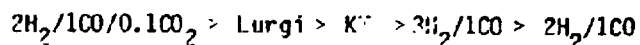


one base case with the Lurgi feed gas was repeated (compare Runs 36-2 and 47-2). The respective conversions were 41.0 and 29.2 percent; these values are consistent with the estimated catalyst loss. Nevertheless, the results indicate distinct differences in performance due to the difference in feed compositions. Figures 4-4 and 4-5 present the raw data for the -12 +16 mesh particles and Figures 4-6, -7, -8 and -9 present the raw data for the -16 +20 mesh particles. Summary curves for the methanol productivity for all the various feed compositions are shown in Figures 4-10 and 4-11. Neglecting differences in absolute reaction rates due to particle size differences, the relative reaction rates as a function of feed gas composition are, in decreasing order:

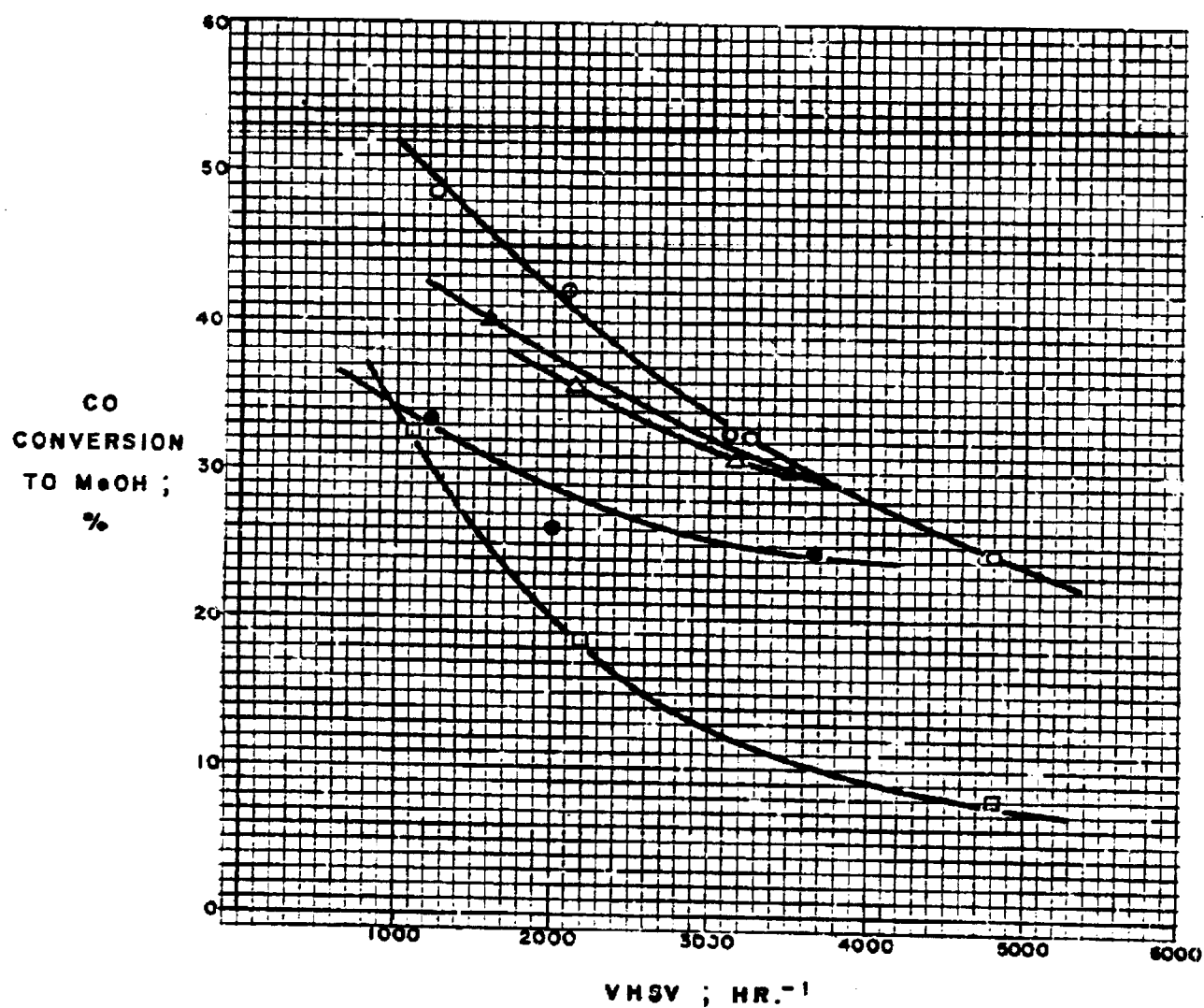


These results confirm previously published work in the respect that CO_2 in the feed gas appears to behave as a catalyst promoter, significantly boosting CO conversion levels while passing through the reactor without measurably reacting itself. The data also strongly indicate that feed gases containing H_2 and CO in the correct stoichiometric ratio ($\text{H}_2/\text{CO}=2$) give superior productivity when compared to those with much lower H_2/CO ratios, such as a KT feed gas ($\text{H}_2/\text{CO} = 0.63$). This is probably a result of the reduced H_2 concentration at the required conversion levels. In addition, while both the $2\text{H}_2/\text{CO}/0.1\text{CO}_2$ and Lurgi feed gases contain the correct stoichiometric ratio, the higher productivity of the $2\text{H}_2/\text{CO}/0.1\text{CO}_2$ feed gas appears to be due solely to its higher concentration of reacting gas (97 percent CO and H_2 vs. 75 percent CO and H_2), indicating that a CO_2 level of as little as 3 percent is sufficient to promote the MeOH reaction.

Effect of Temperature

The MeOH productivity as a function of temperature is presented in Figures 4-12 and -13 for the -12 +16 mesh particles and in Figures 4-14, -15, -16 and -17 for the -16 +12 mesh particles. In all cases, the

