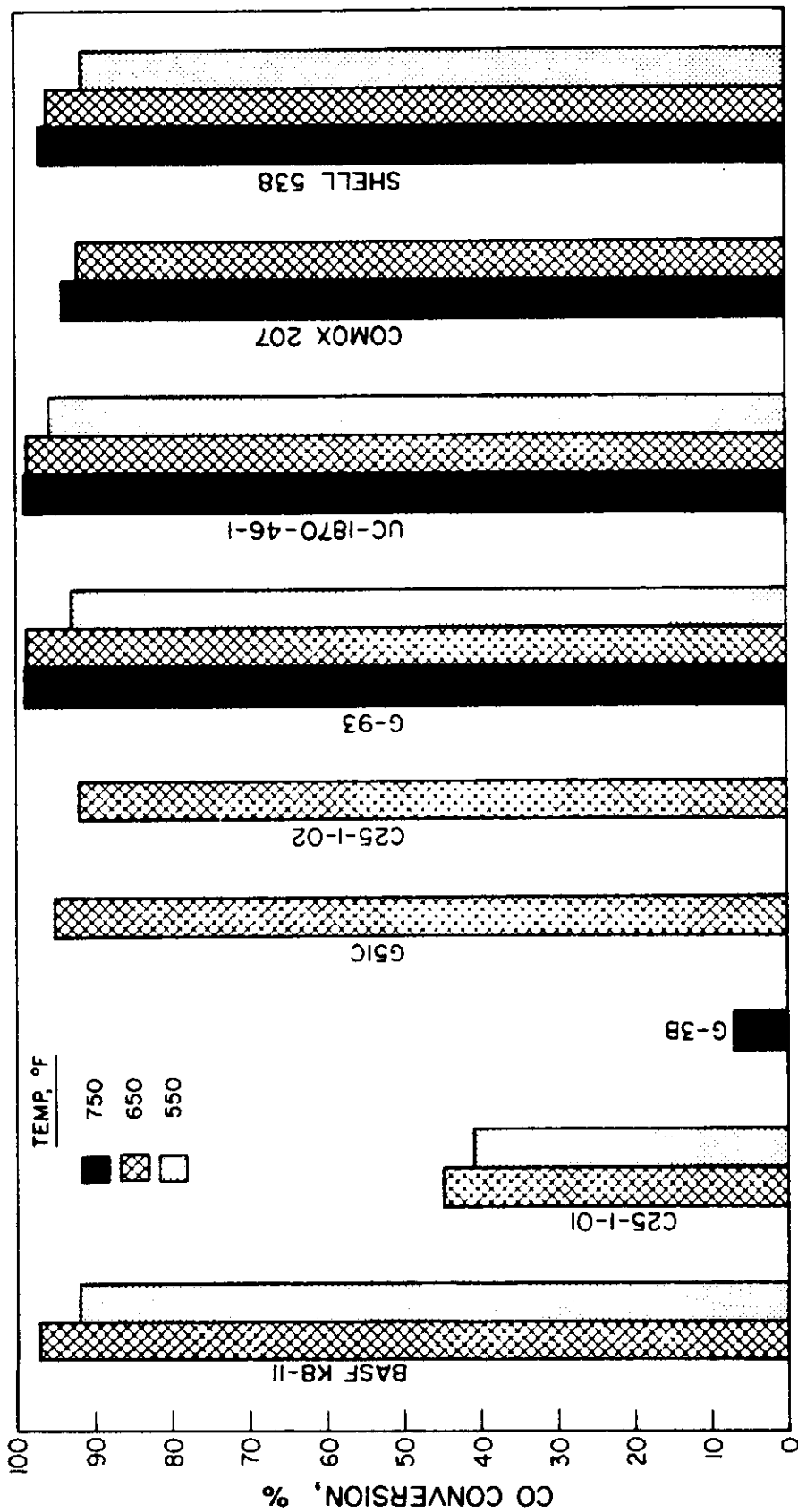
- BASF catalyst K8-11, made by Badische Anilin und Soda-Fabrik AG, consists of oxides of cobalt and molybdenum on a special carrier catalyst. It was used in a commercial plant for the production of ammonia from the gasification of heavy fuel oil (Texaco Process). It was specially developed as a shift conversion catalyst for use in systems at pressures higher than 40 atm. The catalyst performance was greatly improved when it was pretreated with a high sulfur-containing gas. Without the pretreatment, the catalyst was rapidly deactivated in the presence of ammonia. Benzene retarded both the percent and the rate of carbon monoxide conversion (Figure 90), and phenol poisoned the catalyst (Figure 92), but the catalyst was regenerable. Carbon formation was detected at 650°F and a steam/benzene ratio of 6 (mole ratio, dry basis).



