KINETICS TESTS

Kinetics of the Water-Gas Shift Reaction

Reaction kinetics include the rate of formation or conversion of a specific component; the rate of deactivation; the effectiveness factor or the effect of diffusion and particle size; and the effect of a component or components, which do not take part in the reaction under investigation, but cause competing reaction at certain conditions. In this study of the water-gas shift reaction in coal gasification product gases, we have all the above-mentioned conditions: the rate of formation of hydrogen or the rate of conversion of carbon monoxide, and the rate of deactivation by ammonia and by phenol. Although the particle size is constant, the average pore length (as defined in the Thiele modulus) changes with time. The presence of excess aromatics at low steam/aromatics ratios promotes carbon formation reaction at high temperatures.

The experimental work reported here was planned on the basis of the work reported in the previous section. A continuous-stirred-tank-reactor (CSTR), which gives the isothermal conditions and eliminates the concentration gradient, was used for this study. The carbon oxides were analyzed by infrared analyzers, a gas partitioner, and a mass spectrograph. All components except hydrogen were analyzed by gas partitioning and mass spectrography, and hydrogen is analyzed by mass spectrography alone.

Experiments were started using a feed consisting of carbon monoxide, carbon dioxide, hydrogen, methane, ethane, propane, mercaptan, hydrogen sulfide, carbonyl sulfide, nitrogen, helium, and water. Three water/gas ratios were used to determine the effect of water concentration on the reaction. Benzene was added, and the conditions at which the first set of tests were studied were run again. Close observations were made of the carbon balance. The effect of benzene on the reaction and the carbon formation reactions were studied at benzene feed concentrations of about 10 and 20 mol %.

The isolation method was used to determine the order of reaction with respect to each component involved in the reaction. Previous studies have shown that components such as carbon dioxide, methane, helium, nitrogen, sulfurs, and small amounts of heavier hydrocarbons were of zero order with respect to the water-gas shift reaction. By holding other component concentrations constant and varying H_2O concentration, the reaction order with respect to H_2O was determined. Similarly, the order of carbon monoxide was estimated. Other components, such as benzene, ammonia, and phenol were added one at a time. The experiments were repeated for the same sets of conditions, and the deactivation effect of these components was estimated. The temperature and pressure were then changed, and for every change, the same set of data were taken. Once the initial effect of each component was established, the total rate expression was formulated, and the reaction orders were finalized for all components with the experimental data.

The initial rate analysis is summarized in Figure 15. The reaction orders with respect to carbon monoxide and water are positive, and that with carbon dioxide is zero. The reaction order with respect to benzene is negative. Deactivation by phenol is a side-by-side reaction, and will be included in the water-gas shift rate equation by means of a separate factor.

Kinetics Test Results – G93

A total of 110 runs were made for this study. The detailed data are presented in Appendix B, Tables B-1 and B-2. In addition to the data needed for the development of a rate equation, we also obtained information to estimate the effect of benzene, ammonia, and phenol on the conversion, and on the rate of conversion, of carbon monoxide in the water-gas shift reaction. Most of the experiments were conducted at conditions well away from equilibrium conversions in order to obtain meaningful rate data.

The effects of temperature, pressure, and the steam/gas ratio can be graphically represented as shown in Figures 16 (for feeds containing approximately 10% carbon monoxide) and 17 (for feeds containing approximately 20% carbon monoxide). In general, the conversion of carbon monoxide increases with temperature, pressure, and steam; the rate of conversion of carbon monoxide also increases with temperature, pressure, and steam/gas ratio, as shown in Figures 18 (for feeds containing approximately 10% carbon monoxide) and 19 (for feeds containing approximately 20% carbon monoxide).

The effect of the presence of benzene in the feed was studied at benzene concentrations of about 10 and 20 mole %, and is illustrated in Figure 20. The results of these experiments can be summarized as follows:

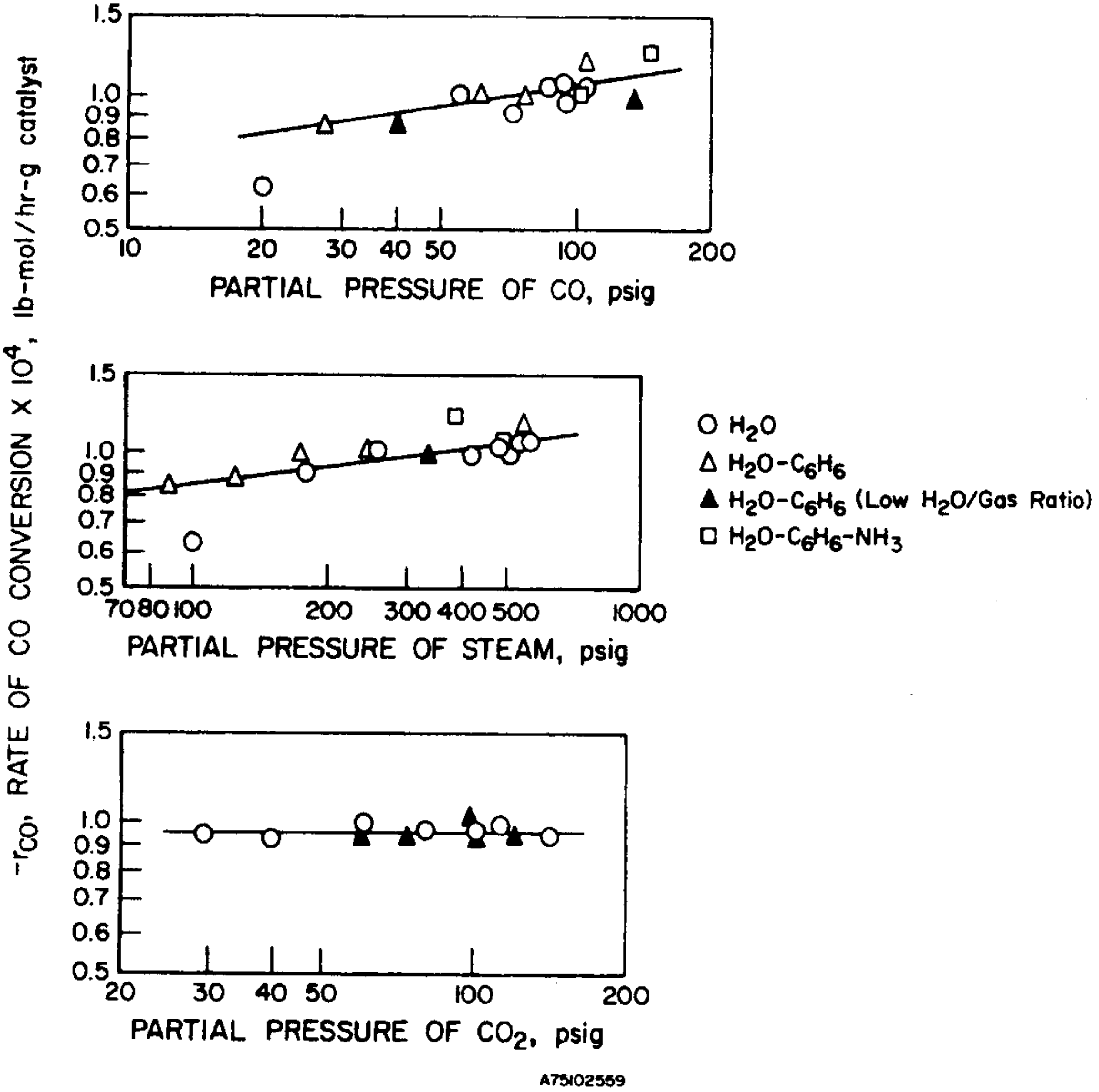
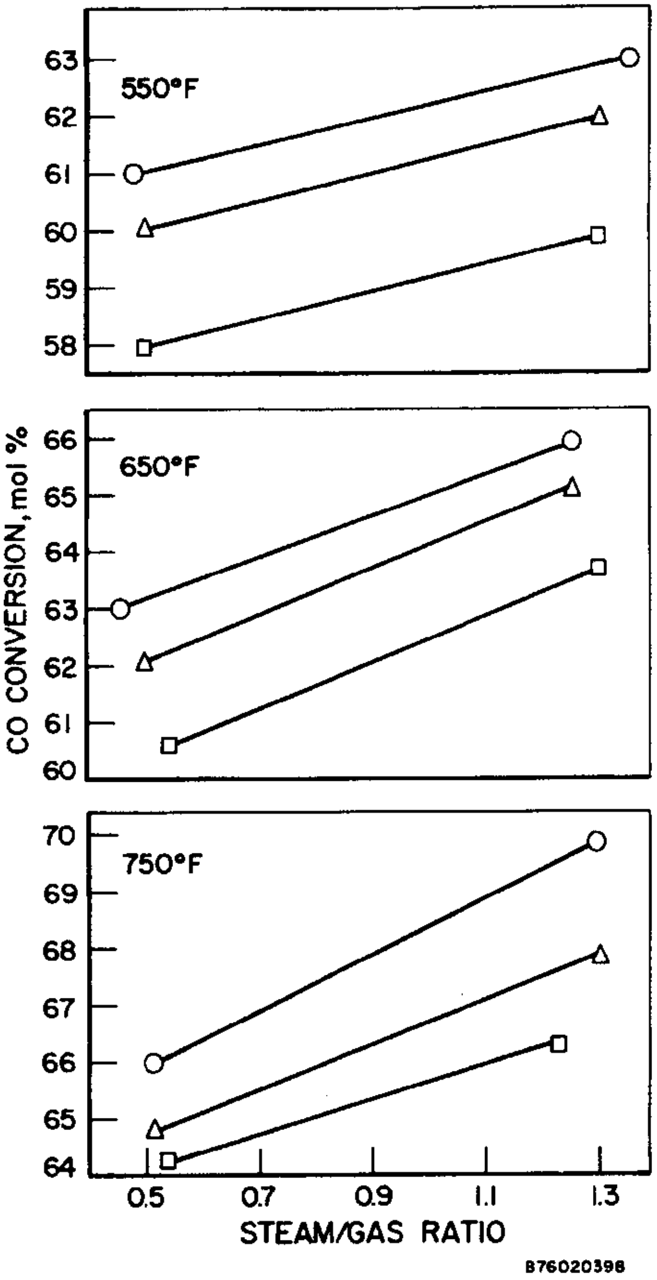


Figure 15. EFFECT OF PARTIAL PRESSURES OF FEED COMPONENTS AND CARBON DIOXIDE ON THE RATE OF CARBON MONOXIDE CONVERSION

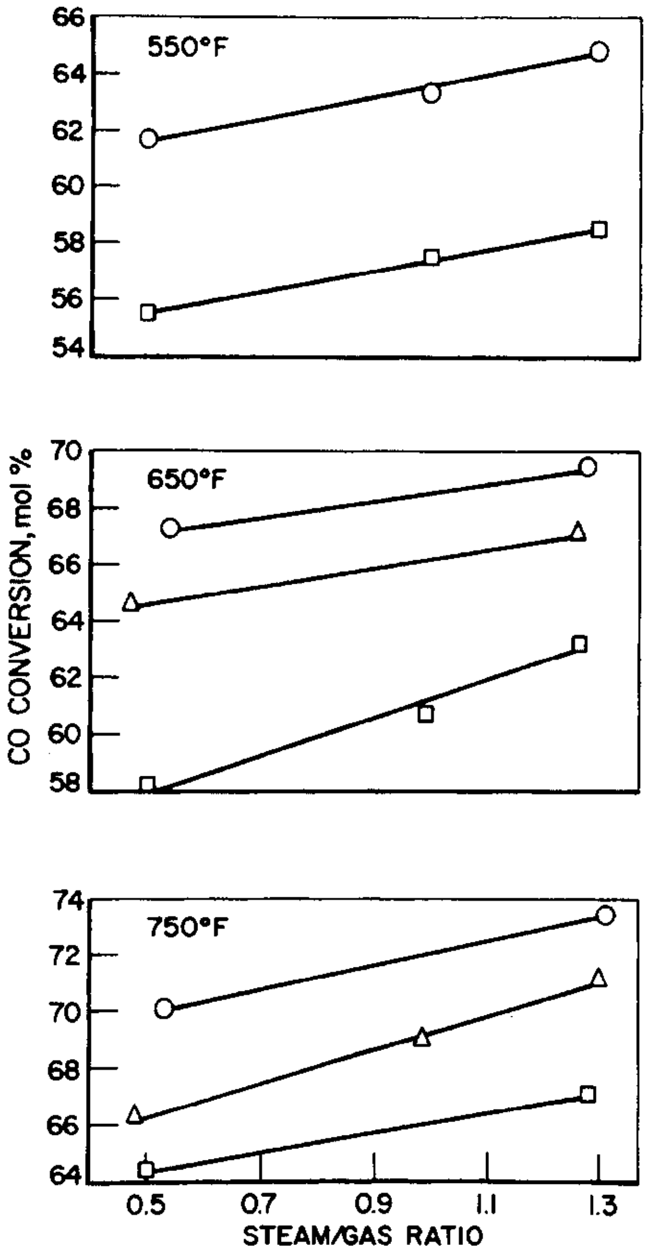


SYMBOL	PRESSURE, psig
○	1000
△	500
□	200

FEED GAS COMPOSITION, Dry Basis

COMPONENT	
CO, mol %	9.01
CO_2, mol %	18.56
H_2, mol %	34.14
CH_4, mol %	23.87
C_2H_6, mol %	0.90
C_3H_8, mol %	0.27
C_4H_{10}, mol %	0.19
H_2S, mol %	1.79
N_2, mol %	1.35
He, mol %	0.01
NH_3, mol %	0.44
C_6H_5OH, mol %	0.09
C_6H_6, mol %	9.28
COS, mol %	0.10
CH_3SH, ppm	114
TOTAL	100.00

Figure 16. EFFECT OF STEAM/GAS RATIO ON CONVERSION OF CARBON MONOXIDE



SYMBOL	PRESSURE, psig
○	1000
△	500
□	200

FEED GAS COMPOSITION, Dry Basis

COMPONENT	
CO, mol %	17.4
CO_2, mol %	20.2
H_2, mol %	25.6
CH_4, mol %	20.4
C_2H_6, mol %	1.3
C_3H_8, mol %	0.88
C_4H_{10}, mol %	0.09
H_2S, mol %	1.4
N_2, mol %	1.2
He, mol %	0.03
NH_3, mol %	0.35
C_6H_5OH, mol %	0.08
C_6H_6, mol %	11.07
COS, ppm	31.4
CH_3SH, ppm	235.6
C_2H_5SH, ppm	2.6
C_4H_4S, ppm	1.6
TOTAL	100.00

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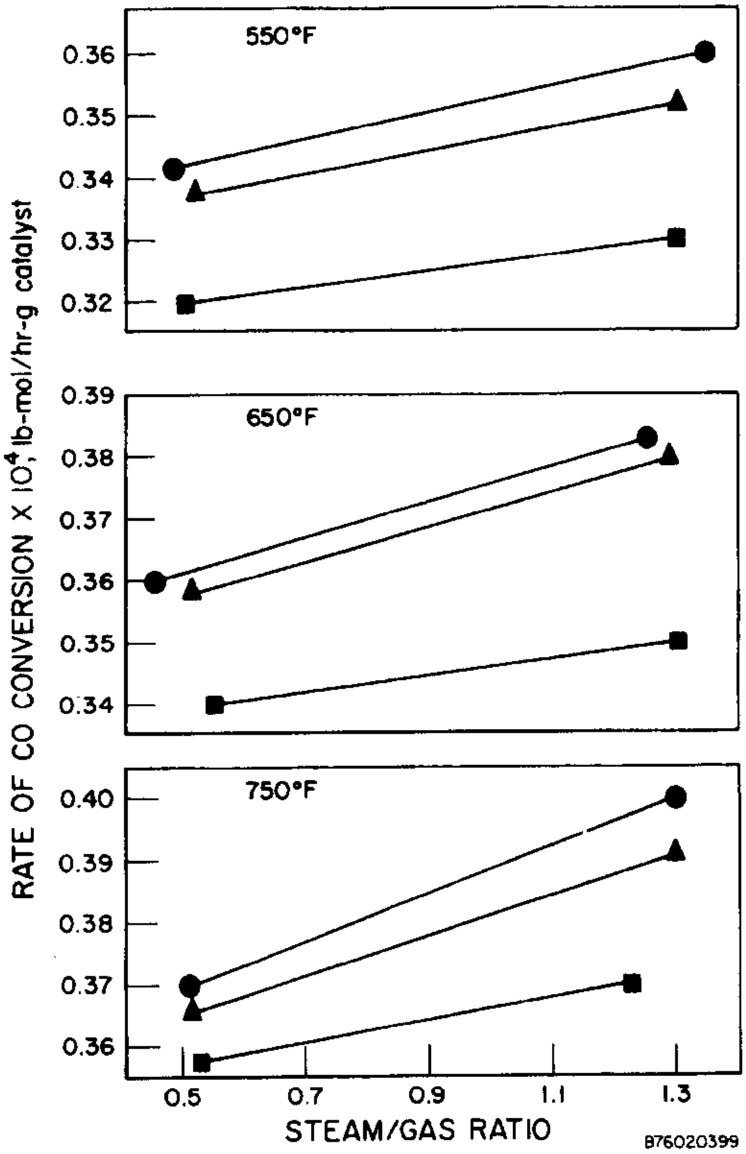
Figure 17. EFFECT OF STEAM/GAS RATIO ON CONVERSION OF CARBON MONOXIDE

