

## Effect of CO<sub>2</sub> on Catalyst Activity

Experiments were conducted to quantify the advantage of higher CO<sub>2</sub> concentration in the feed on catalyst activity. The results of these runs on the 400 hour old catalyst are shown in Figure 17. Improvement in methanol outlet concentration is very significant, going from 0.5 to 2% CO<sub>2</sub>. It reaches a maximum of about 9.8 mole% at around 5% CO<sub>2</sub>, and then decreases slightly with higher CO<sub>2</sub> concentration. The maximum productivity of about 38 gmole/hr-kg was obtained at 5% CO<sub>2</sub>, which is about 40% higher than 27 gmole/hr-kg obtained at the 0.5% CO<sub>2</sub> (see Figure 18).

## Field Test # 2

### Improvements in Field Test # 2

A second field test was conducted using the knowledge gained from Field Test #1, analytical results, and the lab test on CO<sub>2</sub> effect. The strategy was to give the catalyst the best chance to stabilize. Several modifications were made to the unit:

- Install a 4 ft column containing molecular sieve 3A (Bed 1) to remove water from the feed. Install panametric monitors to measure water content of Bed 1 inlet and outlet.
- Install knockout pots in the adsorption as well as autoclave feed system to remove liquids, including water.
- Move the feed line so that it goes up (instead of down) from the inlet to the existing DGC methanol unit to avoid liquids in the feed.
- Modify H<sub>2</sub>S injection system to inject CO<sub>2</sub> into the feed. According to the lab test, low CO<sub>2</sub> does not cause catalyst deactivation. However, additional CO<sub>2</sub> enhances catalyst activity. Also, it may maintain a certain oxidation level and reduce catalyst susceptibility to poisons. Another benefit of CO<sub>2</sub> addition is that the effluent of the methanol reactor in the demonstration plant will have a more balanced C to H ratio.
- Install a carbon bed downstream of compressor to remove any Fe or Ni formed after the adsorption system.

Adsorbents were regenerated every three days, despite the absence of sulfides and carbonyls. This would regenerate the capacities for acetonitrile, water, benzene, toluene, Fe(CO)<sub>5</sub> and any other poison that was picked up. Dakota Gas Company's (DGC) analytical department provided spot-checks for acetonitrile breakthrough. There was some risk of ethylene (detected by on-line GC with a PID and confirmed by DGC) poisoning the catalyst. Ethylene removal would require additional research and the literature suggested that ethylene was probably benign to the catalyst.

Figure 17

# CO<sub>2</sub> ADDITION TO SYNTHESIZED GP COAL GAS

(250 G, 750 PSIG @ 10,000 GHSV)

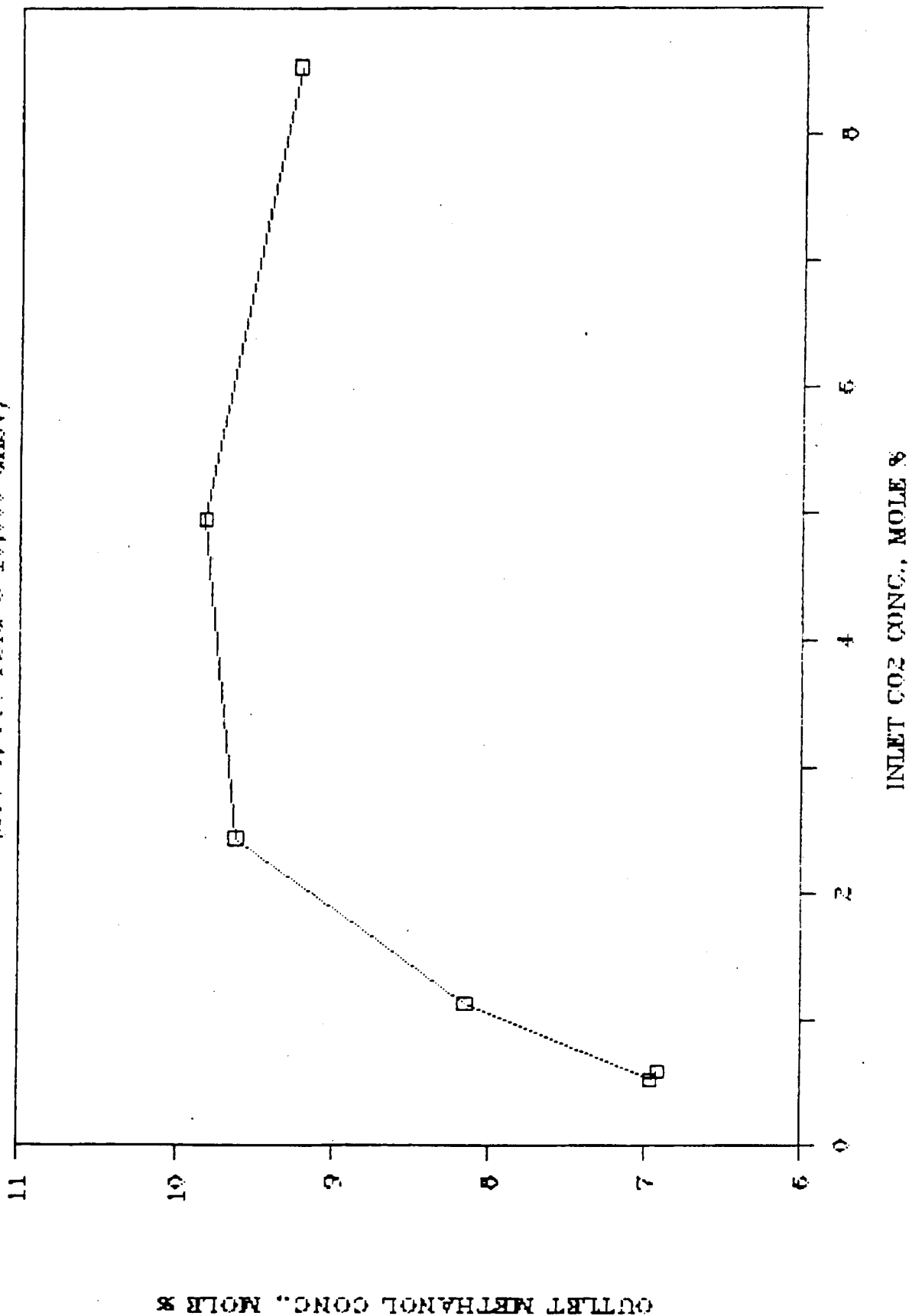
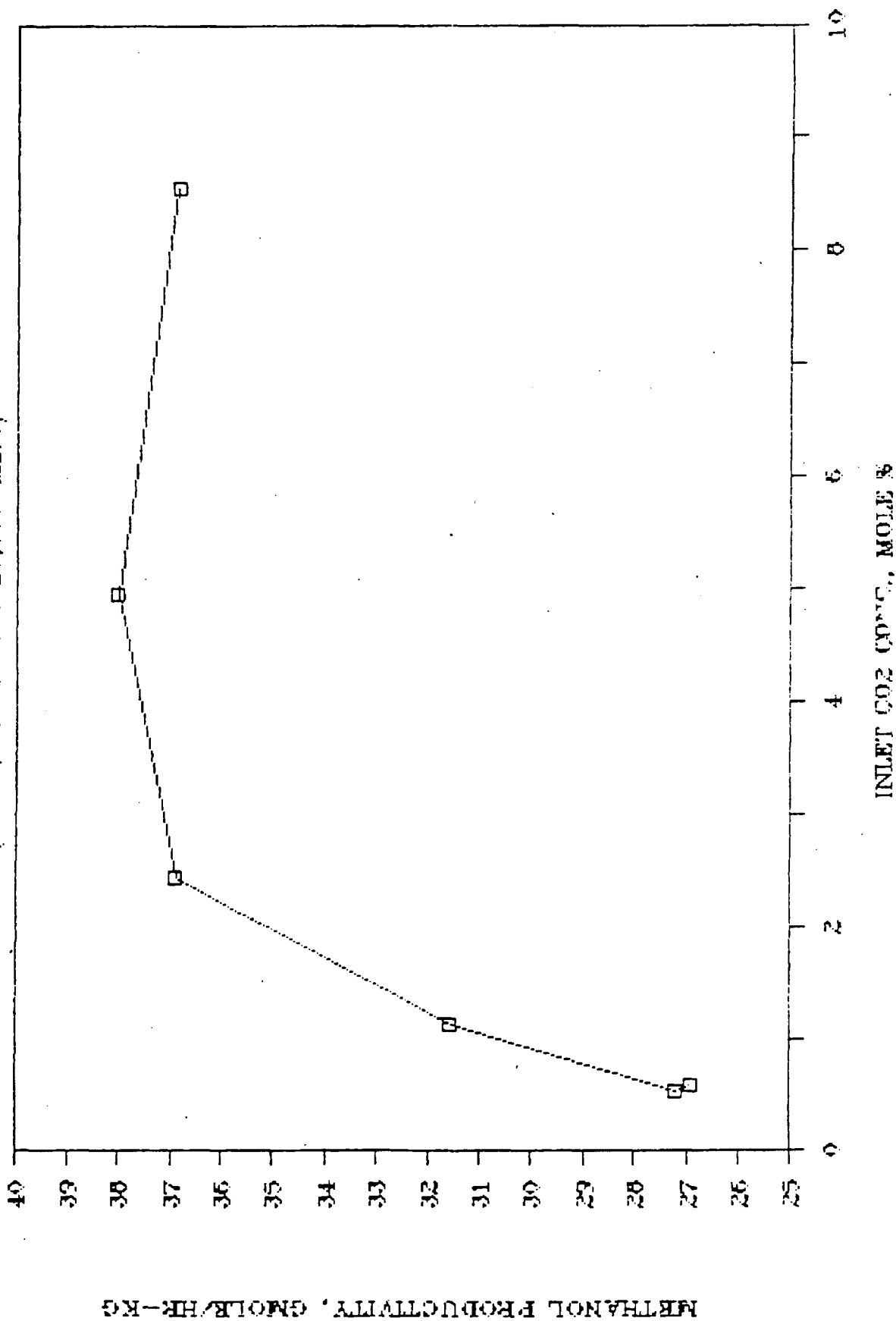