FIGURE 4-4
CONVERSION WITH LURGI GAS
 CATALYST A (-12 + 16 MESH) / WITCO 40
 1000 PSIG

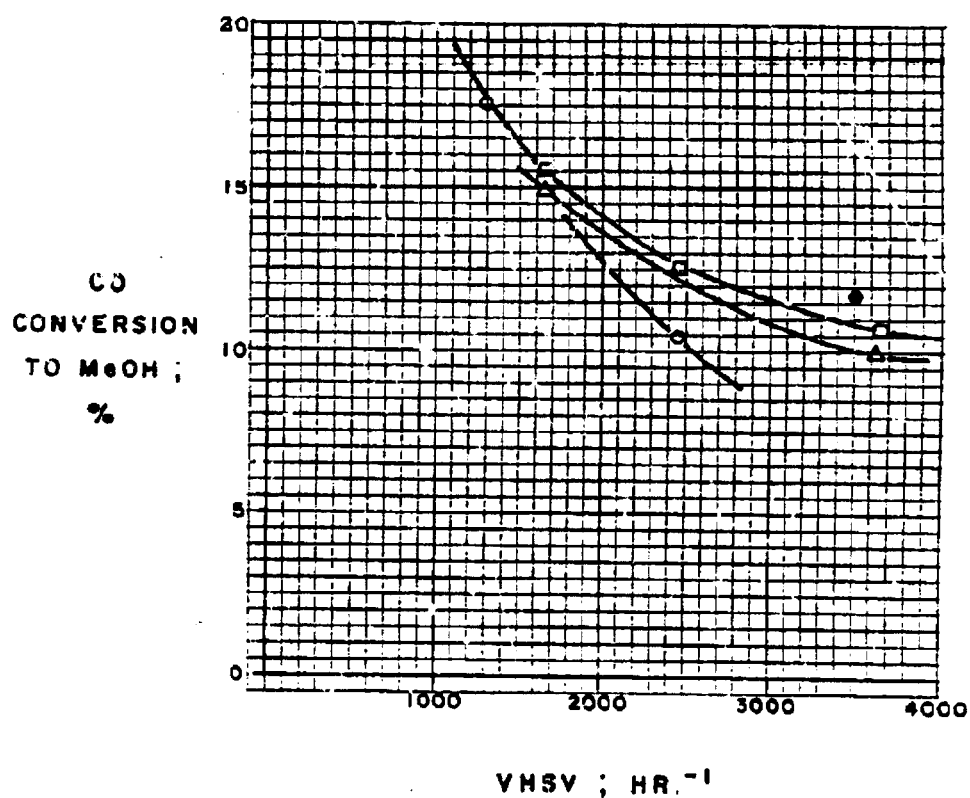


	T ; °C
□	220
○	225
▲	235
△	250
◆	275

FIGURE 4-5

CONVERSION WITH KT GAS

CATALYST A (-12+ 16 MESH) / WITCO 40
1000 PSIG

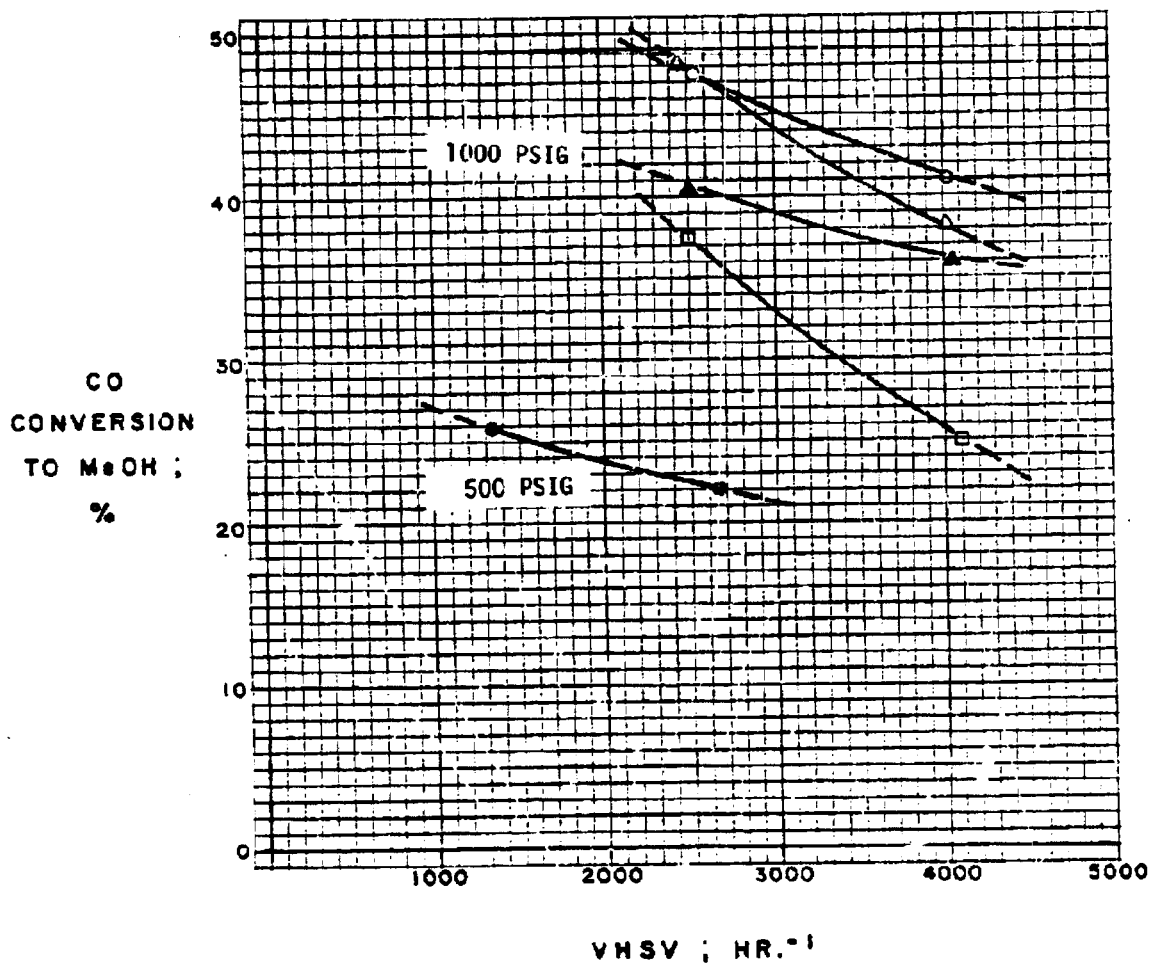


	T , °C
○	225
●	235
□	250
△	275

FIGURE 4-6

CONVERSION WITH LURGI GAS

CATALYST A (-16+20 MESH) / WITCO 40



T ; °C	
□	200
△	220
○ ●	235
▲	250

FIGURE 4-7

CONVERSION WITH KT GAS

CATALYST A (-16+20 MESH) / WITCO 40

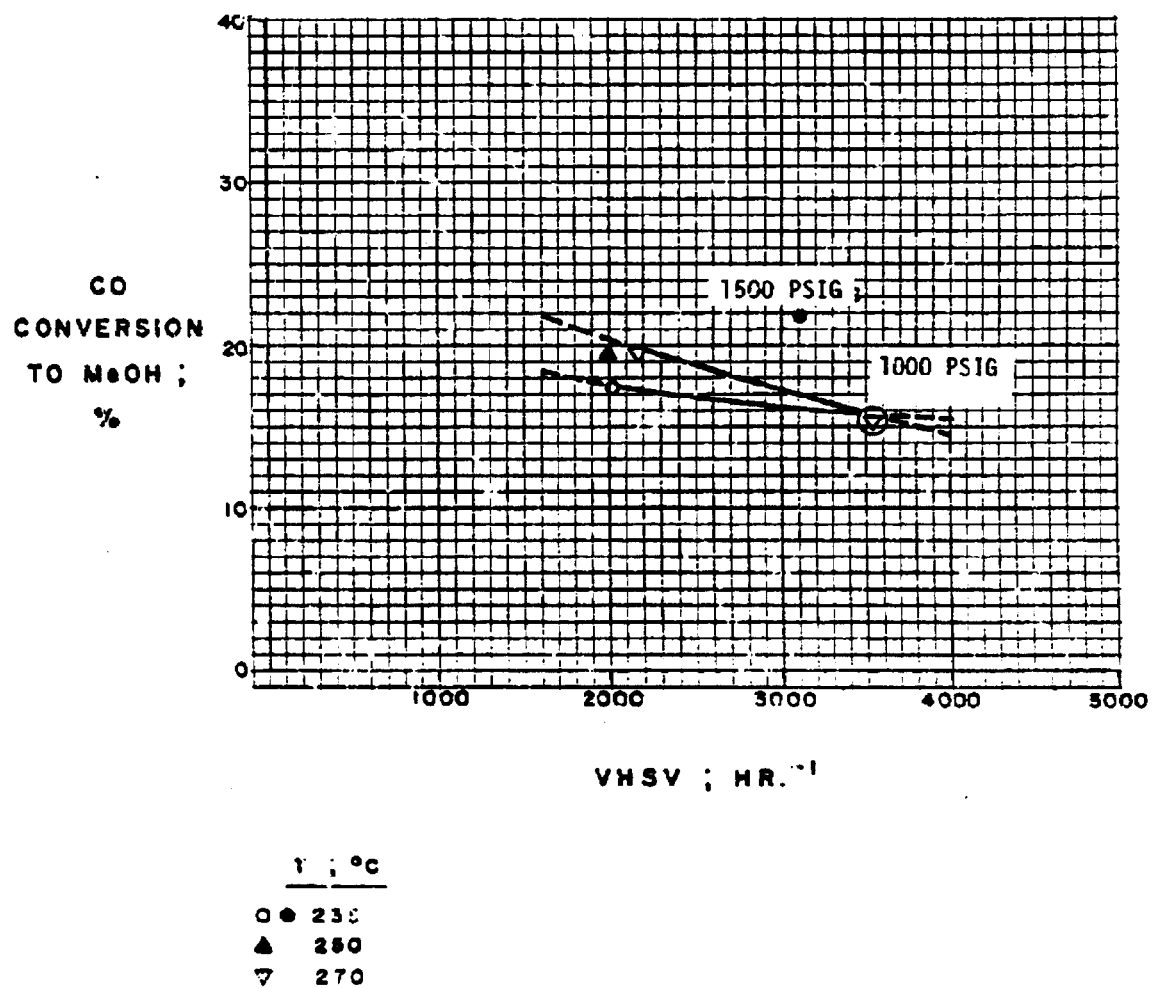


FIGURE 4-8

CONVERSION WITH $2\text{H}_2/\text{ICO}/0.1\text{CO}_2$ GAS

CATALYST A (-16+20 MESH) / WITCO 40
1000 PSIG

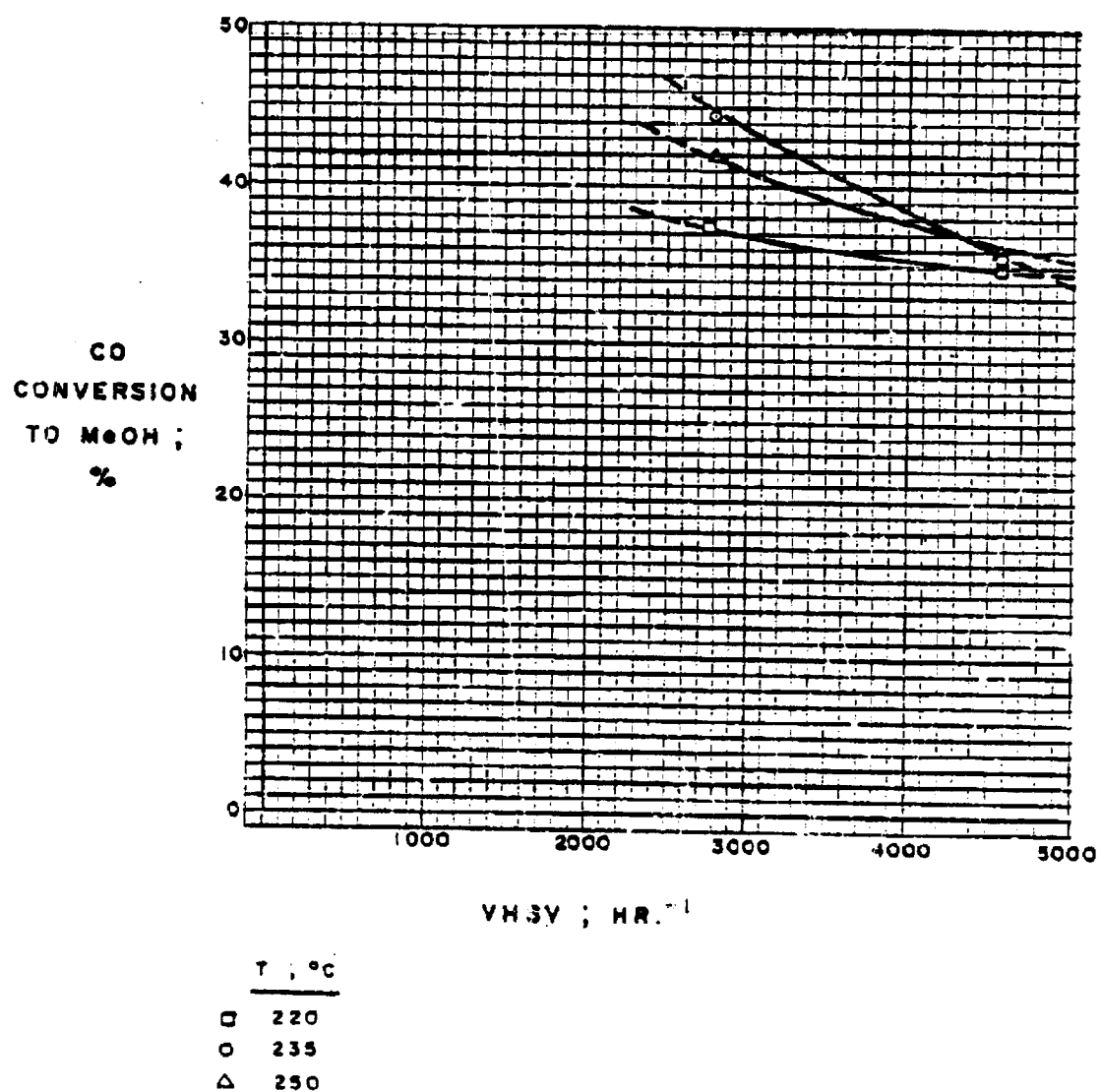
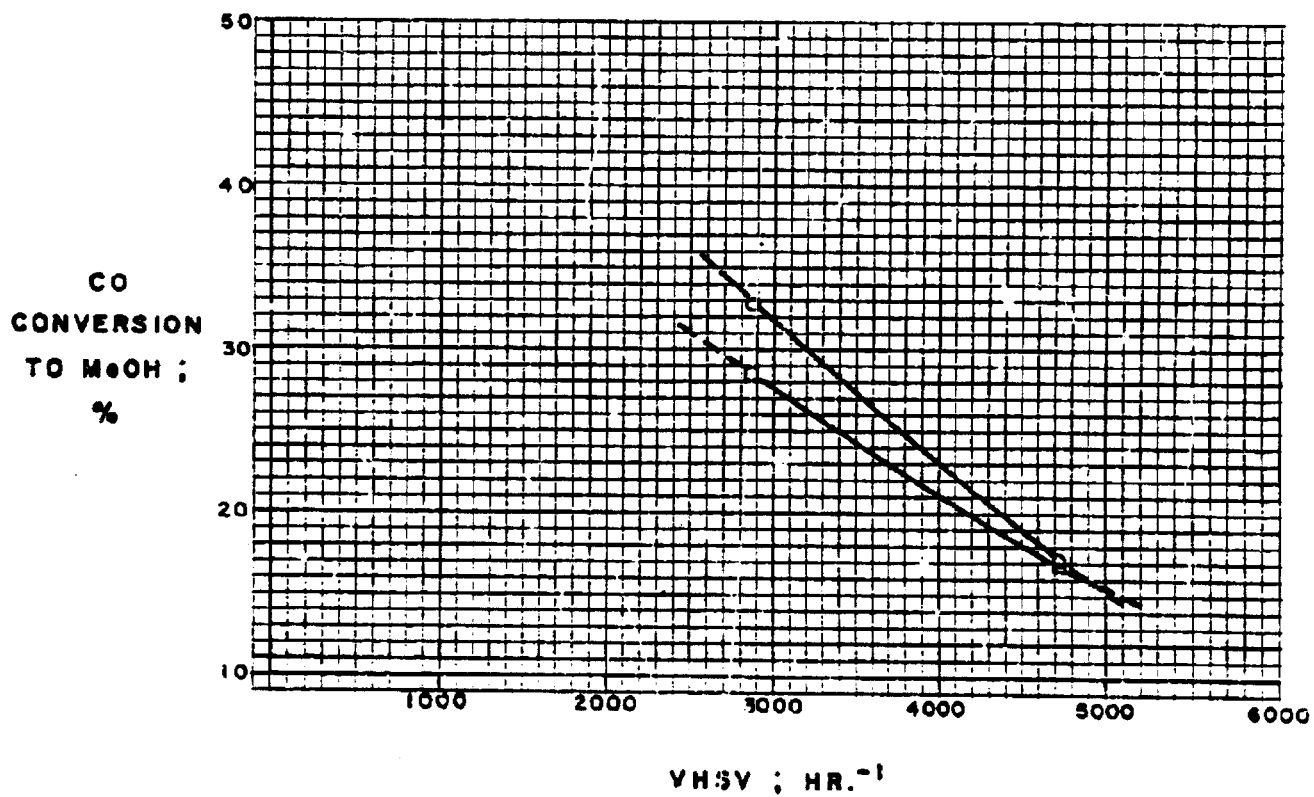