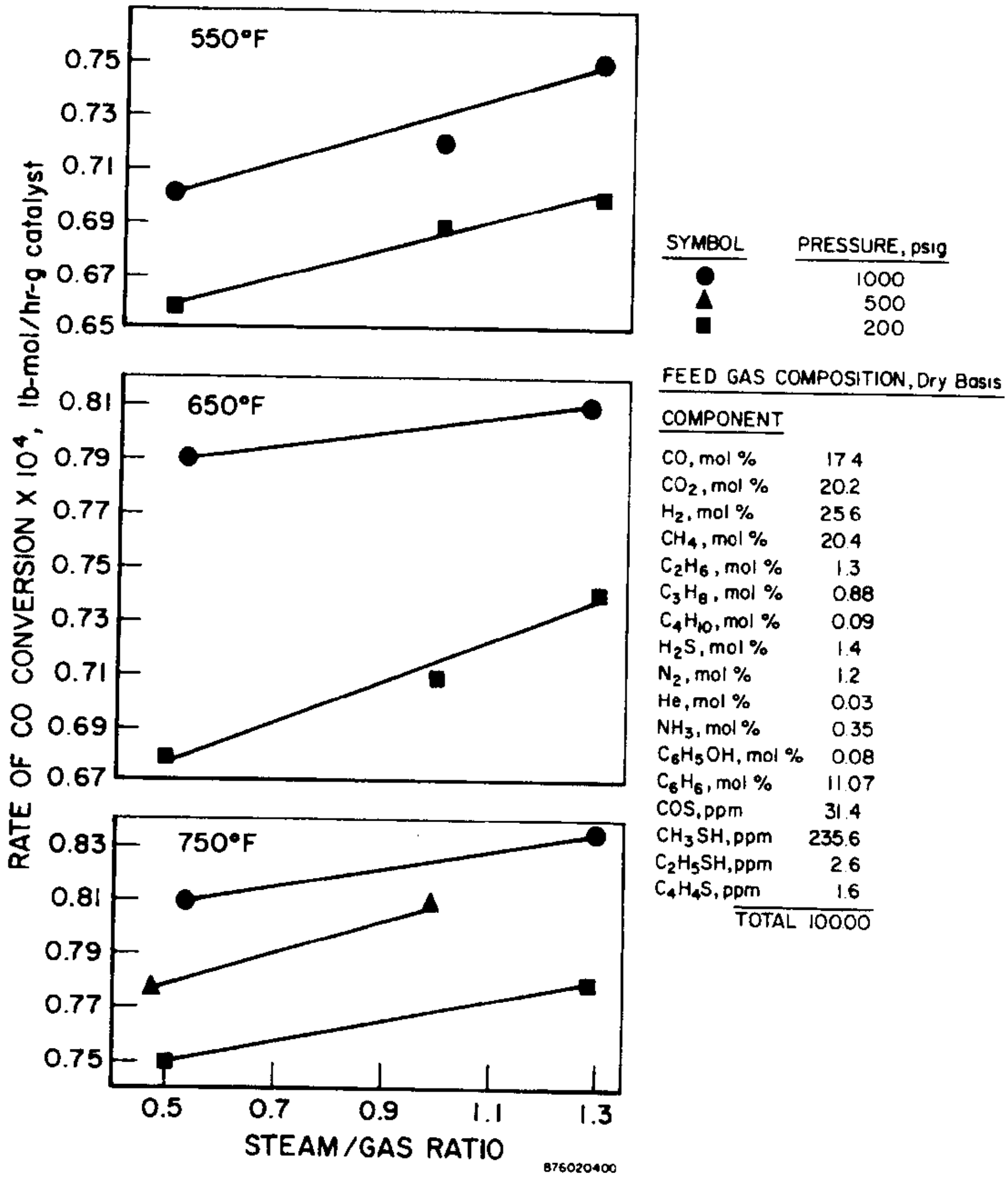


SYMBOL	PRESSURE, psig
●	1000
▲	500
■	200

FEED GAS COMPOSITION, Dry Basis

COMPONENT	
CO, mol %	9.01
CO_2, mol %	18.56
H_2, mol %	34.14
CH_4, mol %	23.87
C_2H_6, mol %	0.90
C_3H_8, mol %	0.27
C_4H_{10}, mol %	0.19
H_2S, mol %	1.79
N_2, mol %	1.35
He, mol %	0.01
NH_3, mol %	0.44
C_6H_5OH, mol %	0.09
C_6H_6, mol %	9.28
COS, mol %	0.10
CH_3SH, ppm	114
TOTAL	100.00

Figure 18. EFFECT OF STEAM/GAS RATIO ON RATE OF CARBON MONOXIDE CONVERSION



FEED GAS COMPOSITION, Dry Basis

COMPONENT	
CO, mol %	17.4
CO_2, mol %	20.2
H_2, mol %	25.6
CH_4, mol %	20.4
C_2H_6, mol %	1.3
C_3H_8, mol %	0.88
C_4H_{10}, mol %	0.09
H_2S, mol %	1.4
N_2, mol %	1.2
He, mol %	0.03
NH_3, mol %	0.35
C_6H_5OH, mol %	0.08
C_6H_6, mol %	11.07
COS, ppm	31.4
CH_3SH, ppm	235.6
C_2H_5SH, ppm	2.6
C_4H_4S, ppm	1.6
TOTAL	100.00

Figure 19. EFFECT OF STEAM/GAS RATIO ON RATE OF CARBON MONOXIDE CONVERSION

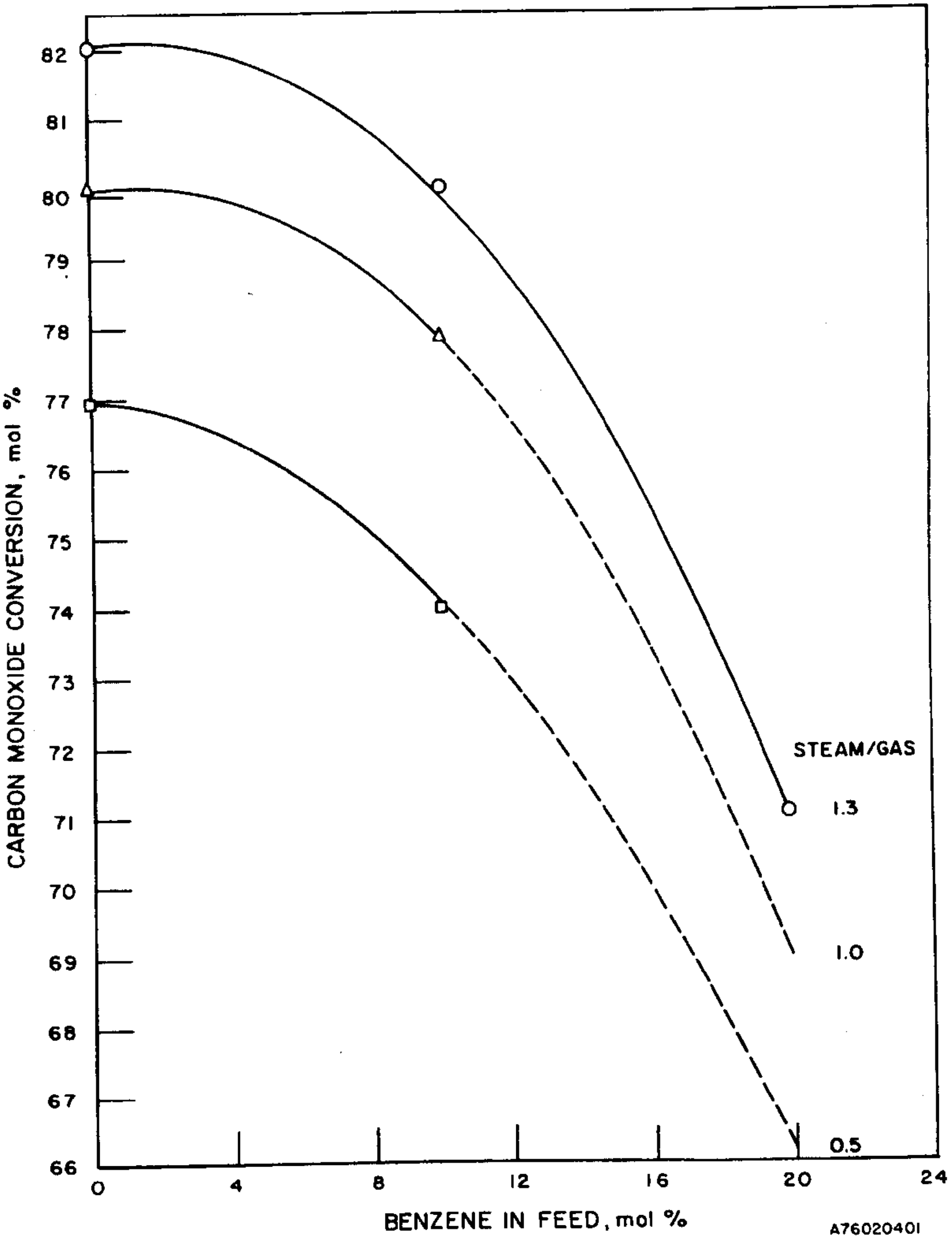


Figure 20. EFFECT OF BENZENE ON CONVERSION OF CARBON MONOXIDE (at 1000 psig, 650°F, and CSTR Space Velocity of 0.2755 SCF/hr-g)

- No carbon formation was detected at temperatures up to 750°F, 1000 psig, with a feed benzene concentration of 10% for the steam/gas ratios studied here.
- Carbon formation was detected at temperature of 802°F, 1000 psig, 10% benzene, and a steam/gas ratio of 0.5.
- No carbon formation was detected at temperatures up to 650°F, 1000 psig, 20% benzene, and a steam/gas ratio of 1.3.
- Slight carbon formation was detected at 650°F, 1000 psig, 20% benzene, and a steam/gas ratio of 1.0.
- Definite carbon formation was detected at 650°F, 1000 psig, 20% benzene, and a steam/gas ratio of 0.5.
- Definite carbon formation was detected at 750°F, 1000 psig, 20% benzene, and all steam/gas ratios studied here.

As shown in Figure 21, the presence of up to 0.36 mole % ammonia in the feed had no effect on the water-gas shift reaction when this improved shift catalyst was used. (Ammonia deactivated other catalysts tested in this program.) Phenol deactivates all catalysts tested so far, but the rate of deactivation is slow, as illustrated in Figure 22.

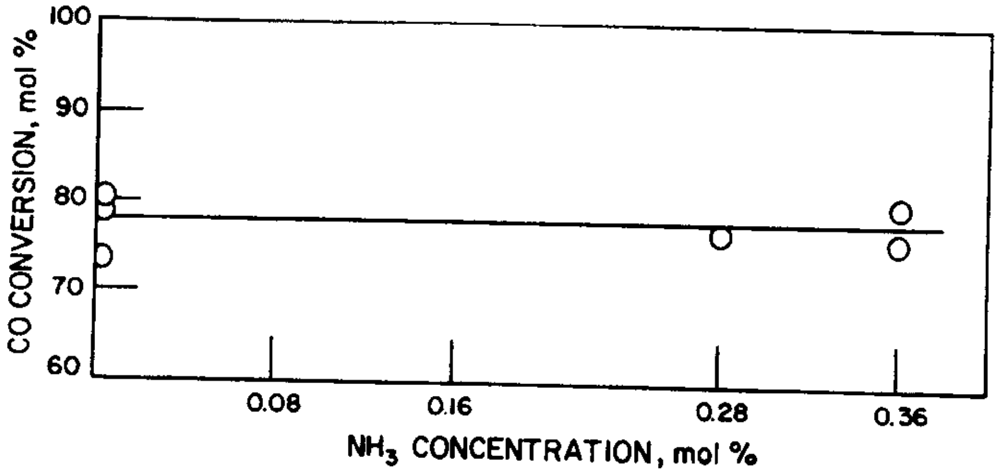


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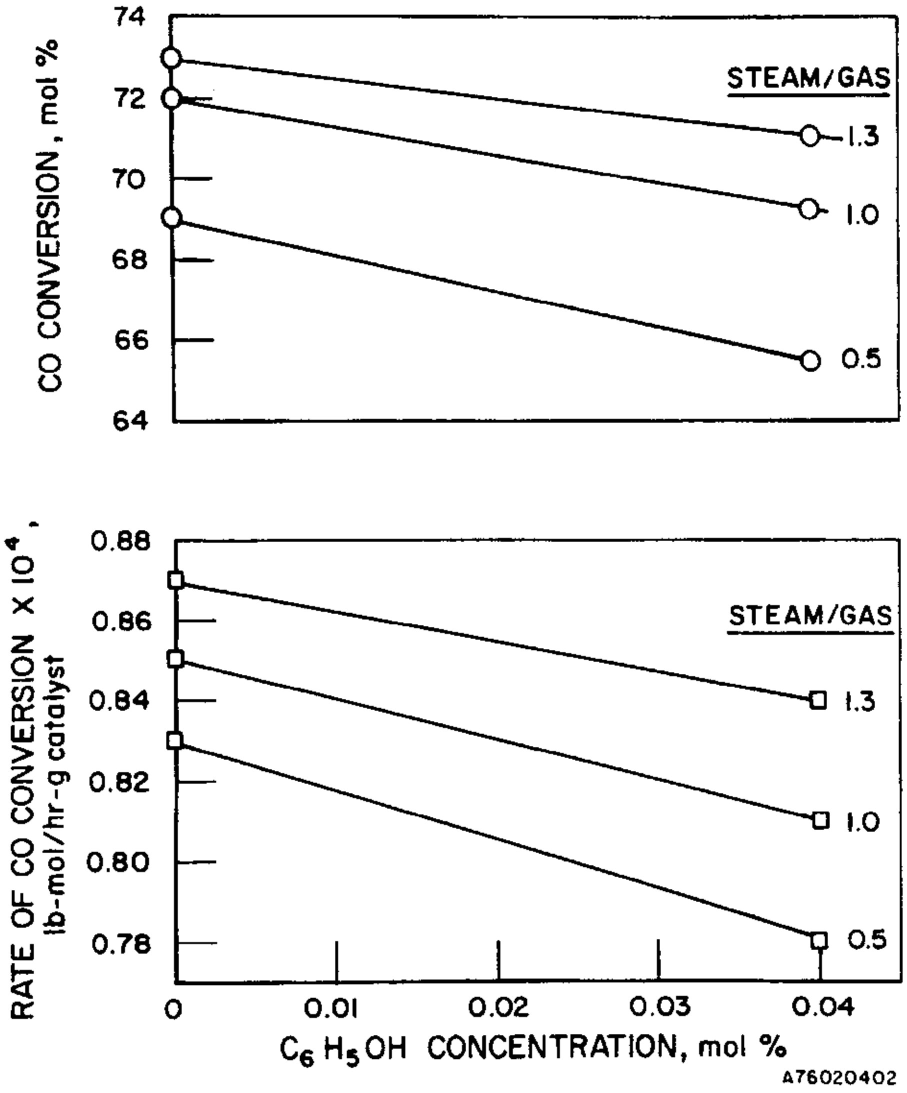
Figure 21. EFFECT OF AMMONIA ON CONVERSION OF CARBON MONOXIDE (Data Obtained at 660°F and 1000 psig)



FEED GAS COMPOSITION, Dry Basis

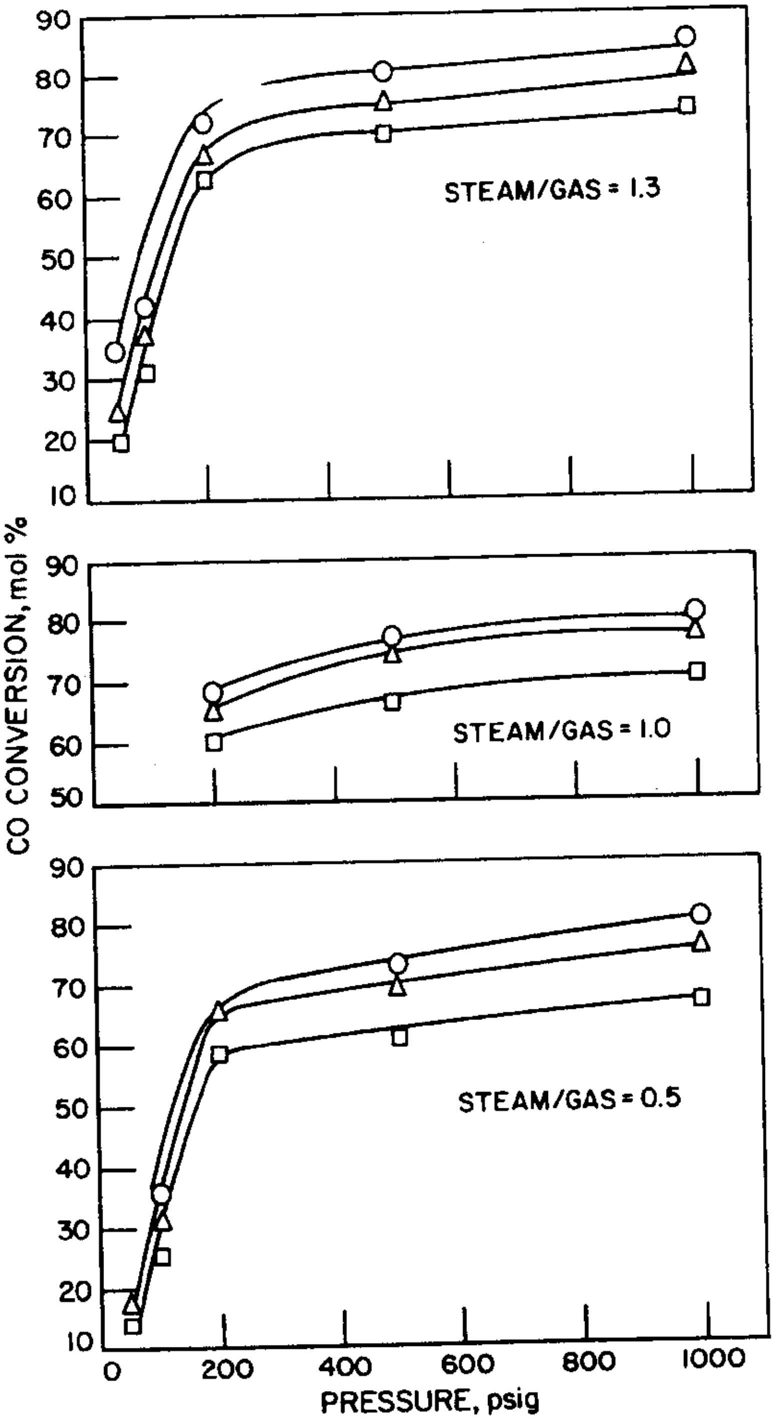
COMPONENT	
CO, mol %	17.4
CO_2, mol %	20.2
H_2, mol %	Balance
CH_4, mol %	20.4
C_2H_6, mol %	1.3
C_3H_8, mol %	0.88
C_4H_{10}, mol %	0.09
H_2S, mol %	1.4
N_2, mol %	1.2
He, mol %	0.03
NH_3, mol %	0.35
C_6H_5OH, mol %	As indicated
C_6H_6, mol %	11.07
COS, ppm	31.4
CH_3SH, ppm	235.6
C_2H_5SH, ppm	2.6
C_4H_4S, ppm	1.6
TOTAL	100.00

Figure 22. EFFECT OF PHENOL ON RATE OF CONVERSION AND ON CONVERSION OF CARBON MONOXIDE (Data Obtained at 750°F and 500 psig)

Kinetics Test Results — UC-1870-46-1

The results of the experimental study of the kinetics of the water-gas shift reaction using the UC-1870-46-1 catalyst are presented in Table B-3. The feed gas used had a composition similar to the feed gas used in the previous study with the G-93 catalyst. This study, anticipating the low-pressure operation of some coal gasification plants, included pressures of 50 and 100 psig, in addition to the higher pressures of 200, 500, and 1000 psig. The results (Figure 23) show a sharp decrease in both the carbon monoxide conversion and the rate of carbon monoxide conversion at pressures lower than 200 psig. It appears that diffusion plays an important role at higher pressures. This finding is useful in the final rate analysis because our rate equation is a function of partial pressures, and there are two different ways to obtain the partial pressure of any component. One is to maintain constant pressure and change the feed composition; the other is to maintain constant composition and change the total pressure. The results from these two methods were not the same in our case, indicating an effect of pressure over and above the partical pressure-concentration effect. This finding points out the danger of doing experimental work only at low pressures and extrapolating it to high pressures, and shows that it is insufficient to study the thermodynamics of these reactions alone.