COMPARISON OF GENERAL BEHAVIOR OF CATALYSTS  
TOTAL EVALUATION TIME, hr

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Figure 85. EFFECT OF TIME ON CARBON MONOXIDE CONVERSION



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EFFECT OF TEMPERATURE ON THE CONVERSION OF CO

Figure 86. EFFECT OF TEMPERATURE ON CARBON MONOXIDE CONVERSION

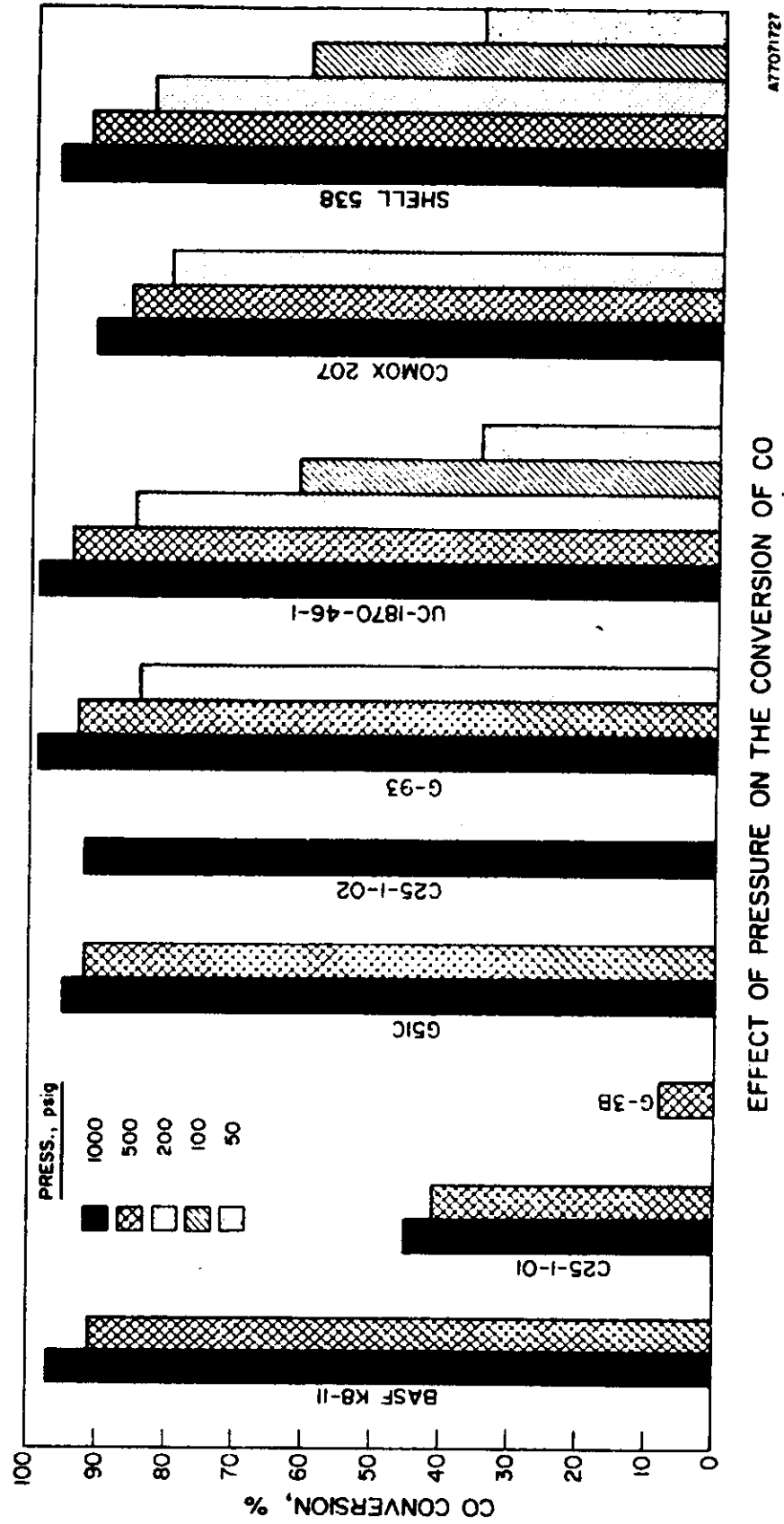


Figure 87. EFFECT OF PRESSURE ON CARBON MONOXIDE CONVERSION

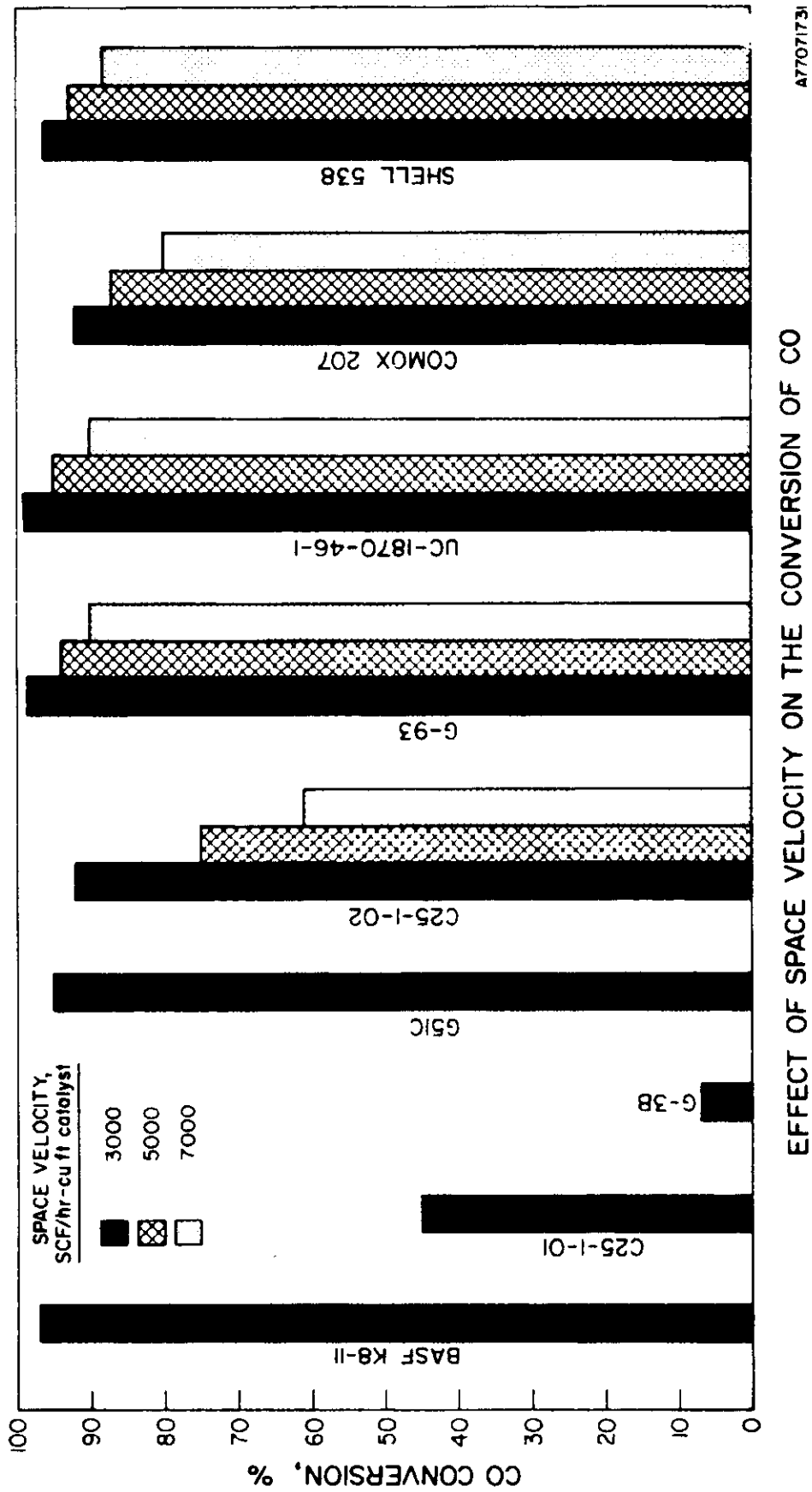
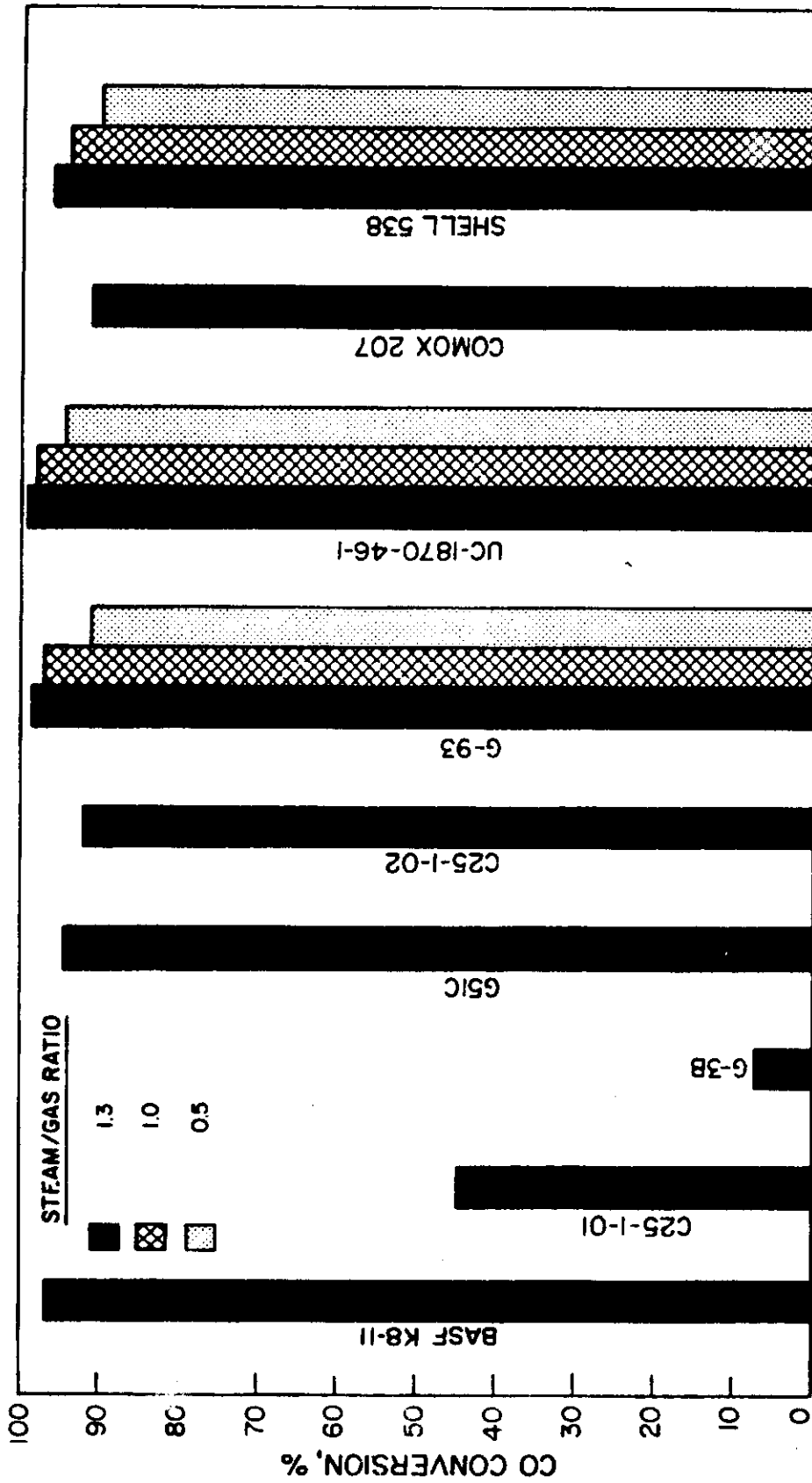