FIGURE 4-9

CONVERSION WITH $2H_2/CO$ GAS

CATALYST A (-16+20 MESH) / WITCC 40
1000 PSIG



T ; °C
○ 220
□ 235

FIGURE 4-10

MEOH PRODUCTIVITY FOR VARIOUS SYNTHESIS GASES

CATALYST A (-12 + 16 MESH) / WITCO 40
1000 PSIG 225°C

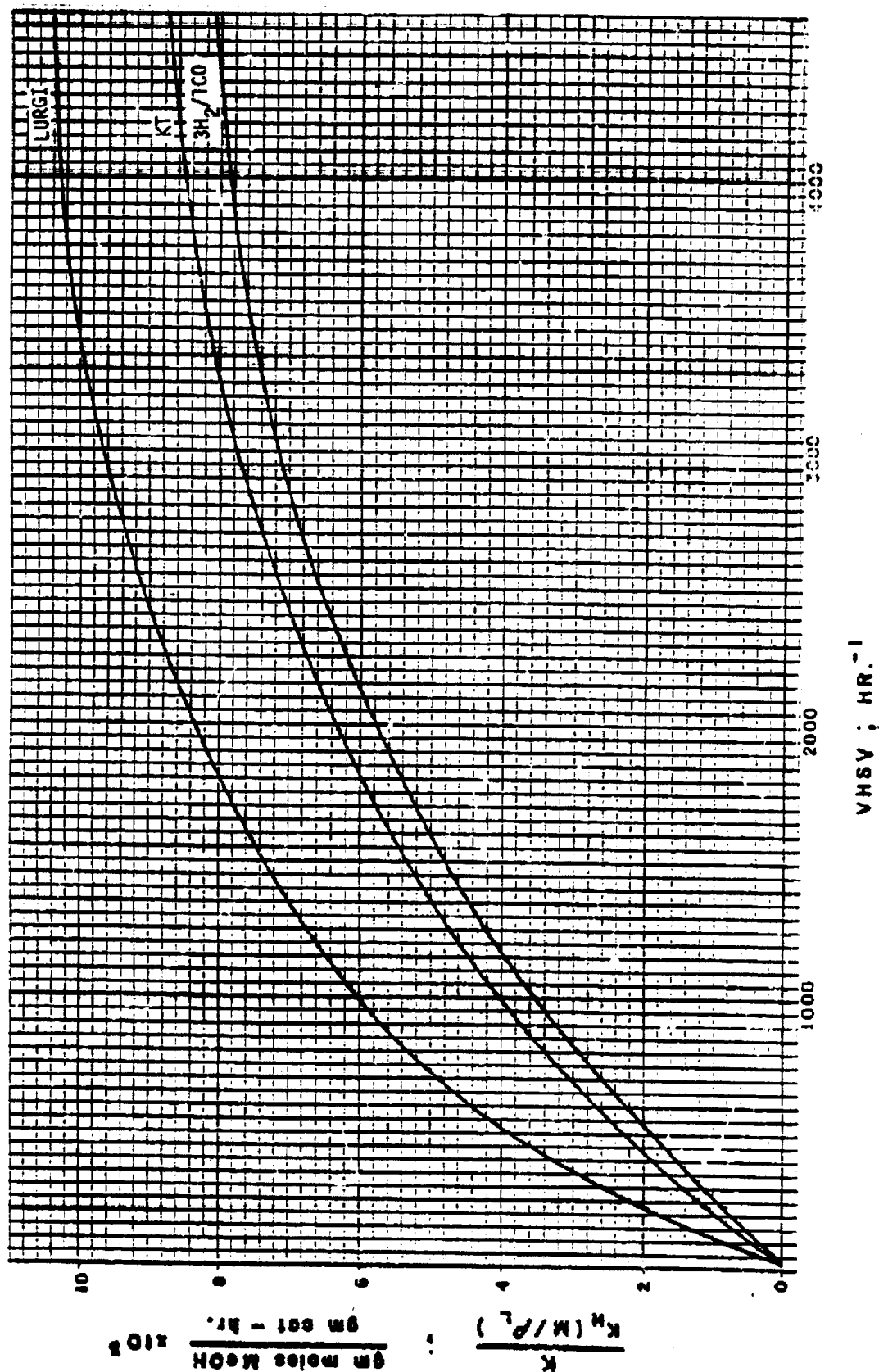


FIGURE 4-11

MeOH PRODUCTIVITY FOR VARIOUS SYNTHESIS GASES

CATALYST A (-16+20 MESH) / WITCO 40
1000 PSIG 235°C

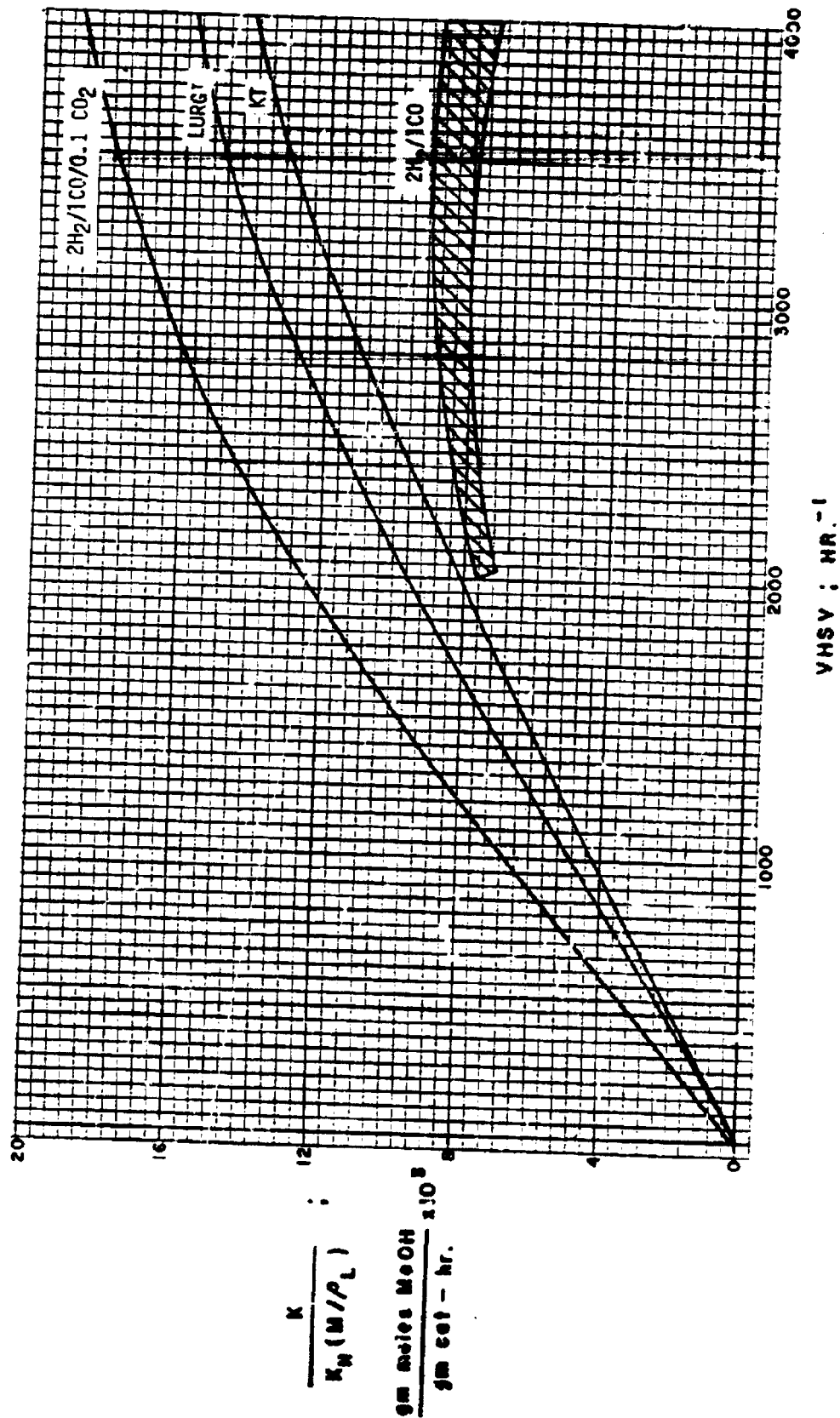


FIGURE 4-12

EFFECT OF TEMPERATURE WITH LURGI GAS

CATALYST A (-12 + 16 MESH) / WITCO 40
1000 PSIG

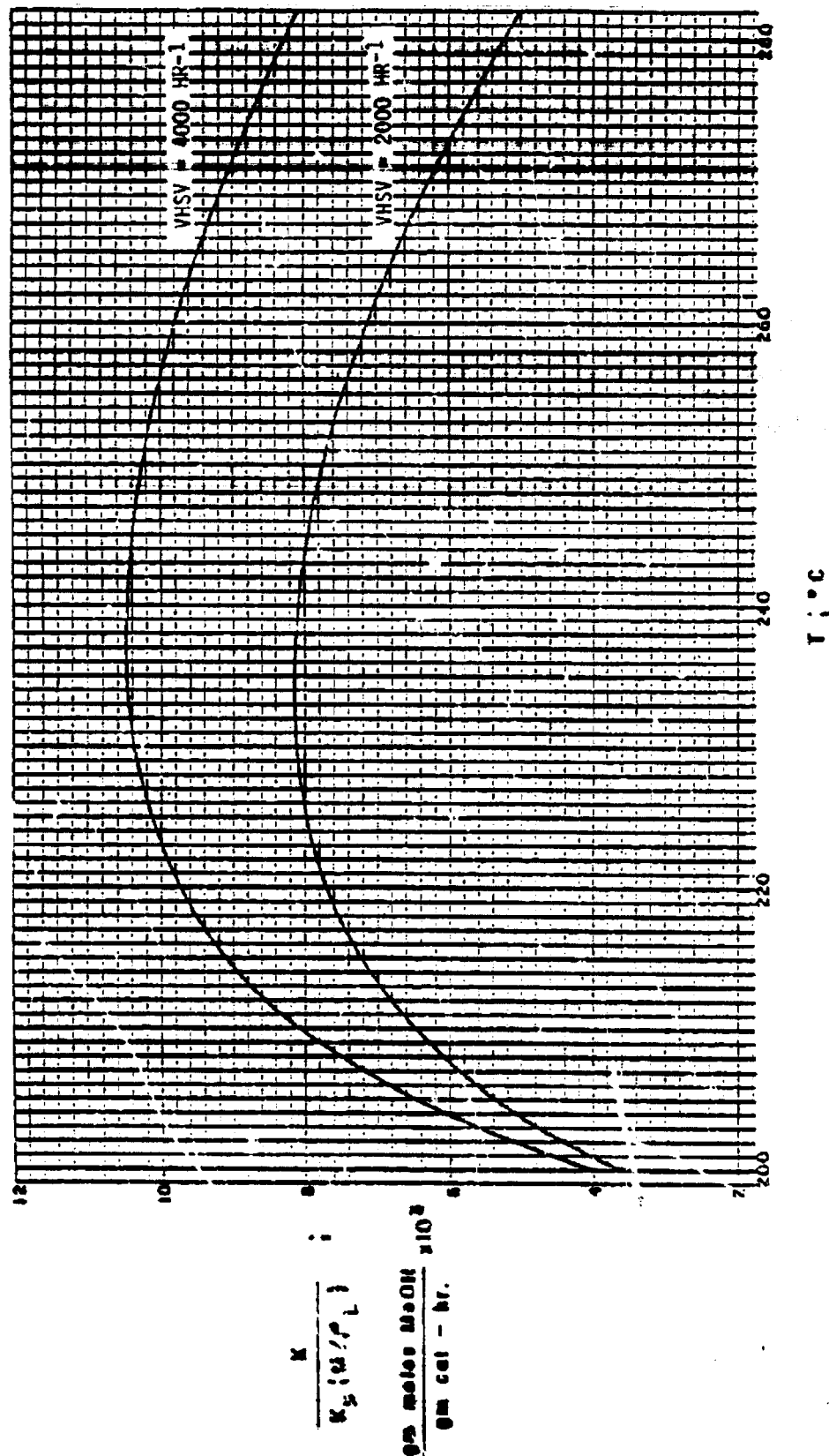
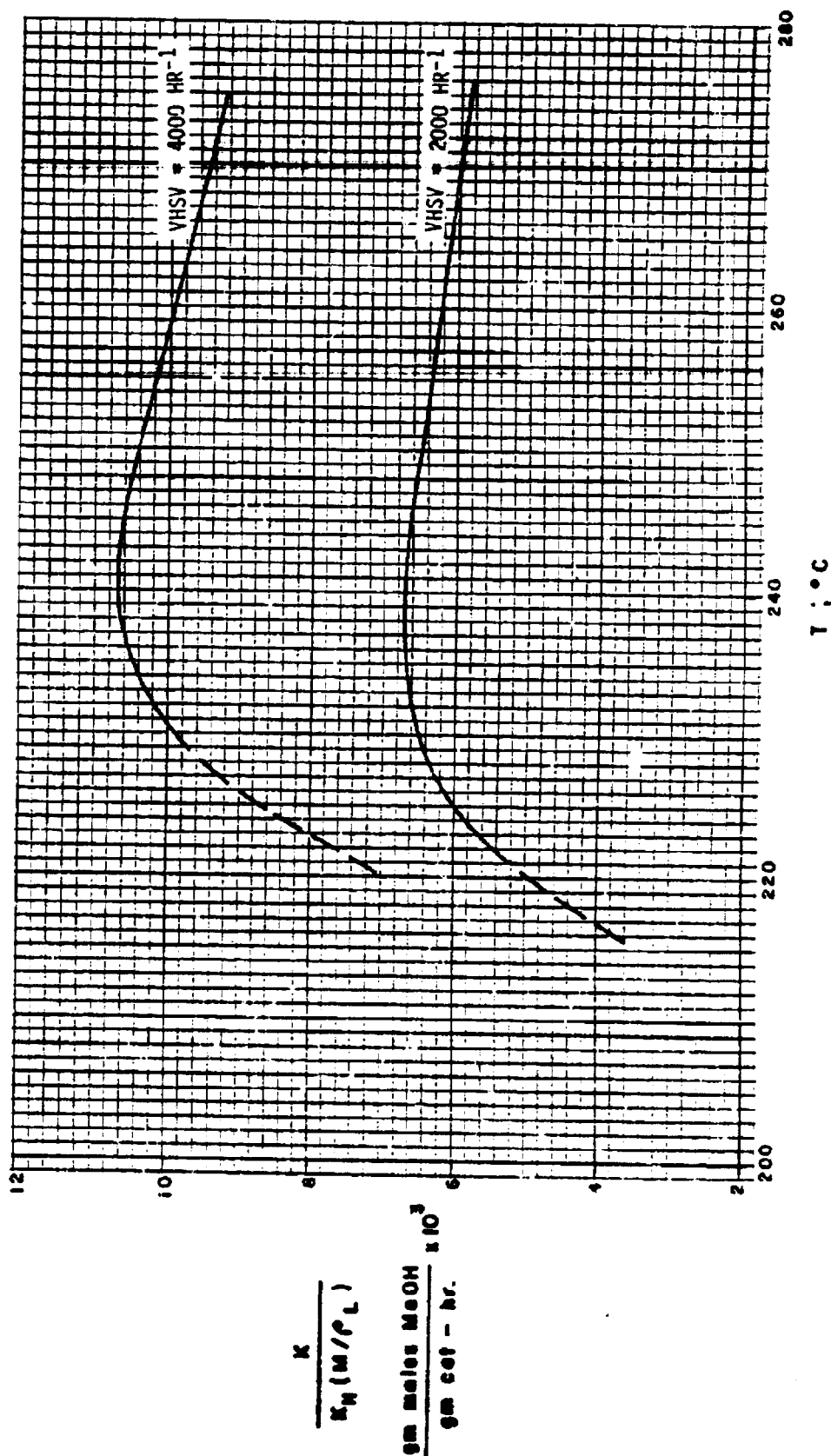


FIGURE 4-13

EFFECT OF TEMPERATURE WITH KT GAS