We evaluated this catalyst at temperatures of 550°, 650°, and 750°F. This is well within the temperature limitations of the catalyst; however, it is limited by our feed compositions. The dew point of steam at 1000 psia is about 545°F, which atuomatically dictates the lower temperature limit because liquid water destroys the catalyst. With about 10 mole % of benzene or oil in the feed, carbon formation was detected at about 600°F, and with about 20 mole % (dry basis), carbon formation was detected at 750°F. Therefore, the upper temperature limit is determined by the reactants. The effect of temperature on this reaction is small within the above-mentioned range. (See Figures 24 and 25.)



SYMBOL	TEMPERATURE, °F
○	750
△	650
□	550

FEED GAS COMPOSITION, dry basis

COMPONENT	mol %
CO	13.2
CO_2	16.4
H_2	37.5
CH_4	27.18
C_2H_6	1.1
C_3H_8	0.8
C_4H_{10}	0.1
H_2S	2.4
N_2	1.2
He	0.02
NH_3	0
C_6H_5OH	0
C_6H_6	0
COS	0.1
C_2H_5SH, ppm	4.3
$\underline{n}$-C_3H_7SH, ppm	1.4
$\underline{i}$-C_3H_7SH, ppm	4.6
DISULFIDES, ppm	2.6
TOTAL	100.00

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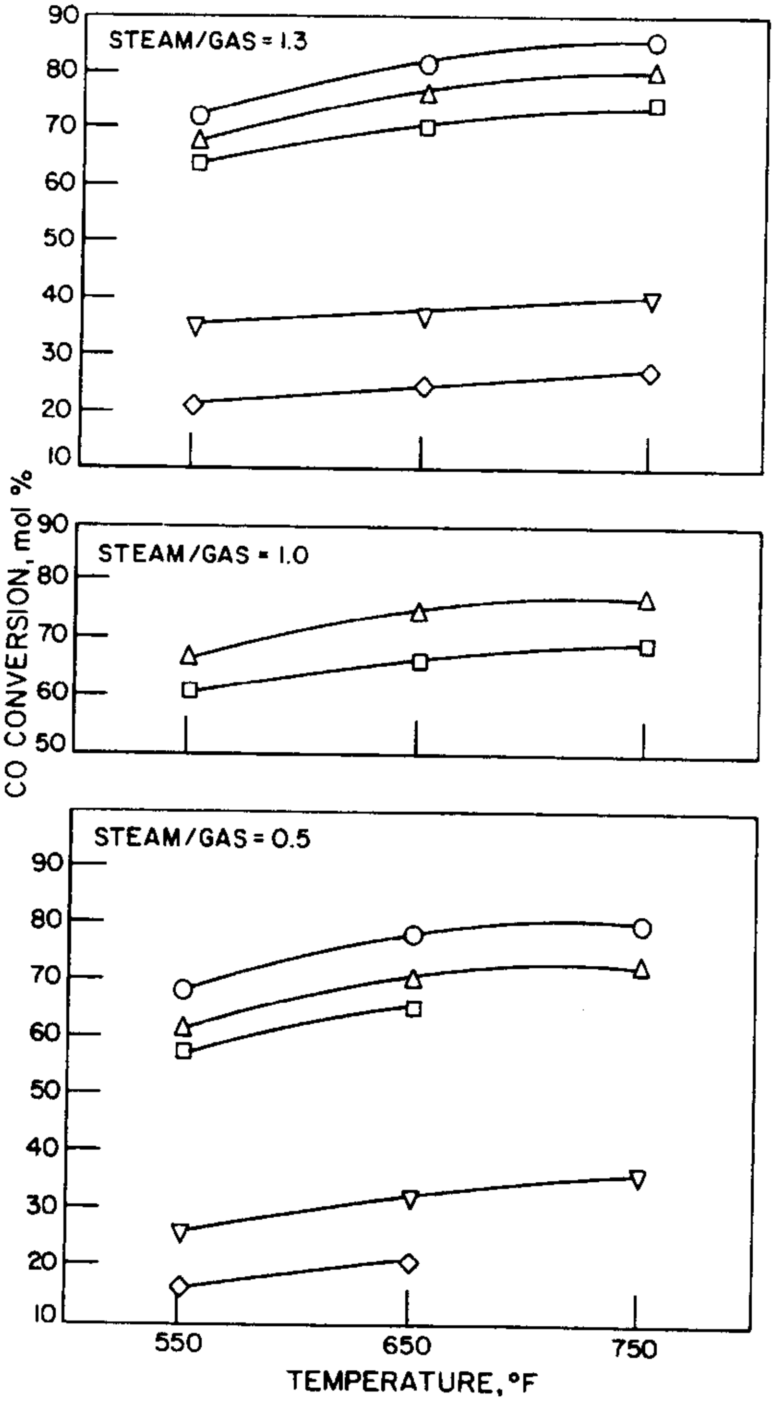
Figure 23. EFFECT OF PRESSURE ON THE CONVERSION OF CARBON MONOXIDE (UC-1870-46-1 Catalyst at a CSTR Space Velocity of 0.2230 SCF/hr-g)



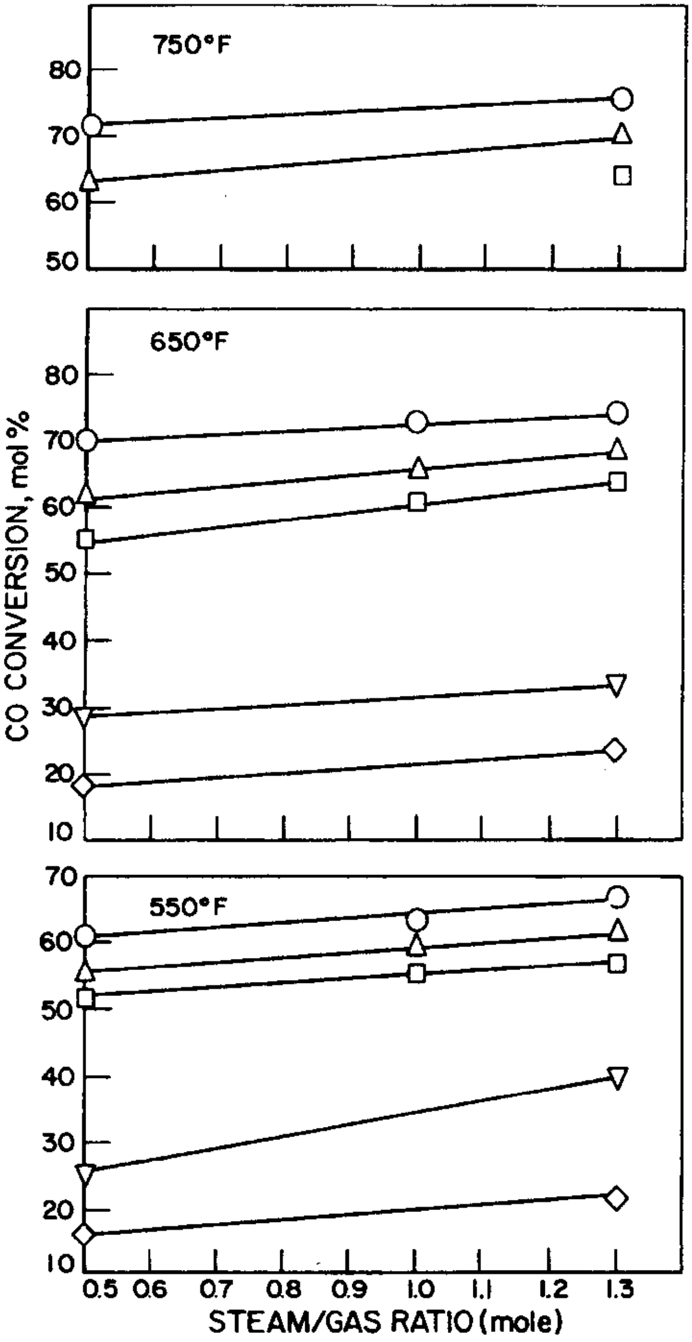
SYMBOL	PRESSURE, psig
○	1000
△	500
□	200
▽	100
◇	50

FEED GAS COMPOSITION, dry basis

COMPONENT	mol %
CO	13.2
CO_2	16.4
H_2	37.5
CH_4	27.18
C_2H_6	1.1
C_3H_8	0.8
C_4H_{10}	0.1
H_2S	2.4
N_2	1.2
He	0.02
NH_3	0
C_6H_5OH	0
C_6H_6	0
COS	0.1
C_2H_5SH, ppm	4.3
$\underline{n}$-C_3H_7SH, ppm	1.4
$\underline{i}$-C_3H_7SH, ppm	4.6
DISULFIDES, ppm	2.6
TOTAL	100.00

A76102232

Figure 24. EFFECT OF TEMPERATURE ON THE CONVERSION OF CARBON MONOXIDE (UC-1870-46-1 Catalyst at a CSTR Space Velocity of 0.2230 SCF/hr-g)



SYMBOL	PRESSURE, psig
○	1000
△	500
□	200
▽	100
◇	50

FEED GAS COMPOSITION, dry basis

COMPONENT	mol %
CO	20.14
CO_2	15.20
H_2	26.88
CH_4	23.84
C_2H_6	1.0
C_3H_8	0.8
C_4H_{10}	0.1
H_2S	0.5
N_2	1.2
He	0.02
NH_3	0
C_6H_5OH	1.0
C_6H_6	9.3
COS	0.1
C_2H_5SH, ppm	4.3
n-C_3H_7SH, ppm	1.4
i-C_3H_7SH, ppm	4.6
DISULFIDES, ppm	2.6
TOTAL	100.00

A76102233

Figure 25. EFFECT OF THE STEAM/GAS RATIO ON THE CONVERSION OF CARBON MONOXIDE (UC-1870-46-1 Catalyst at a Space Velocity of 0.2230 SCF/hr-g)

The steam/gas ratio in the feed does not seem to have a great influence on the percent conversion on carbon monoxide as shown in Figure 25 for steam/gas ratios of 0.5, 1.0, and 1.3, but the effect on the rate of carbon monoxide conversion is quite pronounced, as can be seen in Figure 18.* However, the more important hidden fact is that the steam/benzene ratio is crucial for carbon formation reactions. The chance for carbon to form increases greatly at steam/benzene ratios of less than 6.

The rate of deactivation due to phenol was also studied at phenol concentrations of 0, 0.1%, 0.4%, and 0.9% (Runs 67 through 100, and 103 through 143), and the results are presented in Figures 26 through 28. The deactivation appears to be both by poisoning and, at high phenol concentrations, by promoting carbon deposition, as was observed in Runs 67 through 69, 74 and 75, 78, 80 and 81, 86 through 90, 94 through 96, 111 through 118, 120 through 126, 130 through 133, 135 through 138, 140, and 141.

Kinetics Test Results — Shell Oil 538 and Comparison of Three Catalysts

The detailed experimental results of our study of the kinetics of the water-gas shift reaction using the Shell Oil 538 catalyst are presented in Table B-4. This study was started without any special pretreatment of the catalyst. The catalyst was activated with the standard 16-component sulfur-containing feed mixture, but without benzene, ammonia, or phenol (Runs 1 to 32). Ammonia and benzene were added (Runs 33 to 65) and then discontinued (Runs 66 to 71). The carbon monoxide concentration was changed (Runs 72 to 80). Ammonia and benzene were added again (Runs 81 to 95), and phenol was added at three different concentrations for the remainder of this program (Runs 96 to 145). The experimental program is outlined in Table 5.

In this study, we observed that —

- The general behavior of this catalyst is similar to that of G-93; both catalysts are cobalt-molybdenum on an alumina-carrier type.
- Its dependence on pressure is gradual (Figures 29 and 30) by comparison, and it is not as active as the UC-1870-46-1 or the G-93, but the difference is small (Figure 31).
- The presence of benzene retards the conversion (Figure 32), but benzene is not a poison. Excess benzene will cause carbon formation, which in turn will cause deactivation.

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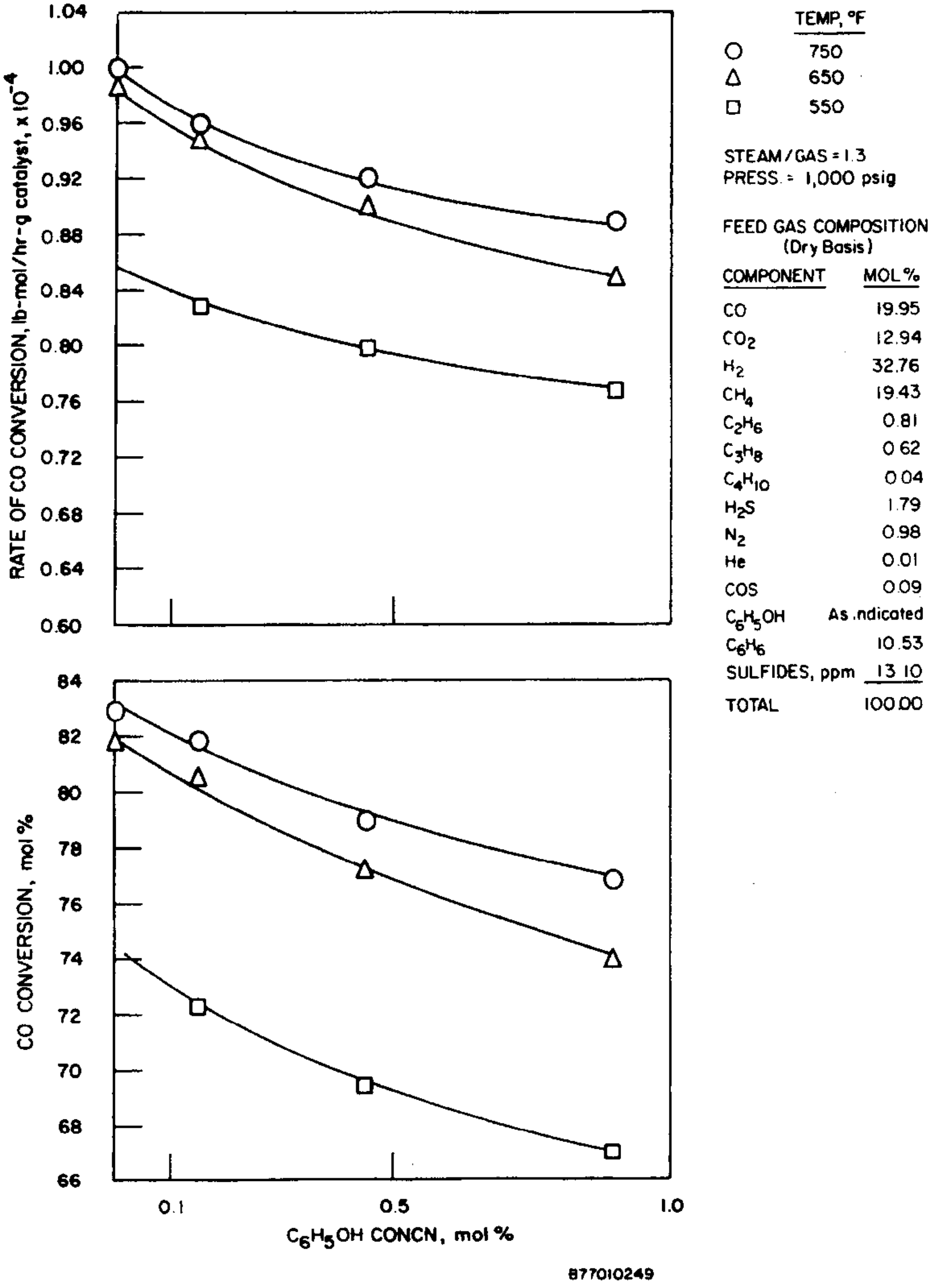
* See page 44.