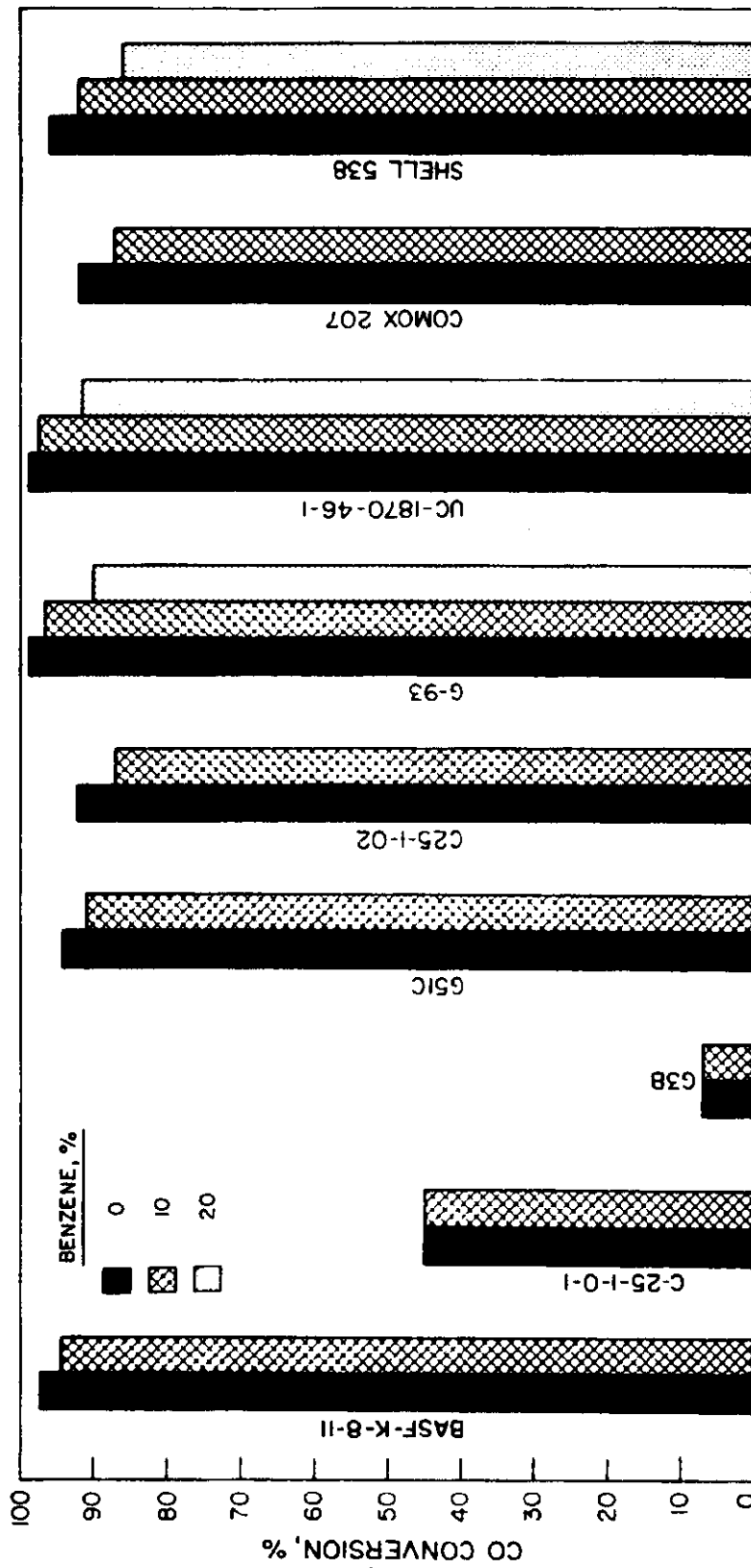
Figure 88. EFFECT OF SPACE VELOCITY ON CARBON MONOXIDE CONVERSION