CATALYST A (-16+20 MESH) / WITCO 40
1000 PSIG



$$\frac{K}{K_H (M/P_L)}$$

$$\frac{\text{gm moles MeOH}}{\text{gm cat} - \text{hr.}} \times 10^3$$

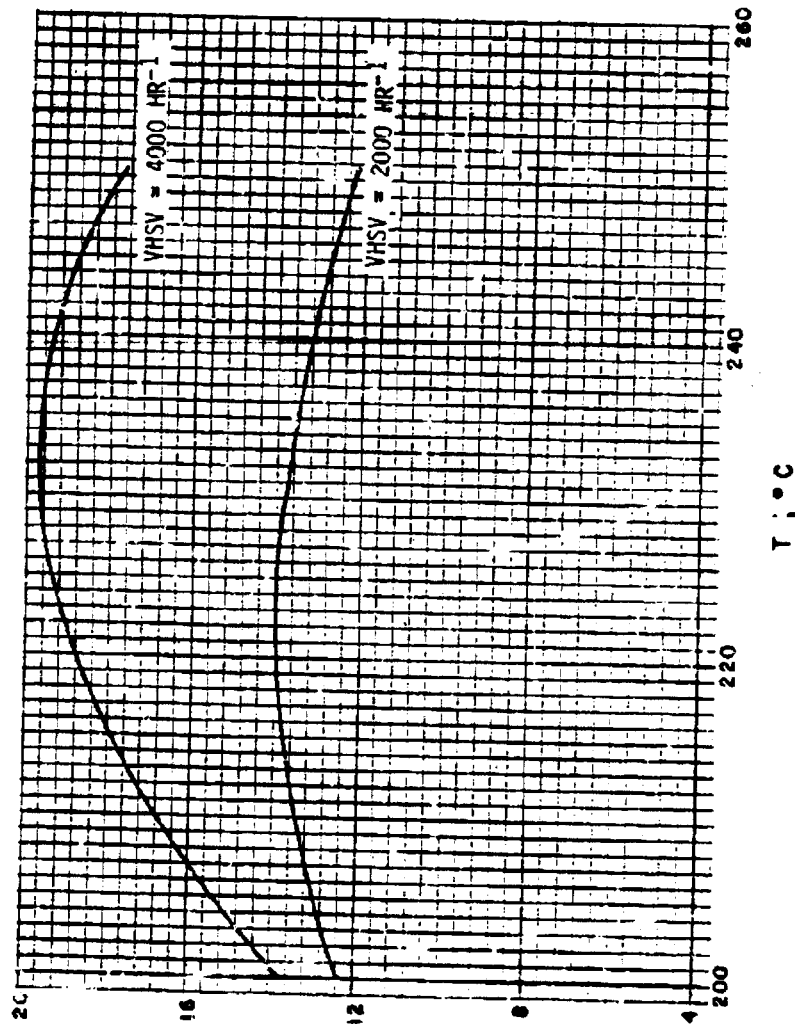
FIGURE 4-14

EFFECT OF TEMPERATURE

WITH

LURGI GAS

CATALYST A (-16+20 MESH) / WITCO 40
1000 PSIG



$$\frac{K}{K_H (M/P_L)}$$

$$\frac{\text{gm moles MeOH}}{\text{gm cat} \cdot \text{hr.}} \times 10^3$$

FIGURE 4-15

EFFECT OF TEMPERATURE

WITH

KT FEED GAS

CATALYST A (-16+20 MESH) / WITCO 40

1000 PSIG

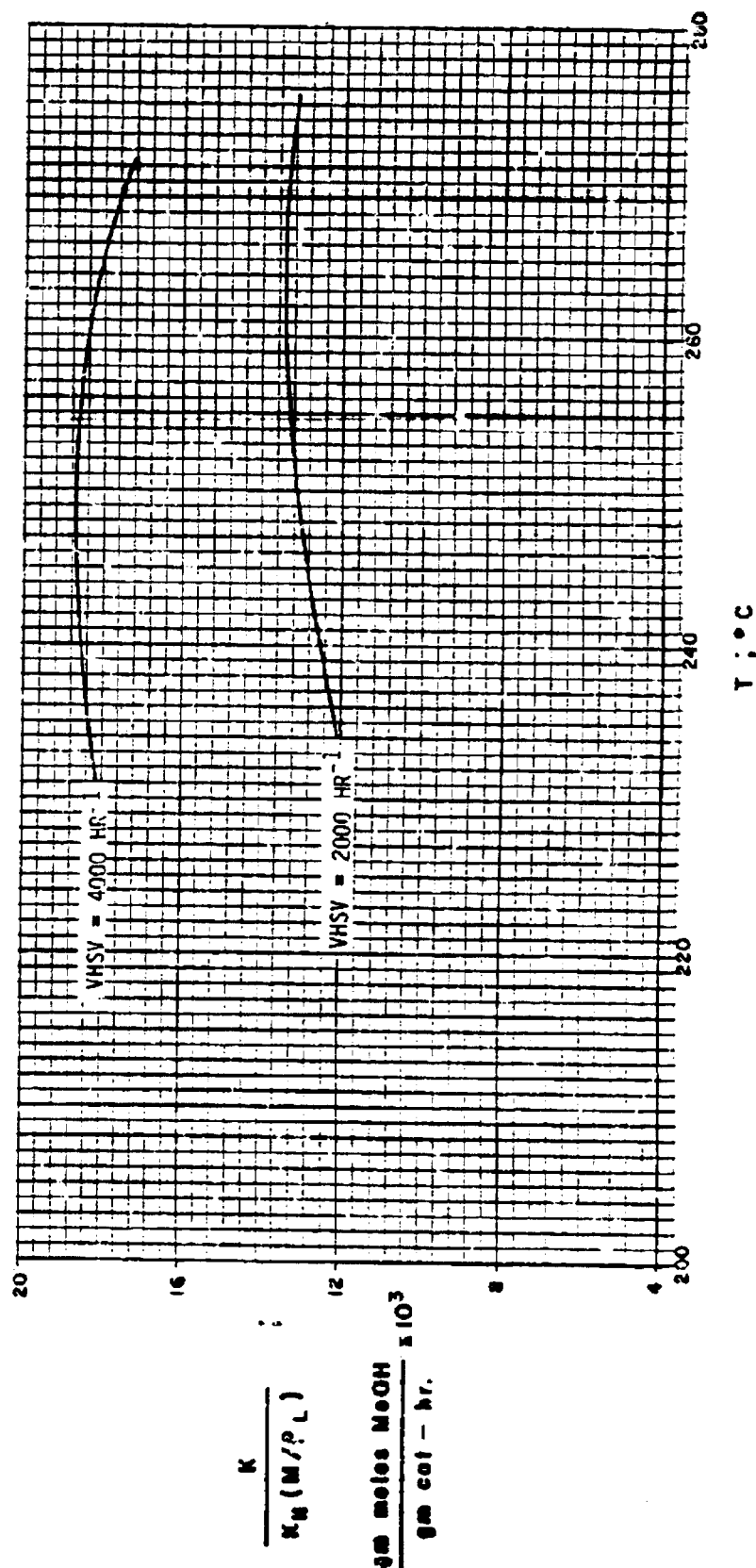


FIGURE 4-16

EFFECT OF TEMPERATURE
WITH
 $2\text{H}_2 / 1\text{CO} / 0.1\text{CO}_2$ FEED GAS
CATALYST A (-16+20 MESH) / WITCO 40
1000 PSIG