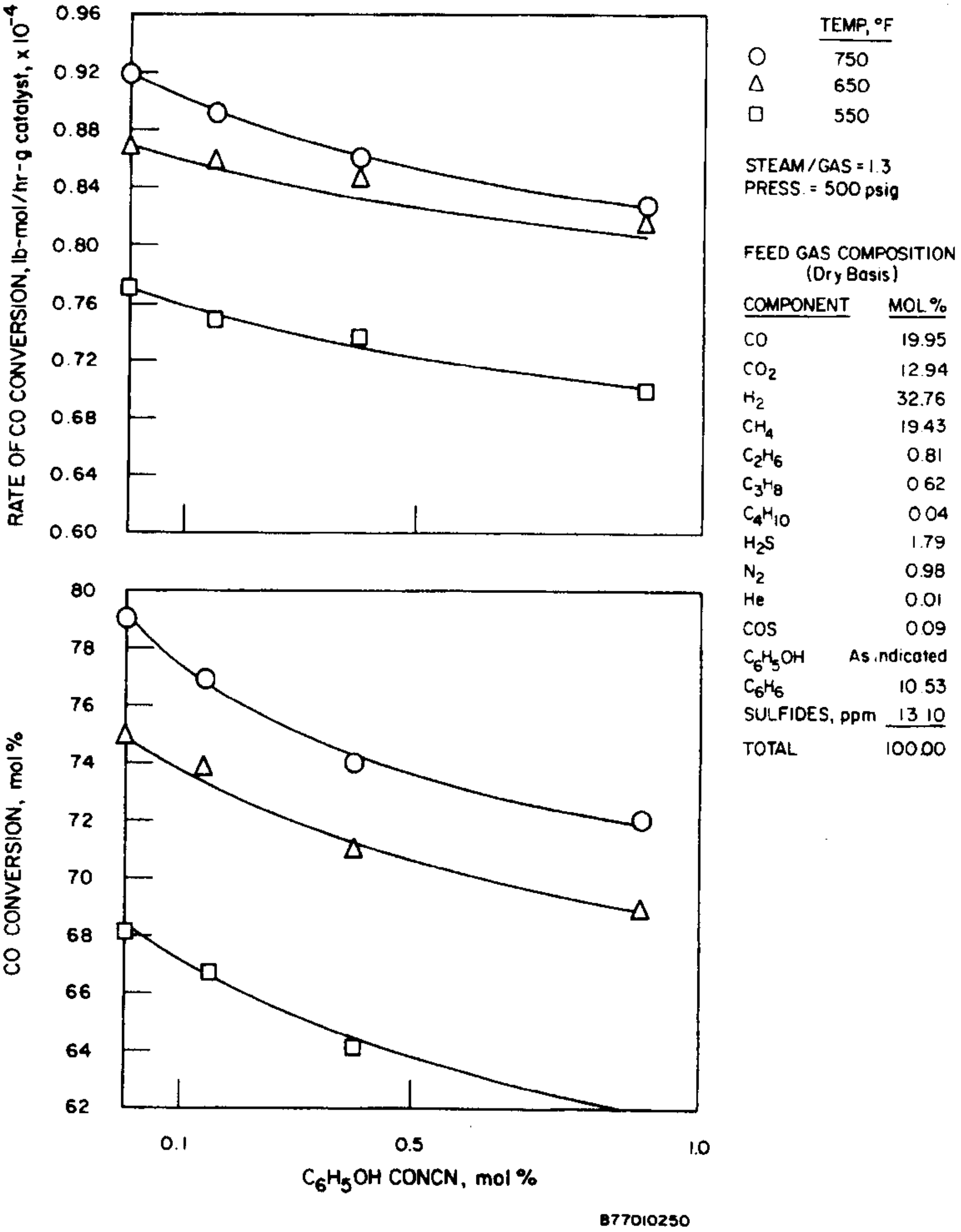


STEAM/GAS = 1.3
PRESS. = 1,000 psig

FEED GAS COMPOSITION
(Dry Basis)

COMPONENT	MOL %
CO	19.95
CO_2	12.94
H_2	32.76
CH_4	19.43
C_2H_6	0.81
C_3H_8	0.62
C_4H_{10}	0.04
H_2S	1.79
N_2	0.98
He	0.01
COS	0.09
C_6H_5OH	As indicated
C_6H_6	10.53
SULFIDES, ppm	13.10
TOTAL	100.00

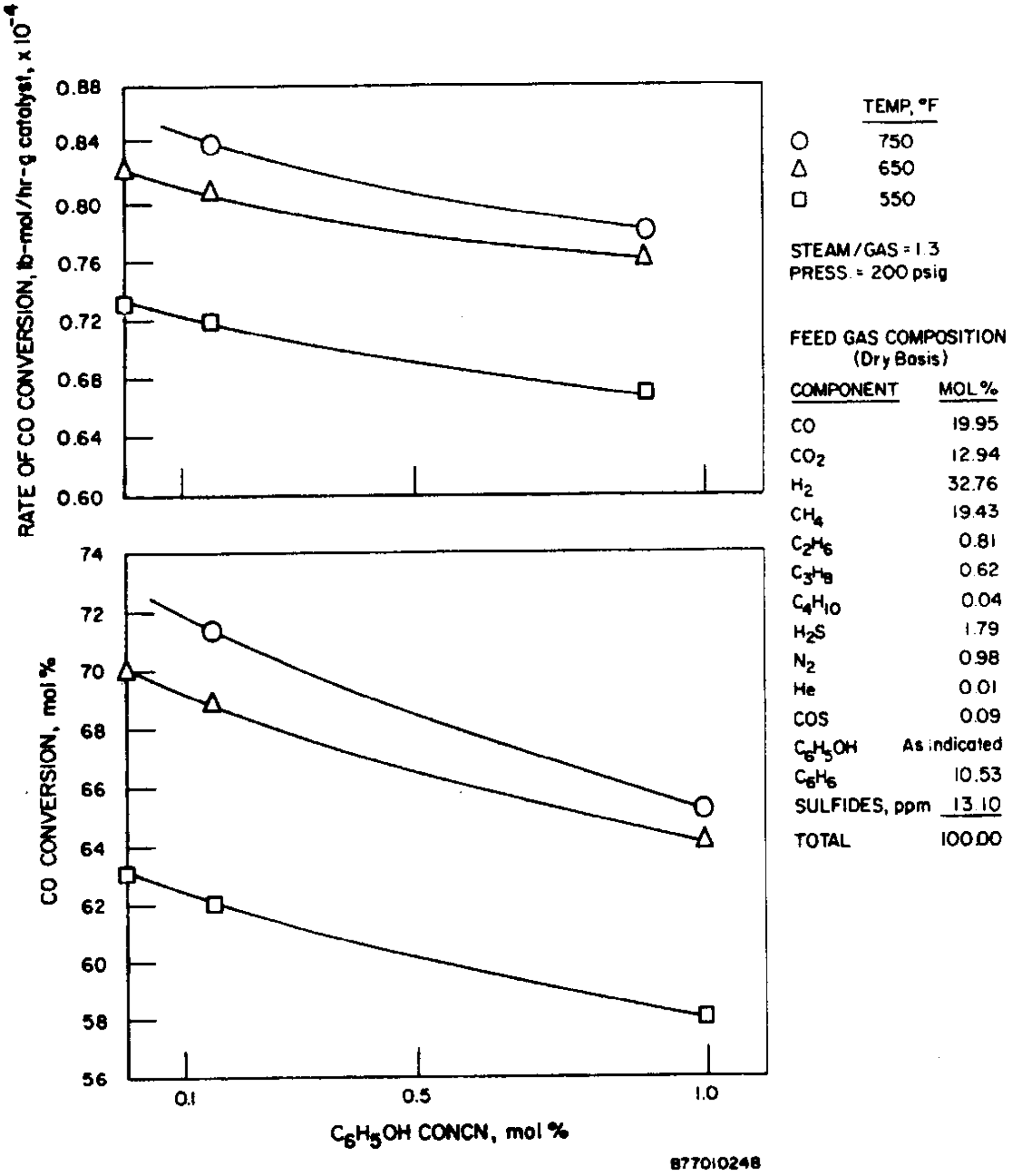
Figure 26. EFFECT OF PHENOL ON THE CONVERSION AND RATE OF CONVERSION OF CARBON MONOXIDE (UC-1870-46-1 Catalyst at a Space Velocity of 0.2230 SCF/hr-g; Pressure = 1000 psig)



FEED GAS COMPOSITION
(Dry Basis)

COMPONENT	MOL %
CO	19.95
CO_2	12.94
H_2	32.76
CH_4	19.43
C_2H_6	0.81
C_3H_8	0.62
C_4H_{10}	0.04
H_2S	1.79
N_2	0.98
He	0.01
COS	0.09
C_6H_5OH	As indicated
C_6H_6	10.53
SULFIDES, ppm	13.10
TOTAL	100.00

Figure 27. EFFECT OF PHENOL ON THE CONVERSION AND RATE OF CONVERSION OF CARBON MONOXIDE (UC-1870-46-1 Catalyst at a Space Velocity of 0.2230 SCF/hr-g; Pressure = 500 psig)



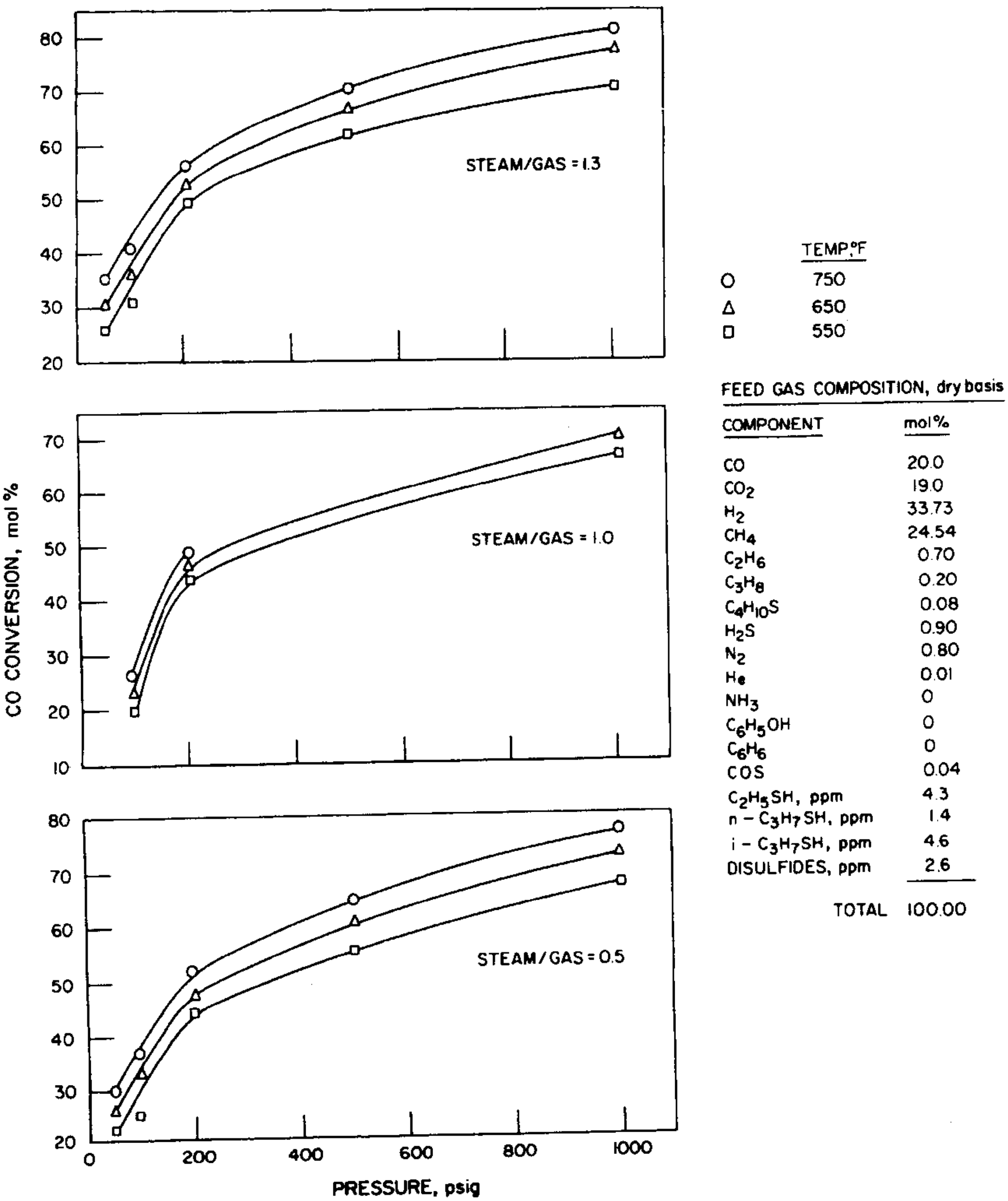
FEED GAS COMPOSITION
(Dry Basis)

COMPONENT	MOL %
CO	19.95
CO_2	12.94
H_2	32.76
CH_4	19.43
C_2H_6	0.81
C_3H_8	0.62
C_4H_{10}	0.04
H_2S	1.79
N_2	0.98
He	0.01
COS	0.09
C_6H_5OH	As indicated
C_6H_6	10.53
SULFIDES, ppm	13.10
TOTAL	100.00

Figure 28. EFFECT OF PHENOL ON THE CONVERSION AND RATE OF CONVERSION OF CARBON MONOXIDE (UC-1870-46-1 Catalyst at a Space Velocity of 0.2230 SCF/hr-g; Pressure = 200 psig)

Table 5. EXPERIMENTAL PROGRAM FOR THE COMPLETE STUDY OF THE WATER-GAS SHIFT REACTION KINETICS USING THE SHELL OIL 538 CATALYST (4 x 6 Mesh Spheres, 10.0 g)

Run No.	Temperature, °F	Pressure, psig	Component	Objective
1-32	550, 650, 750	50, 100, 200, 500, 1000	Standard 16-component feed gas with 20% CO and steam/gas of 0.5, 1.0 and 1.3	To activate the catalyst at a simulated plant operating conditions and to establish the initial reaction order of water and carbon monoxide.
33-65	550, 650, 750	50, 100, 200, 500, 1000	0.3% NH_3 and 10% C_6H_6 were added	To determine the effect of ammonia and benzene on the rate of reaction.
66-71	550, 650, 750	50	Same conditions as that used in Runs 1-32	To determine the after-effect of ammonia and benzene on the rate of reaction.
72-80	550, 650, 750	200, 500	Standard 16-component feed with 10% CO and Steam/gas of 0.5, 1.0, and 1.3	To determine the reaction order of water and carbon monoxide.
81-95	550, 650, 750	50, 100, 200, 500	0.3% NH_3 and 10% C_6H_6 were added	To determine the effect of ammonia and benzene on the rate of reaction.
96-109	550, 650, 750	50, 100, 200, 500	Standard 16-component with 20% CO, 0.3% NH_3, 10% C_6H_6 and 0.1% C_6H_5OH	To determine the effect of and the rate of deactivation due to phenol.
110-123	550, 650, 750	50, 100, 200, 500, 1000	C_6H_5OH was increased to 0.4%	To determine the rate of deactivation due to phenol.
124-132	550, 650, 750	100, 200, 500	C_6H_5OH was increased to 1.0%	To determine the rate of deactivation due to phenol.
133-145	650	500	Same as that used in Runs 124-132	To establish the rate of deactivation with a mini-life test of about 160 hours.



FEED GAS COMPOSITION, dry basis

COMPONENT	mol%
CO	20.0
CO_2	19.0
H_2	33.73
CH_4	24.54
C_2H_6	0.70
C_3H_8	0.20
$C_4H_{10}S$	0.08
H_2S	0.90
N_2	0.80
He	0.01
NH_3	0
C_6H_5OH	0
C_6H_6	0
COS	0.04
C_2H_5SH, ppm	4.3
n – C_3H_7SH, ppm	1.4
i – C_3H_7SH, ppm	4.6
DISULFIDES, ppm	2.6
TOTAL	100.00

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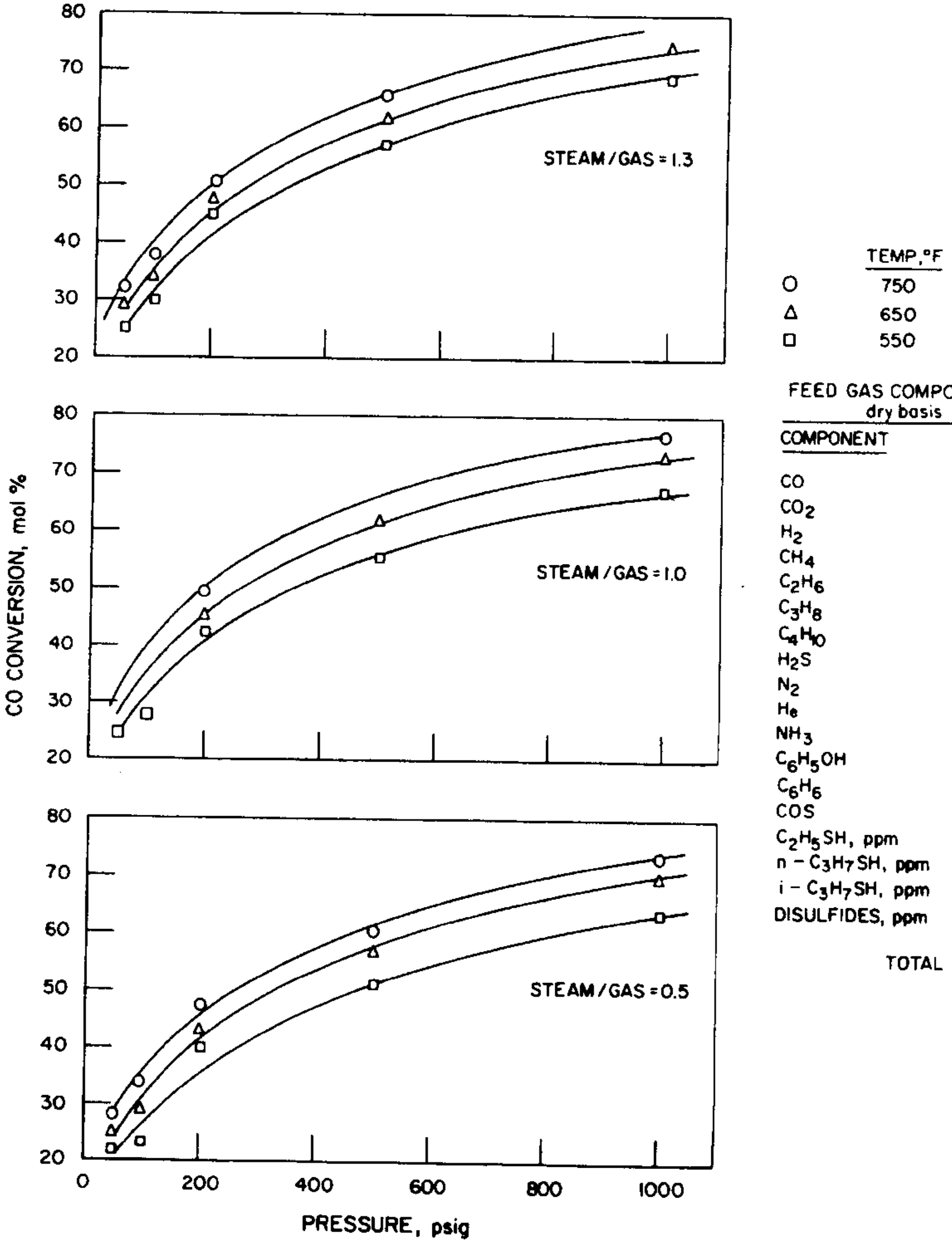
Figure 29. EFFECT OF PRESSURE ON THE CONVERSION OF CARBON MONOXIDE (Shell Oil 538 Catalyst at a CSTR Space Velocity of 0.2230 SCF/hr-g)



FEED GAS COMPOSITION, dry basis

COMPONENT	mol %
CO	18.00
CO_2	17.00
H_2	30.55
CH_4	21.14
C_2H_6	0.68
C_3H_8	0.19
C_4H_{10}	0.08
H_2S	0.85
N_2	0.80
He	0.02
NH_3	0.32
C_6H_5OH	0.10
C_6H_6	10.23
COS	0.04
C_2H_5SH, ppm	4.3
n − C_3H_7SH, ppm	1.4
i − C_3H_7SH, ppm	4.6
DISULFIDES, ppm	2.6
TOTAL	100.00

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Figure 30. EFFECT OF PRESSURE ON THE CONVERSION OF CARBON MONOXIDE (Shell Oil 538 Catalyst at a CSTR Space Velocity of 0.2230 SCF/hr-g)