EFFECT OF STEAM/GAS RATIO ON THE CONVERSION OF CO

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Figure 89. EFFECT OF STEAM/GAS RATIO ON CARBON MONOXIDE CONVERSION



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EFFECT OF BENZENE ON THE CONVERSION OF CO

Figure 90. EFFECT OF BENZENE ON CARBON MONOXIDE CONVERSION

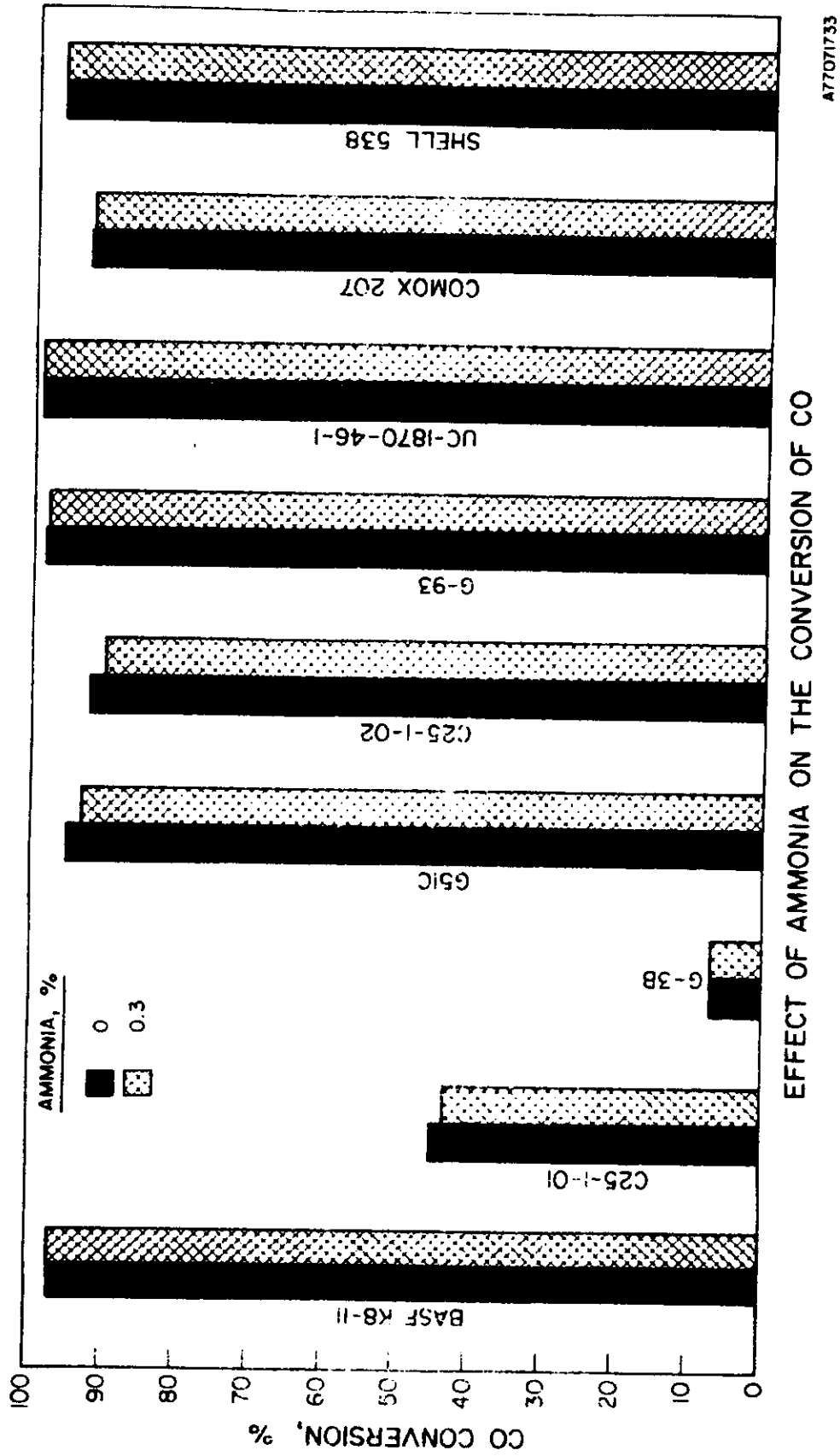