Figure 18

# CO<sub>2</sub> ADDITION TO SYNTHESIZED GP COAL GAS

(250 G, 750 PSIG @ 10,000 GHSV)



### Catalyst Life Test with Adsorbents On-stream

The adsorption columns were loaded with fresh adsorbents as given in Table 11. The H-Y zeolite and BPL carbon were loaded twice as much as in the earlier field test to get higher capacities. The Cu/Zn catalyst in column #2 was reduced using 2% H<sub>2</sub> in N<sub>2</sub> at 100 psig with temperature ramping. The molecular sieve in column #1 and the zeolite in column #3 were dried using N<sub>2</sub> at 500°F for about 12 hours. The autoclave was loaded with about 25 grams of F21/OE75-43 catalyst powder and 125 grams of Drakeol-10 oil. The catalyst slurry was reduced in the autoclave using 2% H<sub>2</sub> in N<sub>2</sub> at 100 psig with temperature ramping.

The first cycle was started up with the autoclave bypassed, in order to purge the system. The reactor inlet was monitored by GCs to insure that the feed was free of sulfides and carbonyls. The adsorption system was operated at 300 psig inlet pressure and an 8% higher flow rate than in the autoclave (4.5 vs. 4.2 lit/min). No H<sub>2</sub>S, COS, or Fe(CO)<sub>5</sub> were detected in the feed. Initially, some Ni(CO)<sub>4</sub> (in the range of 10-30 ppb) was detected in the system. After cleaning the suspected section right before the autoclave, the Ni(CO)<sub>4</sub> gradually diminished.

The autoclave was then started up at 10,000 sl/kg-hr, 250°C and 750 psig. The feed gas, with CO<sub>2</sub> added, had a composition of about 19.5% CO, 60% H<sub>2</sub>, 5% CO<sub>2</sub>, and 15.5% CH<sub>4</sub>. Initially, DGC found ppm levels of acetonitrile in the feed to the adsorption system but none in the feed to the autoclave. We were on-stream with 5% CO<sub>2</sub> for about 120 hours. The catalyst appeared to be stable with methanol concentration over 10% in the outlet (see Figure 19). Methanol productivity was about 38 gmole/hr-kg (see Figure 20).

After 120 hours on-stream, CO<sub>2</sub> injection was stopped to see if the catalyst remained stable. Methanol concentration dropped to about 7% in the outlet (methanol productivity of 27 gmole/hr-kg). However, the catalyst was still stable for the next 150 hours on-stream. The downturns in the early (on-stream time 130 hours) as well as the last stage (on-stream time 270 hours) of this study were believed to be due to the decrease of CO<sub>2</sub> in the feed.

After on-stream time of about 280 hours, CO<sub>2</sub> injection resumed to check productivity level. Methanol concentration came back up to about 10% in the outlet with productivity of about 38 gmole/hr-kg. This confirmed the stability of the catalyst.