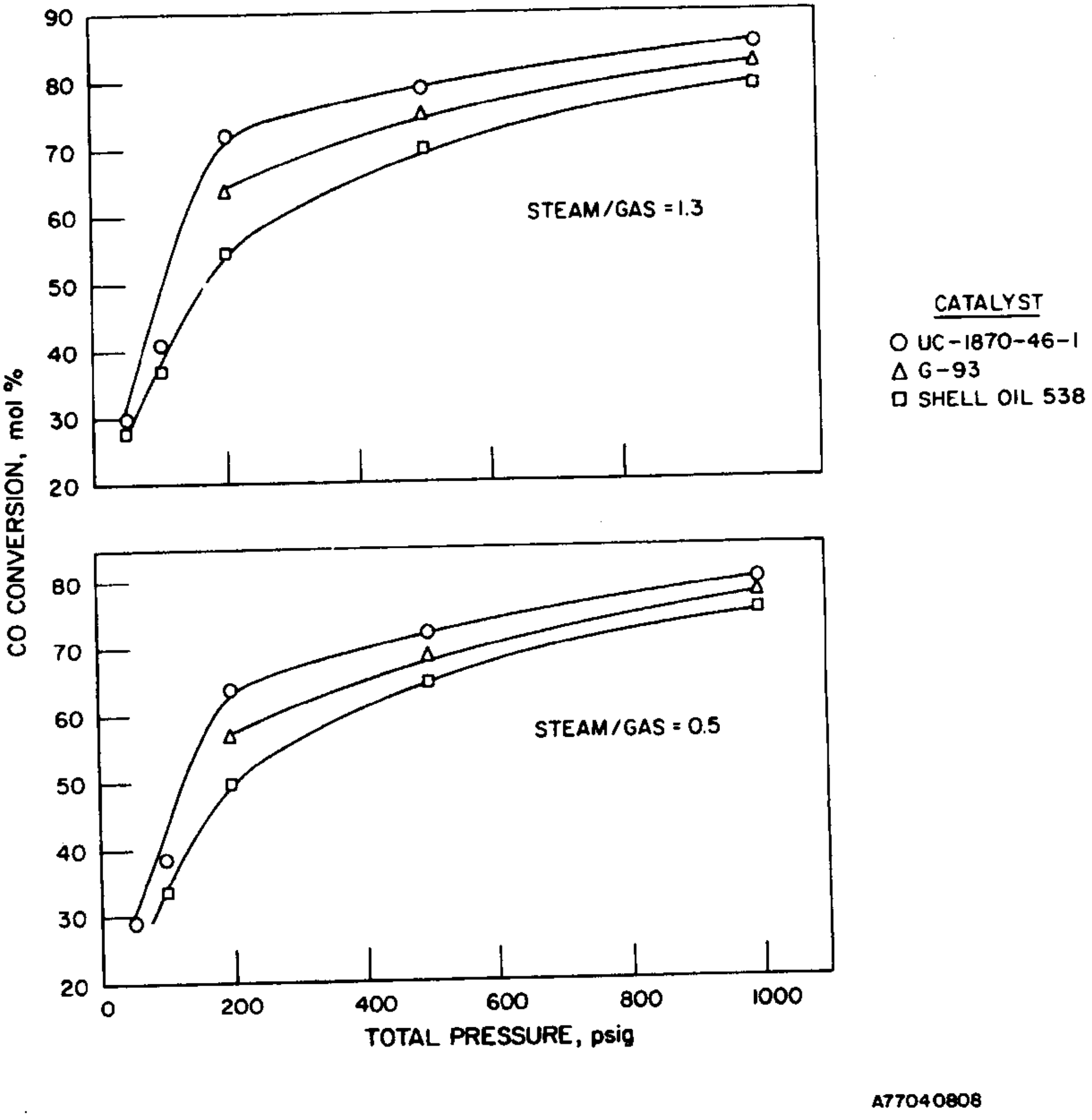
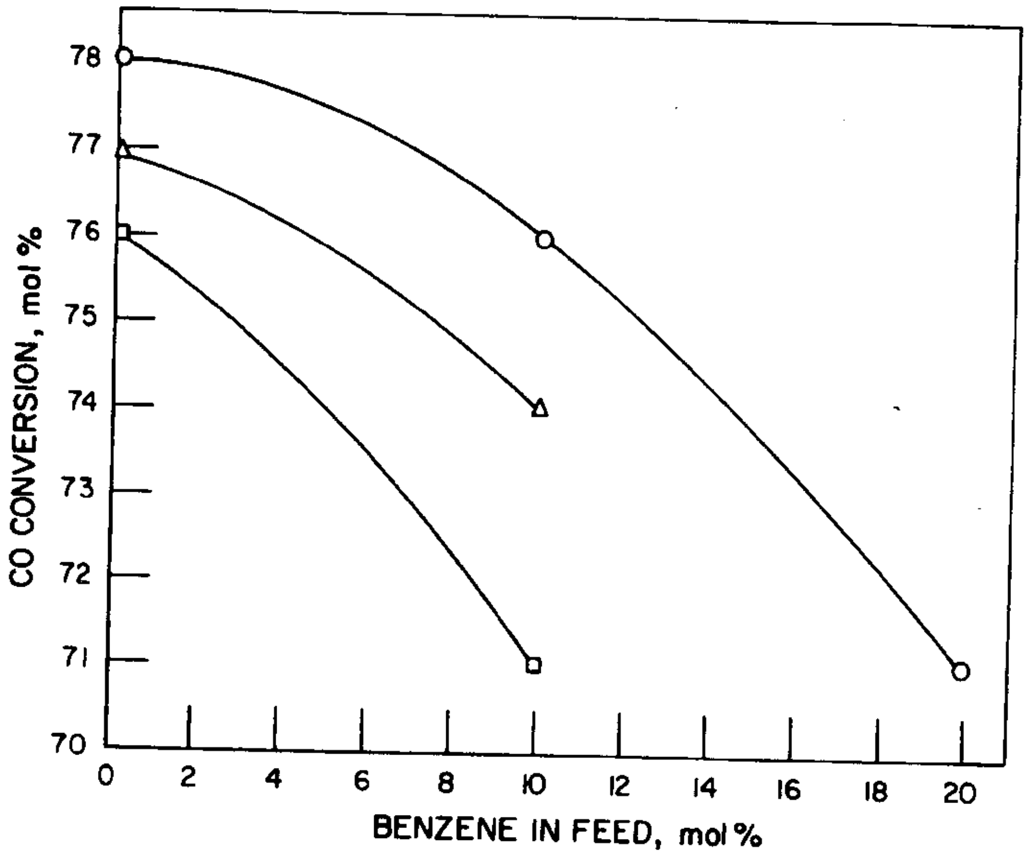


Figure 31. COMPARISON OF CATALYST PERFORMANCE AS A FUNCTION OF PRESSURE AT 750°F (CSTR Space Velocity of 0.2230 SCF/hr-g)



FEED GAS COMPOSITION, dry basis

COMPONENT	mol %
CO	20.0
CO_2	19.0
H_2	33.73
CH_4	24.54
C_2H_6	0.70
C_3H_8	0.20
C_4H_{10}s	0.08
H_2S	0.90
N_2	0.80
He	0.01
NH_3	0
C_6H_5OH	0
C_6H_6	0
COS	0.04
C_2H_5SH, ppm	4.3
n-C_3H_7SH, ppm	1.4
i-C_3H_7SH, ppm	4.6
DISULFIDES, ppm	2.6
TOTAL	100.00

Figure 32. EFFECT OF BENZENE ON THE CONVERSION OF CARBON MONOXIDE (Shell Oil 538 Catalyst, 4 x 6 Mesh Spheres, at 1000 psig, 650°F, and a CSTR Space Velocity of 0.2230 SCF/hr-g)

- At an H_2O/C_6H_6 ratio of less than 6 in the feed, carbon formation occurs, especially at temperatures higher than 750°F. This behavior was also detected with the other two catalysts. A comparison of the effect of benzene on the conversion of carbon monoxide is presented in Figure 33.

- The effect of temperature from 550° to 750°F on the percent and the rate of conversion is small (Figures 34 and 35), which means that the activation energy is also small.

- The effect of steam on the conversion is small (Figures 36 and 37), but the effect on the rate of conversion is not.

- 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. If the steam/gas ratio were less than 0.5, carbon formation reactions would make operation of the process difficult, so lower steam/gas ratios are not of practical significance.

- The reaction orders with respect to methane, carbon dioxide, and ammonia are zero, as shown in Figures 38 through 40.

- The reaction orders with respect to carbon monoxide and water are close to those obtained with the G-93 catalyst (Figures 41 and 42).

- The rate of deactivation by phenol is exemplified in Figures 43 through 48. The rate decreases with increasing phenol concentration (Figures 43 through 45), and it is also a function of total pressure (Figures 46 through 48).

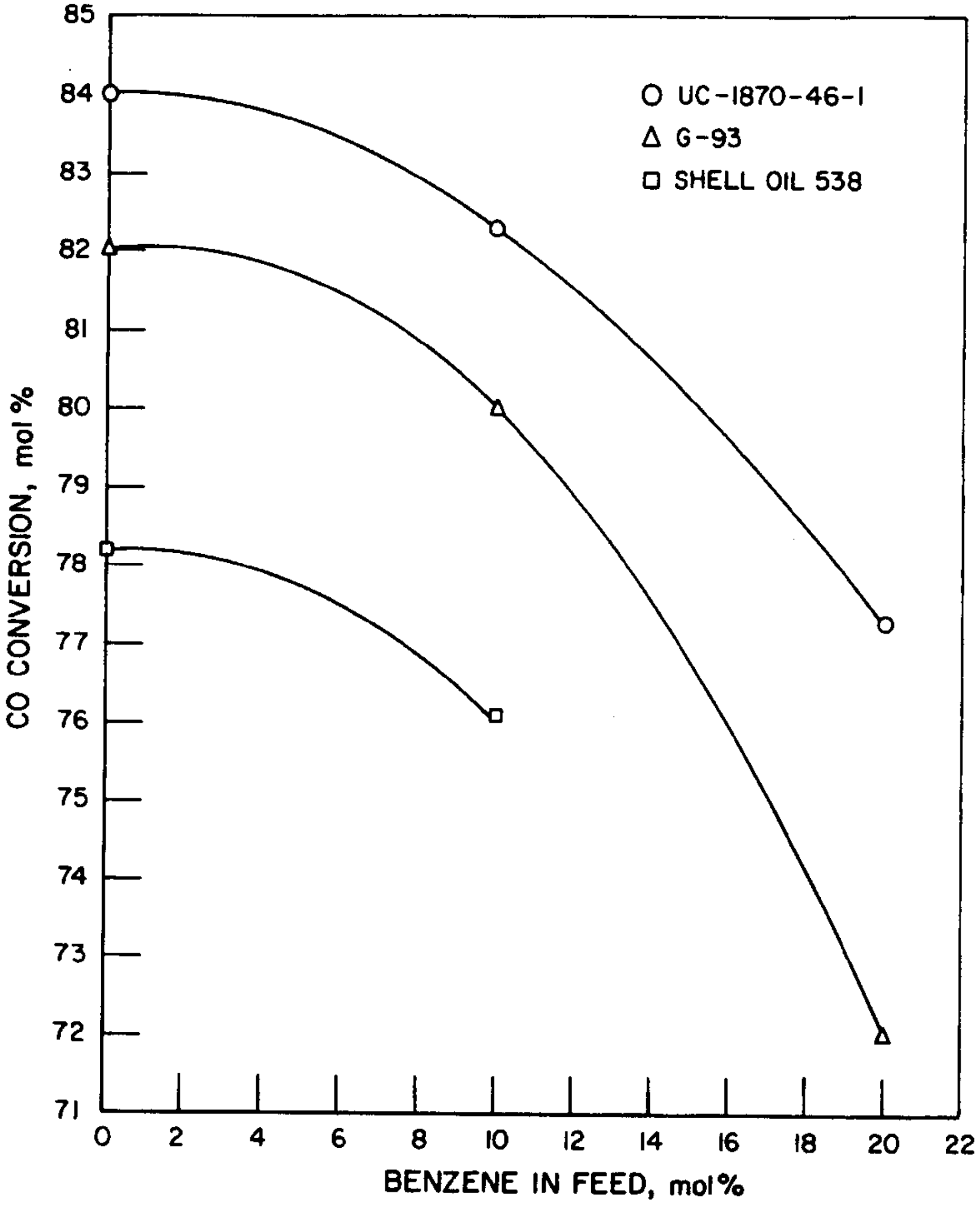


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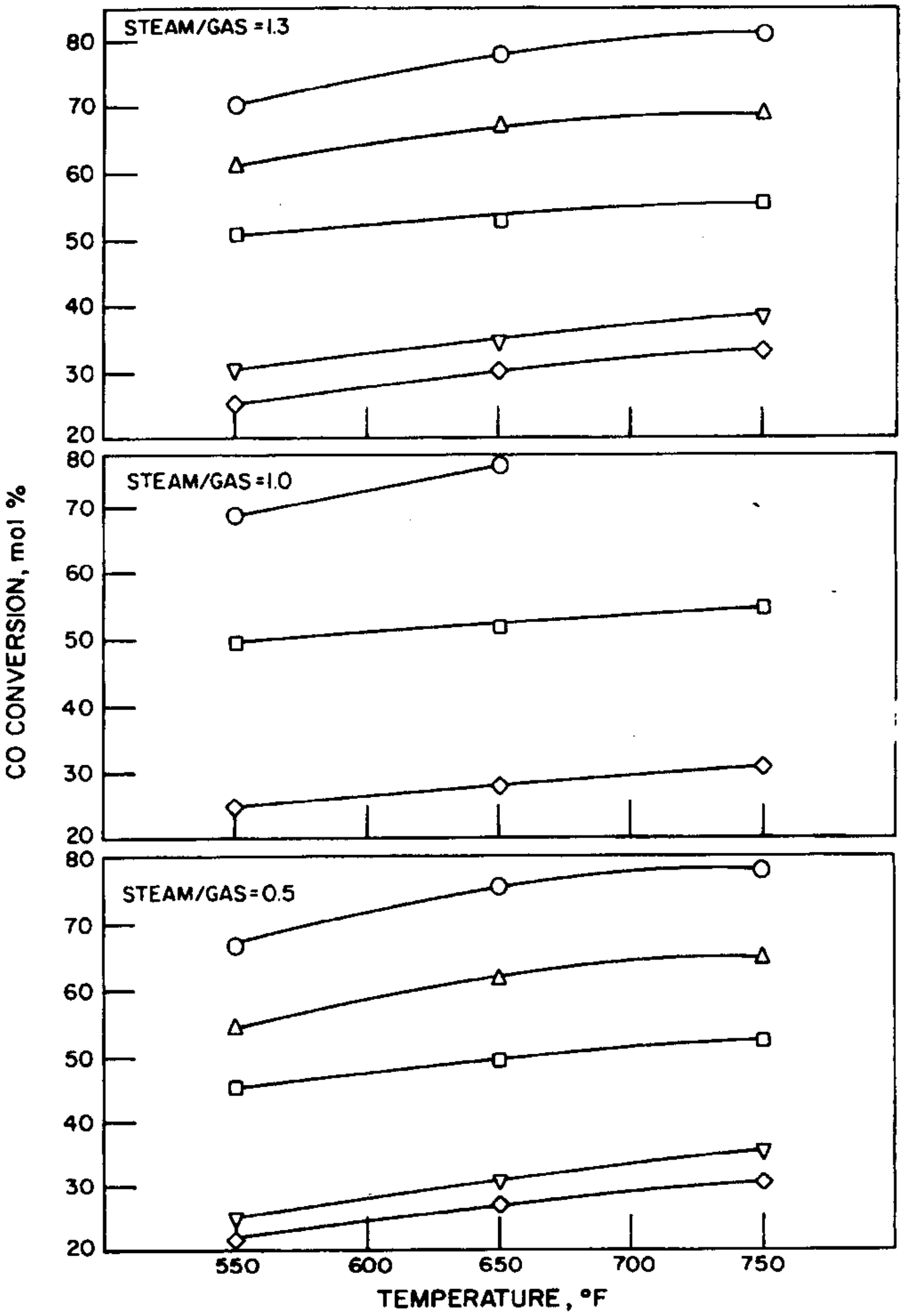
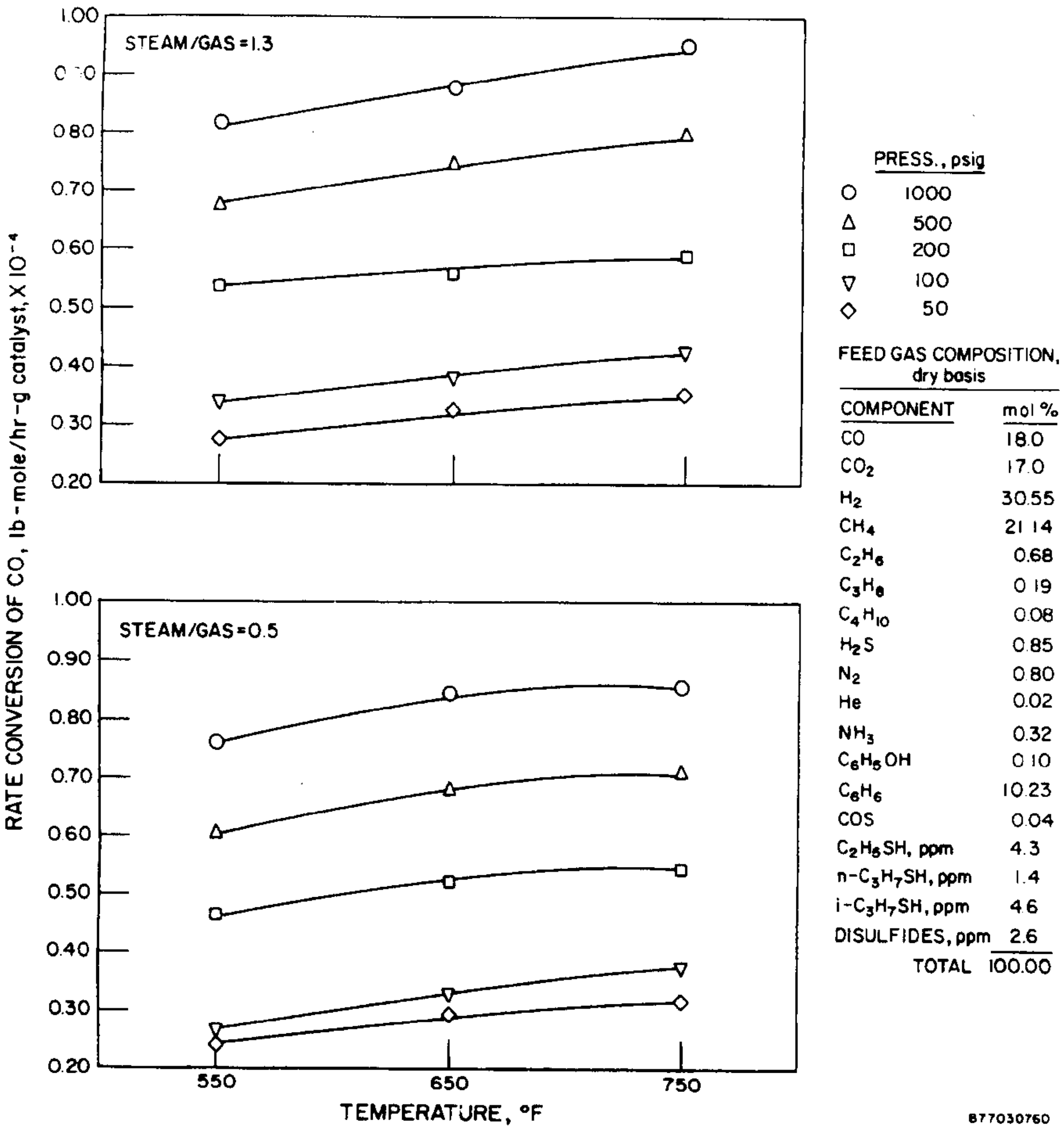
Figure 33. COMPARISON OF CATALYST PERFORMANCE IN PRESENCE OF BENZENE



