Section 8

SUPPORTING STUDIES

REACTION MODELLING

Kinetic Model

One approach taken to develop a kinetic model for the liquid phase methanol reaction was a simplified, semi-empirical method.

This work was based on the kinetic model successfully developed for the analogous liquid phase methanation system. The methanol system is an equilibrium limited reaction system. The terms used in the model derivation are defined at the end of this section. The initial study was performed specifically for a Lurgi type synthesis gas, but can be generalized to handle other feed gas composition. A Lurgi type synthesis gas has the nominal composition:

50% H_2, 25% CO, 10% CO_2, and 15% CH_4

Experimental data indicate that under nearly all reaction conditions, both CO_2 and CH_4 behave as inerts and this gas composition can be represented by:

50% H_2, 25% CO, and 25% inerts.

In terms of the total pressure, P_T, and the conversion X, the reaction stoichiometry for the Lurgi synthesis gas can be written as:

$$
\begin{array}{ccccccc}
CO & + & 2H_2 & + & \text{Inerts} & \rightleftharpoons & CH_3OH \\
\left(\frac{1-X}{4-2X}\right) P_T & + & \left(\frac{2-2X}{4-2X}\right) P_T & + & \left(\frac{1}{4-2X}\right) P_T & \rightleftharpoons & \left(\frac{X}{4-2X}\right) P_T
\end{array}
$$

* In cases where the circulating liquid phase exhibits a relatively high vapor pressure, P_T should be replaced by the term $(P_T - P^*)$.

A mass balance over a reactor element is given by

$$FdX = rdW$$

If the reaction rate is assumed to be first order in the difference between CO liquid phase concentration, C, and the CO liquid phase concentration that would exist at equilibrium reaction conditions, C_{EQ}, then,

$$r = K(C-C_{EQ})$$

By introducing the Henry's law constant, K_H, and a suitable conversion factor, the rate may be expressed in terms of the CO partial pressures, P and P_{EQ},

$$r = \frac{K}{K_H(M/\rho_L)} \quad (P - P_{EQ})$$

$$r = \frac{K}{K_H(M/\rho_L)} \left[\frac{1-X}{4-2X} - \frac{1-X_{EQ}}{4-2X_{EQ}}\right] P_T$$

Introducing this rate expression into the reactor element mass balance, recognizing that the term, $\left[(1-X_{EQ}) \ / \ (4-2X_{EQ})\right]$, is a constant ($\phi$) for fixed temperature, pressure, and feed gas composition, the following differential rate equation is obtained:

$$\frac{dX}{\left(\frac{1-X}{4-2X}\right) - \phi} = \frac{KP_T}{K_H(M/\rho_L)} \quad \frac{dW}{F}$$

This equation can be rearranged and integrated:

$$\int_0^X \frac{(4-2X)dX}{(1-4\phi) - (1-2\phi)X} = \int_0^W \frac{KP_T}{K_H(M/\rho_L)} \quad \frac{dW}{F}$$

resulting in the expression:

$$\frac{2}{(1-2\phi)}\left[\left(2-\frac{(1-4\phi)}{(1-2\phi)}\right)\ln\left(\frac{(1-4\phi)}{(1-4\phi)-(1-2\phi X)}\right)+X\right]=K_1P_T\frac{W}{F}$$

One can see that even for this simple reaction model, the resulting expression is very complex. Using this model the effect of the feed gas flow rate on CO conversion at fixed temperature and pressure levels was investigated.

The main intent of the series of reaction runs presented in Table 8-1 was to isolate the system response to a single process variable, feed gas rate, at fixed temperature and pressure, and compare the results with those predicted by the reaction model. While the initial activity level was lower than normally achieved with this reaction system(1), the data on any given day of operation were internally consistent. In fact, the activity level held fairly constant through Run 122-2, when a singular sharp drop in activity was noted. Thereafter, the catalyst activity remained at the new, lower level. When the catalyst was removed from the reactor, it had a peculiar copper sheen to it, as opposed to its normal black color. Whether or not this is evidence of some alternation of the important catalytic properties is unkown. Under the temperature and pressure conditions tested, a Lurgi type synthesis gas would have an equilibrium CO conversion of 43 percent at 230°C and 500 psig, and 64.7 percent at 230°C and 1000 psig. Substituting these values into the kinetic model, reaction rate constants were calculated for the different feed flow rates (Table 8-2). It can be seen that at the higher feed gas rates (lower conversion), the calculated K_1 values appear to be fairly constant, as they should be. However, as the feed gas rate approaches zero, the calculated K_1 value falls rapidly. This behavior is true at both pressure levels and indicates that the present form of the model is insufficient to represent the actual reaction system at low VHSV. One reason for this behavior could be that the circulating oil

(1) Catalyst A/Witco 40/Lurgi Gas

TABLE 8-1

APPROACH TO EQUILIBRIUM FOR LOW FEED GAS RATES

COMMERCIAL CATALYST A(1) (16 X 20 MESH)/WITCO 40/LURGI FEED GAS(2)

RUN NO.	TEMP (°C)	PRESS. (psig)	VHSV (Hr^{-1})	CO CONVERSION TO MeOH (%) (3)
119-1	230	500	1680	24.2
120-1	230	500	1665	13.3(4)
120-2	230	500	680	19.5(4)
120-3	230	500	2525	10.6(4)
121-1	230	500	1700	20.3
121-2	230	500	720	28.7
121-3	230	500	2715	16.0
122-1	230	500	1700	22.5
122-2	230	500	245	37.0
123-1	230	500	485	25.6
124-1	230	500	2175	14.6
124-2	230	1000	[illegible]	30.9
125-1	230	1000	2475	33.6
125-2	230	1000	900	44.8
125-3	230	1000	3725	26.3
126-1	230	1000	2370	29.2
126-2	230	1000	350	51.9
127-1	230	1000	2390	25.3(5)
127-2	230	1000	2335	23.8(6)
127-3	230	1000	2335	23.8(7)
127-4	230	1000	2255	13.7(4)
128-1	230	1000	2315	23.2

(1) Catalyst Loading = 219.6 gm

(2) Lurgi feed gas nominal composition 50% H_2, 25% CO, 10% CO_2, 15% CH_4.

(3) Includes small selectivity to higher alcohols.

(4) No liquid flow through bed; gas sparged through stagnant submerged bed.

(5) Liquid flow reduced to 1/3 normal rate.

(6) Liquid flow reduced to 1/6 normal rate.

(7) Liquid flow reduced to 1/12 normal rate.

TABLE 8-2
CALCULATED REACTION RATE CONSTANT

CONDITIONS	X_{EQ}	RUN NO.	F: ARBITRARY UNITS	X	$K_1 = (\frac{F}{P_T W})(X, X_{EQ})$ ARBITRARY UNITS
230°C, 500 psig	0.430	119-1	1680	0.242	1015
	0.430	121-1	1700	0.203	785
	0.430	121-2	720	0.287	575
	0.430	121-3	2715	0.160	930
	0.430	122-1	1700	0.225	920
	0.430	122-2	245	0.370	225
Unexplained incremental loss in activity at Run 123-1;					
230°C, 500 psig	0.320	124-1	2175	0.146	665
230°C, 1000 psig	0.647	124-2	2965	0.309	620
	0.547	125-1	2476	0.336	575
	0.647	125-2	900	0.448	325
	0.647	125-3	3725	0.263	630
	0.647	126-1	2370	0.292	465
	0.647	126-2	350	0.519	170

contains a small but measurable quantity of methanol and dissolved gas, and the molar flow rate of the oil, relative to the gas feed rate, is high (20/1) at low VHSV. It is probable that the reactor is closer to that of continuous stirred tank reactor rather than the assumed plug flow model. Accounting for this difference would have the desired result of adjusting the high conversion K_1 values sharply upward.

The kinetic model is probably applicable for a range of gas compositions over a reasonable operating range except at lower values of gas to liquid flows. Also the catalytic effect of CO_2 concentration of rate will have to be handled empirically.

Nomenclature

C	Liquid Phase CO Concentration; gm moles/cm^3
F	Molar Feed Rate; gm moles/hr
K	Reaction Rate Constant; gm moles/hr-gm cat-(gm moles/cm^3)
K_1	Reaction Rate Constant; gm moles/hr-gm cat-atm
K_H	Henry's Law Constant; atm/mole fraction
M	Liquid Phase Molecular Weight; gm/gm moles
P	CO Partial Pressure; atm
P_T	Total Pressure; atm
P^*	Liquid Phase Vapor Pressure; atm
r	Reaction Rate; gm moles/hr - gm cat
W	Catalyst Weight; gm
X	CO Fractional Conversion
ρ_L	Liquid Phase Density

Subscript

EQ At reaction equilibrium conditions.

Empirical Model

At a later stage of the development program another approach was taken to develop an empirical model. This method calculated the CO conversion in terms of an approach to equilibrium (measured in ^0C) rather than as an absolute value for CO conversion.

Lurgi-Type Feed Gas. Equilibrium conversion for a Lurgi-type feed gas (50 % H_2, 25% CO, 10% CO_2, 15% CH_4) at 1000 psig is shown on Figure 8-1. This curve was used to transform the experimentally observed CO conversion value into an approach to the equilibrium temperature. Figure 8-2 presents the data for this gas composition showing conversion versus space velocity and temperature for 850 runs with a coarse-crushed catalyst (-12+16 Mesh). By definition the conversion at zero space velocity (infinite residence time) is the equilibrium conversion at the reaction temperature. The crossing of the various isotherms is a result of the inverse relationship of equilibrium conversion with temperature offset by the direct relationship of reaction rate with temperature. When these data are transformed into an approach to equilibrium value and plotted versus space velocity for the various temperatures, the result is an easily discernible family of curves as shown in Figure 8-3. Note that at zero space velocity, equilibrium conversion is assumed (zero approach).