Figure 91. EFFECT OF AMMONIA ON CARBON MONOXIDE CONVERSION



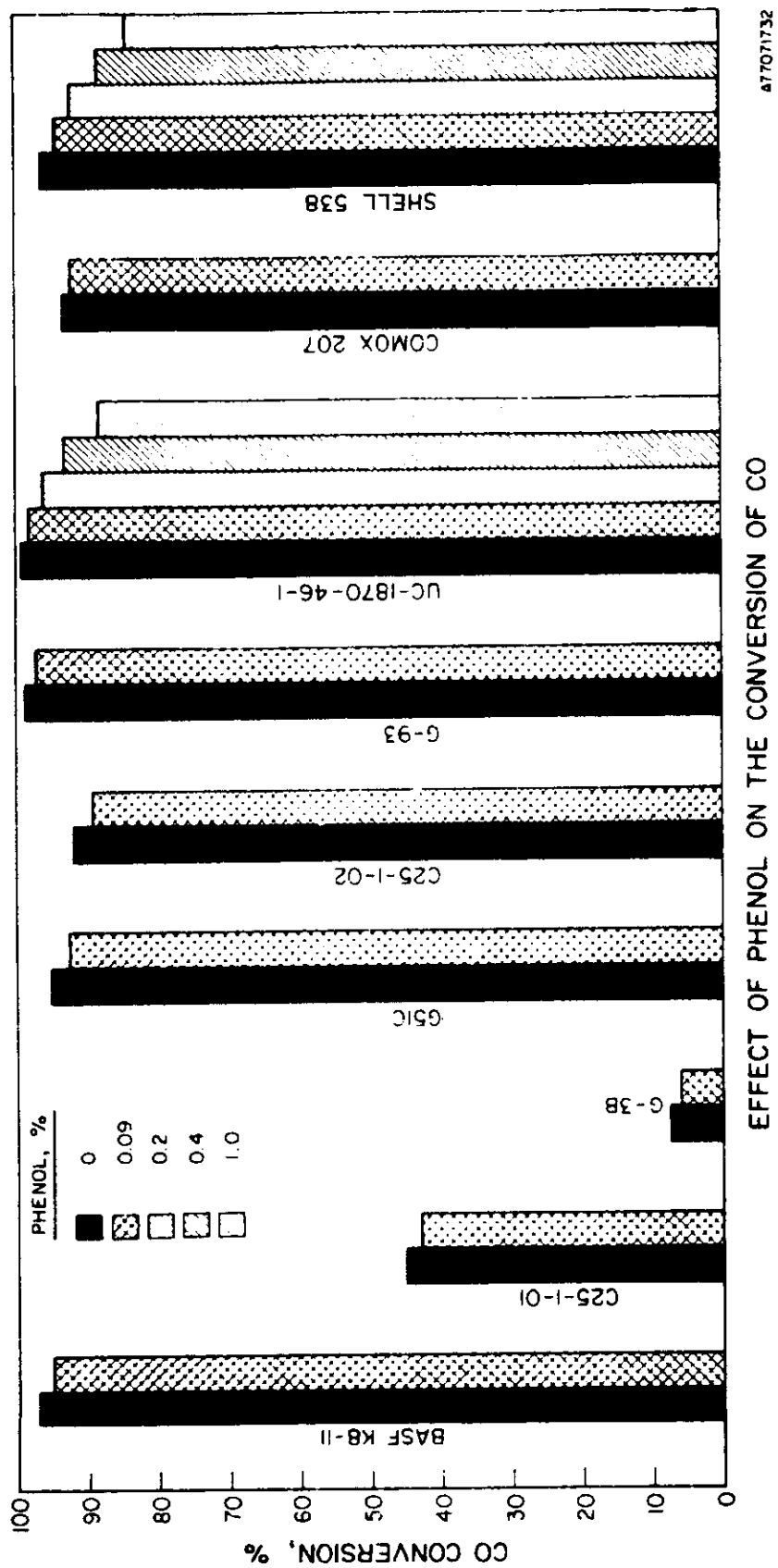


Figure 92. EFFECT OF PHENOL POISON ON CARBON MONOXIDE CONVERSION

It was not selected for further studies of the kinetics of the water-gas shift reaction because of its need for pretreatment, lower ammonia poisoning resistance, lower carbon formation conditions (Figure 93), and weaker physical strength.