FEED GAS COMPOSITION, dry basis

COMPONENT	mol %
CO	20.0
CO_2	19.0
H_2	33.73
CH_4	24.54
C_2H_6	0.70
C_3H_8	0.20
$C_4H_{10}S$	0.08
H_2S	0.90
N_2	0.80
He	0.01
NH_3	0
C_6H_5OH	0
C_6H_6	0
COS	0.04
C_2H_5SH, ppm	4.3
n-C_3H_7SH, ppm	1.4
i-C_3H_7SH, ppm	4.6
DISULFIDES, ppm	2.6
TOTAL	100.00

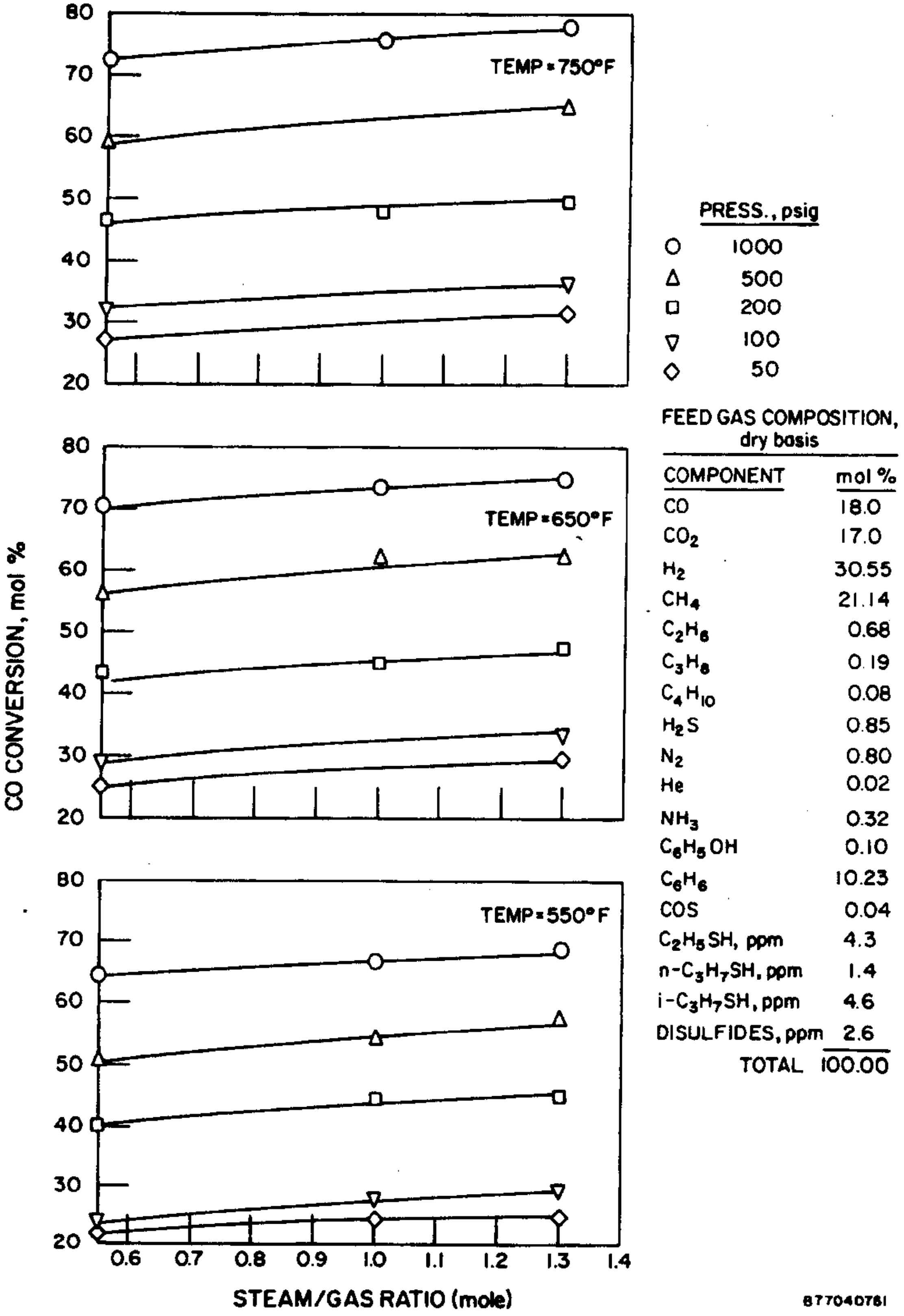
Figure 34. EFFECT OF TEMPERATURE ON THE CONVERSION OF CARBON MONOXIDE (Shell Oil 538 Catalyst at a CSTR Space Velocity of 0.2230 SCF/hr-g)



FEED GAS COMPOSITION, dry basis

COMPONENT	mol %
CO	18.0
CO_2	17.0
H_2	30.55
CH_4	21.14
C_2H_6	0.68
C_3H_8	0.19
C_4H_{10}	0.08
H_2S	0.85
N_2	0.80
He	0.02
NH_3	0.32
C_6H_5OH	0.10
C_6H_6	10.23
COS	0.04
C_2H_5SH, ppm	4.3
n-C_3H_7SH, ppm	1.4
i-C_3H_7SH, ppm	4.6
DISULFIDES, ppm	2.6
TOTAL	100.00

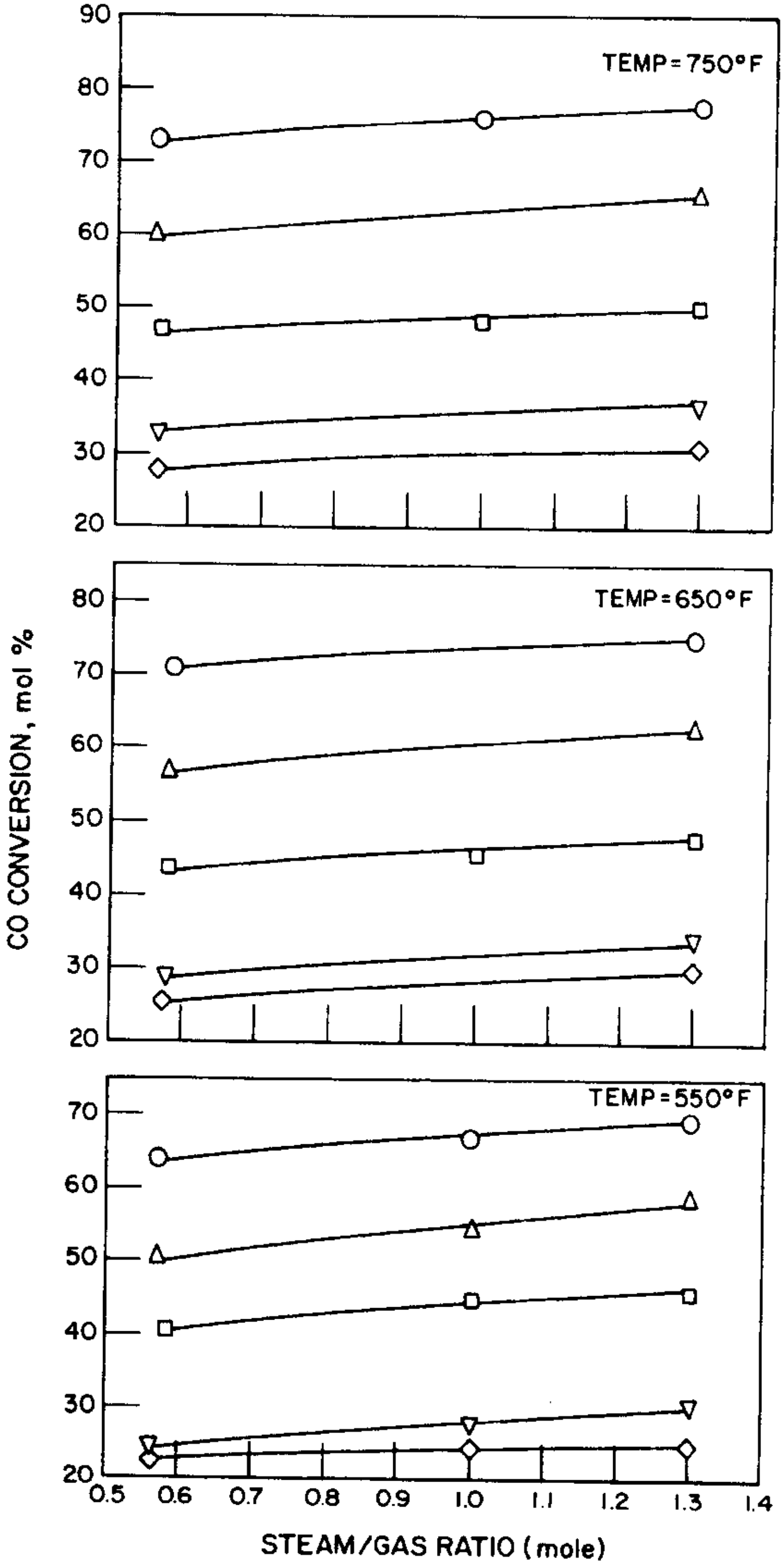
Figure 35. EFFECT OF TEMPERATURE ON THE RATE OF CONVERSION OF CARBON MONOXIDE (Shell Oil 538 Catalyst at a CSTR Space Velocity of 0.2230 SCF/hr-g)



FEED GAS COMPOSITION, dry basis

COMPONENT	mol %
CO	18.0
CO_2	17.0
H_2	30.55
CH_4	21.14
C_2H_6	0.68
C_3H_8	0.19
C_4H_{10}	0.08
H_2S	0.85
N_2	0.80
He	0.02
NH_3	0.32
C_6H_5OH	0.10
C_6H_6	10.23
COS	0.04
C_2H_5SH, ppm	4.3
n-C_3H_7SH, ppm	1.4
i-C_3H_7SH, ppm	4.6
DISULFIDES, ppm	2.6
TOTAL	100.00

Figure 36. EFFECT OF THE STEAM/GAS RATIO ON THE CONVERSION OF CARBON MONOXIDE (Shell Oil 538 Catalyst at a CSTR Space Velocity of 0.2230 SCF/hr-g)



FEED GAS COMPOSITION, dry basis

COMPONENT	mol %
CO	20.0
CO_2	19.0
H_2	33.73
CH_4	24.54
C_2H_6	0.70
C_3H_8	0.20
C_4H_{10}	0.08
H_2S	0.90
N_2	0.80
He	0.01
NH_3	0
C_6H_5OH	0
C_6H_6	0
COS	0.04
C_2H_5SH, ppm	4.3
n-C_3H_7SH, ppm	1.4
i-C_3H_7SH, ppm	4.6
DISULFIDES, ppm	2.6
TOTAL	100.00

Figure 37. EFFECT OF THE STEAM/GAS RATIO ON THE CONVERSION OF CARBON MONOXIDE (Shell Oil 538 Catalyst at a CSTR Space Velocity of 0.2230 SCF/hr-g)

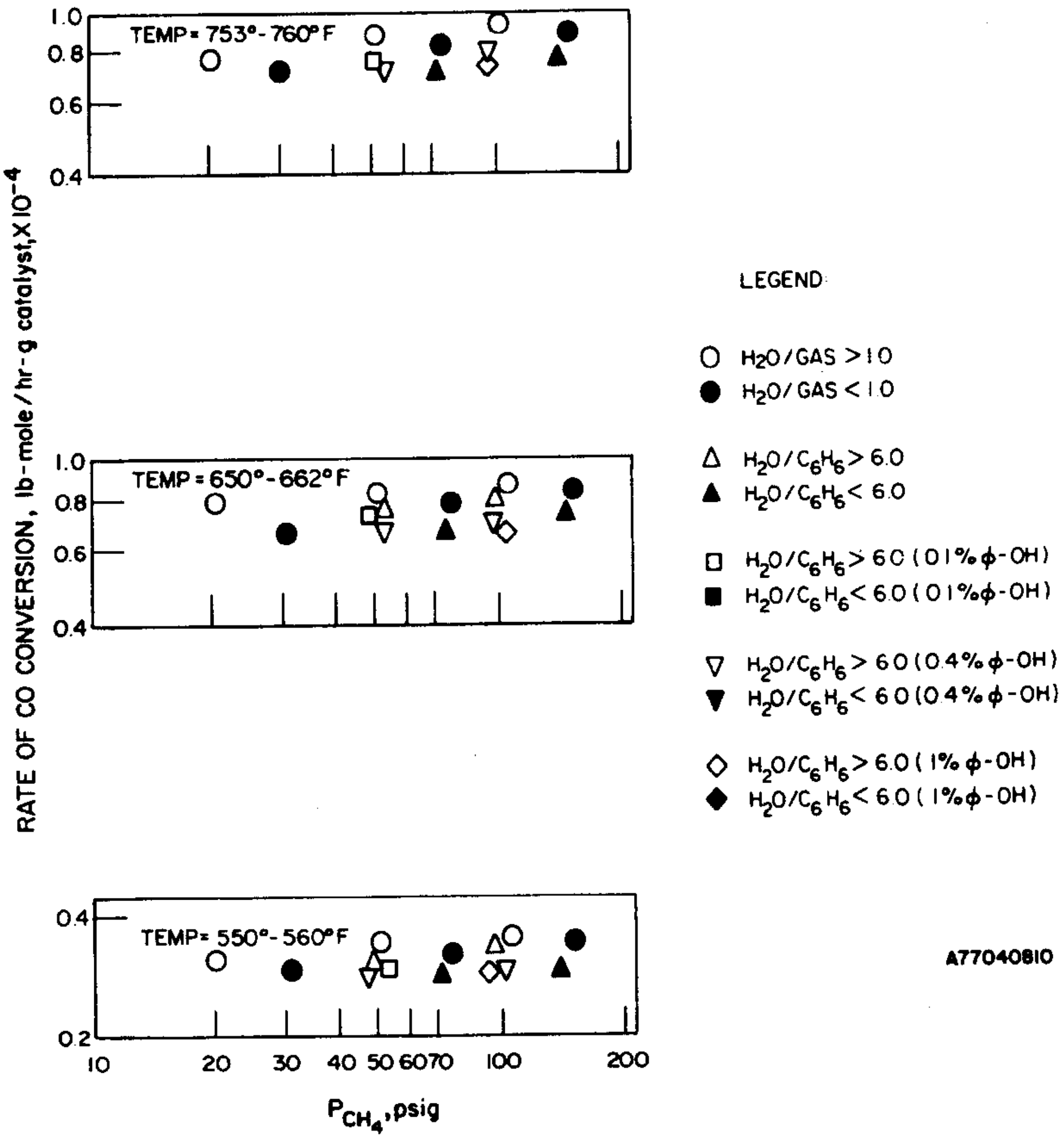


Figure 38. REACTION ORDER OF METHANE (Shell Oil 538 Catalyst, 4 x 6 Mesh Spheres)