Data obtained with different size catalyst particles, -16+20 mesh and 3/32" 0 tablets, were also subjected to the same analysis. The results are shown on Figures 8-4, 8-5, 8-6, and 8-7. Again, a good correlation is obtained.

One advantage to this correlating technique is that it provides a clear visual assessment of relative catalyst activities. The data in Figures 8-3, -5, and -7 are combined on Figure 8-8 to provide such a perspective. At 250^{0}C the coarse-crushed catalyst (-12+16 mesh) has no activity advantage over the 3/32" tablets while the finely-crushed catalyst (-16+20 mesh) offers significant advantages over both

FIGURE 8-1

EQUILIBRIUM CONVERSION FOR A LURGI FEED GAS AT 1000 PSIG

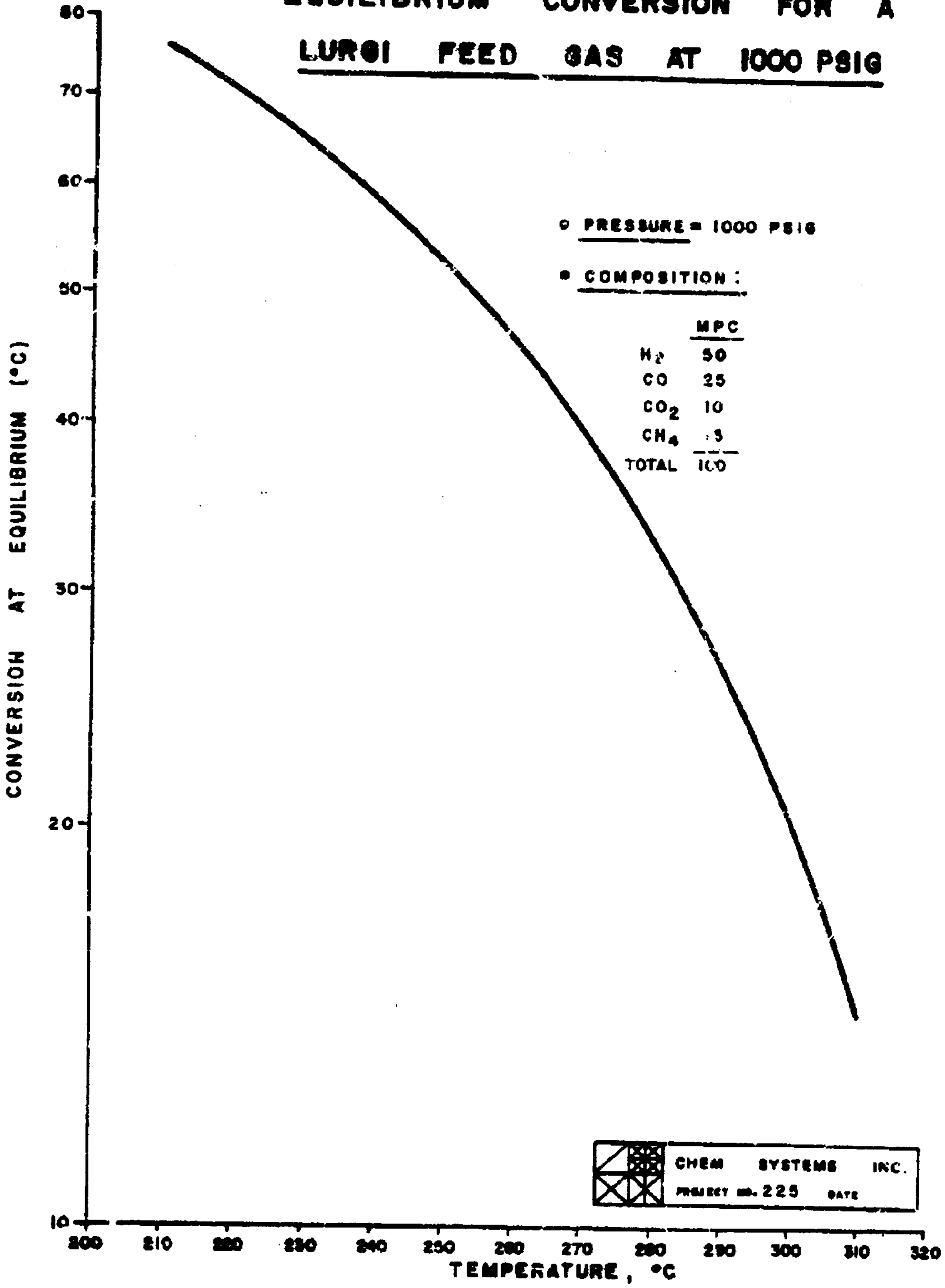


FIGURE 8-2

CO CONVERSION VS. SPACE VELOCITY FOR A LURGI FEED GAS AT 1000 PSIG WITH 12 – 16 MESH CATALYST A

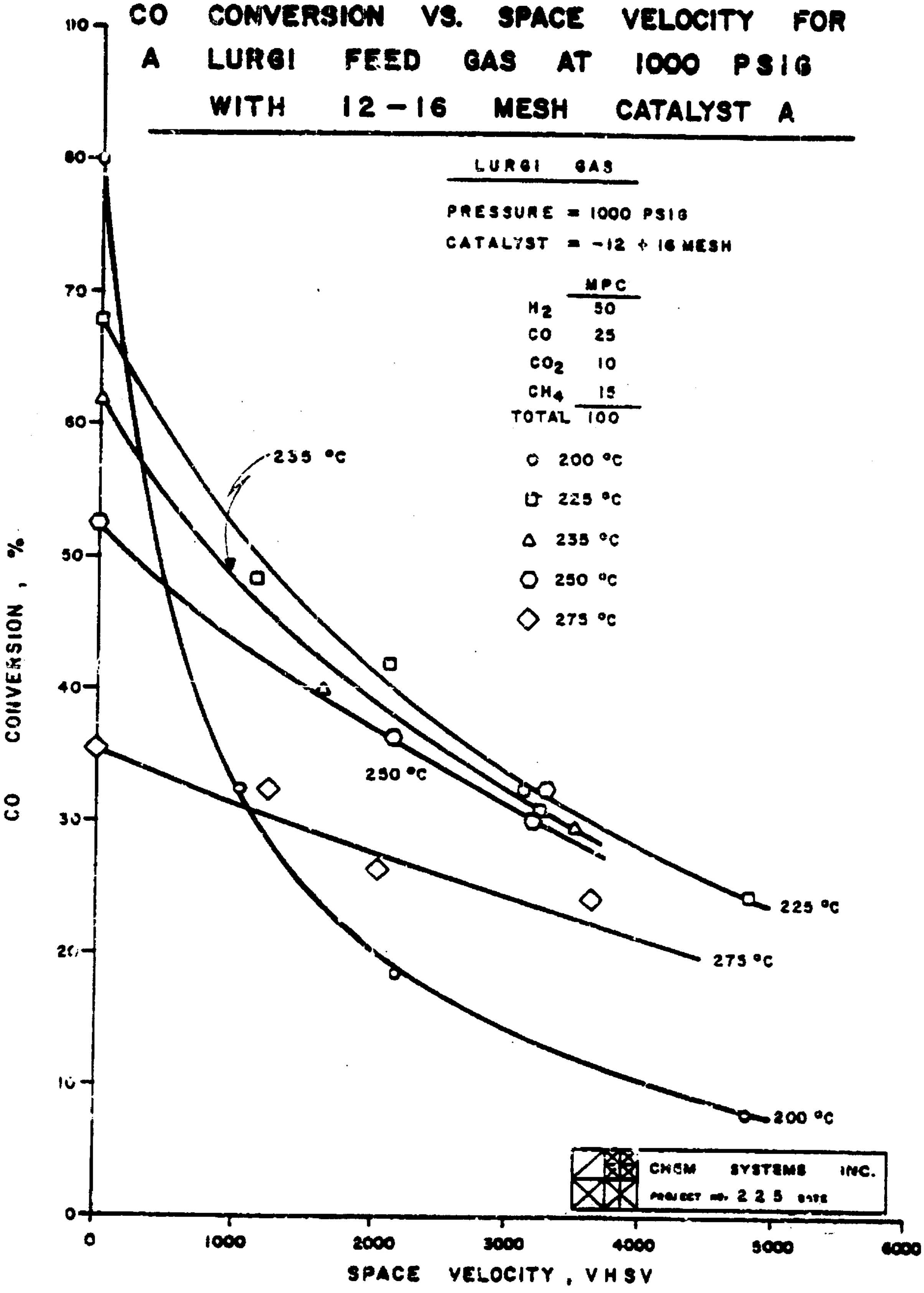


FIGURE 8-3

APPROACH TO EQUILIBRIUM VERSUS SPACE VELOCITY FOR A LURGI FEED GAS AT 1000 PSIG WITH 12-16 MESH CATALYST A

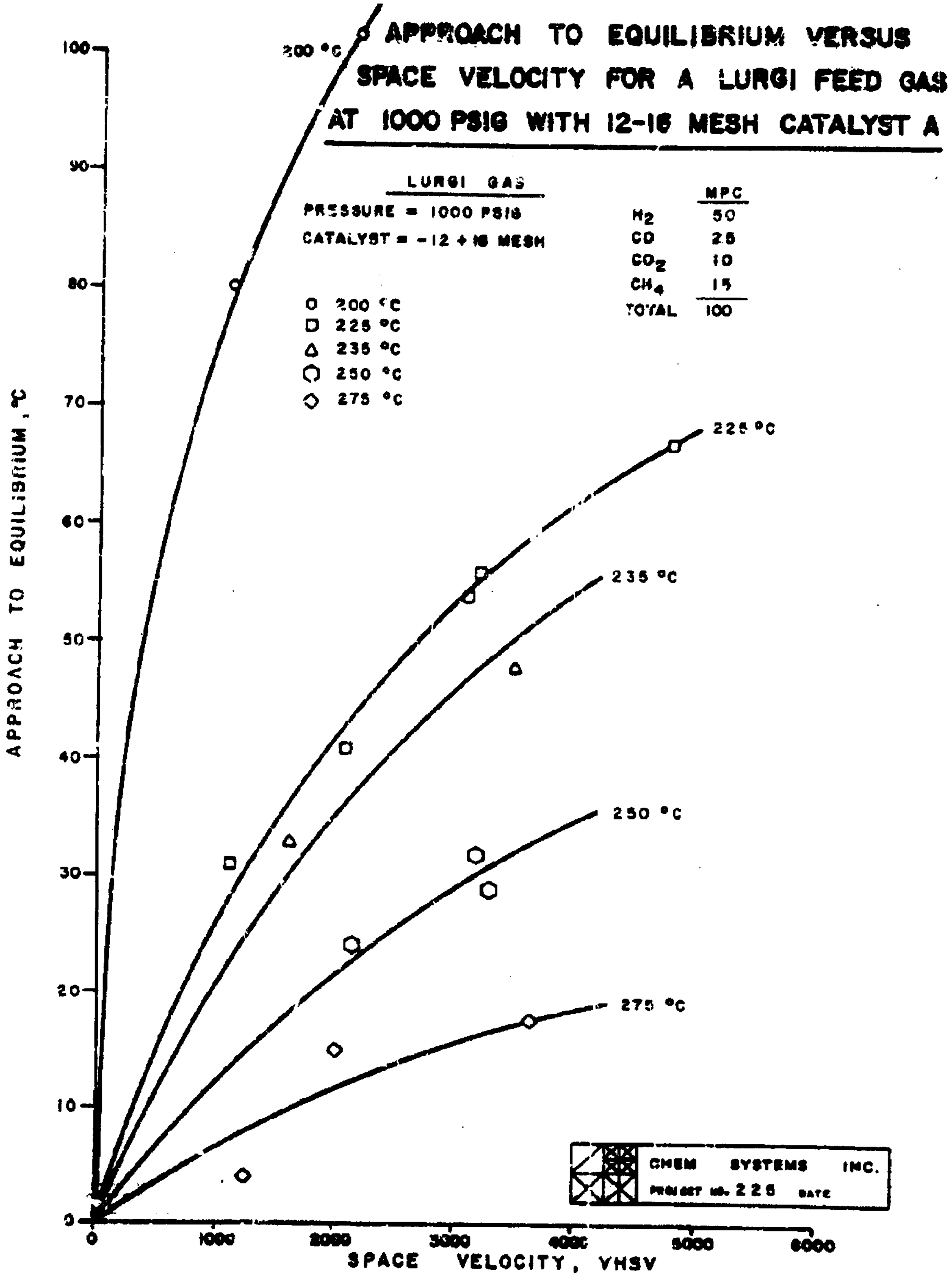


FIGURE 8-4

CO CONVERSION VS. SPACE VELOCITY FOR A LURGI FEED GAS AT 1000 PSIG WITH 16-20 MESH CATALYST A

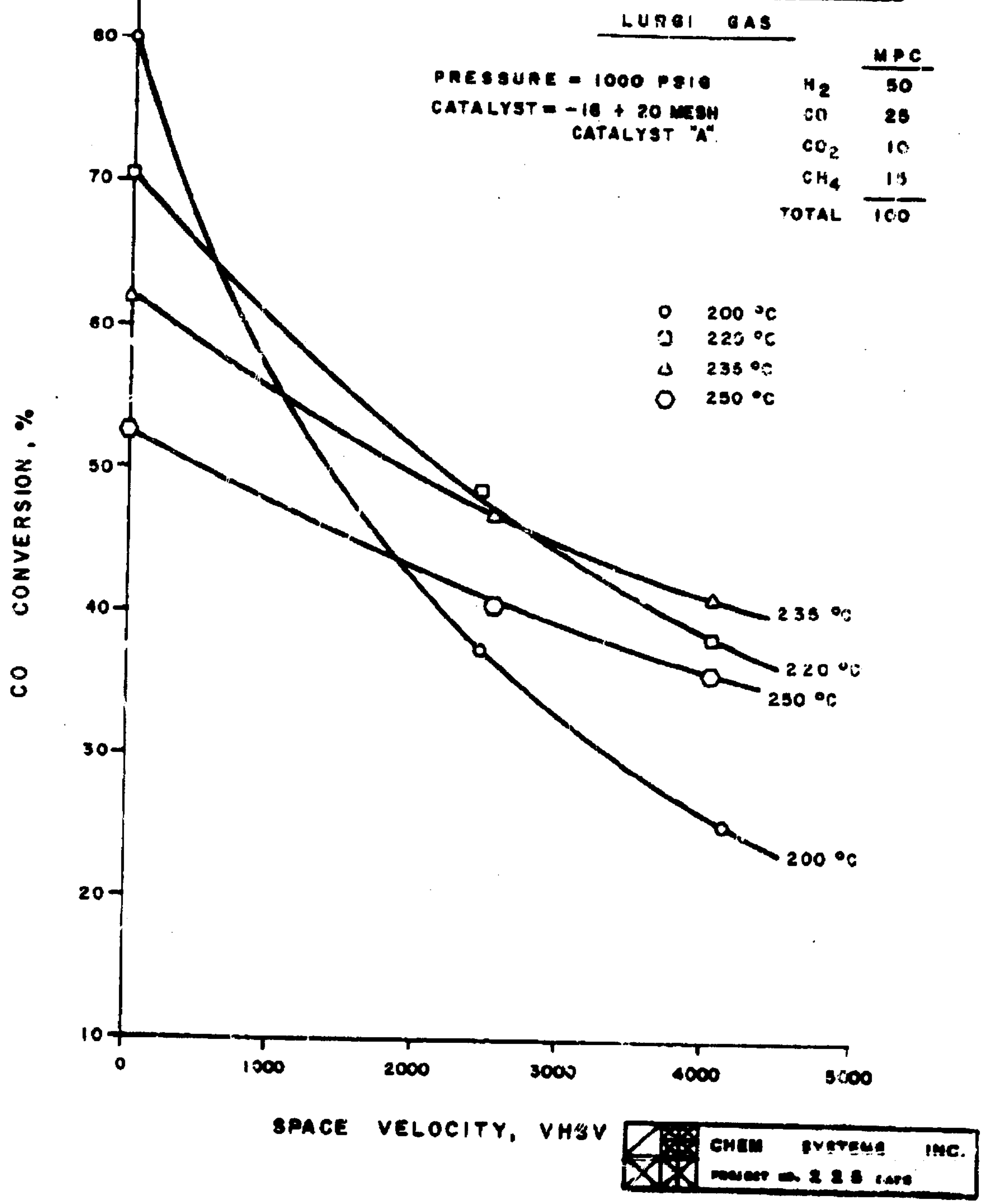
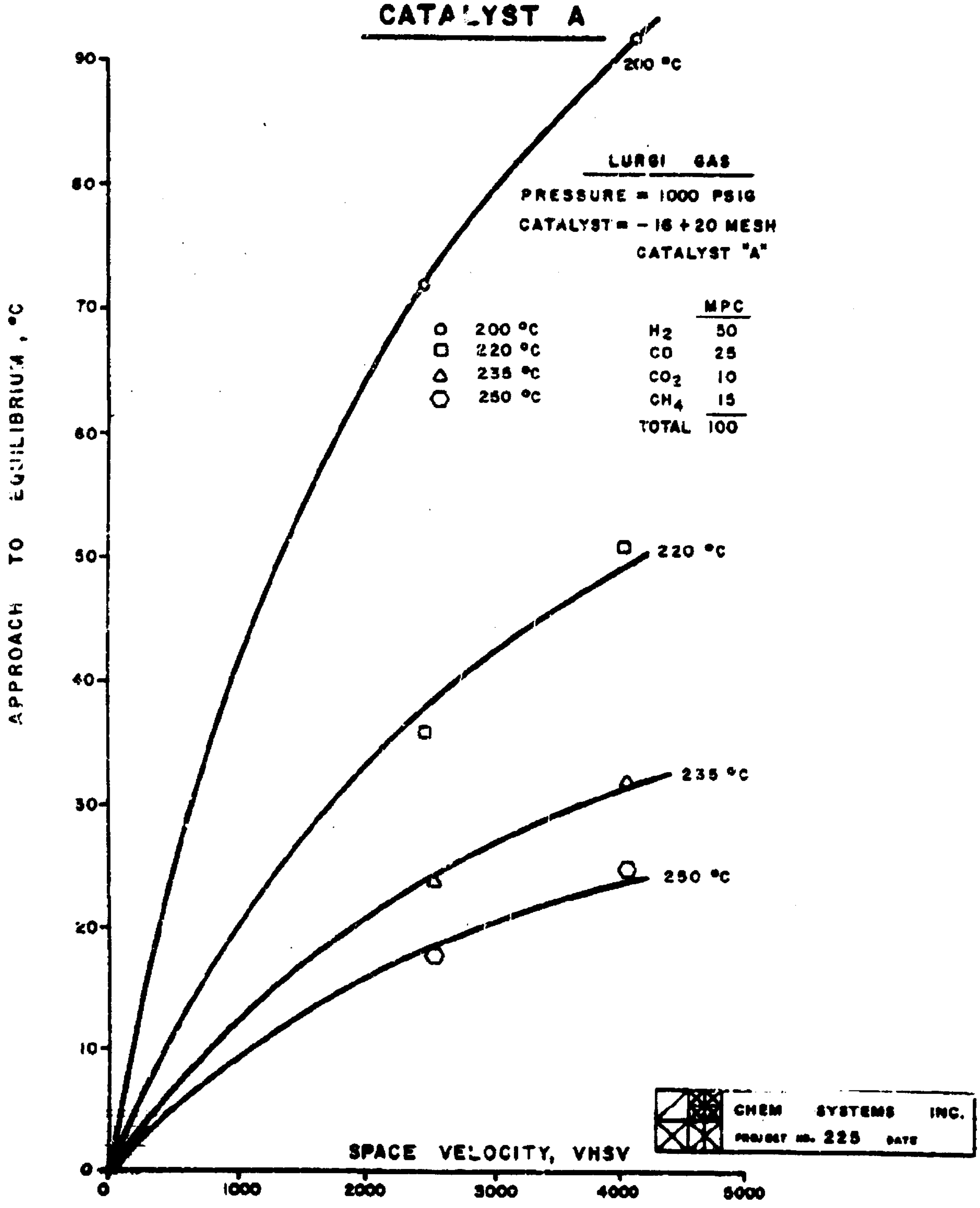