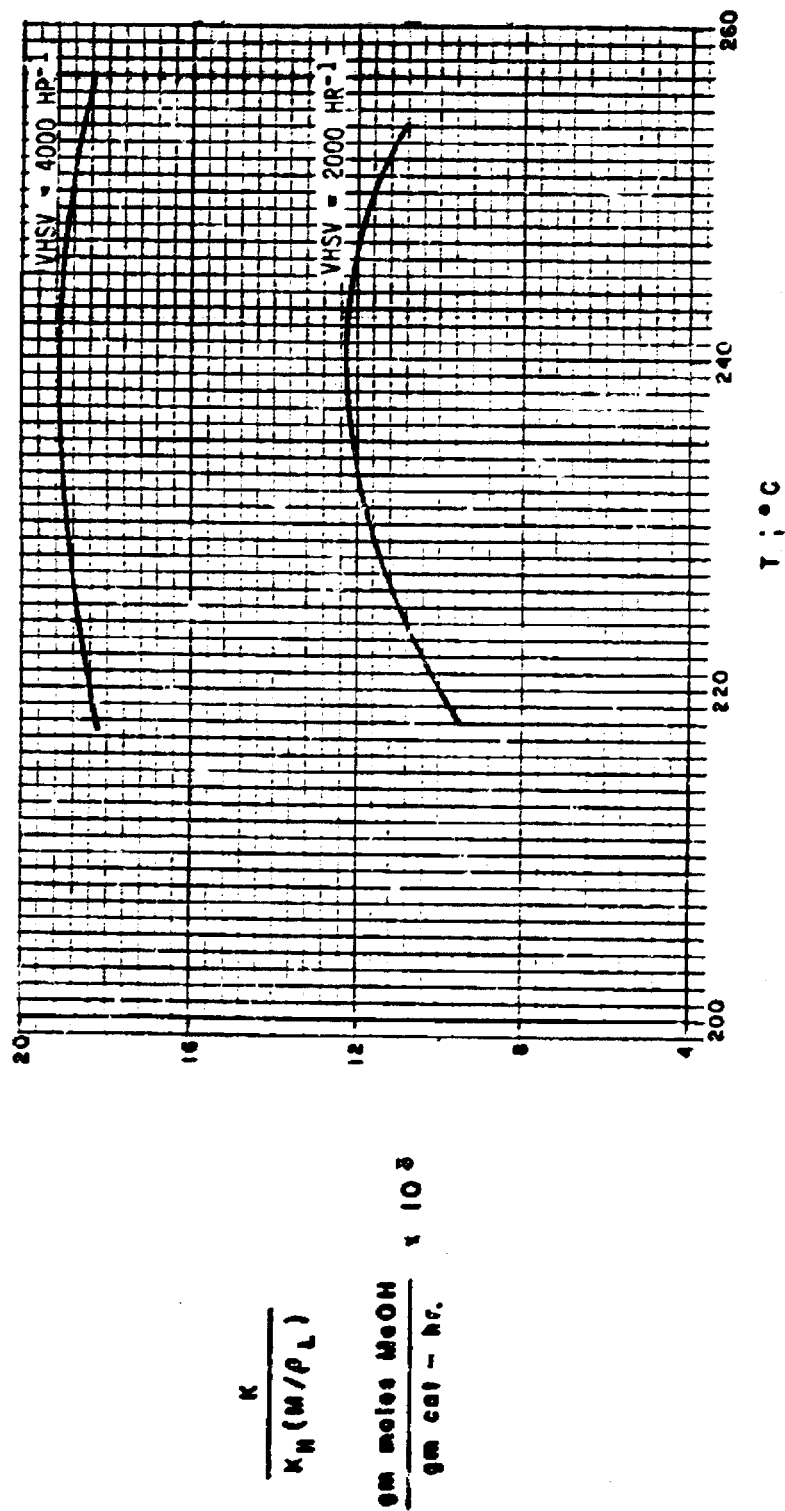


FIGURE 4-17

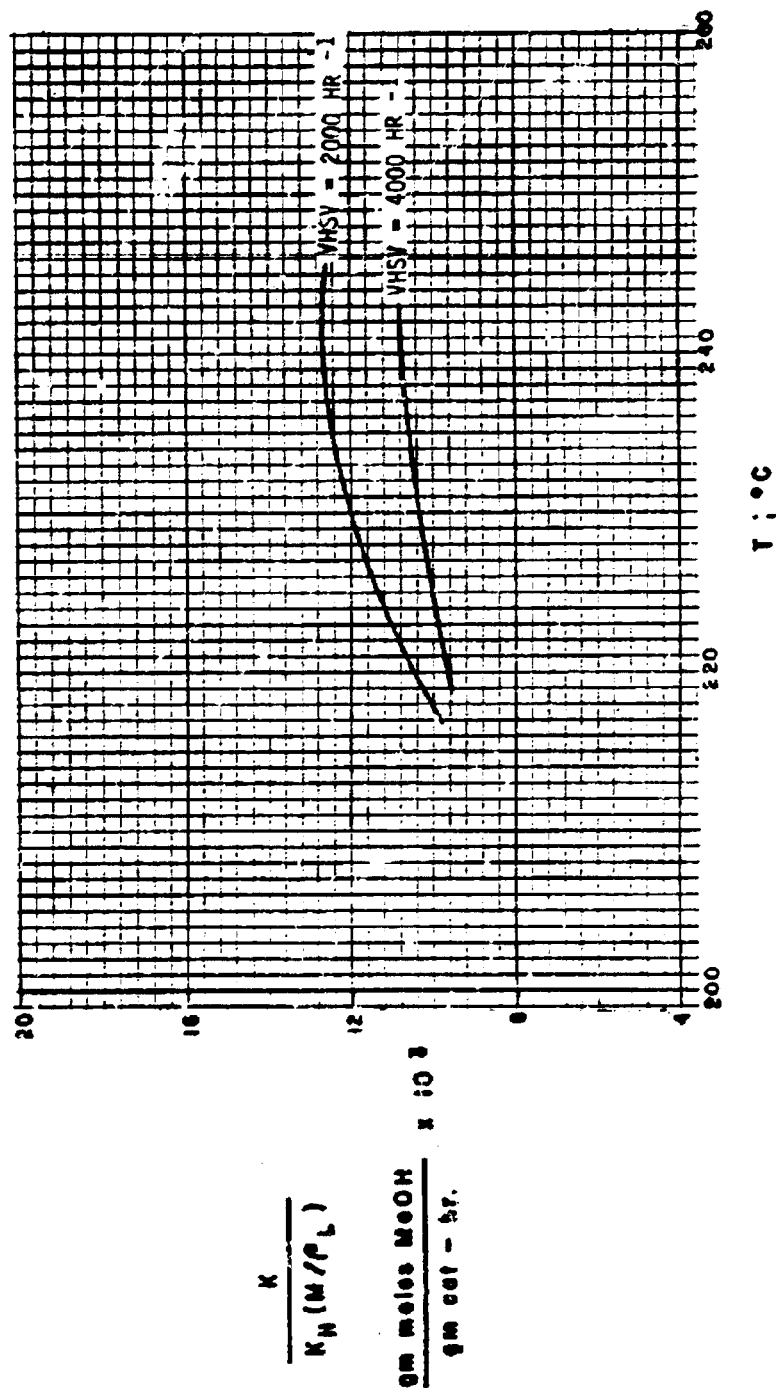
EFFECT OF TEMPERATURE

WITH

$2H_2/1CO$ FEED GAS

CATALYST A (-16+20 MESH) / WITCO 40

1000 PSIG



productivity curve forms a broad maximum over the 230-250°C temperature range, with the more reactive systems favoring the lower temperatures and vice versa. At lower temperatures, the productivity is limited by the catalyst activity, while at the higher temperatures, equilibrium constraints are responsible for the drop in productivity.

Effect of Pressure

Figures 4-18 and 19 present the data for the comparison runs performed at both lower (500 psig) and higher (1,500 psig) pressure levels. In general, the conversion is proportional to the reaction pressure. Examination of the equilibrium curves for these reaction conditions indicates that despite the change in the absolute conversion levels, the approach to equilibrium remains on the order of 50-80 percent over a VHSV range of from 2000-4000 hr⁻¹.

Effect of Particle Size

Figure 4-20 presents the summary results for both the Lurgi and KT feed gases under constant reaction conditions for both the -12 +16 mesh and -16 +20 mesh particle sizes. In both cases, the reaction rates for the smaller size particles are some 30-50 percent greater than those obtained with the larger particles. A similar experience with the analogous liquid phase methanation system was attributed to pore diffusion limitations for the larger sized particles. A more accurate interpretation of these results will depend on future ability to formulate the catalyst particles into a more regular particle shape.

Throughout these runs with the smaller particle size, highly erratic feed gas flow was experienced which was eventually traced to the existence of a partial catalyst plug at the reactor exit. This plug resulted in high pressure surges with each stroke of the positive displacement circulating oil pump causing a corresponding surge in the feed gas flow. All attempts to back flush the reactor were unsuccessful and ultimately the