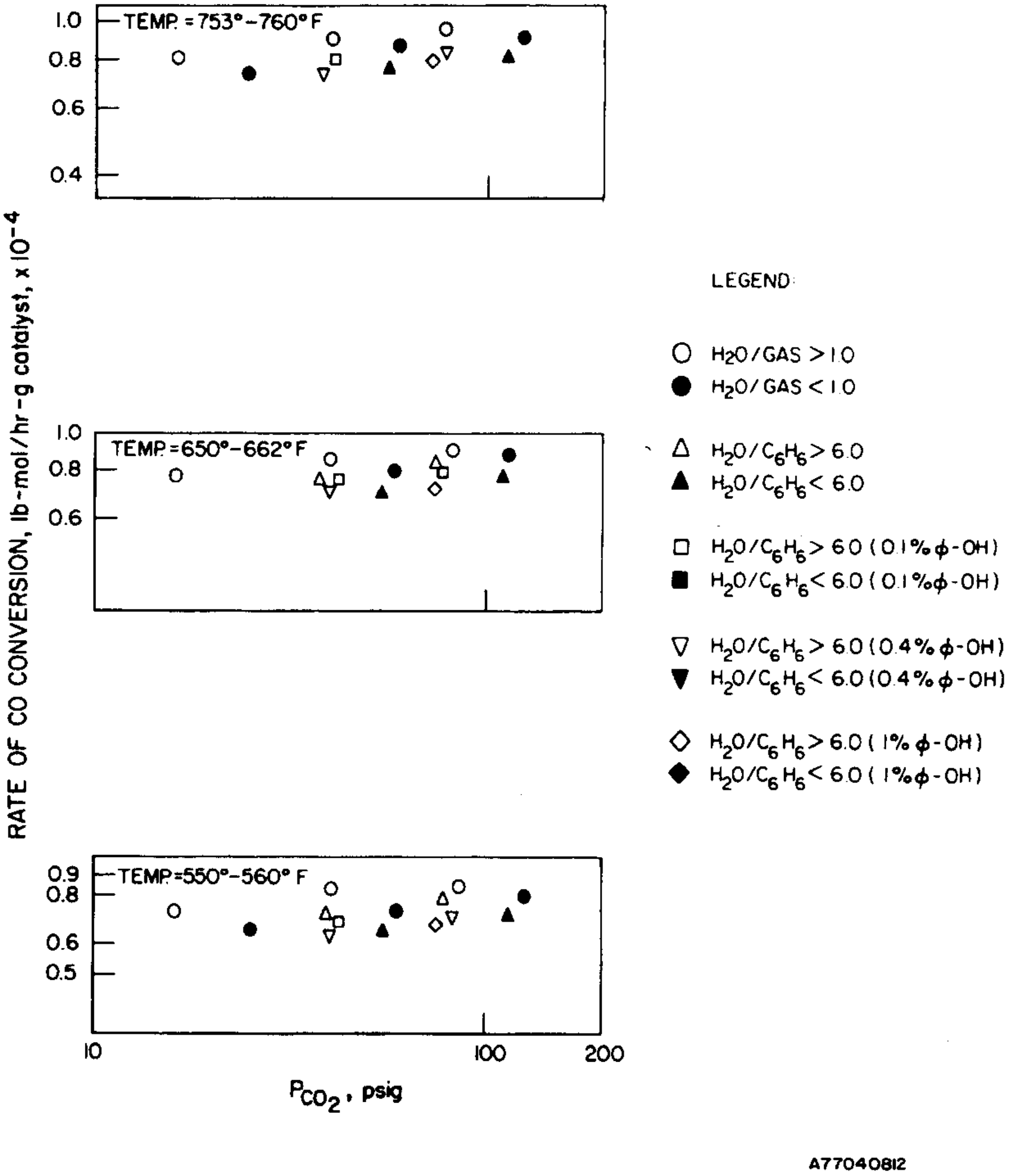
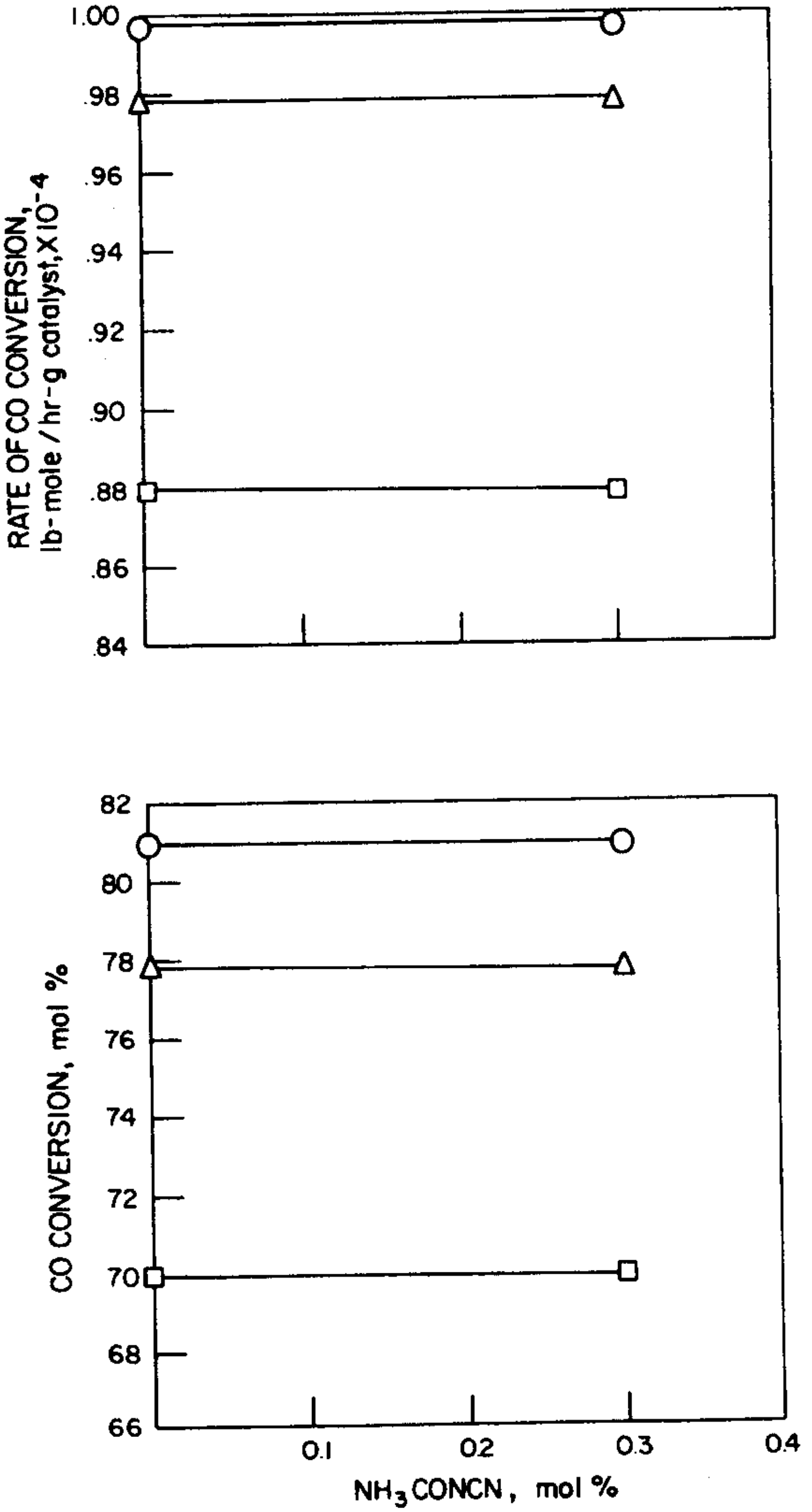


Figure 39. REACTION ORDER OF CARBON DIOXIDE (Shell Oil 538 Catalyst, 4 x 6 Mesh Spheres)



FEED GAS COMPOSITION, dry basis

COMPONENT	mol %
CO	20.0
CO_2	19.0
H_2	33.73
CH_4	24.22
C_2H_6	0.70
C_3H_8	0.20
$C_4H_{10}S$	0.08
H_2S	0.90
N_2	0.80
He	0.01
NH_3	As indicated
C_6H_5OH	
COS	0.04
C_2H_5SH, ppm	4.3
n-C_3H_7SH, ppm	1.4
i-C_3H_7SH, ppm	4.6
DISULFIDES, ppm	2.6
TOTAL	100.00

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Figure 40. EFFECT OF AMMONIA ON THE CONVERSION AND RATE OF CONVERSION OF CARBON MONOXIDE (Shell Oil 538 Catalyst, 4 x 6 Mesh Spheres)

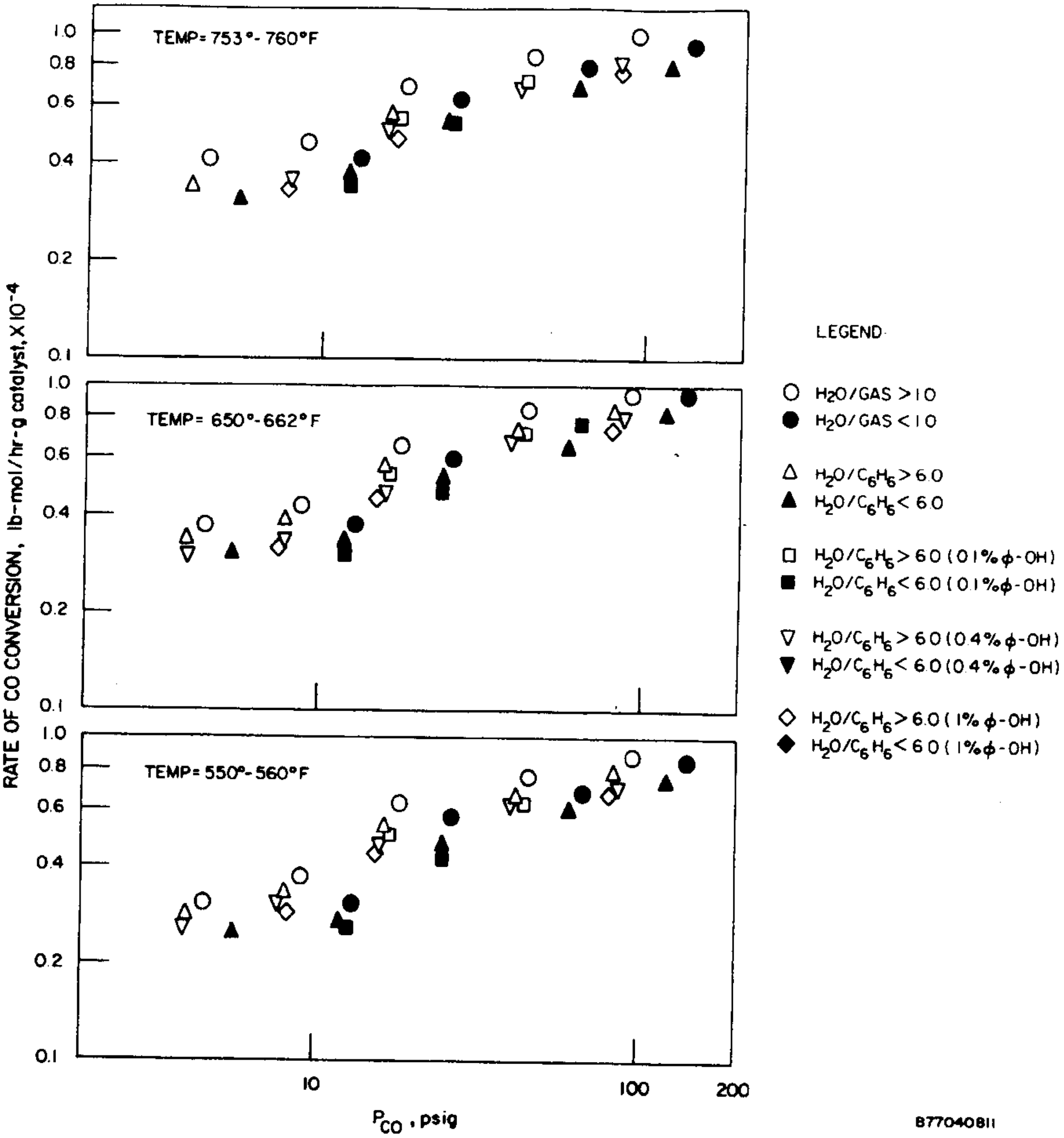

Figure 41. REACTION ORDER OF CARBON MONOXIDE (Shell Oil 538 Catalyst, 4 x 6 Mesh Spheres)

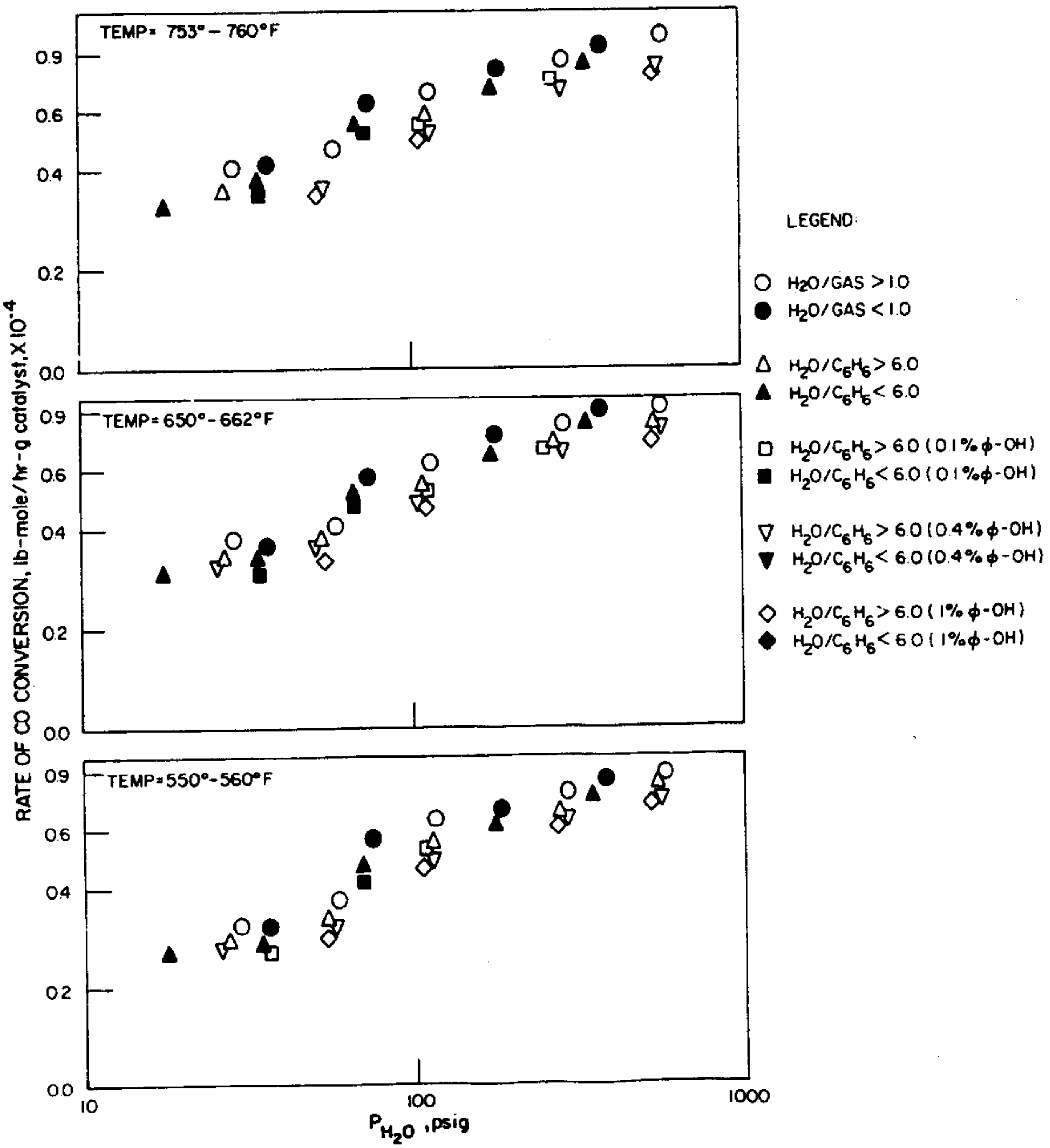

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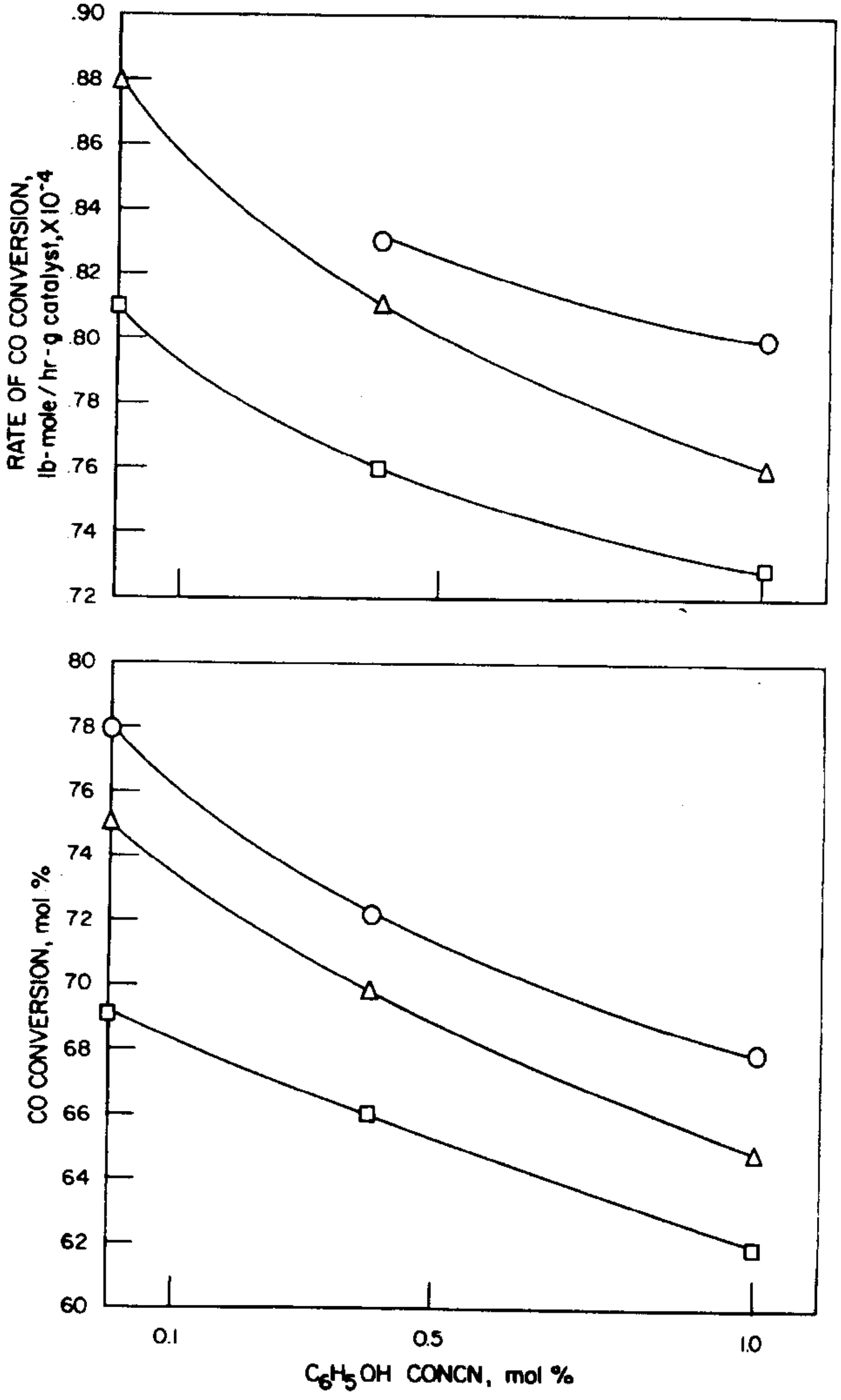
Figure 42. REACTION ORDER OF WATER (Shell Oil 538 Catalyst, 4 x 6 Mesh Spheres)



TEMP, °F

○	750
△	650
□	550

STEAM/GAS = 1.3
PRESS. = 1000 psig

FEED GAS COMPOSITION, dry basis

COMPONENT	mol %
CO	18.0
CO_2	17.0
H_2	30.55
CH_4	21.14
C_2H_6	0.68
C_3H_8	0.19
C_4H_{10}	0.08
H_2S	0.85
N_2	0.80
He	0.02
NH_3	0.32
C_6H_5OH	As indicated
C_6H_6	10.33
COS	0.04
C_2H_5SH, ppm	4.3
n-C_3H_7SH, ppm	1.4
i-C_3H_7SH, ppm	4.6
DISULFIDES, ppm	2.6
TOTAL	100.00