FIGURE 8-5

APPROACH TO EQUILIBRIUM VS. SPACE VELOCITY FOR A LURGI FEED GAS AT 1000 PSIG WITH 16-20 MESH CATALYST A



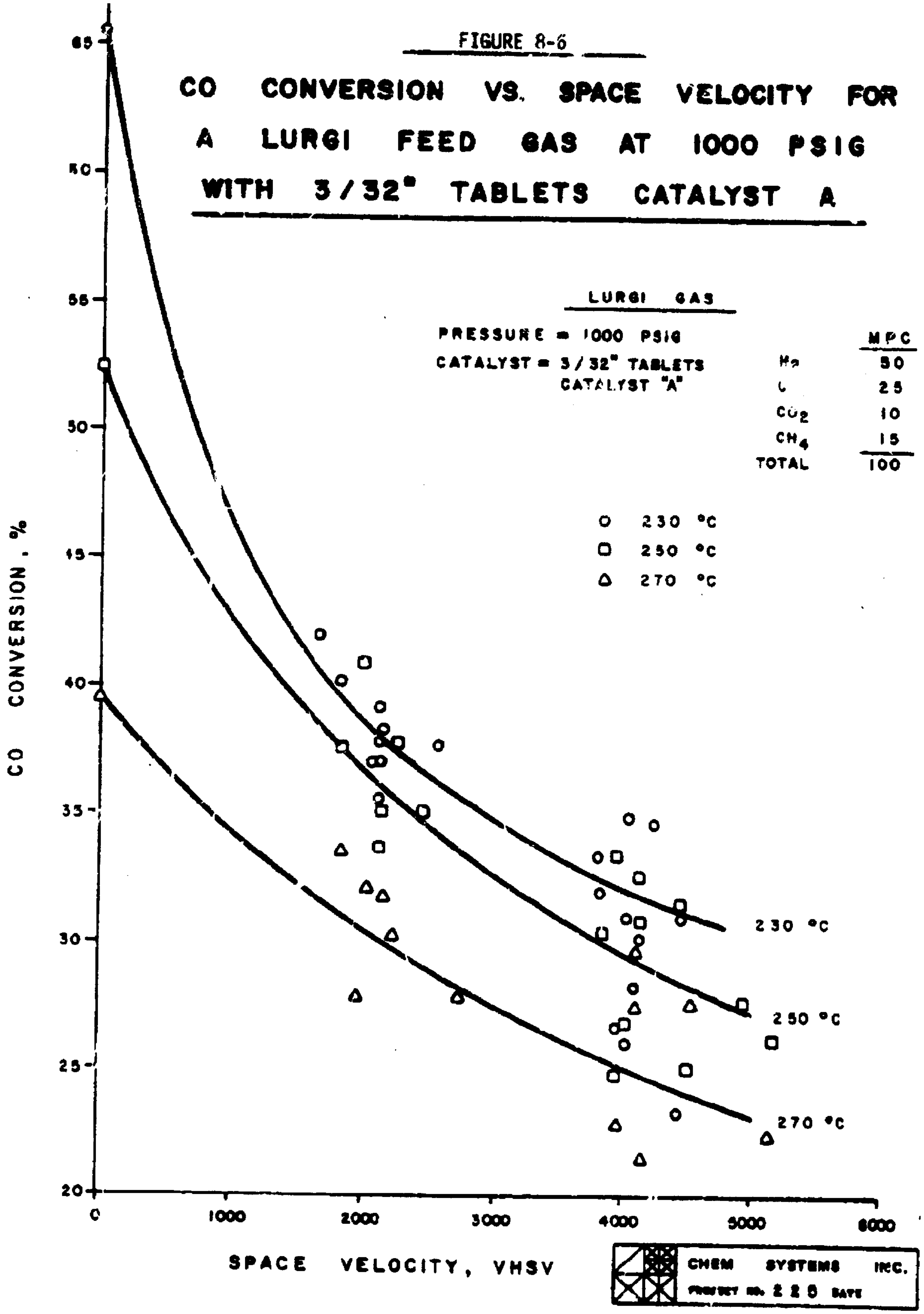


FIGURE 8-6

CO CONVERSION VS. SPACE VELOCITY FOR A LURGI FEED GAS AT 1000 PSIG WITH 3/32" TABLETS CATALYST A

CHEM SYSTEMS INC.
PROJECT NO. 2 2 5 DATE

FIGURE 8-7

APPROACH TO EQUILIBRIUM VS. SPACE VELOCITY FOR A LURGI FEED GAS AT 1000 PSIG WITH 3/32" TABLETS CATALYST A

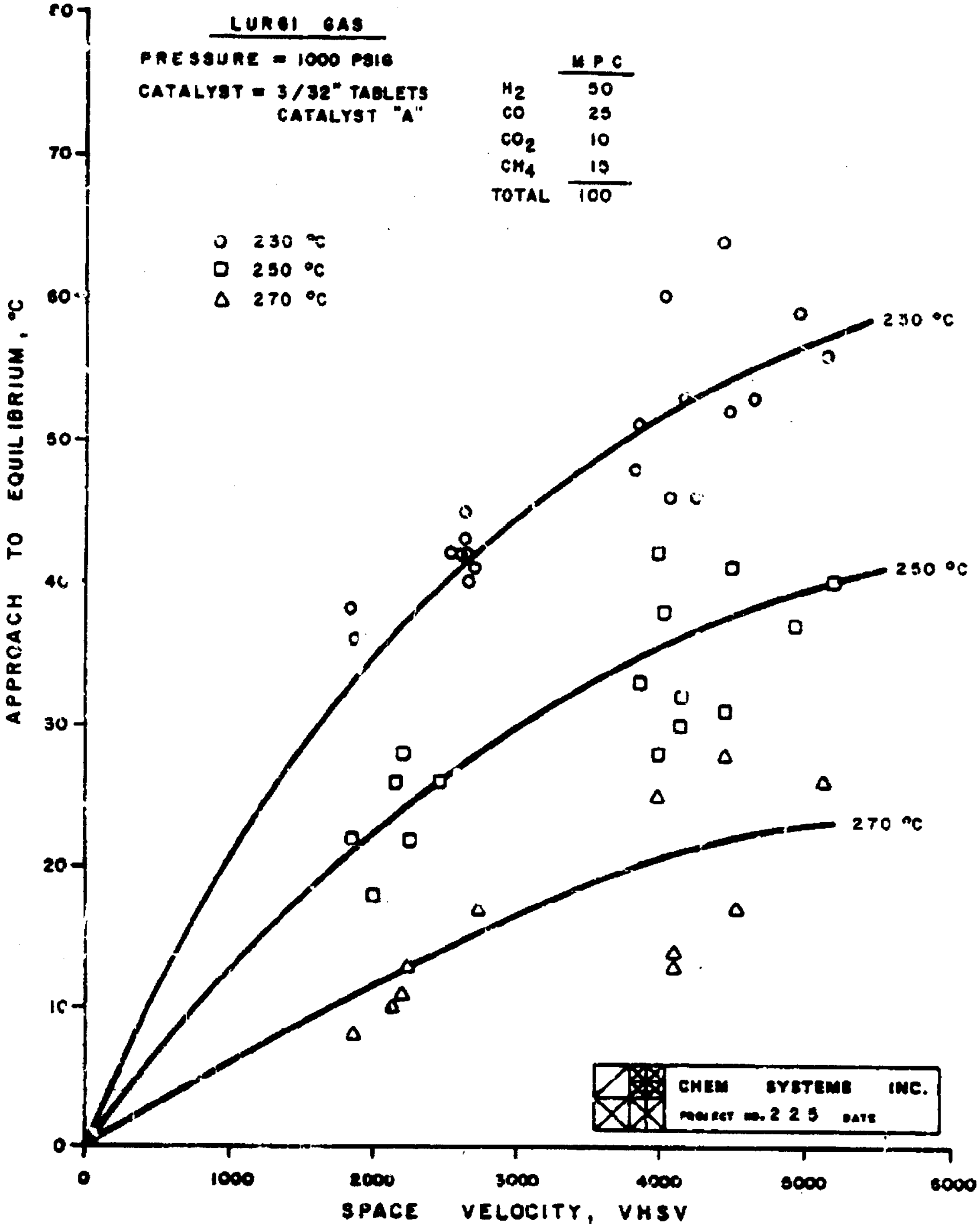
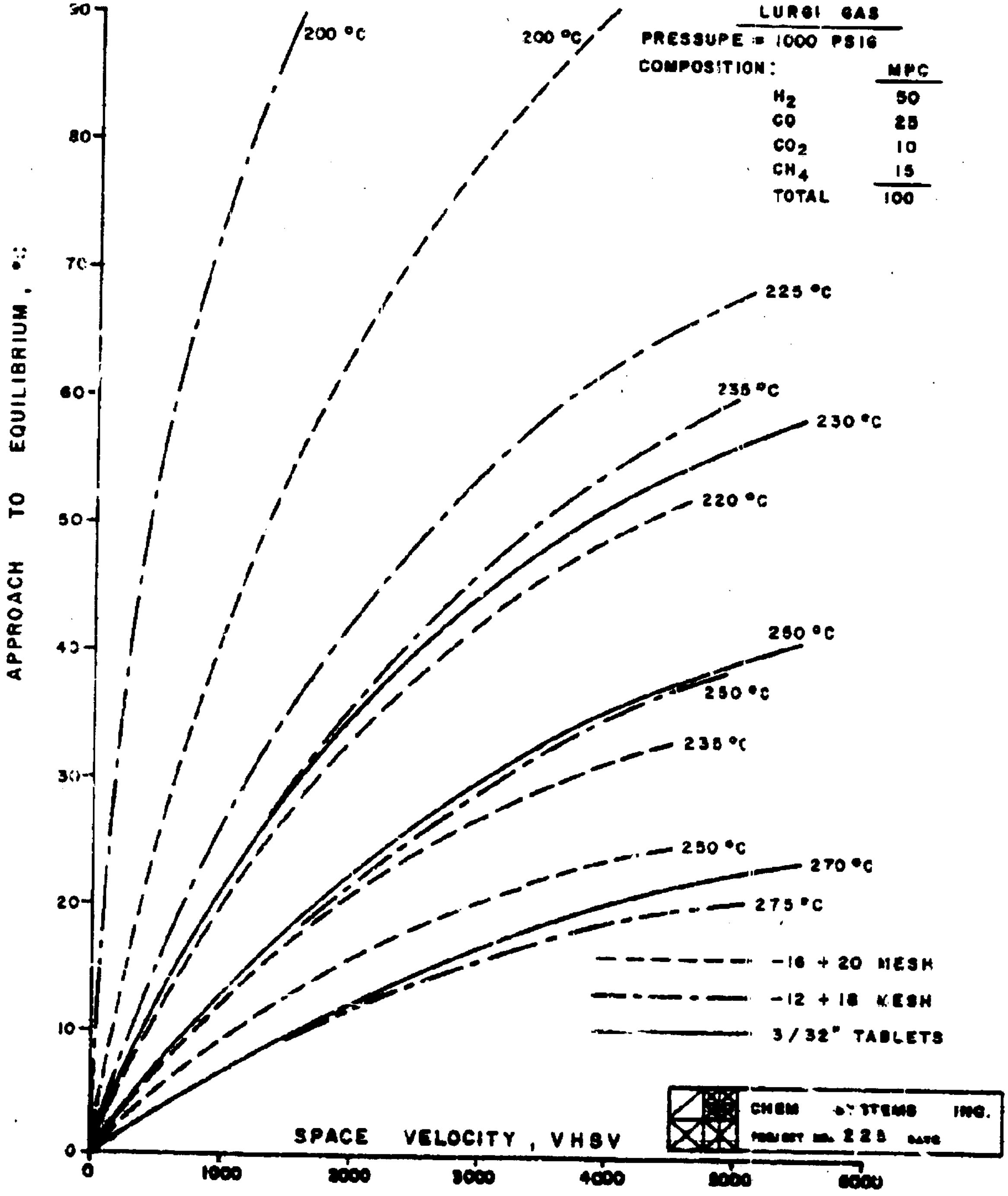


FIGURE 8-8

APPROACH TO EQUILIBRIUM VS. SPACE VELOCITY FOR A LURGI FEED GAS AT 1000 PSIG FOR THREE CATALYST SIZES



coarse-crushed and tablets. It is hard to believe that the difference in catalyst diameter (833-991 microns vs 991-1400 microns) accounts for the increased rate in this particular instance. Thus the data for the -12+16 mesh is somewhat suspect.

K-T Type Feed Gas. Experimental data from runs using a K-T feed gas were also analyzed. Figure 8-9 is the equilibrium CO conversion versus temperature at 1000 psig for a gas composition of; 36% H_2, 56% CO, 2% CO_2, 6% Ar. Figures 8-10 and 8-11 show experimental data for 3/32" Ø catalyst tablets while Figures 