FIGURE 4-18

EFFECT OF PRESSURE

CATALYST A (-12+16 MESH) / WITCO 40

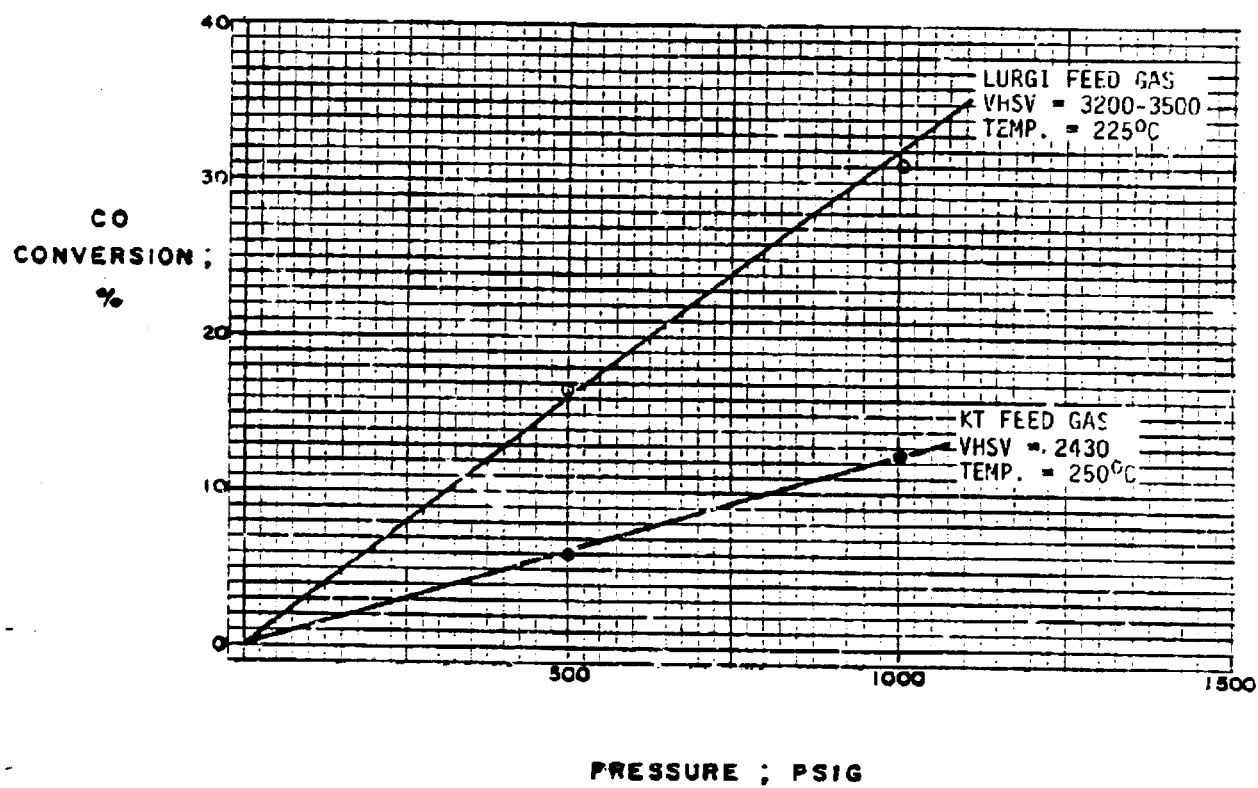


FIGURE 4-19

EFFECT OF PRESSURE

CATALYST A (-16+20 MESH) / WITCO 40

235 °C

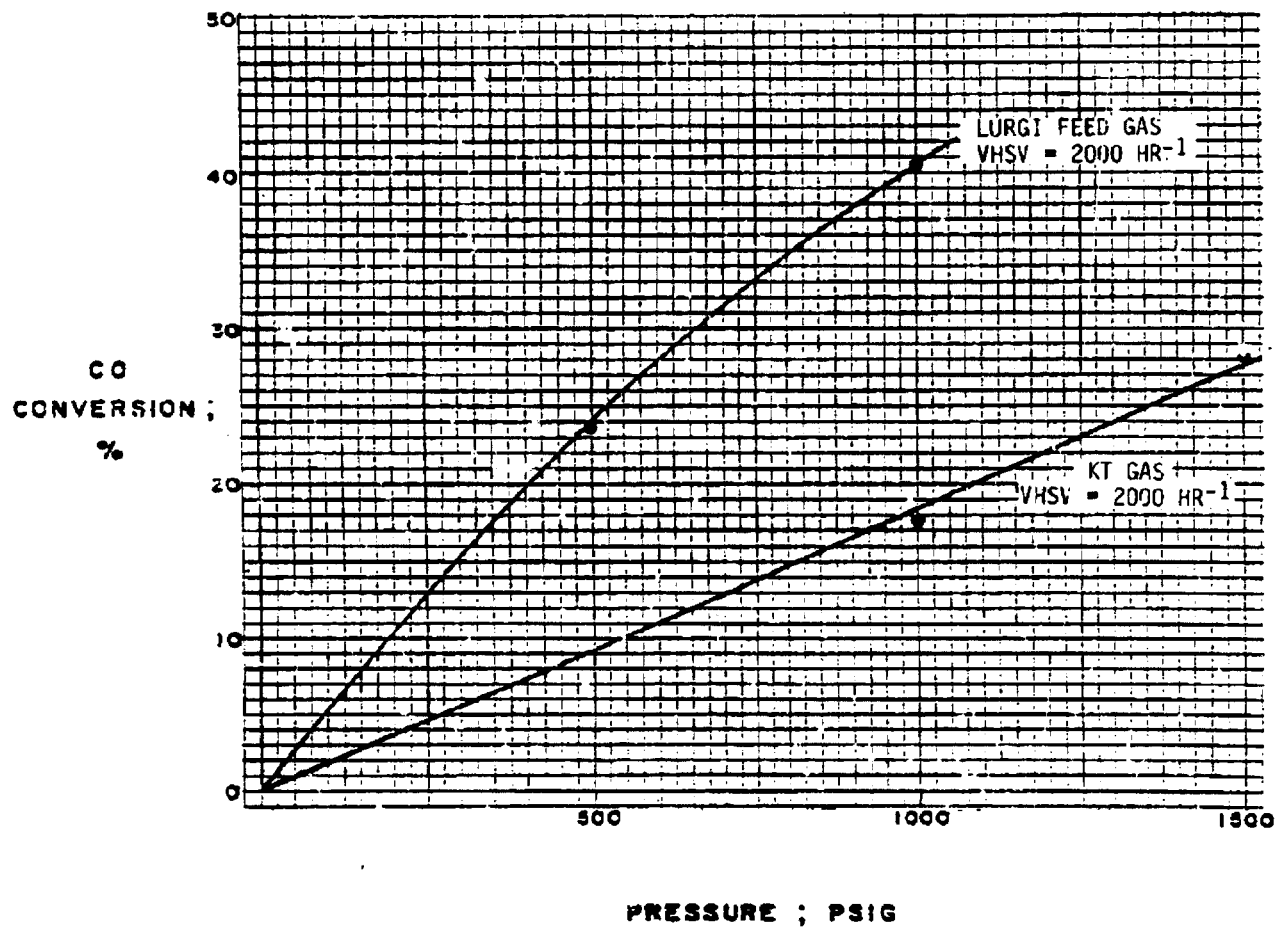
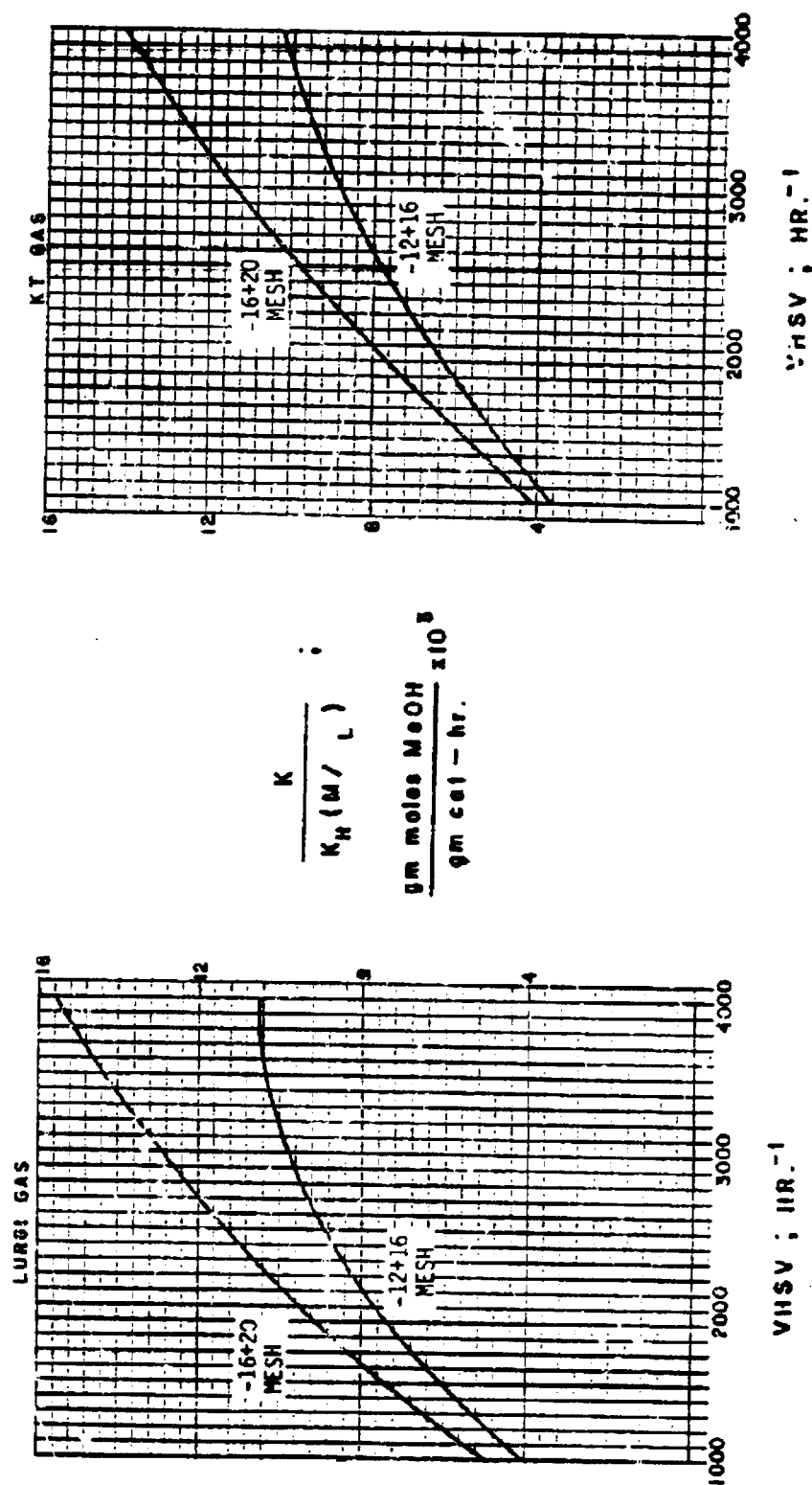


FIGURE 4-20

EFFECT OF PARTICLE SIZE

CATALYST A ; WITCO 40
1000 PSIG 235°C



reactor had to be cooled and vented in order to manually remove the plug. Notwithstanding, when the reactor was put back on-stream, the conversion levels were still quite high when compared to the results for the larger, -12 +16 mesh particles (see Table 4-2). However, because of the uncertainty in the amount of catalyst remaining in the reactor, this charge was dumped and reloaded with a similar -16 +20 mesh charge in order to complete this variable scan (see Table 4-4).

The catalyst particles are formed by grinding 1/4" $\emptyset$ x 1/4" tablets and grading according to size. The collected particles are irregular in shape and subject to attrition. This attrition behavior is comparable to experiences with the analogous liquid phase methanation system where early experimental work with crushed particles also displayed high attrition rates and subsequent catalyst loss. These problems were subsequently overcome by formulating the catalyst into 1/16" $\emptyset$ spheres. Present contact with a catalyst manufacturer indicates that these catalysts might also be processed into a regular spherical shape with superior physical properties. This would allow careful control of the particle size of the loaded catalyst and more reliable data on the effect of particle size.

Effect of Process Liquid and Catalyst Composition

Work performed during the last three months of 1975 focused on (1) the effect of circulating liquid composition, and (2) the effect of catalyst composition - Commercial Catalyst A vs. Commercial Catalyst B. Table 4-5 lists the properties of the two different liquids tested, Witco 40 mineral oil and Exxon Aromatic 150.

The reaction results are summarized in Table 4-6 (Catalyst A/Exxon Aromatic 150), Table 4-7 (Catalyst B/Witco 40), and Table 4-8 (Catalyst B/Witco 40). The repetition of the Catalyst B data points with a new catalyst loading was brought about because it was felt that its significantly poorer performance as compared to Catalyst A might have

TABLE 4-5
PHYSICAL PROPERTIES OF LIQUIDS USED

<u>Witco 40 Mineral Oil</u>		<u>Exxon Aromatic 150</u>		
Hydrocarbon				
Type	72 % Paraffinic, 28% Naphthenic	98+% Aromatic		
Carbon Number	C ₁₄	5%	C ₈	-
Distribution	C ₁₄ -C ₁₅	15%	C ₉	5.6
	C ₁₆ -C ₁₇	20%	C ₁₀	12.8
	C ₁₈ -C ₁₉	25%	C ₁₁	18.2
	C ₂₀ -C ₂₁	20%	C ₁₂	1.4
	> C ₂₁	15%	Non-Aromatic	2.0
API Gravity 60/60°F	43.2	25.4		
Viscosity at 100°F	3.4 cP (SUS = 40)	0.87 cP (SUS 32)		
Distillation (ASTM D86)				
18P	518°F	362°F		
5	528	370		
10	540	372		
50	568	380		
90	634	394		
95	657	402		
EP	659	410		
Sulfur (ASTM D1266)	1 ppm	1ppm		

TABLE 4-6
COMMERCIAL CATALYST A⁽¹⁾ (-16+20 MESH)/EXXON AROMATIC 150

Run No.	Feed Gas	Temp. °C	Pressure psig	VHSV Hr ⁻¹	CO Conversion To MeOH ⁽²⁾ , %
53-1	Lurgi ⁽³⁾	235	500	1,270	18.5
54-1	Lurgi ⁽³⁾	235	1,000	3,555	37.7
55-1	Lurgi ⁽³⁾	250	1,000	3,755	31.6
55-2	Lurgi ⁽³⁾	250	1,000	2,490	35.3
56-1	Lurgi ⁽³⁾	220	1,000	2,475	32.6
56-2	Lurgi ⁽³⁾	220	1,000	3,895	21.1

(1) Catalyst loading = 219.6 gm = 200 cm³.

(2) Includes small selectivity to higher alcohols.

(3) Nominal composition: 50% H₂, 25% CO, 10% CO₂ and 15% CH₄.

TABLE 4-7
COMMERCIAL CATALYST B⁽¹⁾ (-16+20 MESH)/Witco 40 MINERAL OIL

<u>Run No.</u>	<u>Feed Gas</u>	<u>Temp. °C</u>	<u>Pressure psig</u>	<u>VHSV Hr⁻¹</u>	<u>CO Conversion To MeOH⁽²⁾, %</u>
57-1	Lurgi ⁽³⁾	235	1,000	4,580	29.5
57-2	Lurgi ⁽³⁾	235	1,000	2,830	35.6
58-1	Lurgi ⁽³⁾	220	1,000	2,595	27.3
58-2	Lurgi ⁽³⁾	220	1,000	4,590	16.0
59-1	Lurgi ⁽³⁾	250	1,000	2,720	28.8
60-2	Lurgi ⁽³⁾	270	1,000	2,780	24.0
61-1	Lurgi ⁽³⁾	270	1,000	2,695	26.0

(1) Catalyst loading = 215.6 gm = 155 cm³.