Table 11

# GREAT PLAINS COAL GAS STUDY

## FIELD TEST # 2

### ADSORPTION BEDS

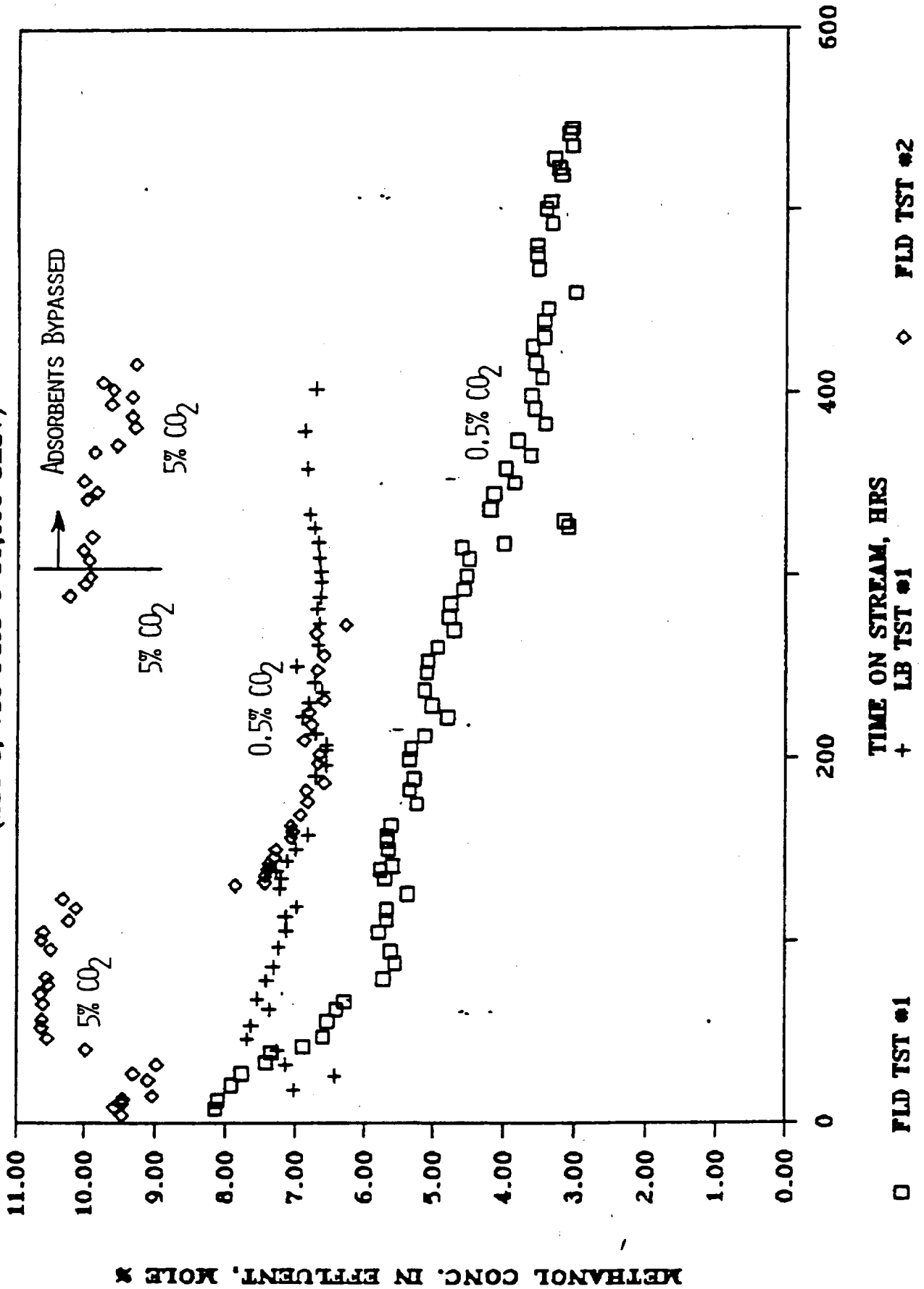
COLUMN	ADSORBENT	POISON	LENGTH	WEIGHT
1	LINDE MOLECULAR SIEVE 3A	H <sub>2</sub> O	4 FT	186 GM
2	CU/ZN BASF S3-86 CATALYST	HCL, H <sub>2</sub> S	1.2 FT	90.8 GM
3	LINDE H-Y ZEOLITE	FE(CO) <sub>5</sub>	1.2 FT	44.5 GM
4	BPL CARBON	NI(CO) <sub>4</sub>	1.2 FT	33.8 GM
4	FCA CARBON (WITH CU/CR OXIDE)	COS	3 FT	107.1 GM

THE COLUMNS HAVE 3/4" OD X .049" WALL  
AND ARE MADE UP OF 316 SS.

Figure 1b

# FIELD/LAB TESTS WITH GP COAL GAS

(250 C, 750 PSIG @ 10,000 GHSV)