8-12 and 8-13 show data for the -12+16 mesh catalyst size. The limited amount of BSU data for a K-T feed gas and the slightly different gas compositions for various runs inhibit firm conclusions about relative catalyst activity. Provisionally, analysis of Figures 8-11 and 8-13 shows that the 3/32" Ø tablets are more active than the coarse-crushed catalyst (-12+16 Mesh). Since the actual runs were performed at different time periods, these results are suspect. Additional data on a consistent basis must be obtained before any definitive conclusions can be made regarding catalyst activity.

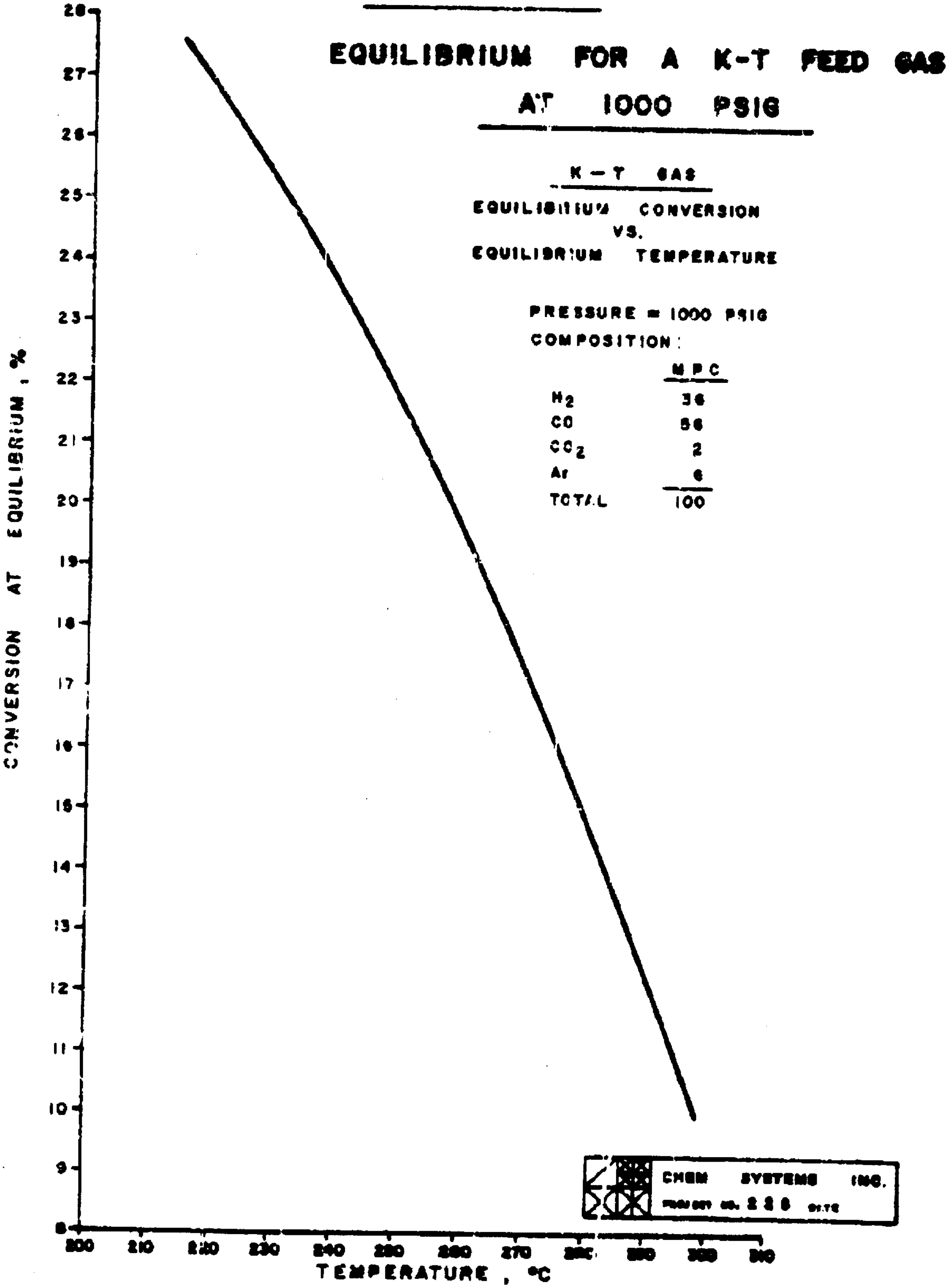
The empirical method of using an approach to equilibrium concept is valuable for evaluating LPMeOH experimental data and should be used in future laboratory analyses and presentations. This technique also provides a foundation for performing future regression analyses which will relate operating pressure, space velocity, catalyst type, and operating temperature to predicted conversions. Its use, in conjunction with more rigorous analytical models should greatly improve the ability to predict performance under a wide variety of operating conditions.

