

LIQUID PHASE METHANOL LAPORTE PROCESS DEVELOPMENT UNIT:
RESEARCH AND ENGINEERING SUPPORT STUDIES

Topical Report

Task 3.8: Catalyst Poisons Field Demonstration

Contractor

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Abstract

As part of the DOE-sponsored liquid phase methanol process development program (Contract No. DE-AC22-87PC90005), the present study (Task 3.8) evaluated adsorptive schemes to remove catalyst poisons from coal gas at pilot scale. In addition to a lab test with coal gas from Coolwater, two field tests were performed at Great Plains with live coal gas.

In the lab test with Coolwater gas, iron carbonyl, carbonyl sulfide, and hydrogen sulfide were effectively removed from the coal gas. The capacities of H-Y zeolite and BPL carbon for $\text{Fe}(\text{CO})_5$ agreed well with the previous bench scale results at similar CO_2 partial pressure. Significant Fe deposition was observed during regeneration. This was minimized by regenerating at lower temperatures. COS appeared to be chemisorbed on FCA carbon; its capacity was non-regenerable by hot nitrogen purge. A Cu/Zn catalyst, used to remove H_2S adsorptively, worked adequately. With the adsorption system on-line, a downstream methanol catalyst showed stable activity for 120 hours of operation.

In the two field tests, it was demonstrated that the Great Plains (GP) syngas could be treated by adsorption for LPMEOH process. The catalyst deactivation observed in the first field test was much improved in the second field test 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, needed to be modified to accommodate other unexpected impurities, such as acetonitrile and ethylene which were observed during both field tests. A lab test with a simulated GP gas indicated that low CO_2 content (0.5%) in the GP gas does not cause catalyst deactivation. Adjusting the CO_2 content of the feed to 5% by CO_2 addition, increased methanol productivity by 40% in both the lab and the second field test.

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INTRODUCTION:

Since 1982, Air Products and Chemicals, Inc. and Chem Systems Inc. have been developing a liquid phase process to produce methanol from synthesis gas. Conventionally, the commercial catalytic conversion of synthesis gas to methanol is carried out in a gas phase fixed bed reactor. In the liquid phase methanol (LPMEOH*) process, the catalyst is suspended in an inert liquid and synthesis gas is bubbled through it. The liquid phase provides an effective medium for heat removal and enables excellent temperature control, allowing isothermal operation of the highly exothermic and equilibrium-limited methanol synthesis. High conversions per pass are achieved even with coal gas, which contains a high amount of CO. However, the coal gas typically contains catalyst poisons such as carbonyls and sulfides, which must be removed from the feed prior to its introduction into the reactor.

A study was conducted to screen adsorbents as guard bed materials for the removal of poisons from coal gas (Task 3.4). Both equilibrium and kinetic adsorptive characteristics of various commercial adsorbents were measured for catalyst poisons such as iron carbonyl, nickel carbonyl, hydrogen sulfide, carbonyl sulfide and hydrochloric acid. A coal gas clean-up system was designed based on these data (1). The current study (Task 3.8) involved testing of the clean-up system at pilot scale with actual coal gasifier off-gas.

A pilot unit consisting of an adsorption system and an autoclave reactor was set up in a trailer. Coal gas was filled in a tube trailer at the Coolwater site and transported to Allentown, Pennsylvania. Two lab tests were conducted with the Coolwater coal gas. The pilot unit trailer was then transported to Great Plains Synfuels Plant near Beulah, North Dakota, where two field tests were conducted with live Great Plains gas.

OBJECTIVES:

1. To investigate the removal of methanol catalyst poisons from coal gas by adsorption.
2. To confirm the effectiveness of an optimum adsorption design via lab tests by measuring LPMEOH catalyst performance.
3. To test the effectiveness of the adsorption system via field tests by monitoring catalyst performance with live coal gas.

*A trademark of Chem Systems Inc.

PATENT SITUATION:

An idea proposal entitled "Improved Regeneration of H-Y Zeolite and BPL Carbon for Iron Carbonyl Removal" was submitted (I-C2304).