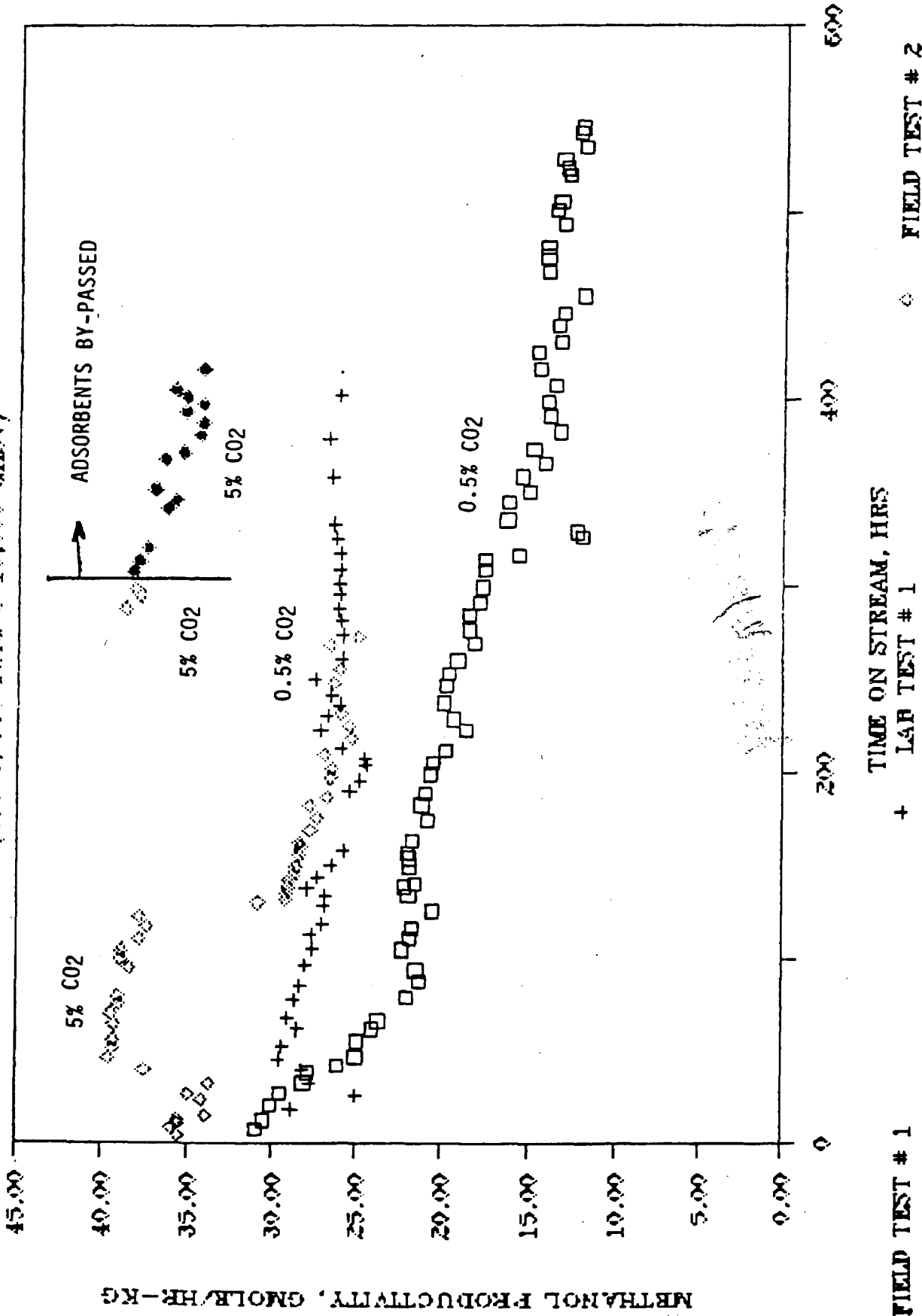


ADSORBENTS REGENERATED EVERY 72 HOURS

Figure 20

# FIELD/LAB TEST WITH GP COAL GAS

(250 C, 750 PSIG @ 10,000 GHSV)



### Catalyst Life Test with Adsorbents Bypassed

The adsorption system as well as the carbon guard bed were bypassed next to check the stability of the catalyst without the gas clean-up. There was a lot of scatter in the data. However, catalyst activity seemed to be declining. Two days into this bypass study, there was a sulfur spike in the feed (from 30 to 60 ppb), which may have contributed to the decline. However, there was no acetonitrile in the feed. This was probably because the flow through the Rectisol unit was lower, as several gasifiers (as many as 3 out of 14) were down at that time. Another reason could be a different type of coal in use. After about 120 hours on-stream in the bypass mode, the test was terminated since a typical feed was not expected.

The feed gas was essentially dry during the entire test. No liquid was collected in any of the traps. The dew point of the inlet gas to column #1 ranged from -55 to -65°C. The outlet gas from column #1 had a dew point of about -75 to -80°C.

### Comparison of Field/Lab Test Results

Results from the second test are compared with those from the first test and the lab test in Figures 19 and 20. The following observations can be made from these plots:

- After 270 hours on-stream, the catalyst was as active as the lab test and significantly more active than the first test.
- The catalyst was much more stable than the first test but may be slightly less stable than the lab test.
- Increasing the CO<sub>2</sub> level from 0.5% to 5% in the feed increased methanol productivity about 40%.

Conversions of CO, H<sub>2</sub>, CO<sub>2</sub> and CH<sub>4</sub> during the test are plotted in Figure 21. CO and H<sub>2</sub> conversion remained stable at a constant CO<sub>2</sub> level. CO<sub>2</sub> conversion was small at 5% CO<sub>2</sub> and negative at 0.5% CO<sub>2</sub>. CH<sub>4</sub> conversion was close to zero as expected.

Molar ratios were calculated to check the proximity to stoichiometry for the reaction:

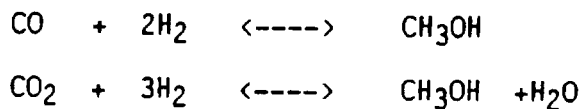
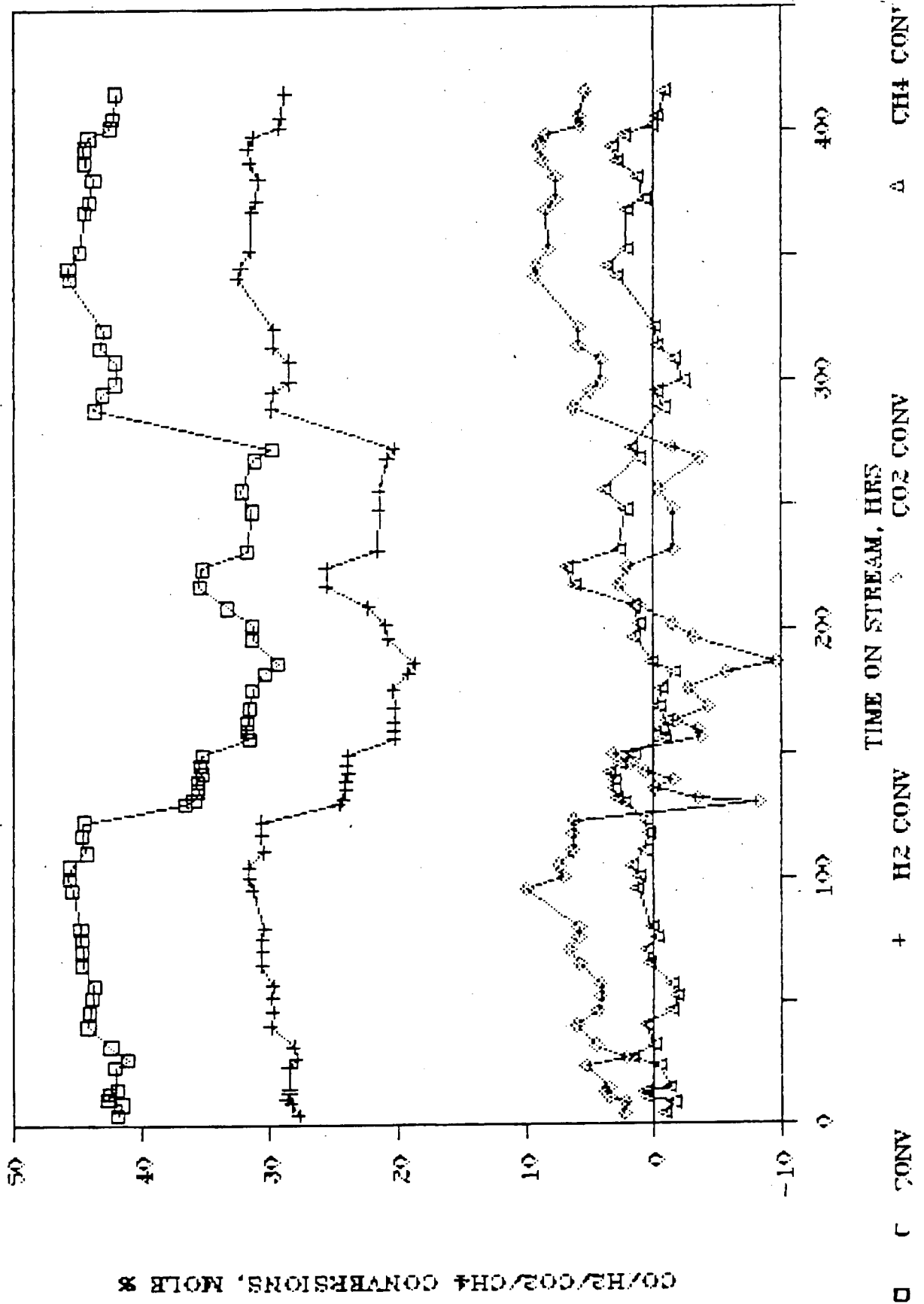