- Catalyst C25-1-01, formerly named C20-6-02 and made by CCI, is a cobalt-molybdenum on alumina catalyst. It was used in oil desulfurization processes and was tested by CCI in shift conversion prior to submission to IGT for evaluation. It was found to be unsatisfactory in all respects (Figures 85 through 92).
- Catalyst C25-1-02, formerly named C20-6-03 and made by CCI, is also a cobalt-molybdenum catalyst. 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 or ammonia or . The results were satisfactory, and it was sent to IGT for further evaluation. It was found that the catalyst was poisoned by ammonia and required pretreatment. The carbon monoxide conversion decreased rapidly with increased space velocity (Figures 85 and 88). Carbon formation was observed at 654°F and 1000 psig when benzene and phenol were added, and deactivation was accelerated. Attempts were made to regenerate the catalyst, but to no avail. The discharged catalyst was analyzed by CCI and found to have retained only 16% of its original crush strength. Recently CCI has improved this catalyst to retain much better physical properties such as surface area and crush strength, and the catalyst is in the form of 3/16 inch x 1/8 inch tablets. This improved C25-1-02 catalyst is less acidic and should be more tolerant to ammonia, but IGT has not evaluated it.
- Catalyst 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. This catalyst was found to be unsuitable for shift conversion in the presence of benzene, ammonia, and phenol. It is also generally accepted that, although the iron-chromium type catalysts were widely used with a clean feed gas in the past, they will not perform satisfactorily in a coal gasifier effluent.
- Catalyst G51C, made by Girdler Chemicals, Inc., is a low-density cobalt-molybdenum catalyst. It is used principally for hydrodesulfurization of hydrocarbons. This catalyst had the weakest physical strength of all the catalysts evaluated, and its resistance to benzene, ammonia, and phenol was the poorest.
- Catalyst G-93, formerly named T-2021 and 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 resist ammonia and phenol poisoning. Its activity is good. Near-equilibrium conversion was obtained at a space velocity of 7000 SCF/hr-ft<sup>3</sup> (dry basis) (Figure 88). It was not affected by ammonia (Figure 91). The rate of conversion was not affected by benzene as long as carbon deposition conditions were avoided, but the percent conversion decreased as the benzene concentration increased (Figure 90). The lowest effective temperature appears to be about 530°F at 1000 psig, and the upper temperature limit appears to be less than 900°F. The problem at high