SAFETY:

The primary hazards associated with the experimental study were toxicity of carbonyls, sulfides, and carbon monoxide as well as flammability of hydrogen and carbon monoxide. Hazards reviews and operation readiness inspections were conducted for the apparatus (2,3). Safeguards included installation of CO and flammable alarms, an adequate ventilation system, and an automatic shutdown system.

REGULATORY MATTERS:

Not Applicable.

FUTURE PROGRAMS:

This study completes the poison removal tasks under DE-AC22-87PC90005. Additional coal gas clean-up work is planned under the Alternative Fuels I contract.

ACKNOWLEDGMENTS:

The author of this report, Bharat Bhatt, would like to thank Tom Dahl, Steve Gaul, and Bob Blum for safe and efficient construction and operation of the pilot unit. In addition, Tom Hsiung and Tim Golden provided valuable guidance and supervisory back-up for the project. The author is grateful to Bob Byerley for excellent analytical support.

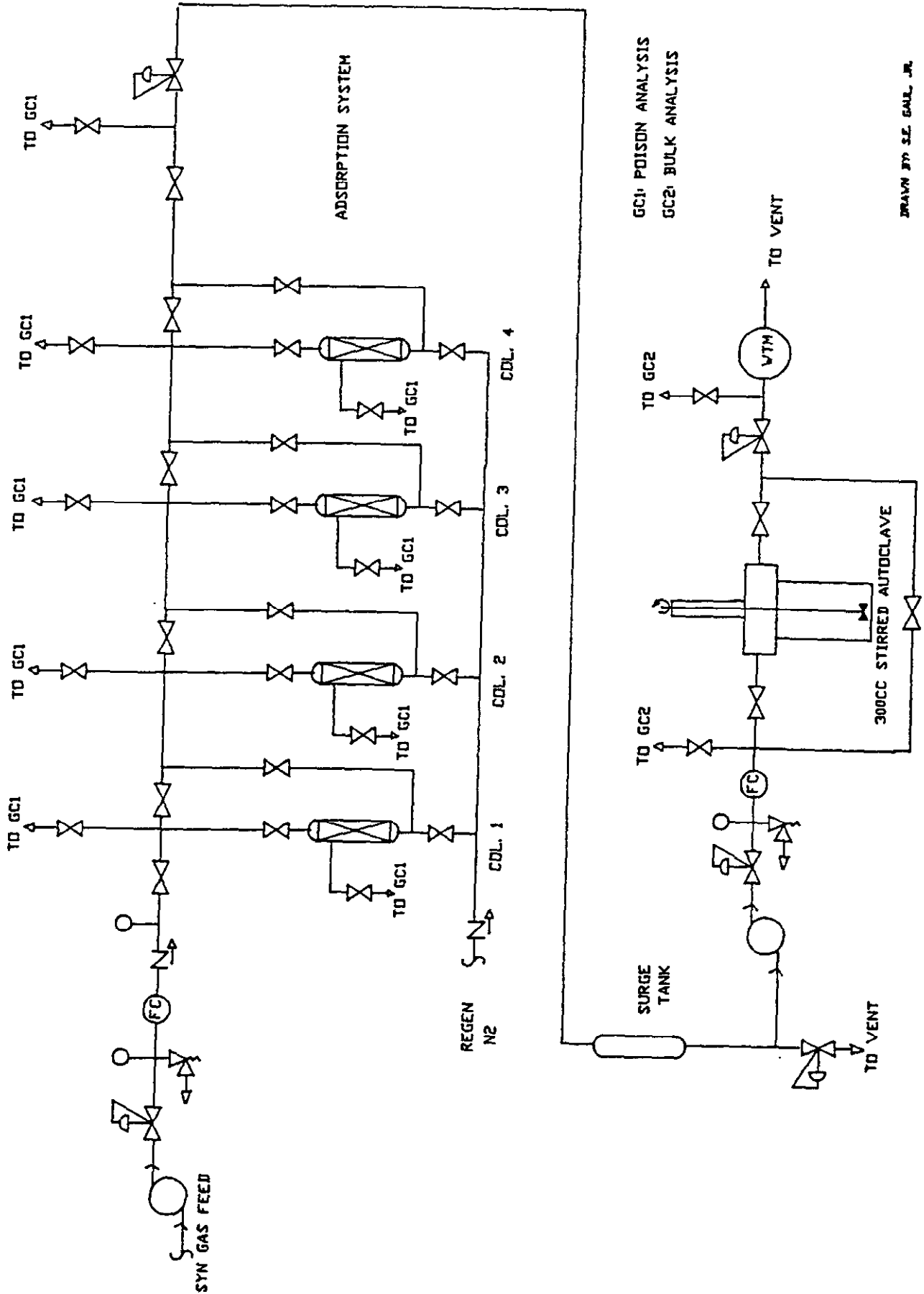
EXPERIMENTAL TECHNIQUES:

The two lab tests with CW coal gas as well as the two field tests with Great Plains coal gas were conducted in a pilot unit built in a trailer. The details of this unit are described in the hazards reviews (2,3). A simplified schematic of the unit is given in Figure 1. The unit consists of an adsorption system and an autoclave reactor.

Adsorption System

Four 3/4" O. D. stainless steel columns were used in series to remove poisons from the coal gas. Column length varied from 1 to 4 ft and each column was filled with a different adsorbent specific for a particular poison. The coal gas was compressed when its source was a tube trailer (i.e., CW coal gas). It was not compressed when a constant pressure source was available (i.e., Great Plains coal gas). Adsorption flow was controlled using a mass flow controller. The flow direction was downward through the columns. Each column had a number of sample ports along the length. A back pressure regulator maintained up to 1000 psig during adsorption. The regeneration was conducted using nitrogen flowing upwards through each column.

FIGURE 1
COAL GAS CLEAN-UP UNIT SCHEMATIC



GC1: POISON ANALYSIS
GC2: BULK ANALYSIS

DRAWN BY S.E. GALL, JR.

Autoclave System

A stirred 300 cc stainless steel autoclave was used as a reactor to conduct methanol synthesis. The clean coal gas from the adsorption system was compressed and fed to the heated autoclave containing a slurry of catalyst and oil. The flow through the autoclave was controlled using a mass flow controller. A back pressure regulator maintained up to 1000 psig in the autoclave. The product was vented after sampling. A one gallon surge tank was used between the adsorption and autoclave system. The adsorption system was operated at a slightly higher flow rate (about 5%) than the autoclave system. The excess flow was vented through a back pressure regulator.

Analytical System

The gas analysis was conducted by using two on-line GCs. One was dedicated to poison analysis, the other was used for bulk components. Details of the analytical system are described in Reference 4. The poison GC consisted of an Electron Capture Detector (ECD) for iron and nickel carbonyl analysis and a Photo Ionization Detector (PID) for hydrogen sulfide and carbonyl sulfide analysis. The bulk components were analyzed by two Thermal Conductivity Detectors (TCDs); one for CO, CO₂, CH₄, N₂, CH₃OH, C₂H₅OH and CH₃OCH₃, and the other for H₂.

RESULTS AND DISCUSSION:

Lab Tests with Coolwater Coal Gas

Lab Test #1

Lab Test #1 studied the removal of Fe(CO)₅, Ni(CO)₄, COS, and H₂S from the Coolwater (CW) coal gas by adsorption. The coal gas was filled in a tube trailer at the Coolwater plant site in August 1988. The gas analysis by Radian analysis during the fill-up indicated, on an average, about 11 ppmv COS, 30 ppmv H₂S, 0.14 ppmv Fe(CO)₅, and no Ni(CO)₄ (see Table 1). Wet chemical analysis before the coal gas clean-up study (February 1989) found no H₂S, about 8 ppmv Fe(CO)₅, and no Ni(CO)₄. GC analysis of the coal gas during the study (March 1989) indicated about 55 ppmv COS in addition to confirming results from the wet chemical analysis. While generation of Fe(CO)₅ could be expected, the apparent conversion of H₂S into COS beyond equilibrium cannot be explained. Bulk analysis of the coal gas indicated about 42.6% CO, 39.2% H₂, 17.3% CO₂, 0.4% N₂, 0.25% CH₄ and 0.17% Ar.

The columns were loaded up with fresh adsorbents as shown in Table 2. The Cu/Zn catalyst in column #1 was reduced using 2% H₂ in N₂ at 100 psig with a temperature ramping. The zeolite in column # 2 was dried using N₂ at 500°F for about 12 hours.