Figure 21

# FIELD TEST # 2 (GREAT PLAINS COAL GAS)

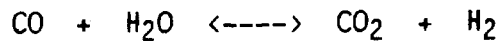
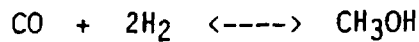
(250 C. 750 PSIG @ 10,000 GHSV)



Ratios of H<sub>2</sub> consumed to CO + CO<sub>2</sub> consumed as well as CH<sub>3</sub>OH produced to CO + CO<sub>2</sub> consumed were calculated for the three tests. If no other reaction occurred, the H<sub>2</sub> consumed/CO+CO<sub>2</sub> consumed ratio would be slightly higher than 2. The CH<sub>3</sub>OH produced/CO+CO<sub>2</sub> consumed ratio would be 1. The actual ratios are plotted as a function of on-stream time in Figures 22-24. The average ratios are given in Table 12. The H<sub>2</sub> consumed/CO+CO<sub>2</sub> consumed ratio was 2.16 (highest) and the CH<sub>3</sub>OH produced/CO+CO<sub>2</sub> consumed ratio was 0.83 (lowest) for Field Test #1. This indicates side reactions consuming higher proportion of hydrogen making by-products (non-methanol) during Field Test #1.

### Estimation of Rate Constants

A rate model developed by Air Products' Process Engineering department (6) was used to estimate rate constants from the data. This would eliminate variations in the results due to operating conditions and feed compositions. The model is based on the following reactions and rate expressions:



$$R_{\text{meoh}} = K_f f_{\text{CO}}^{1/3} f_{\text{H}_2}^{2/3} [1 - f_{\text{meoh}} / K_{\text{eq}} f_{\text{CO}} f_{\text{H}_2}^2]$$

$$K_f = k_0 * \exp [ -14380 / (1.987 * T) ]$$

where

$R_{\text{meoh}}$	=	methanol productivity
$K_f$	=	rate constant
$f_x$	=	fugacity of component x
$K_{\text{eq}}$	=	methanol equilibrium constant
$k_0$	=	pre-exponential factor
$T$	=	reactor temperature

The effect of CO<sub>2</sub> content on methanol productivity is empirically accounted for by correlating  $k_0$  with the CO<sub>2</sub> content of the feed from the LaPorte data.

The rate constants estimated from the actual data were compared with the rate constants predicted by the model based on LaPorte data. This analysis was performed on results from the second test as well as the first test and the lab test. The comparison of the three tests is made in Figure 25. Eta defined as  $(k_0)_{\text{actual}} / (k_0)_{\text{predicted}}$  is plotted as a function of on-stream time. The following observation can be made from Figure 25:

- At 0.5% CO<sub>2</sub> level in the feed, the eta for Field Test #2 was about the same as that for the lab test and close to "1." This indicates good agreement between Field Test #2, the lab test, and the model prediction which is based on LaPorte data.

# FIELD TEST # 1 (GREAT PLAINS COAL GAS)

(250 C, 750 PSIG @ 10,000 GHSV)

Figure 22

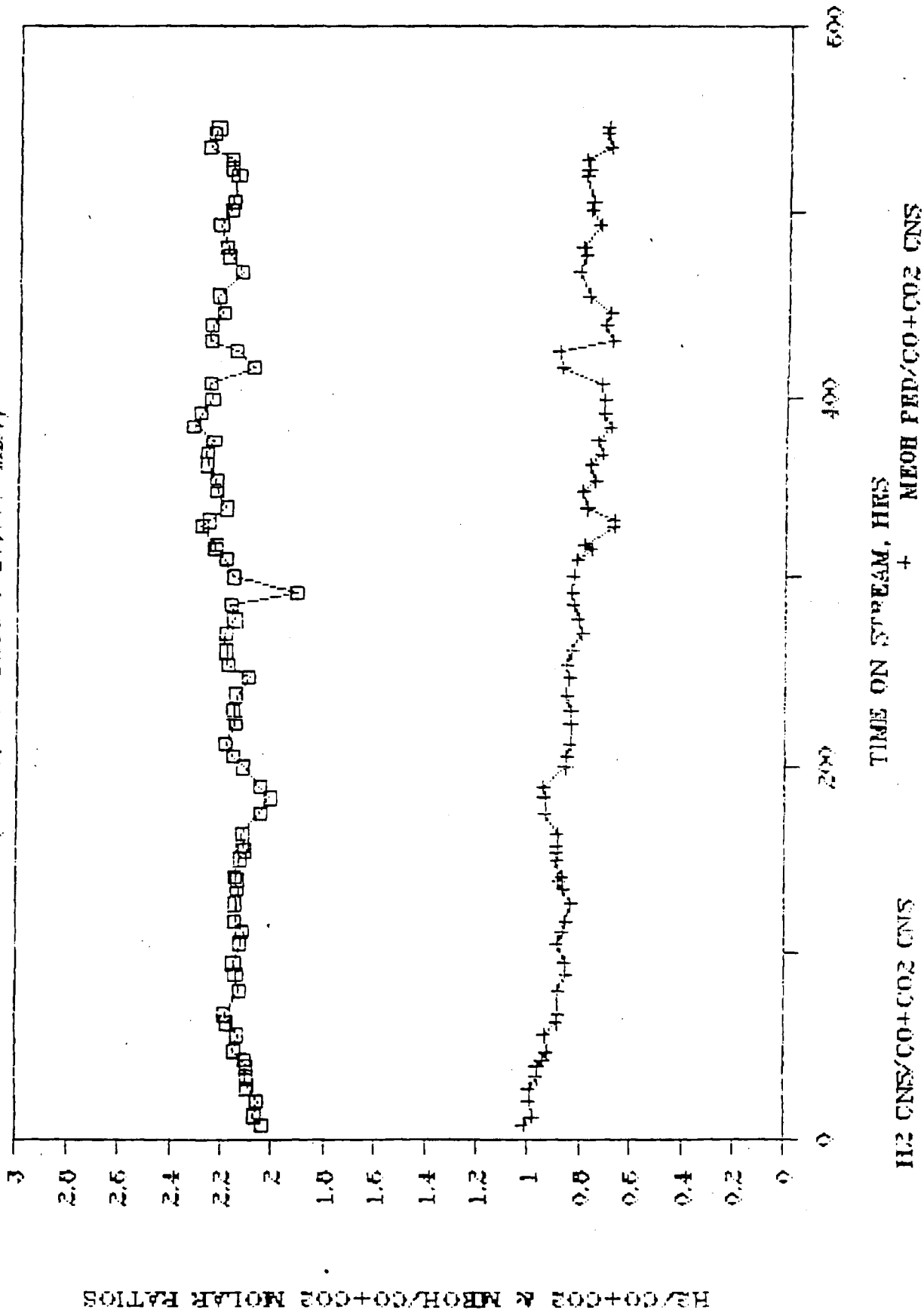


Figure 23

# LAB TEST # 1 (SYNTHESIZED GP COAL GAS)

(250 C, 750 PSIG @ 10,000 GHSV)