(2) Includes small selectivity to higher alcohols.

(3) Nominal composition: 50% H₂, 25% CO, 10% CO₂ and 15% CH₄.

TABLE 4-8
COMMERCIAL CATALYST B⁽¹⁾ (-16+20 MESH)/WITCO 40 MINERAL OIL

Run No.	Temperature °C	Pressure psig	VHSV Hr ⁻¹	CO Conversion to MeOH ⁽³⁾ %
62-1	235	1,000	2,640	39.5
62-2	235	1,000	5,150	32.0
63-1	250	1,000	3,220	35.1
63-2	250	1,000	5,260	29.7
64-1	235	1,000	3,230	33.4
64-2	235	1,000	5,490	24.4
65-1	220	1,000	3,190	25.1
65-2	220	1,000	5,290	15.6
66-1	275	1,000	3,570	24.2
66-2	275	1,000	5,520	20.2
67-1	235	1,000	3,600	25.6
67-2	235	500	3,600	8.0 ⁽⁴⁾
68-1	250	500	2,140	11.6
68-2	250	500	3,610	8.44
69-1	225	500	2,140	12.6
69-2	225	500	3,970	7.86
70-1	275	500	2,210	10.3
70-2	275	500	3,680	7.72
71-1	235	1,000	3,290	NA
71-2	235	500	3,530	7.67

- (1) Catalyst loading = 219.6 gms = 155 cm³.
(2) Nominal composition: 50% H₂, 25% CO, 10% CO₂, and 15% CH₄.
(3) Includes small selectivity to higher alcohols.
(4) Indications that this value could be as high as 12.0%.

been due to a temperature upset during the reduction procedure. The graphical presentation of data from Tables 4-6 and 7 is shown in Figures 4-21, -22, -23 and -24. In general, these catalyst/liquid systems show the same response to the process variables of feed rate and temperature as the Catalyst A/Witco 40 system. However, as indicated in Figure 4-25, there are noticeable differences in their absolute methanol productivities when compared to the Catalyst A/Witco 40 system:

Catalyst A/Witco 40 > Catalyst A/Exxon 150 >> Catalyst B/Witco 40

The results of the second Catalyst B scan confirm the earlier work and indicate that the Catalyst B/Witco 40 system gives the poorest productivity of all the systems examined to date, some 30 percent lower than the next best system (Catalyst A/Exxon Aromatic 150).

It is felt that the higher reaction rates evidenced by the Witco 40 mineral oil system are due to the fact that the equilibrium MeOH solubility in a recycle system would be lower in the mineral oil in comparison to the aromatic oil, providing a greater overall driving force for this reaction. This was verified by subsequent experiments, which are discussed in some detail in Section 8. Briefly, measured activity coefficients for the methanol/Witco 40 mineral oil system were a factor of 2-3 times higher than the values obtained for the methanol/Exxon 150 aromatic oil system. Since solubility is an inverse function of the activity coefficients, the equilibrium methanol concentration would indeed be substantially lower in the Witco 40 as has been theorized.

The superior productivity of Catalyst A over Catalyst B was unexpected since the available literature gives no indication of substantial differences in their relative reactivity. At first it was felt that a temperature upset during the reduction procedure might have been responsible for the lower reactivity. However, experiments with a subsequent catalyst loading gave substantially the same results. Therefore, efforts concentrated on physical property modification of the Catalyst A formulation.