METHANOL PRODUCT ANALYSIS

Lurgi Feed Gas

A detailed chromatographic analysis was performed on representative methanol product samples from the three PDU and one long duration BSU runs made with Lurgi Feed gas. The analyses are presented in Table 8-3. The product is substantially methanol (95 weight percent), with the bulk of the remaining material being co-product water and dissolved

FIGURE 8-9



EQUILIBRIUM FOR A K-T FEED GAS AT 1000 PSIG

FIGURE 8-10

CO CONVERSION VS. SPACE VELOCITY FOR A K-T FEED GAS AT 1000 PSIG WITH 3/32" CATALYST A TABLETS

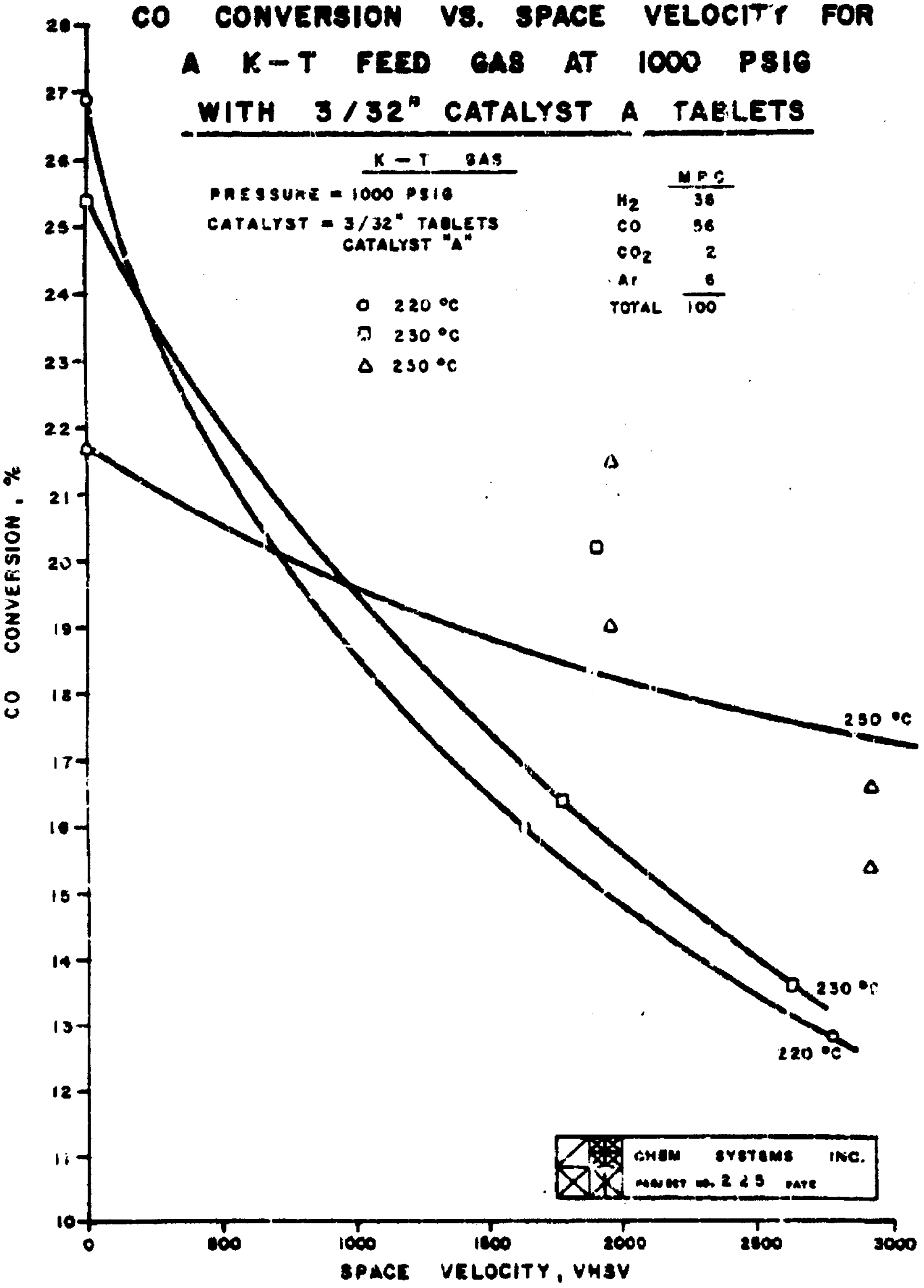


FIGURE 8-11

APPROACH TO EQUILIBRIUM VS. SPACE VELOCITY FOR A K-T FEED GAS AT 1000 PSIG WITH 3/32" CATALYST A TABLETS

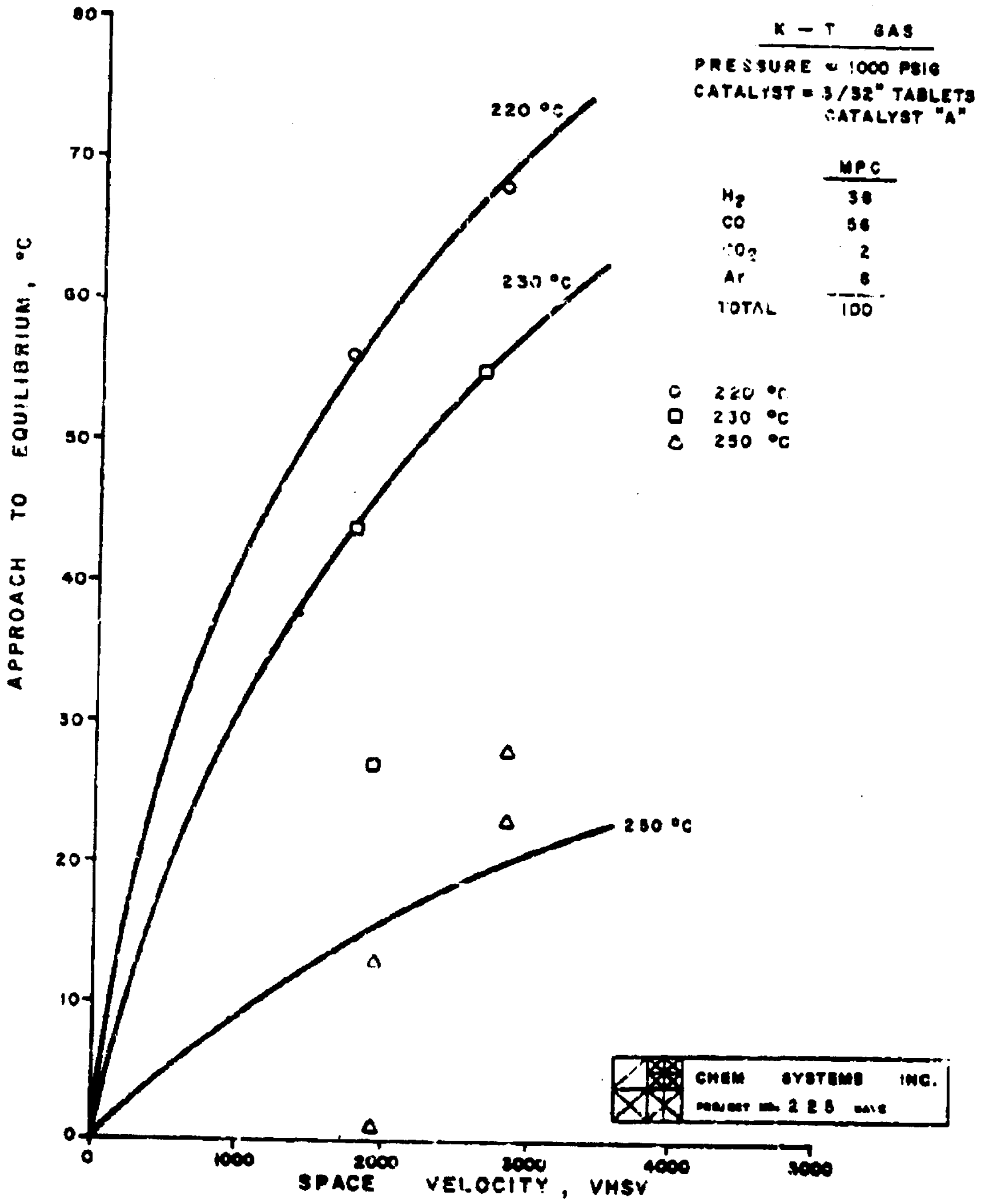


FIGURE 8-12

CO CONVERSION VS. SPACE VELOCITY FOR A K-T FEED GAS AT 1000 PSIG WITH 12-16 MESH CATALYST A

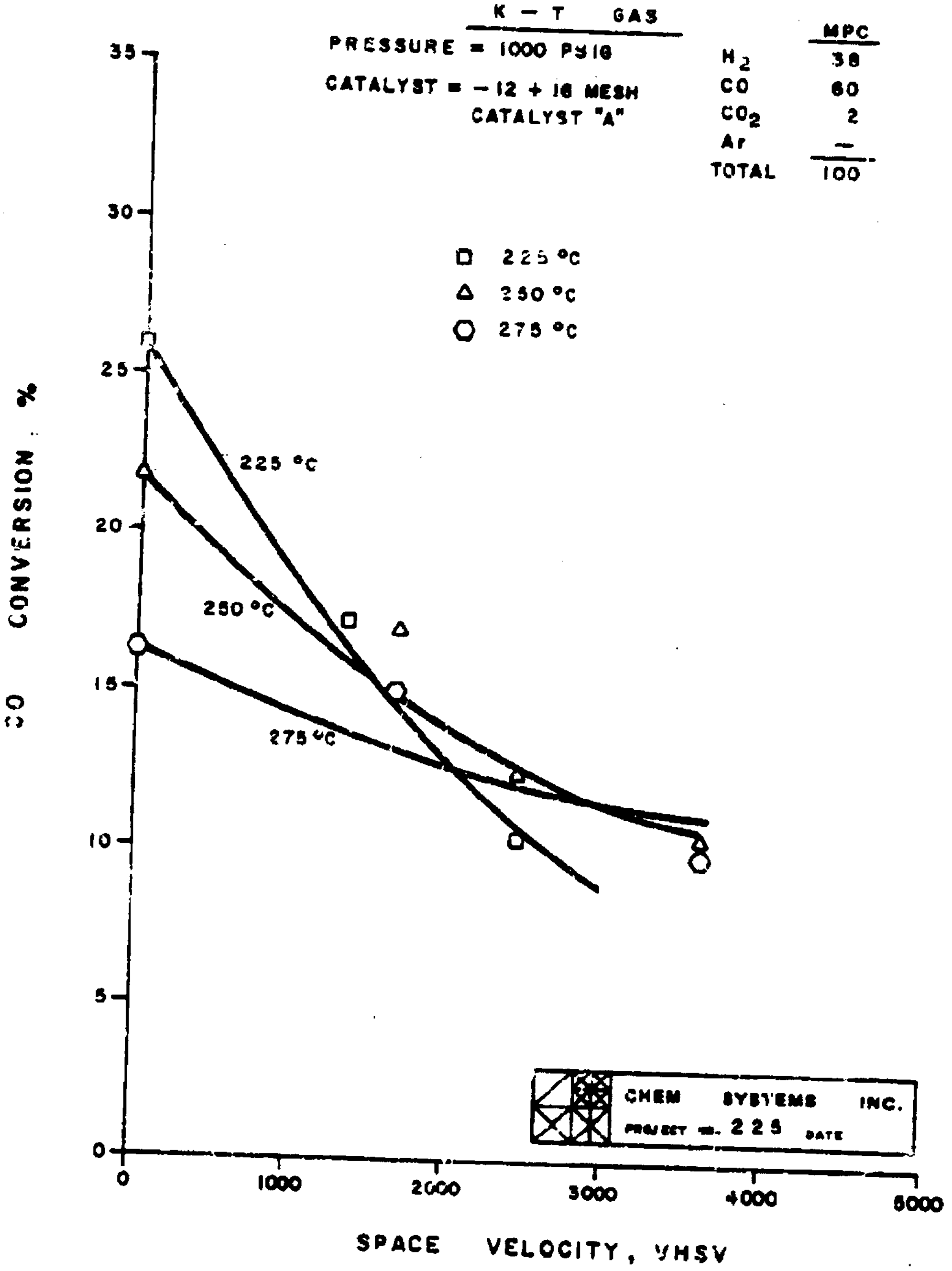


FIGURE 8-13

APPROACH TO EQUILIBRIUM VS. SPACE VELOCITY FOR A K-T FEED GAS AT 1000 PSIG WITH 12 - 16 MESH CATALYST A

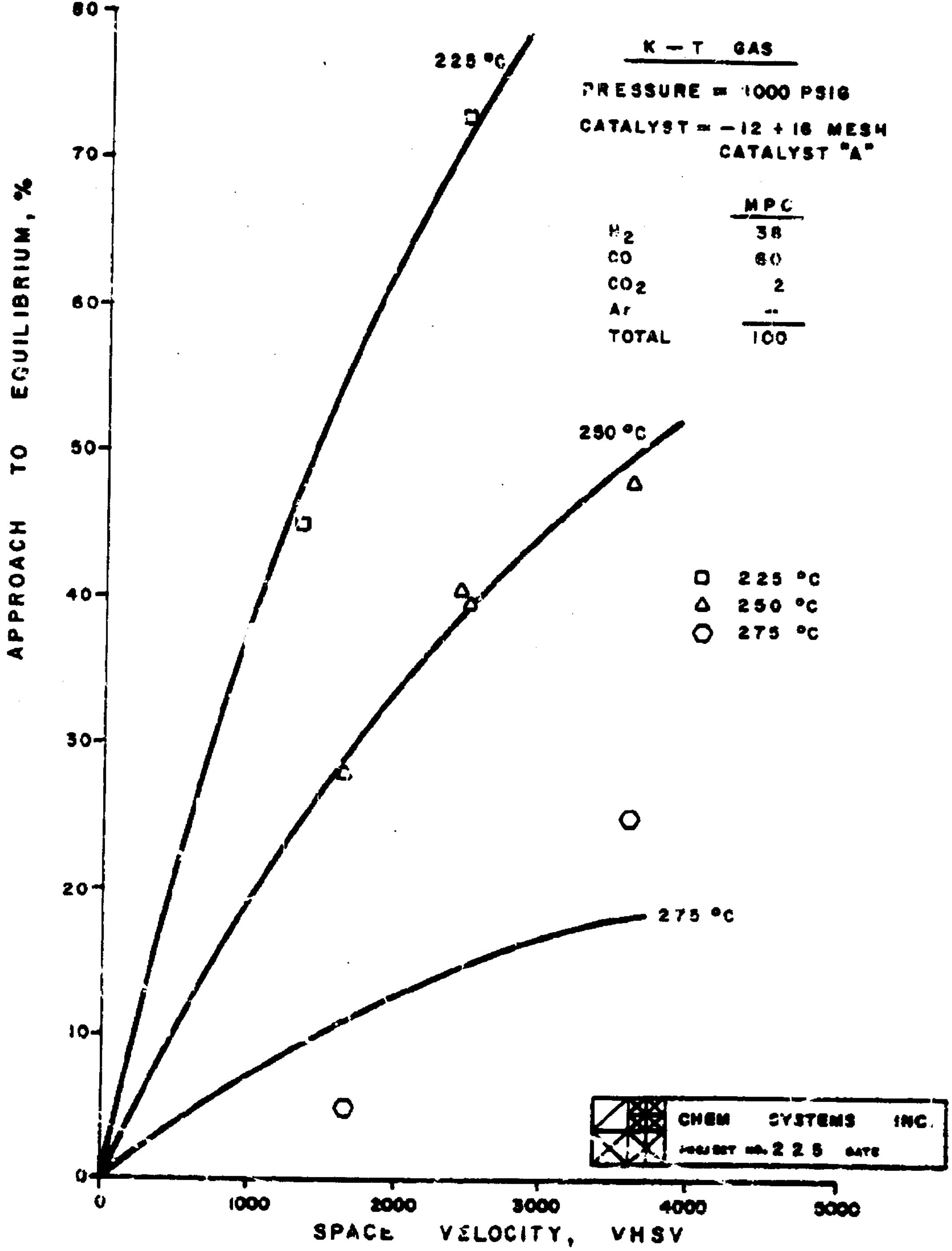


TABLE B-3

CHROMATOGRAPHIC ANALYSIS OF METHANOL SAMPLES
IDENTIFICATION OF MINOR COMPONENTS

COMPONENT	PDU CONTINUOUS RUN No. 1	PDU CONTINUOUS RUN No. 2	PDU CONTINUOUS RUN No. 3	BSU CONTINUOUS RUN No. 1
Methanol	98.00	95.90	96.20	92.70
Methyl Formate	0.20	0.25	0.18	0.09
Ethanol	0.20	0.25	0.31	0.45
i-Propanol	0.02	0.02	0.01	0.01