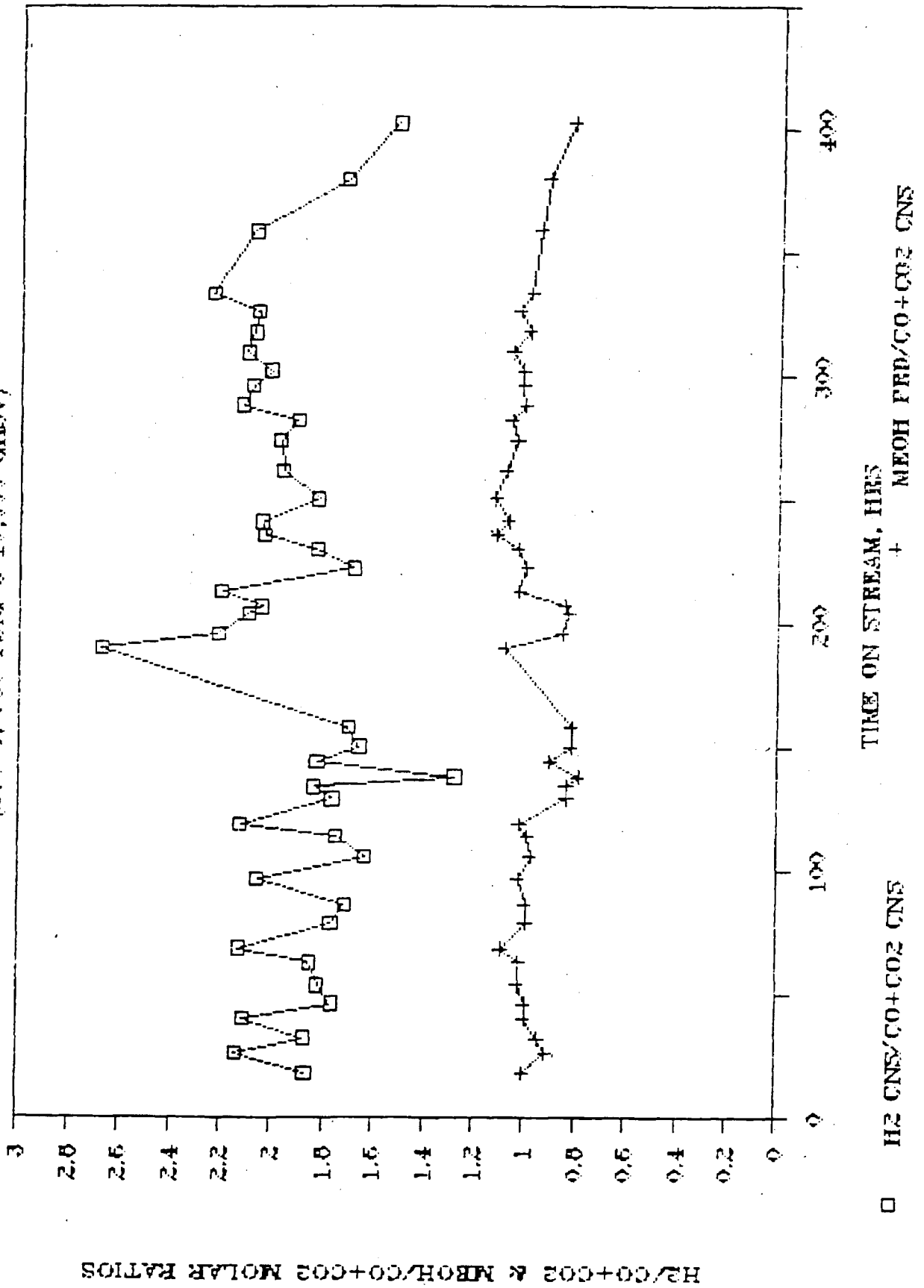
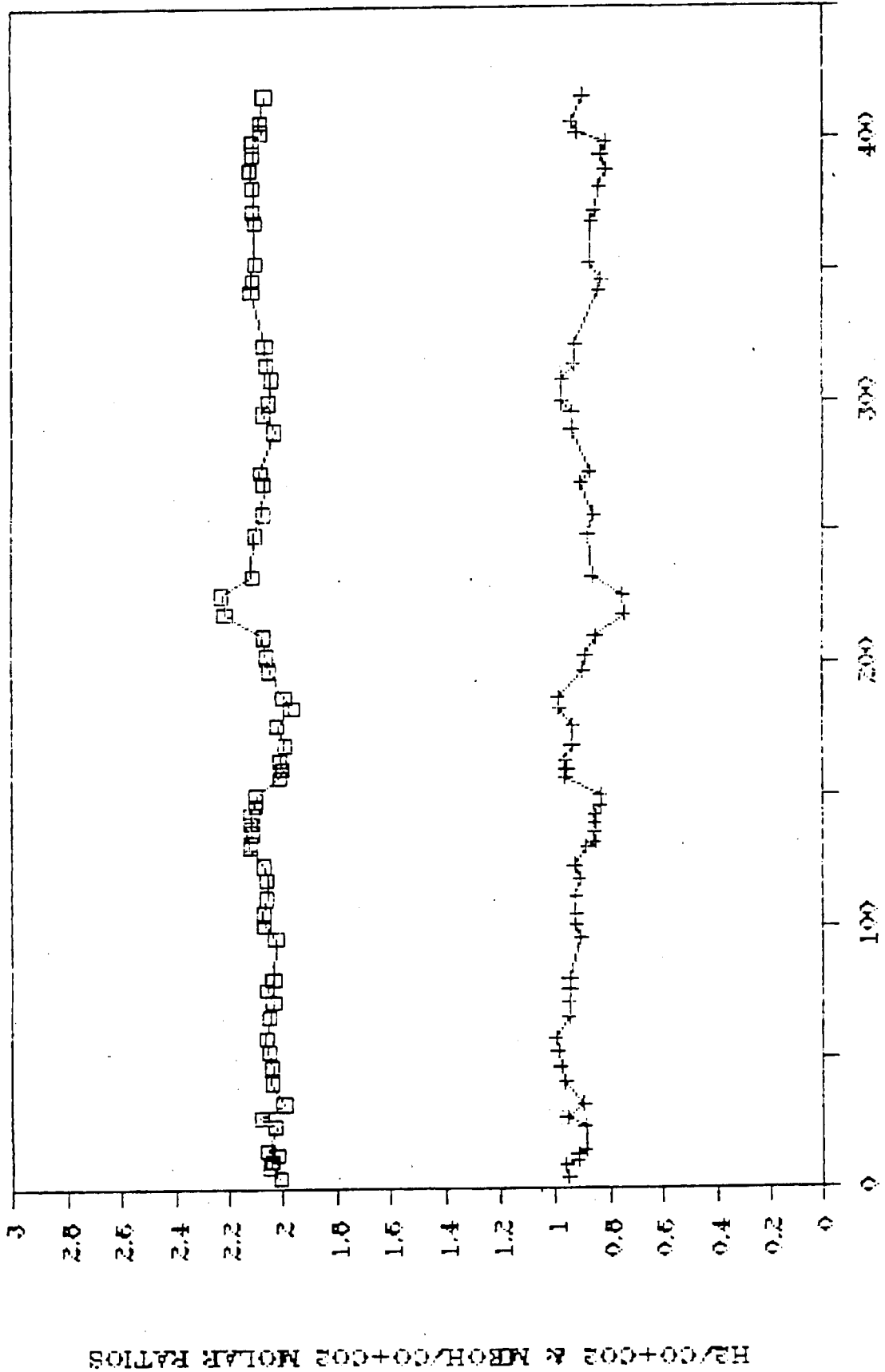