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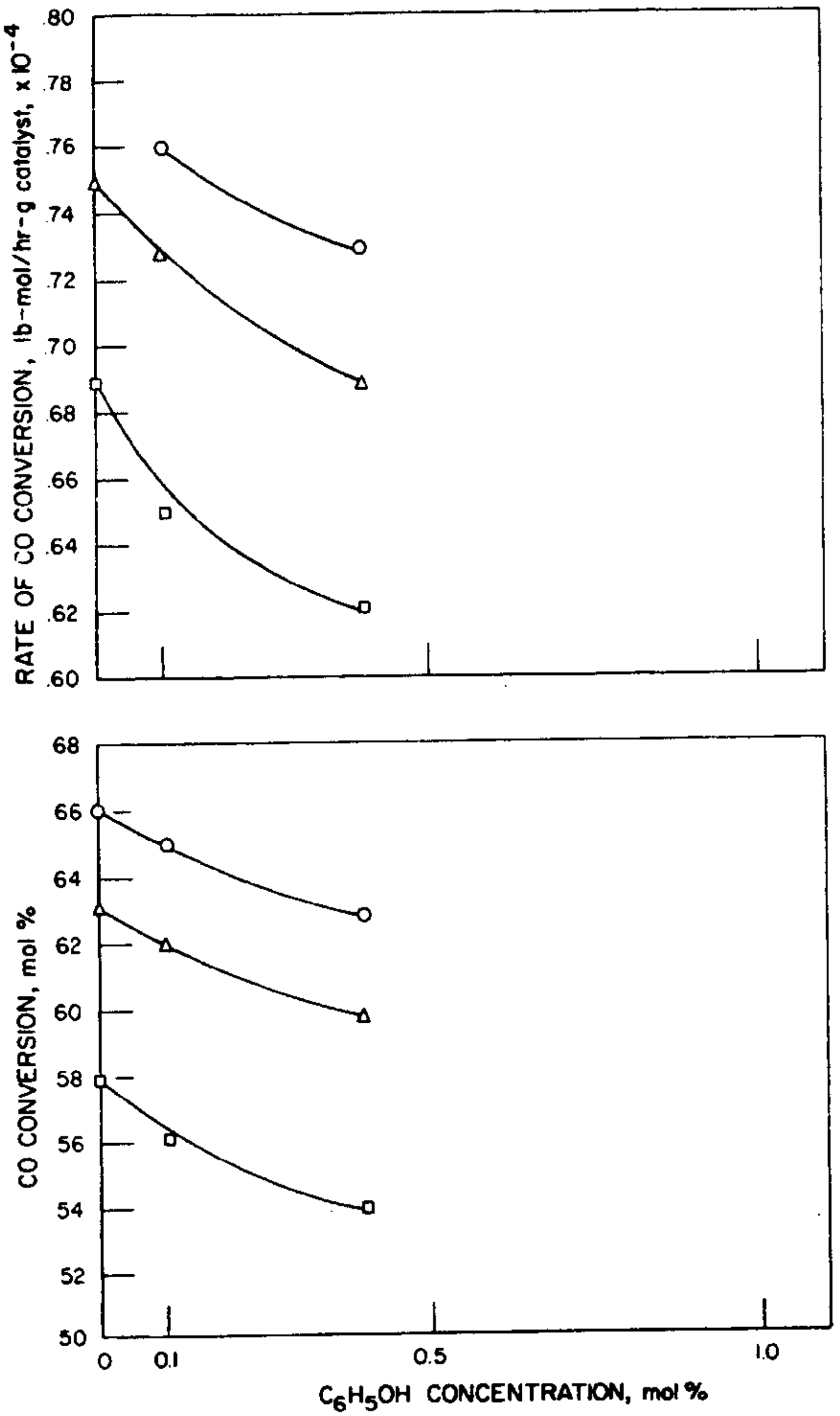
Figure 43. EFFECT OF PHENOL ON THE CONVERSION AND RATE OF CONVERSION OF CARBON MONOXIDE (Shell Oil 538 Catalyst at a CSTR Space Velocity of 0.2230 SCF/hr-g)



TEMP, °F	
○	750
△	650
□	550

STEAM/GAS = 13
PRESS. = 500 psig

FEED GAS COMPOSITION, dry basis

COMPONENT	mol %
CO	18.0
CO_2	17.0
H_2	30.55
CH_4	21.14
C_2H_6	0.68
C_3H_8	0.19
C_4H_{10}	0.08
H_2S	0.85
N_2	0.80
He	0.02
NH_3	0.32
C_6H_5OH	As indicated
C_6H_6	10.33
COS	0.04
C_2H_5SH, ppm	4.3
n-C_3H_7SH, ppm	1.4
i-C_3H_7SH, ppm	4.6
DISULFIDES, ppm	2.6
TOTAL	100.00

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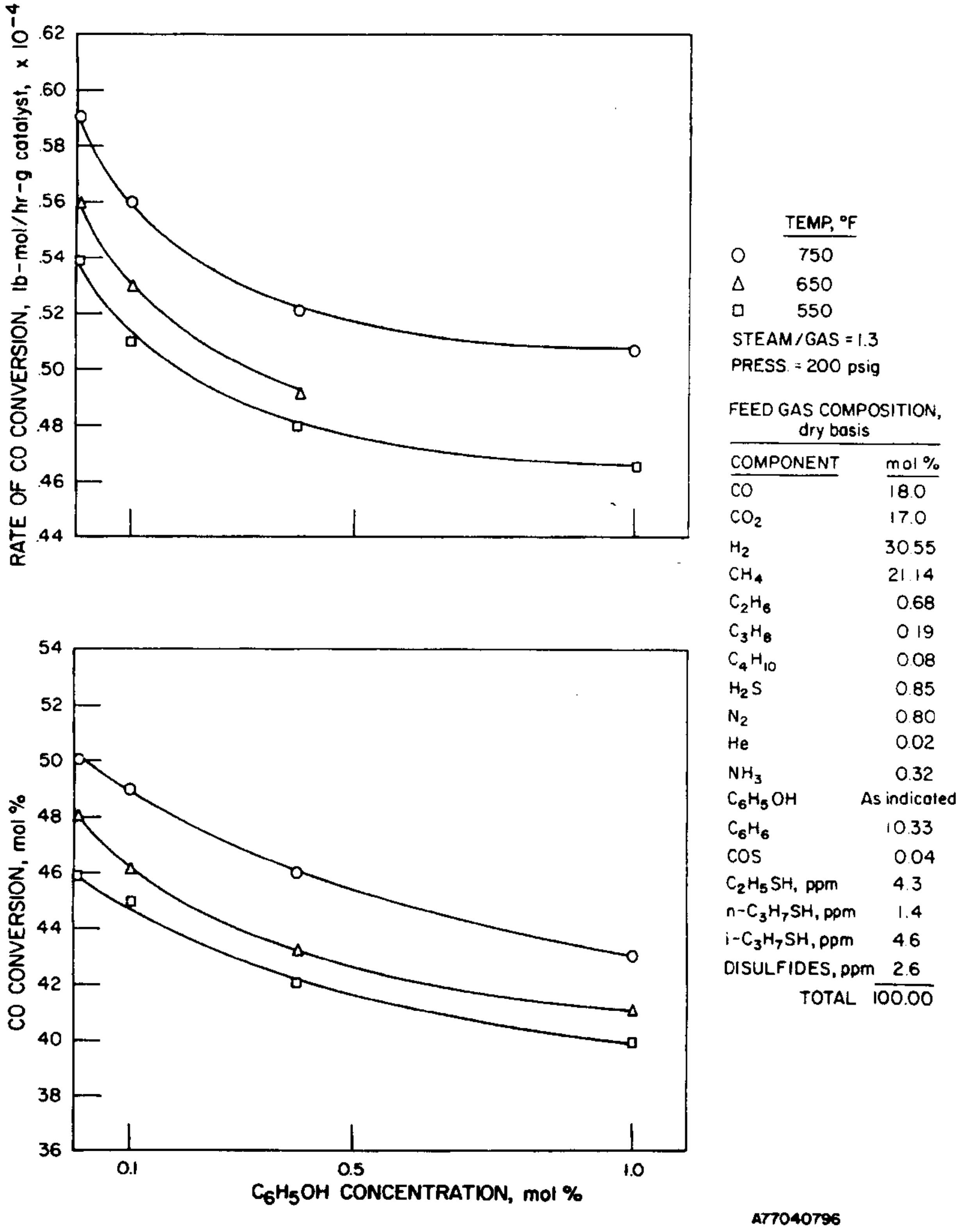
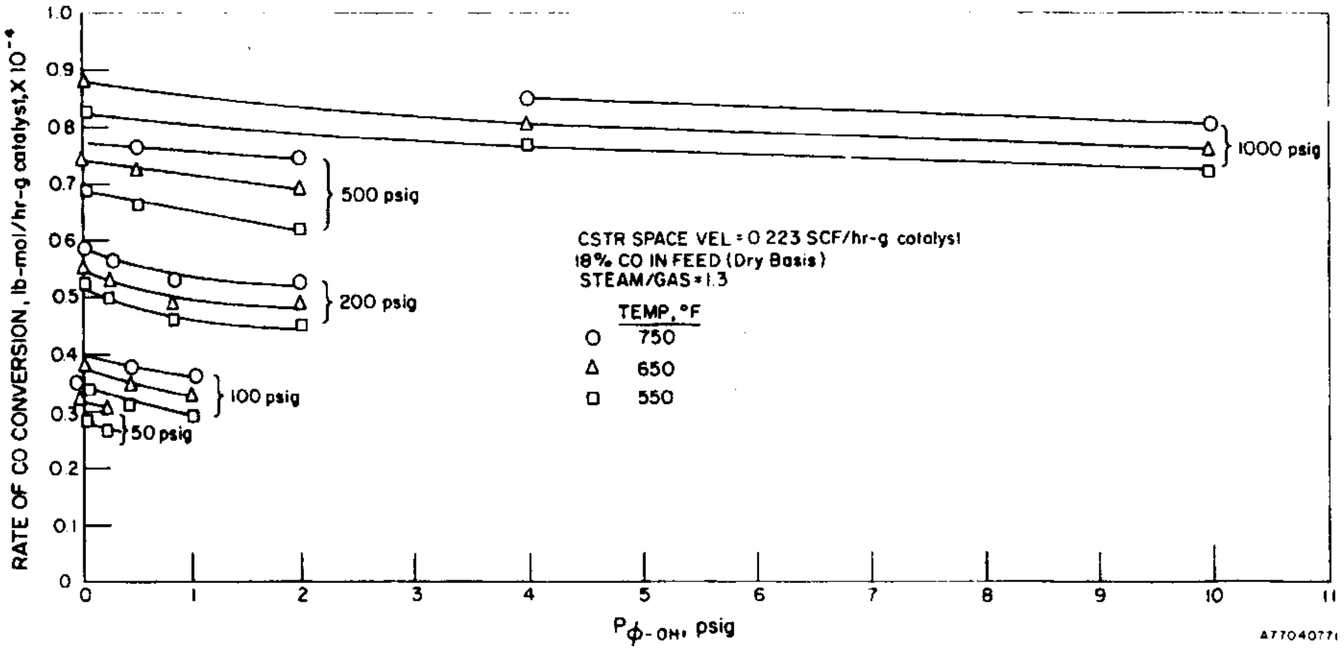
Figure 44. EFFECT OF PHENOL ON THE CONVERSION AND RATE OF CONVERSION OF CARBON MONOXIDE (Shell Oil 538 Catalyst at a CSTR Space Velocity of 0.2230 SCF/hr-g)



FEED GAS COMPOSITION, dry basis

COMPONENT	mol %
CO	18.0
CO_2	17.0
H_2	30.55
CH_4	21.14
C_2H_6	0.68
C_3H_8	0.19
C_4H_{10}	0.08
H_2S	0.85
N_2	0.80
He	0.02
NH_3	0.32
C_6H_5OH	As indicated
C_6H_6	10.33
COS	0.04
C_2H_5SH, ppm	4.3
n-C_3H_7SH, ppm	1.4
i-C_3H_7SH, ppm	4.6
DISULFIDES, ppm	2.6
TOTAL	100.00

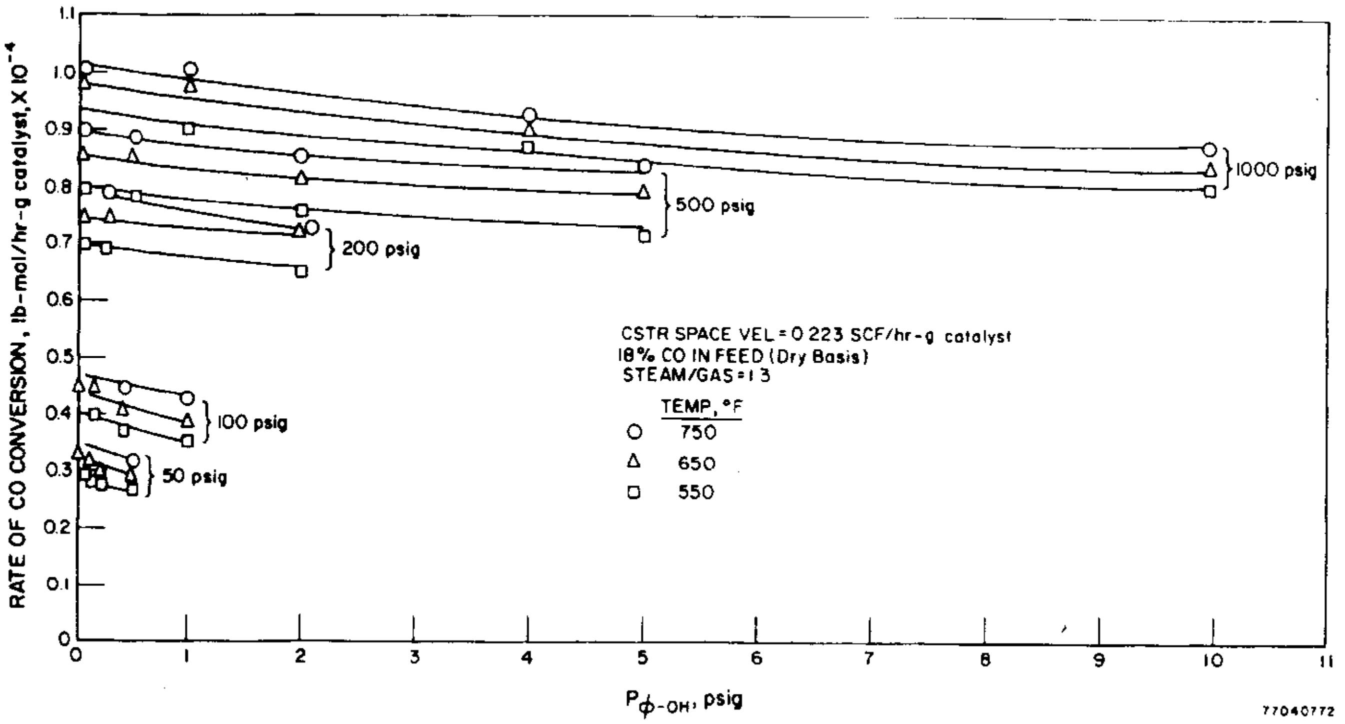
Figure 45. EFFECT OF PHENOL ON THE CONVERSION OF CARBON MONOXIDE (Shell Oil 538 Catalyst at a CSTR Space Velocity of 0.2230 SCF/hr-g)



FEED GAS COMPOSITION, dry basis

COMPONENT	mol %
CO	18.00
CO_2	17.00
H_2	30.55
CH_4	21.14
C_2H_6	0.68
C_3H_8	0.19
C_4H_{10}	0.08
H_2S	0.85
N_2	0.80
He	0.02
NH_3	0.32
C_6H_5OH	As indicated
C_6H_6	10.33
COS	0.04
SULFUR COMPOUND	13.00 ppm
TOTAL	100.00

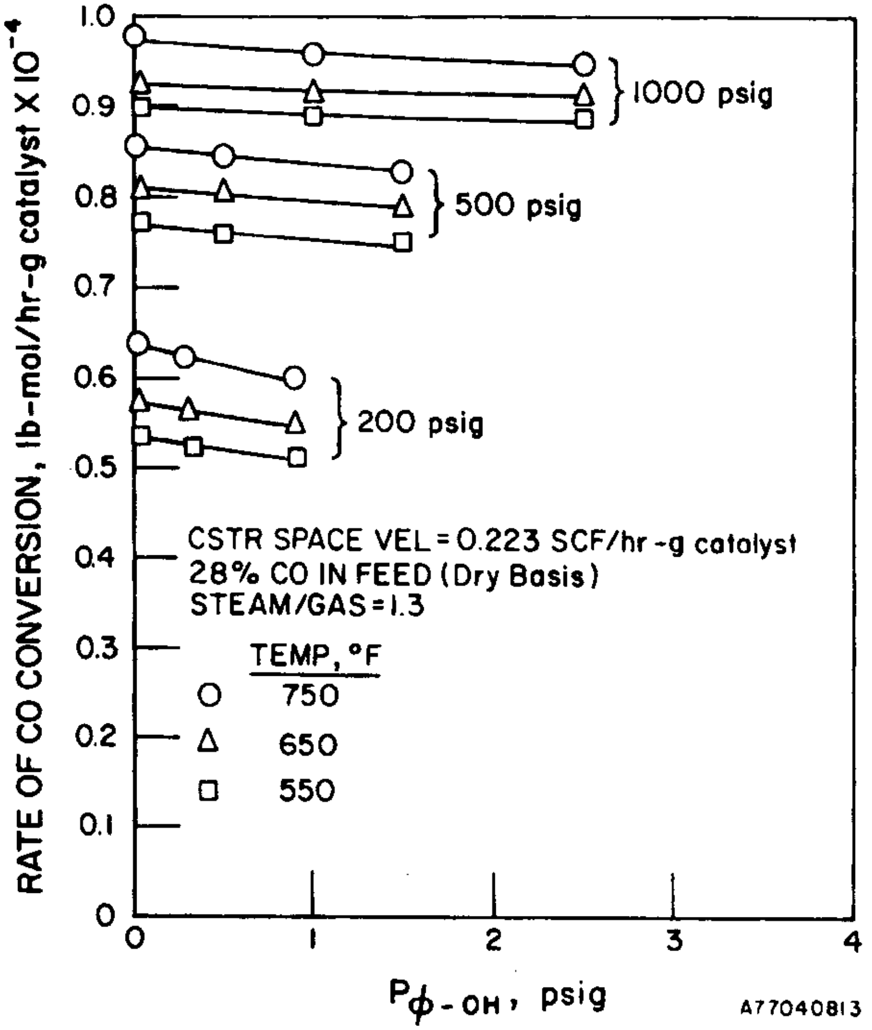
Figure 46. EFFECT OF PHENOL ON THE RATE OF CONVERSION OF CARBON MONOXIDE (Shell Oil 538 Catalyst, 4 x 6 Mesh Spheres)



FEED GAS COMPOSITION,
dry basis

COMPONENT	mol %
CO	18.22
CO_2	12.62
H_2	33.32
CH_4	21.44
C_2H_6	0.90
C_3H_8	0.64
C_4H_{10}	0.09
H_2S	1.86
N_2	0.90
He	0.02
NH_3	—
C_6H_5OH	As indicated
C_6H_6	9.89
COS	0.10
SULFUR COMPOUND	12.9
TOTAL	100.00

Figure 47. EFFECT OF PHENOL ON THE RATE OF CONVERSION OF CARBON MONOXIDE (UC-1870-46-1 Catalyst, 1/16-Inch Extrudates)



FEED GAS COMPOSITION, dry basis

COMPONENT	mol %
CO	18.6
CO_2	20.8
H_2	23.5
CH_4	22.0
C_2H_6	1.4
C_3H_8	0.45
C_4H_{10}	0.09
H_2S	1.07
N_2	1.24
He	0.03
NH_3	0.86
C_6H_5OH	As indicated
C_6H_6	9.89
SULFUR COMPOUND	2.67
TOTAL	100.00

Figure 48. EFFECT OF PHENOL ON THE RATE OF CONVERSION OF CARBON MONOXIDE (G-93 Catalyst, 4 x 6 Mesh Spheres, 10.00 g)