Methyl Acetate	0.02	0.04	0.04	0.03
n-Propanol	0.07	0.19	0.10	0.17
t-Butanol	0.01	0.01	0.01	0.01
sec-Butanol	0.02	0.03	0.03	0.04
i-Butanol	0.03	0.03	0.03	0.04
n-Butanol	0.04	0.04	0.06	0.09
t-Amyl Alcohol	0.07	0.02	0.01	0.01
2- and 3-Pentanol	0.02	0.02	0.03	0.13
i-Pentanol	0.03	0.01	0.01	0.03
1-Pentanol	0.02	0.01	0.02	0.04
C_6 and Higher Alcohols	0.02	0.02	0.02	0.06
Oil	0.67	1.58	1.86	1.40
Water	2.50	1.69	1.12	4.65
TOTALS	100.00	100.00	100.00	100.00

process oil. Small quantities of nearly fifteen co-products (whose total amounted to less than 1 weight percent) were also identified. The higher concentration of water and lower concentration of light components in the BSU product (as compared to the PDU products) is due to the repeated exposure to the atmosphere of the product tank over the thirty-day run period. The process liquid concentration for all of the samples are generally in line with the values obtained in previous runs and in calibrated solubility tests performed and documented in Section 8.

Koppers-Totzek

Subsequent long term BSU and PDU tests with a K-T feed gas yielded product alcohols which were substantially different from those obtained when using a Lurgi feed gas. Methanol content was lower, normally about 90 percent, with nearly 10 percent higher alcohols. Water content was less than 0.5 percent in all cases. Compositions of the K-T products are compared to a Lurgi gas product in Table 8-4.