Figure 24

# FIELD TEST # 2 (GREAT PLAINS COAL GAS)

(250 C, 750 PSIG @ 10,000 GHSV)



□ H<sub>2</sub> CNS/CO+CO<sub>2</sub> CNS  
 + MECH/CO+CO<sub>2</sub> CNS  
 TIME ON STREAM, HRS

Table 12

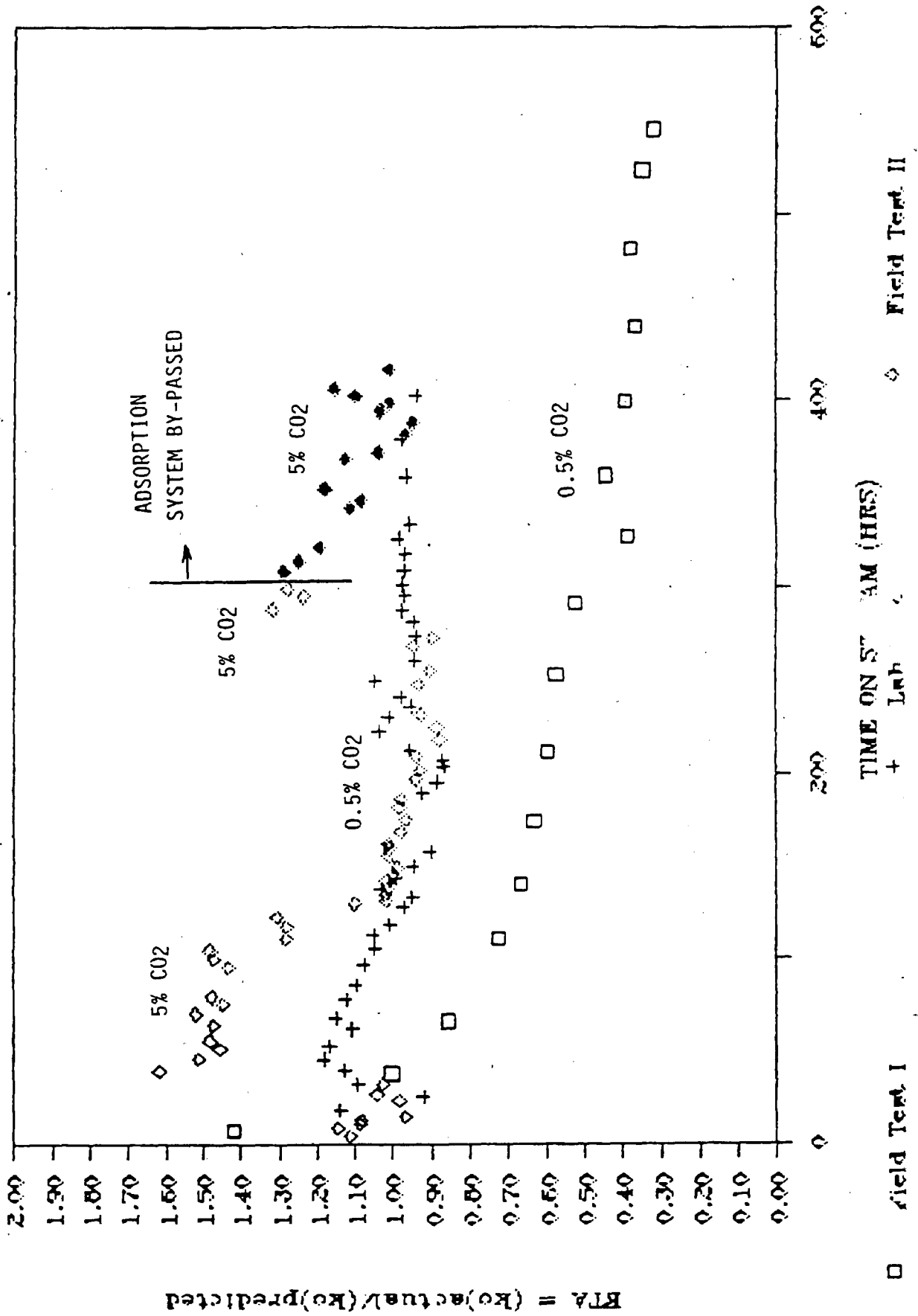
# METHANOL SYNTHESIS FROM GP COAL GAS AVERAGE MOLAR RATIOS

TEST	H <sub>2</sub> CONSUMED/ CO+CO <sub>2</sub> CONSUMED	CH <sub>3</sub> OH PRODUCED/ CO+CO <sub>2</sub> CONSUMED
FIELD TEST # 1	2.16	0.83
LAB TEST # 1	1.94	0.98
FIELD TEST # 2	2.06	0.91
FIELD TEST # 2 (ADSORBENTS BYPASSED)	2.09	0.87
REACTIONS:	CO + 2H <sub>2</sub> ----->	CH <sub>3</sub> OH
	CO <sub>2</sub> + 3H <sub>2</sub> ----->	CH <sub>3</sub> OH + H <sub>2</sub> O

Figure 25

# ETA VS. TIME ON STREAM

(250 C, 750 PSIG & 10,000 GHSV)



- At 5% CO<sub>2</sub> level in feed, the eta was greater than "1". This indicates the model underpredicts the CO<sub>2</sub> advantage.
- The eta for most of Field Test #1 was significantly less than "1" indicating major stability problems.