FIGURE 4-21

CONVERSION VS. SPACE VELOCITY

CATALYST A (-15+20 MESH) / EXXON AROMATIC 150
1000 PSIG LURGI FEED GAS

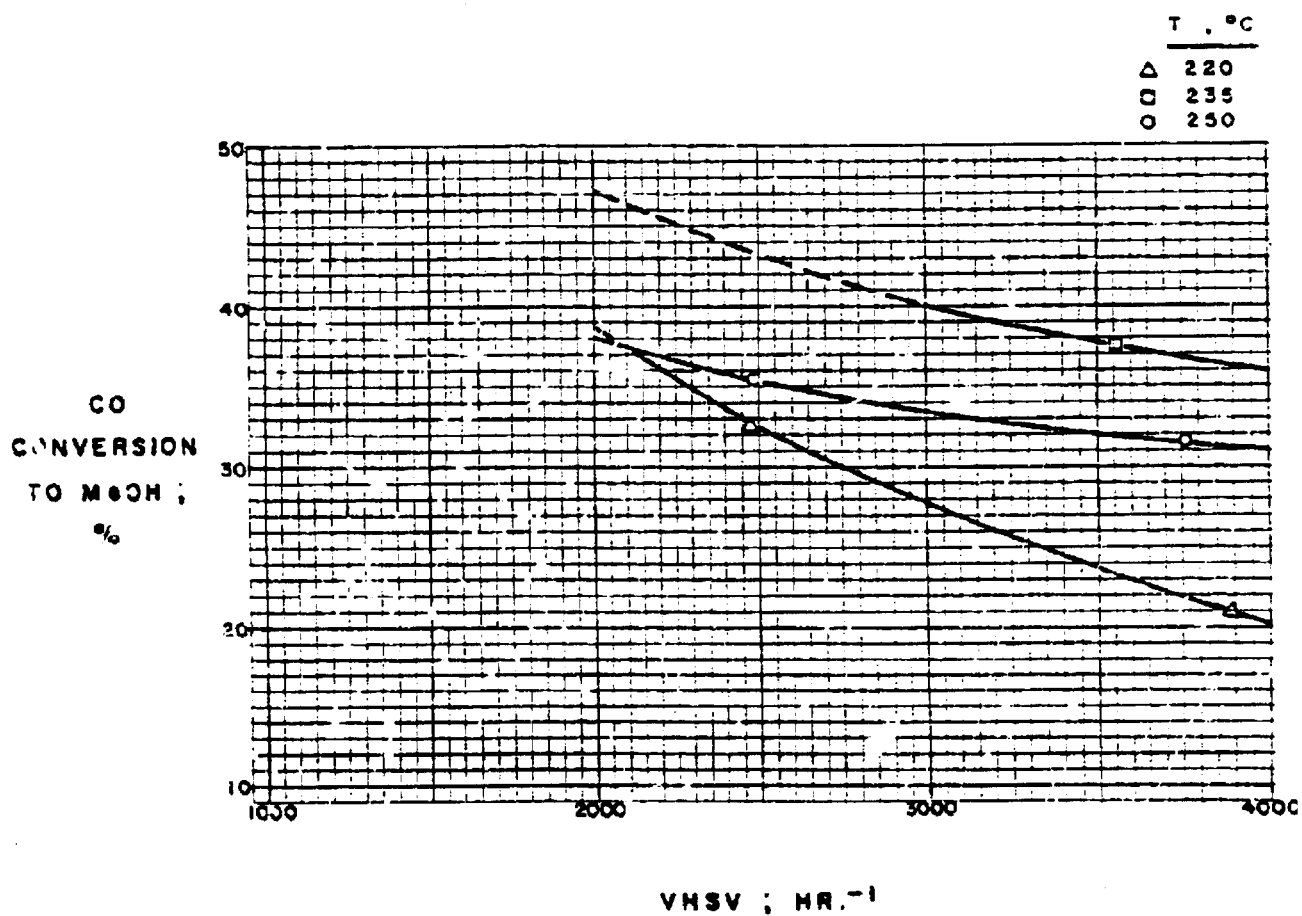


FIGURE 4-22

CONVERSION VS. SPACE VELOCITY

**CATALYST B (-16 + 20 MESH) / WITCO 40
1000 PSIG LURGI FEED GAS**

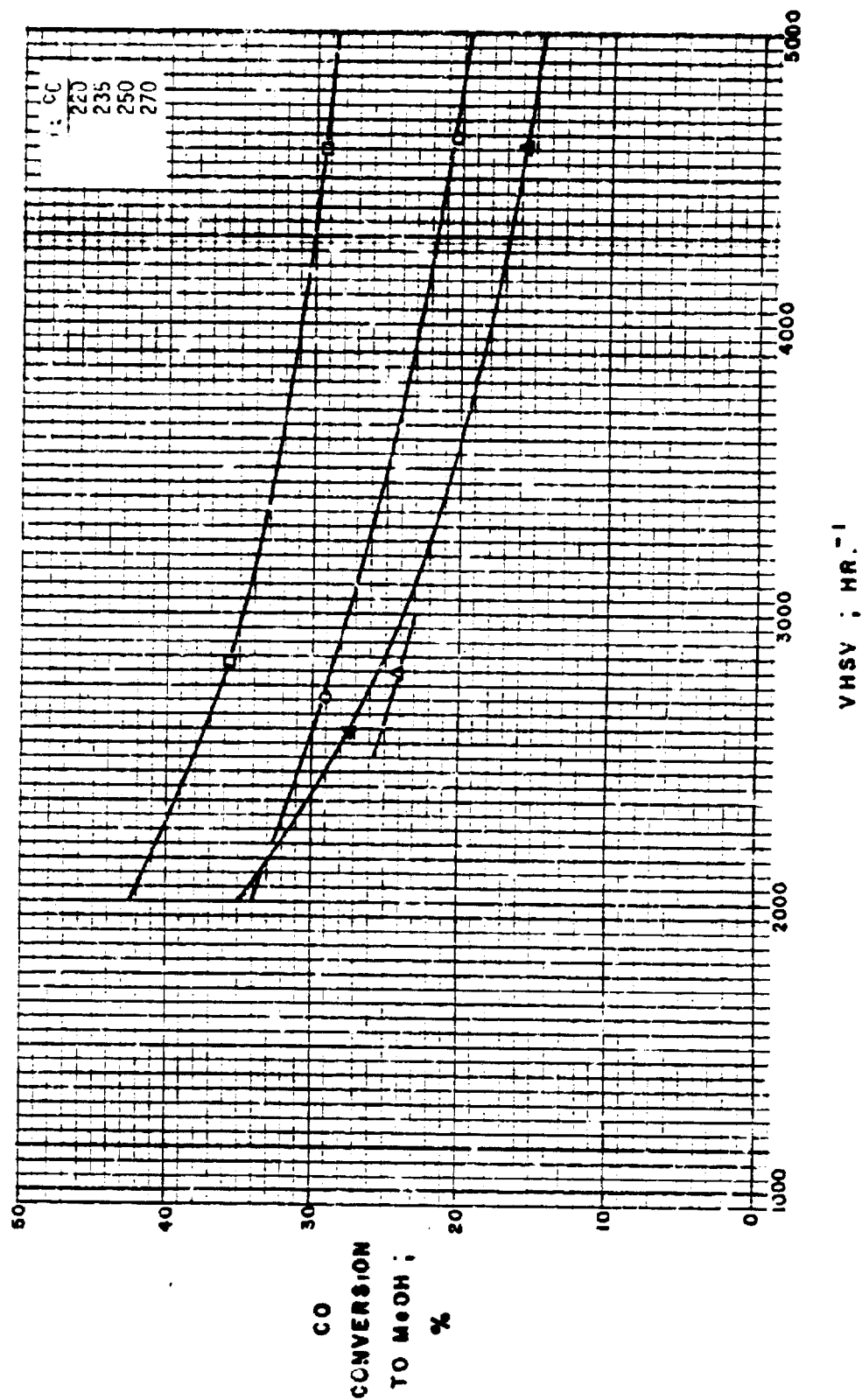


FIGURE 4-23

MeOH PRODUCTIVITY VS. TEMPERATURE

CATALYST A (-16+20 MESH) / EXXON AROMATIC 150

1000 PSIG

LURGI FEED GAS

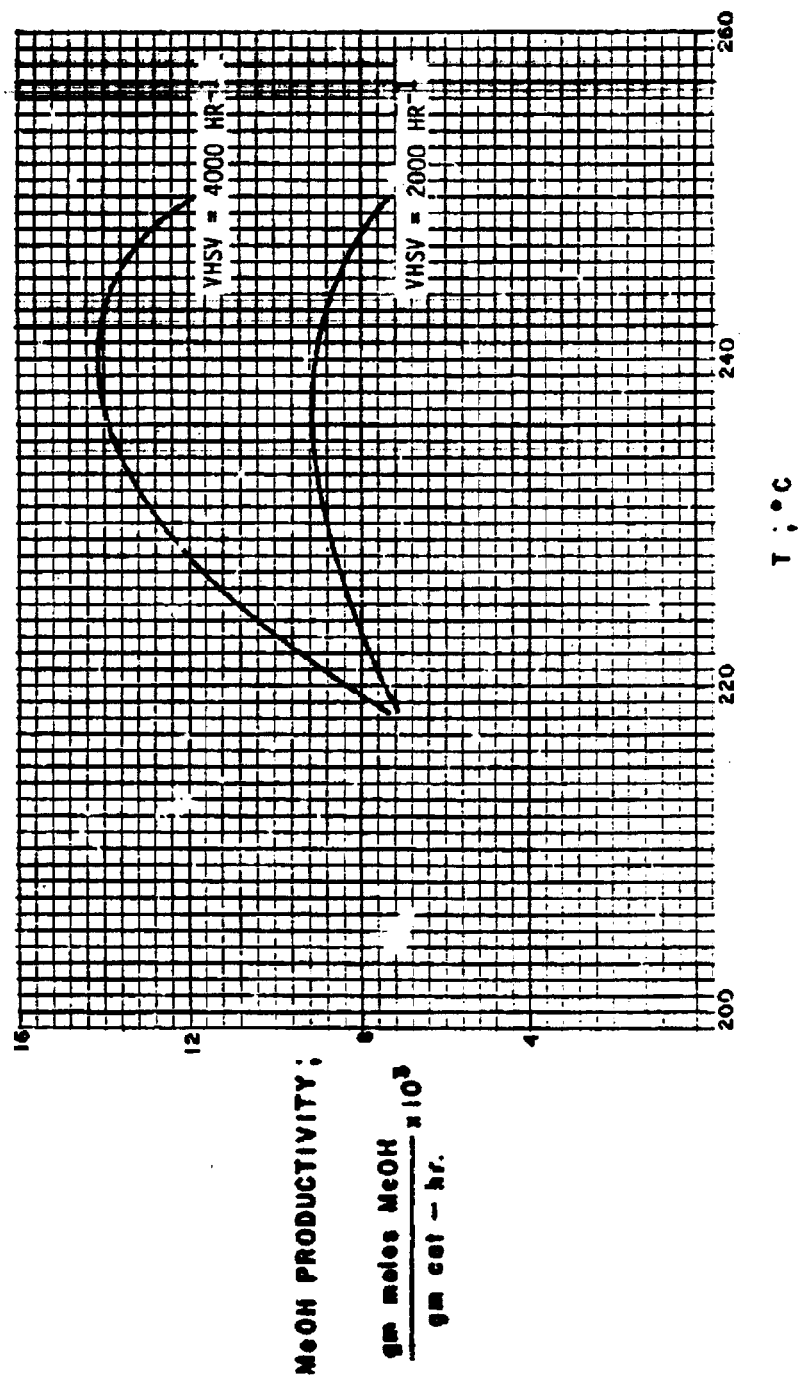


FIGURE 4-24

MeOH PRODUCTIVITY VS. TEMPERATURE

**CATALYST B (-16+20 MESH) / WITCO 40
1000 PSIG LURGI FEED GAS**

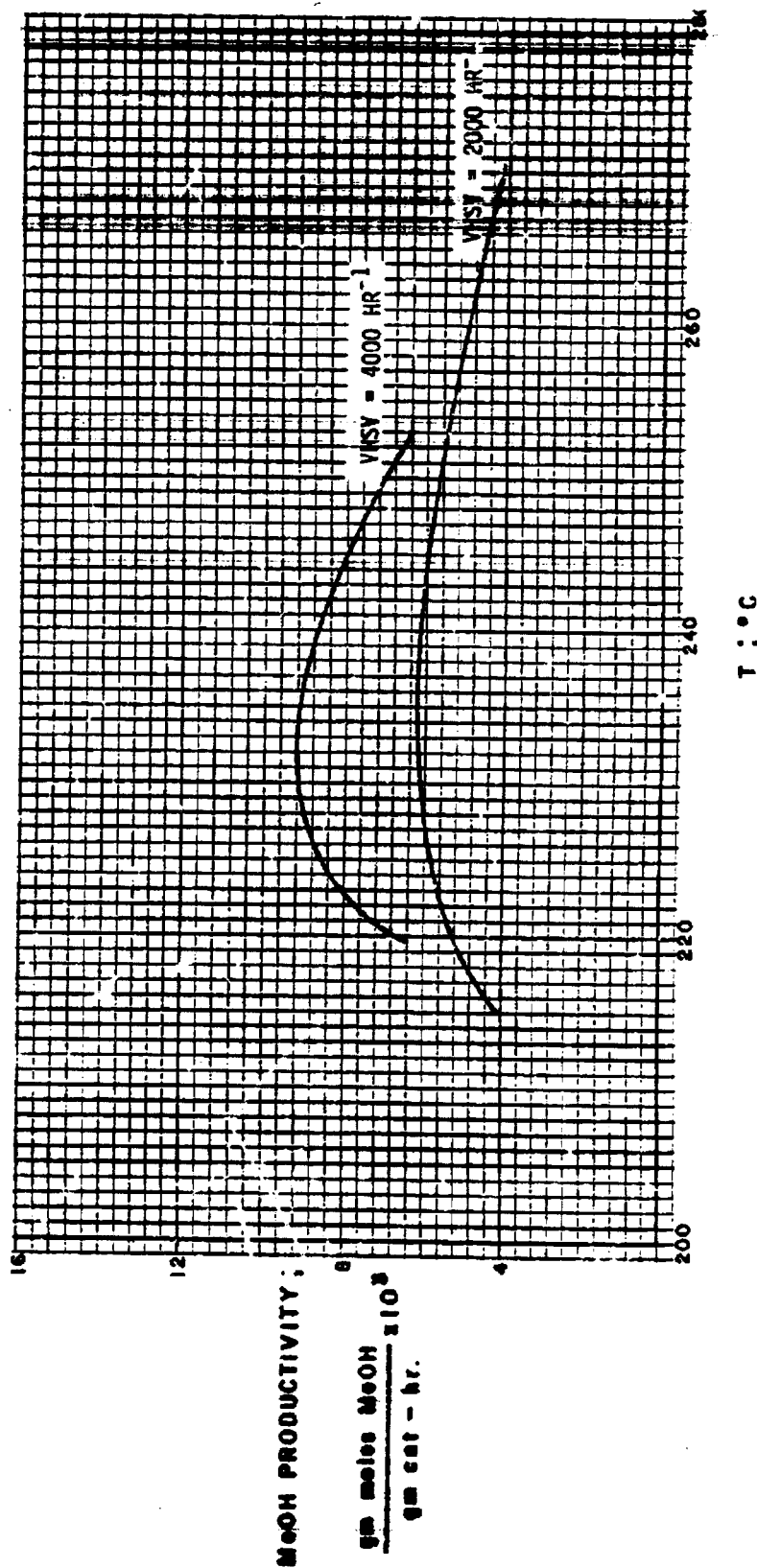
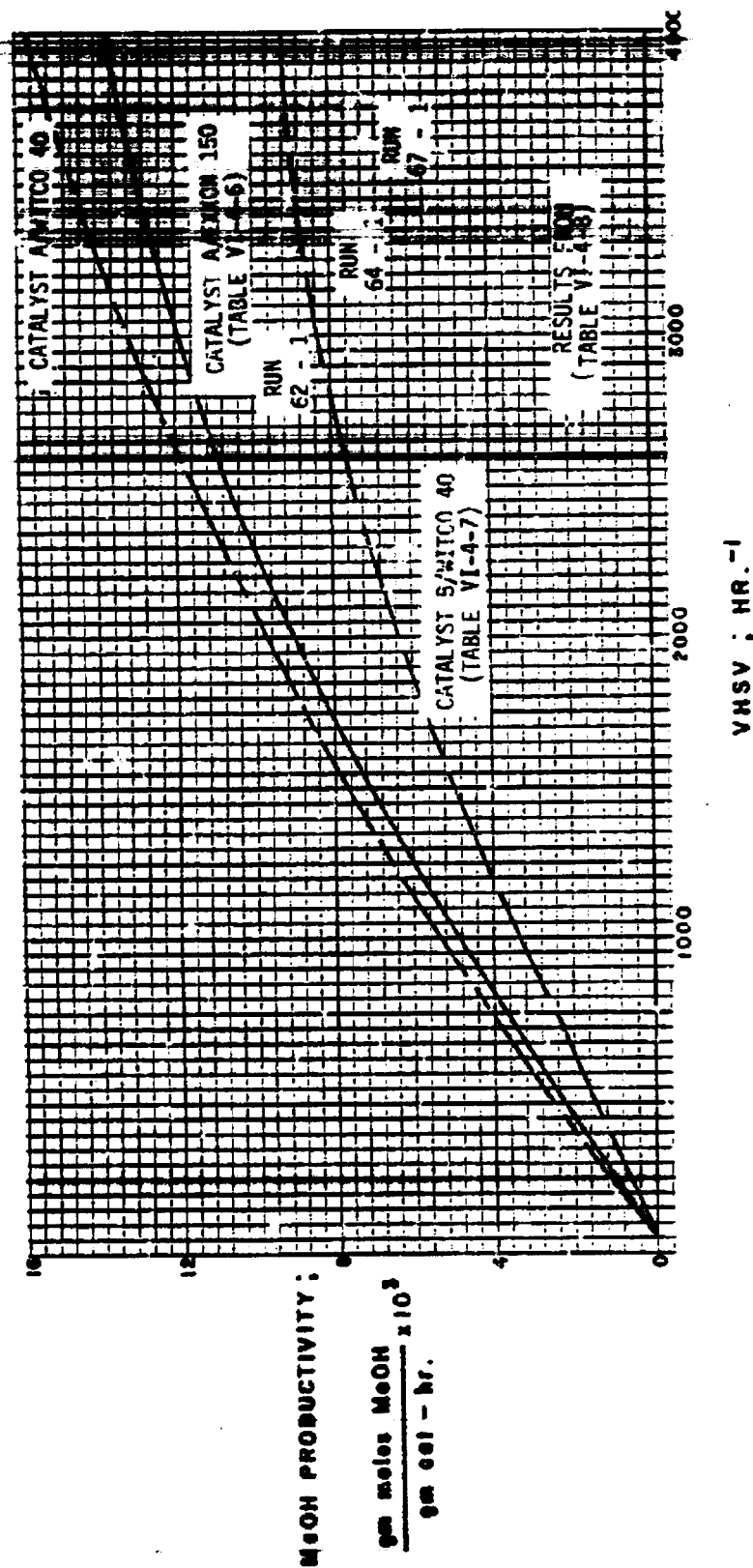


FIGURE 4-25

**MeOH PRODUCTIVITY
FOR
VARIOUS CATALYST - LIQUID PAIRS**
(-16 + 20 MESH) LURGI FEED GAS 235°C
1000 PSIG



The Catalyst A/ethylene glycol system was examined in order to determine the effectiveness of ethylene glycol as a methanol "sink". Immediately upon initiation of the process variable scan, a dark ethylene glycol decomposition product was noticed. The run was terminated and the equipment cleaned up. A second run was started with nitrogen replacing the synthesis gas feed and the same decomposition product was found. Further work with ethylene glycol was abandoned with the conclusion that this compound is unsuitable as a circulating liquid in the liquid phase methanol process.