LIQUID PHASE ACTIVITY COEFFICIENTS

During the study of the physical displacement of the methanol chemical equilibrium via flash vaporization (see Section 5), circulating process liquid samples were collected and analyzed for MeOH content. The data were evaluated to determine the effective methanol/process liquid activity coefficients according to the relationship:

$$\frac{Y}{X} = \frac{\gamma P^*}{P_T} = K$$

where:

Y = Mole fraction MeOH in the vapor

X = Mole fraction MeOH in the liquid

P^* = Vapor pressure of MeOH

P_T = Total system pressure

γ = Activity coefficient of MeOH/oil system: ratio of the actual partial pressure to the partial pressure which could occur if Raoult's law were obeyed

TABLE 8-4

CHROMATOGRAPHIC ANALYSIS OF METHANOL SAMPLES: EFFECT OF FEED GAS
(Composition; wt%)

	Lurgi Gas	Koppers-Totzek	
Component	BSU	BSU	PDU
Methanol	96.16	91.44	89.60
Methyl Formate	0.17	0.24	0.39
Ethanol	0.32	2.55	2.46
i-Propanol	tr	tr	tr
Methyl Acetate	0.07	0.78	1.02
n-Propanol	0.14	1.23	1.31
C_4 Alcohols	0.23	1.43	2.67
C_5 Alcohols	0.33	1.40	1.14
C_{6+} Alcohols	0.06	0.55	1.09
Water	2.71	0.51	0.33

The activity coefficients determined in this manner are summarized in Table 8-5. As expected, the activity coefficients for the mineral oil system are on the order of 2-3 times greater than that calculated for the aromatic oil system. Therefore, for a given MeOH vapor phase concentration, the corresponding MeOH liquid phase concentration will be substantially lower in mineral oil process liquid as compared to an aromatic process liquid.

SOLUBILITY OF MINERAL OIL IN METHANOL-WATER

The solubility of mineral oil in the condensed methanol product is a function of both temperature and water content of the methanol. Water can be produced by the reaction of CO_2 to form methanol.

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$$

It is possible, with partial oxidation gases (which are hydrogen deficient) to operate in a nearly water-free system (e.g., with water concentrations in the methanol product of 0-1 weight percent).

Mineral oil in the methanol product can be removed by either flashing the methanol product or passing it over a carbon absorption bed. In some instances, however, this separation may not be warranted, and the loss rate of oil solvent would have to be ascertained.

The solubility of oil in methanol in the presence of different amounts of H_2O was measured. Five mixtures of 1:1 methanol to Witco 40 oil were prepared containing 0, 0.5, 1, 2.5, and 5 percent H_2O. The mixtures were shaken for five minutes, then left to separate in a constant temperature environment for two to twenty-four hours.

Quantitative analytical standards of oil in methanol and cyclohexane were prepared covering the range from 0.2 to 2.0 percent. Standard injection technique was used to calculate the concentration of oil in methanol layer.

TABLE 8-5

ACTIVITY COEFFICIENTS

Run No.	Catalyst/Liquid System	T, °C	P, atm	P*, atm	Y	X	
50-2	Catalyst A/Witco 40	235	69.0	74.7	0.0901	0.0346	2.40
52-1	Catalyst A/Witco 40	235	69.0	74.7	0.0560	0.0187	2.86
53-1	Catalyst A/Exxon 150	235	35.0	74.7	0.0522	0.0297	0.82
54-1	Catalyst A/Exxon 150	235	69.0	74.7	0.119	0.0726	1.51
55-2	Catalyst A/Exxon 150	250	69.0	95.0[a]	0.109	0.0786	1.00
56-2	Catalyst A/Exxon 150	220	69.0	57.5	0.0636	0.0718	1.06

(a) Estimated.

The solubilities of mineral oil in methanol containing, 0, 1.0, 2.0, 5.0, and 10.0 weight percent water at 20°F, 70°F, and 120°F are listed in Table 8-6 and presented graphically in Figure 8-14. As expected, increased water concentration and lowered temperatures reduce the oil's solubility.

GAS SOLUBILITY IN MINERAL OIL

The experiments performed during the flash vaporization tests (see Section V) provided data on gas component solubility at reaction process conditions. By comparing the "flash gas" flow rate and composition with the component partial pressures prior to flashing the component Henry's Law constant H_i (atm/mole fraction) were calculated using the following equation:

$$H_i = \frac{p_i^*}{\left[Y_{F_i} V\left(\frac{P_T}{P_T-P_F}\right)\right] \Big/ \left[L + V\left(\frac{P_T}{P_T-P_F}\right)\right]}$$

where, P_T = Total pressure prior to flashing; atm
P_F = Flash pressure level; atm
p_i^* = Component partial pressure over liquid prior to flashing; atm
Y_{F_i} = Component composition of "flash" gas; mole fraction
L = Flash oil flow rate; gm mole/hr
V = Flash gas flow rate; gm mole/hr
$V\left(\frac{P_T}{P_T-P_T}\right)$ = Total gas disolved in flash oil; gm mole/hr

All the process runs (Run 137-1 through Run 160-21) during the flash vaporization test series were examined. Individual component Henry's Law constants were calculated, and the averaged values are presented in Table 8-7.

More than 90 percent of the calculated values lie within a 10 percent scatter band.

TABLE 8-6

SOLUBILITY OF WITCO 40 MINERAL OIL IN METHANOL-WATER SOLUTIONS

		WEIGHT % OIL SOLUBLE IN MeOH		
MIXTURE No.	H_2O% BASED ON MeOH WT.	AT 20°F	AT 70°F	AT 120°F
1	.0	1.4	2.9	7.2
2	1.0	1.1	1.9	5.0
3	2.0	0.9	1.5	3.1
4	5.0	0.5	1.3	2.1
5	10.0	0.3	0.4	0.5

FIGURE 8-14

OIL SOLUBILITY IN METHANOL

WITCO 40 MINERAL OIL

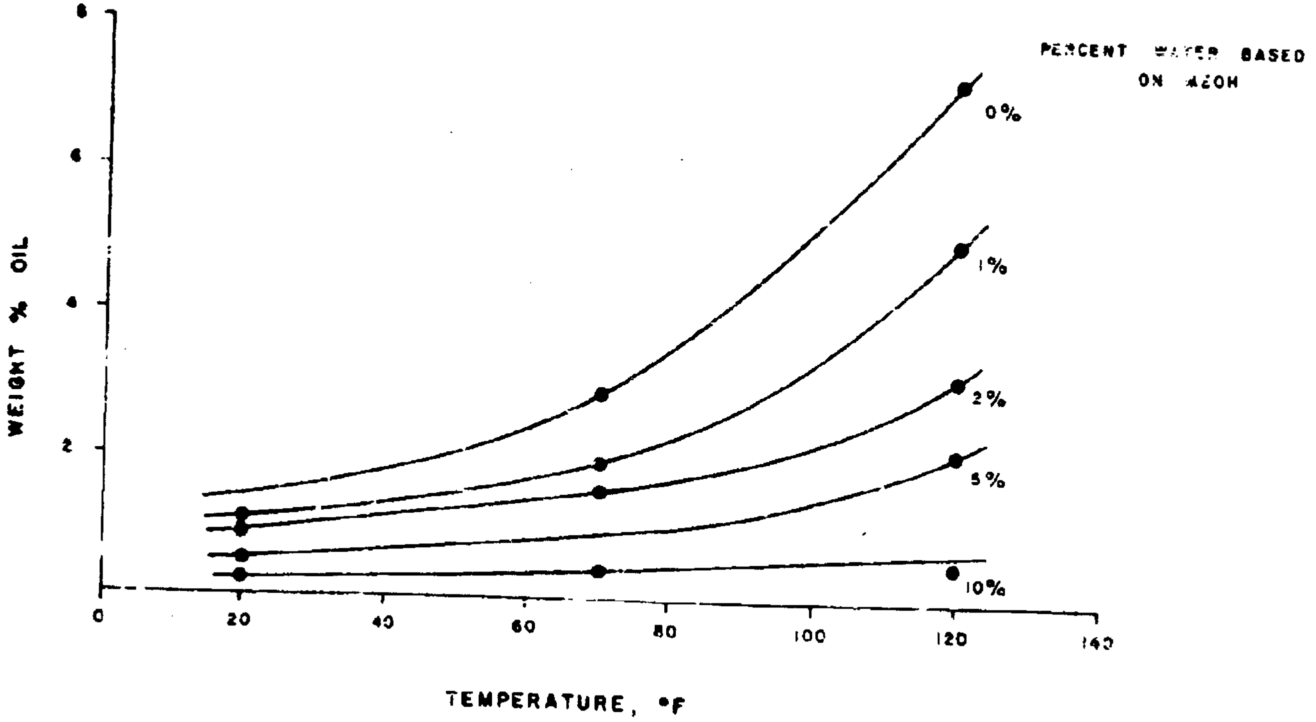


TABLE 8-7

COMPONENT HENRY'S LAW CONSTANTS IN WITCO 40 MINERAL OIL AT 230-250°C

	CSI Experimental H_i; atm/mole fraction	Method of Osburn and Markovic (1) H_i; atm/mole fraction	Literature Value for n-$C_{20}H_{42}$ H_i; atm/mole fraction
H_2	490	600	860 (3) at 150°C (n-$C_{12}H_{26}$)
CH_4	365	110	220 (2) at 200°C
			275 (3) at 150°C
CO	435	230	550 (3) at 60°C (n-$C_{10}H_{22}$)
CO_2	335	--	165 (3) at 100°C

Witco 40 Properties

Molecular Weight = 250
Density at 20°C = 0.81 gm/cm^3
230 - 250°C = 0.62 gm/cm^3
Surface Tension at 20°C = 32 dyne/cm
230 - 240°C = 13 dyne/cm

(1) J.O. Osburn and P.L. Markovic; Chem. Eng. Aug. 25, 1969, pp. 105-108.

(2) C.C. Chappelow and J.M. Prausnitz; AIChEJ, 20 (6), Nov. 1974, pp. 1097-1103.

(3) Institute of Gas Technology - Coal Conversion Databook.

As a basis for comparison, Table B-7 also contains Henry's Law values as predicted by the method of Osburn and Markovic, and experimental values of gas solubility in similar liquids, such as n-decane or n-eicosane. While the absolute values methods vary greatly for each method, all predict the same relative solubilities among the components. In the order of increasing solubility, they are;

$$H_2 < CO < CH_4 < CO_2$$