#### Estimation of Relative Deactivation Rates

To estimate relative stability for each test, a regression was carried out to fit an exponential decay in activity:

$$(\text{Eta}) = (\text{Eta})_0 \exp [-(\text{Alpha})(t)]$$

where Alpha = deactivation rate, and  
t = on-stream time

Average relative deactivation rates for the three tests were calculated and are given in Table 13. The catalyst was much more stable in the second test compared to the first test but may have been slightly less stable than the lab test. The scatter in the lab data makes it difficult to compare the second test results with lab test results. The adsorption system removed all the potential catalyst poisons except olefins like ethylene and propylene. Hence, olefins in the feed may be the cause of slightly higher deactivation. It may be prudent to conduct a lab test with ethylene and propylene in the feed during the Clean Coal III project.

Towards the end of Field Test #2 when the adsorption system was bypassed, the deactivation rate was worse than Field Test #1. This could be due to a brief sulfur breakthrough which was noted in the plant during the bypass test. Or, normal amounts of benzene and toluene in the feed could have caused the deactivation. Looking back at Field Test #1, it appears that Fe and Ni carbonyls from the system was responsible for the initial deactivation. The deactivation continued further, probably due to acetonitrile breakthrough.

#### Analytical Results on Gas/Catalyst Samples

Feed gas and catalyst samples from Field Test #2 were analyzed. Results are compared with those from the other tests are shown in Table 14. XRD tests indicate no growth in crystallite size of Cu (140 A) in Field Test #2. This is consistent with data from the lab test. However, the Cu crystallite size grew to about 400 A during Field Test #1. The crystallite size results support our claim that the catalyst was stable during Field Test #2. Results from AA analyses on the spent catalyst sample indicate no Fe, Ni, or Cl pickup, but some sulfur pickup (120 ppm). Wet chemical analysis on the feed gas sample taken towards the end of Field Test #2 revealed no Fe, H<sub>2</sub>S or CN<sup>-</sup> in the gas. GC analysis of the feed indicated 50 ppmv of ethylene. GC-MS analysis of the feed did not detect any acetonitrile.



Table 13

# METHANOL SYNTHESIS FROM GP COAL GAS DEACTIVATION RATES

TEST	AVG RELATIVE DEACTIVATION RATE (Alpha), % / day
FIELD TEST # 1	4.6
LAB TEST # 1	1.0
FIELD TEST # 2	1.8
FIELD TEST # 2	6.0

(ADSORBENTS BYPASSED)

NOTE:

$$(\text{Eta}) = (\text{Eta})_0 \exp[-(\text{Alpha})(t)]$$

where (Eta) =  $k_0$  (actual) /  $k_0$  (predicted)

Table 14

# ANALYTICAL RESULTS

SAMPLE	METHOD	FRESH	FIELD TEST 1	LAB TEST 1	FIELD TEST 2
CATALYST	XRD: CU	140 A	400 A	140 A	140 A
	AA: FE	70 PPM	430 PPM	NA	80 PPM
	AA: NI	20 PPM	120 PPM	NA	50 PPM
	AA: S	NA	60 PPM	NA	120 PPM
COAL GAS	GCMS: BENZENE		5 PPMV	NA	NA
FROM RECTISOL	GCMS: TOLUENE		0.5 PPMV	NA	NA
OUTLET	GCMS/GC: ETHANE		>> 6 PPMV	NA	340 PPMV
	GCMS/GC: PROPANE		>> 6 PPMV	NA	24 PPMV
	GCMS: ACETONITRILE		> 6 PPMV	NA	ND
	GC: ETHYLENE		NA	NA	50 PPMV

NA - NOT AVAILABLE, ND - NOT DETECTED

## SUMMARY AND CONCLUSIONS:

### Lab Tests with Coolwater Coal Gas

An adsorption system designed to clean up coal gas for the LPMEOH process was successfully tested for Coolwater (CW) coal gas. Iron carbonyl, carbonyl sulfide and hydrogen sulfide were removed from the coal gas. The effectiveness of the adsorption system was confirmed by measuring LPMEOH catalyst performance downstream.

H-Y zeolite showed stable capacity for  $\text{Fe}(\text{CO})_5$  through three adsorption/regeneration cycles (0.19 mmole/gm). In contrast, BPL carbon had higher but unstable capacity for  $\text{Fe}(\text{CO})_5$  (reduced from 0.64 mmole/gm in Cycle 1 to 0.29 mmole/gm in Cycle 3). The capacities for both adsorbents agreed well with those observed in a recirculating apparatus (Task 3.4). The formation of  $\text{Fe}(\text{CO})_5$  on-stream from Fe deposited on adsorbents was observed during regeneration at 500°F. The Fe deposition was minimized by regenerating at lower temperatures (<250°F).

COS appeared to be chemisorbed on FCA carbon. The capacity was non-regenerable by hot nitrogen purge (up to 500°F). This is in contrast with the earlier results from the recirculating apparatus where on-stream times were much lower. Investigation of different regeneration methods (e.g., use of steam) for FCA carbon as well as use of hot ZnO for COS removal is recommended.

The Cu/Zn catalyst appeared to remove  $\text{H}_2\text{S}$  adequately. With about 7 ppm of  $\text{H}_2\text{S}$  added in the coal gas stream, no breakthrough was observed during 100 hours of  $\text{H}_2\text{S}$  injection.

Performance of the F21/OE75-43 catalyst for methanol synthesis was monitored downstream of the adsorption system. At 5000 sl/kg-hr, 750 psig and 250°C, the expected concentration of about 10 % methanol was observed in the effluent with the cleaned-up CW feed. No significant deactivation was evident during the 120 hours on-stream.

### Field/Lab Tests with Great Plains Coal Gas

The Great Plains (GP) syngas can be treated by adsorption for the LPMEOH process. The catalyst deactivation observed in Field Test #1 was much improved in Field Test #2 after regular (every three days) regeneration of the adsorbents was practiced. The adsorption system, which was designed for the removal of iron/nickel carbonyls, hydrogen/carbonyl sulfide, and hydrochloric acid, must be modified to accommodate other unexpected impurities, such as acetonitrile and ethylene, which were observed during both field tests.

The low  $\text{CO}_2$  content (0.5%) in the GP gas does not cause catalyst deactivation. A lab test with a simulated GP gas indicated stable catalyst activity.

Adjusting the CO<sub>2</sub> content of the feed to 5% by CO<sub>2</sub> addition increased methanol productivity by 40%. This improvement, observed in the lab test, was demonstrated in Field Test #2.

Future research is recommended to investigate the impact of acetonitrile and ethylene on the LPMeOH process. Their individual effects on catalyst activity should be quantified. Methods for removal should be developed if they are proven to be detrimental.

#### REFERENCES:

1. Golden, T. C., "Adsorbent Evaluation for Removal of Catalyst Poisons from Synthesis Gas," RRRS Report No. APCI/PSG-90-004, December 1989.
2. Bhatt, B. L., "Full Hazards Review for LPMeOH Poisons Unit," 9 February 1989.
3. Bhatt, B. L., "Hazards Review/ORI for Autoclave Addition to LPMeOH Poisons Unit," 5 July 1989.
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5. Hsiung, T. H., "Hazards Review of #1 300 cc Autoclave in Lab 17 at Iron Run," 17 March 1988.
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