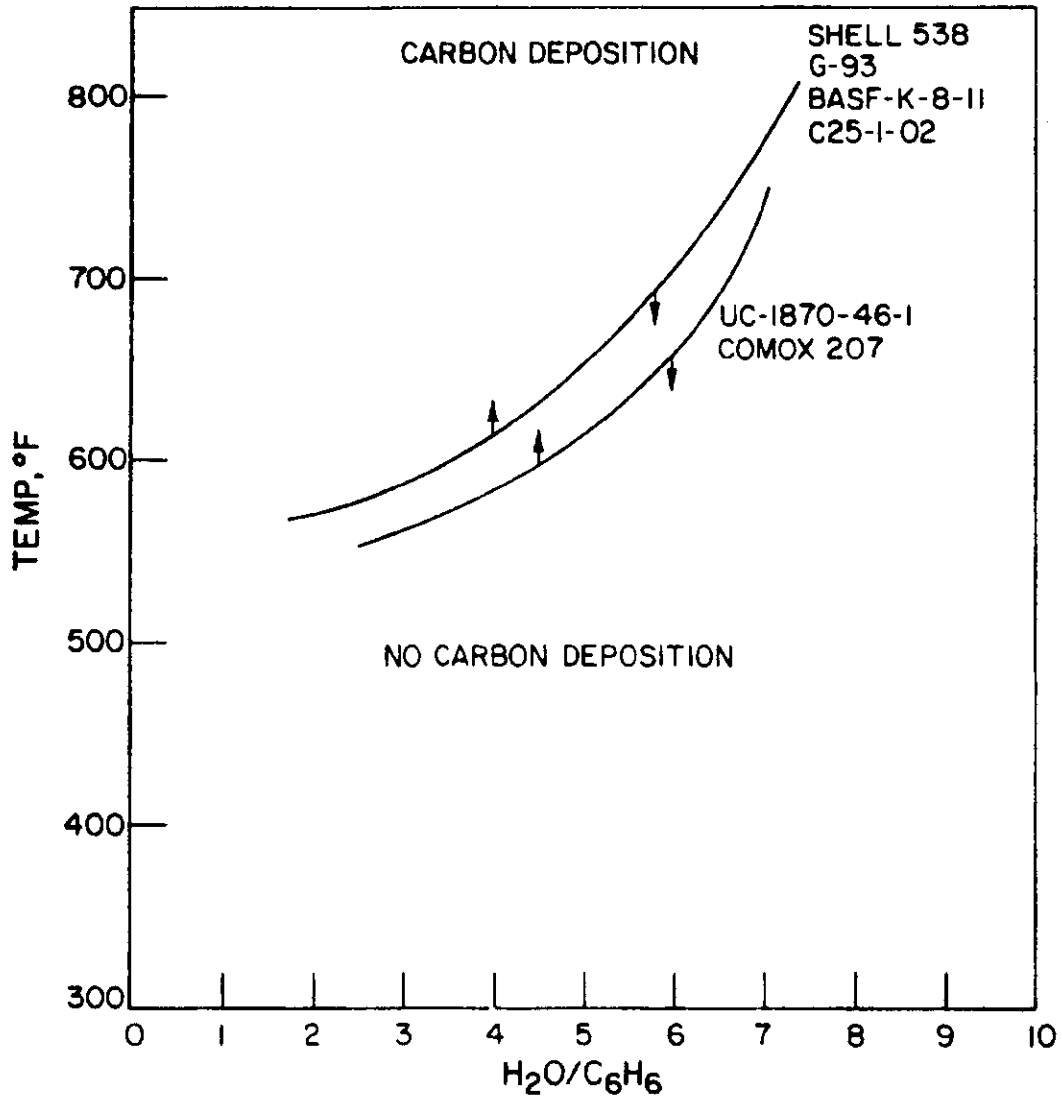


Figure 93. CARBON DEPOSITION CONDITIONS

temperatures is not the loss of catalyst activity but the deposition of carbon due to the large amount of benzene in the feed. It was found that the steam/benzene ratio (mole) of 6 was critical to carbon deposition. Carbon will still form at this ratio, especially at higher temperatures, but will be small in amount and tolerable. Large amounts of carbon will form and will result in high pressure drops at steam/benzene ratios less than 6 (Figure 93). For the feed compositions studied here and for most of the coal gasification processes proposed to date, the concentration of hydrocarbons such as  $C_2$ ,  $C_3$ , and  $C_4$  in the effluent are small, usually about 2%. Although hydrogenolysis reactions occurred, the reaction orders of these components with respect to the water-gas shift reaction are zero. Small quantities of inert gases, such as nitrogen and helium, had no effect on the reaction. However, it is expected that both the reaction rate and the conversion will be retarded if the concentration of the inert gases in the feed exceeds 10%. It is desirable to maintain 1% total sulfur (dry basis) in the feed to avoid deactivation. Phenol is a poison to all the catalysts studied (Figure 92), and the rate of poisoning is relatively independent of temperature and pressure. This poisoning effect is reversible, and the catalyst can be regenerated in situ. The rate of reaction increases with increasing carbon monoxide concentration in the feed. We found that carbon monoxide does not inhibit the rate of the water-gas shift reaction as long as the steam/gas ratio is higher than 0.5.

- Catalyst UC-1870-46-1, made by Union Carbide Corp., is a nickel-molybdenum on zeolite catalyst. Prior to submitting this catalyst to IGT for extensive evaluation, Union Carbide tested it and other shift catalysts, including 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. We found that this catalyst had the highest activity of all the catalysts tested to date (Figure 85 through 87). It was not affected by ammonia (Figure 91). The presence of benzene has the same effect on this catalyst that it had on the G-93 catalyst (Figure 90), but the carbon formation range was greater (Figure 93). This catalyst compares well with other catalysts, as can be seen from Figures 85 through 93. Using this catalyst and anticipating the low-pressure operation of some coal gasification plants, we expanded our pressure studies to include pressures of 50 and 100 psig, in addition to the higher pressures of 200, 500, and 1000 psig. The results showed a sharp decrease in both the percent and the rate of carbon monoxide conversion at pressures lower than 200 psig. At steam/gas ratios larger than 0.5, the influence of steam on the percent conversion of carbon monoxide is small, but its influence on the rate of reaction is quite pronounced until the ratio reaches 1.3 after which its influence on the rate decreases sharply. However, the most important fact is that the steam/benzene ratio is crucial for carbon formation reactions. It is conceivable that the steam/gas ratio may be reduced to less than 0.5 with no effect on the rate of reaction if the benzene and/or oil concentration in the feed were also reduced. To define the poisoning effects due to phenol, phenol concentrations of 0, 0.1%, 0.4%, and 0.9% were used in this study. The deactivation appears to be both by poisoning and, at high phenol concentrations, by promoting carbon deposition.

- Shell Oil Company catalyst 538 is a cobalt-molybdenum catalyst that was used in oil gasification plants and has been modified to fulfill our requirements. In performance, this catalyst compared well with catalysts G-93 and UC-1870-46-1 (Figures 85 through 88, and Figure 90). It did not require pretreatment, was not affected by ammonia, had the same dependency on temperature, pressure, steam/gas ratio, steam/benzene ratio, and was poisoned by phenol just as the G-93 and UC-1870-46-1 catalysts.
- Catalyst Comox 207, made 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. It also showed potential for operation prior to water quenching. It compared well with catalysts G-93, UC-1870-46-1, and Shell Oil 538 (Figures 85 through 93), but was deactivated slightly by ammonia. It was not used in the kinetics study of the water-gas shift reaction, but based on the screen-life test data, the rate equations developed based on the data of the G-03, UC-1870-46-1, and Shell Oil 538 catalysts should be applicable to Comox 207 as well.