Seven runs were completed in this lab test. The operating parameters for each adsorption and regeneration are summarized in Table 3. All the adsorptions were conducted at 450 psig inlet pressure (430 psig outlet) and ambient temperature. All regenerations were conducted using 1 lit/min nitrogen flow for each column. Capacity and mass transfer zone results for various adsorbents are given in Table 4.

Table 1

TRACE COMPONENT ANALYSIS FOR COOLWATER COAL GAS

COMPONENT (PPMV)	RADIAN ANALYSIS DURING FILLING (8/88)	WET CHEMICAL ANALYSIS BEFORE POISON STUDY (2/89)	GC ANALYSIS DURING POISON STUDY (3/89)
COS	7-13	NA	55
H2S	18-53	<0.2	ND
HCL	<0.022	<0.06	NA
FE(CO)5	0.14	8	7
NI(CO)4	0.01	<0.023	ND

NA - NOT AVAILABLE, ND - NOT DETECTED

Table 2

COOLWATER COAL GAS CLEAN UP LAB TEST # 1 ADSORPTION BEDS

COLUMN	ADSORBENT	POISON	LENGTH	WEIGHT
1	CU/ZN BASF S3-86 CATALYST	HCL, H2S	1 FT	79 GM
2	LINDE H-Y ZEOLITE	FE(CO)5	1 FT	38.6 GM
3	BPL CARBON	NI(CO)4	1 FT	29.6 GM
4	FCA CARBON (WITH CU/CR OXIDE)	COS	4 FT	141.5 GM

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

Table 3

COOLWATER COAL GAS CLEAN UP LAB TEST # 1

RUN NO.	COLUMNS ONLINE	BREAKTHRU INFO	CONDITIONS	COMMENTS
1	1, 2, 3, 4	1, 2, 3, 4	5 L/M FOR 140 HRS 10 L/M FOR 15 HRS	
1R	1, 2, 3, 4		2-3 HRS @ 500 F	
2	1, 2, 3, 4	1, 2, 4	5 L/M FOR 63 HRS	
2R	4		7 HRS @ 500 F	
3	3, 4	3, 4	5 L/M FOR 16 HRS 10 L/M FOR 11 HRS	
3R	1, 2, 3, 4		4 HRS @ 500 F	
4	1, 3	1, 3	10 L/M FOR 14 HRS	+ H2S
5	1, 2	2	10 L/M FOR 16 HRS	+ H2S
5R	1, 2, 3		TO 330 F IN 4 HRS	
6	1, 2, 3	-	10 L/M FOR 6 HRS	
6R	1, 2, 3		TO 260 F IN 28 HRS	
7	1, 2, 3	-	10 L/M FOR 2 HRS	
7R	1, 2, 3		TO 210 F IN 21 HRS	

Table 4

COOLWATER COAL GAS CLEAN UP LAB TEST # 1

POISON	FE(CO)5	FE(CO)5	FE(CO)5	COS	COS
COLUMN #	1	2	3	1	4
LENGTH (*)	12	12	12	12	48
ADSORBENT	S3-86 CAT	H-Y ZEOLITE	BPL CARBON	S3-86 CAT	FCA CARBON
CYCLE 1					
CAP. (MMOLES/GM)	0.02	0.19	0.64	0.19	0.56
MTZ (*)	2	3.3	1	2.7	34
CYCLE 2					
CAP. (MMOLES/GM)	0.005	0.19	0.41	0	0.13
MTZ (*)	10.7	2.2	1.3	-	68
CYCLE 3					
CAP. (MMOLES/GM)	0.006	0.19	0.29	0	0.019
MTZ (*)	14.4	4	3.2	-	14

Removal of Iron Carbonyl

The Cu/Zn catalyst (column #1), which is designed for H₂S and HCl, showed significant capacity for Fe(CO)₅ (0.02 mmole/gm) in the initial cycle. The breakthrough curves are shown in Figure 2. Concentration of Fe(CO)₅ is plotted as a function of on-stream time at inlet, outlet, and various ports in the column. From this information, the mass transfer zone (MTZ) was estimated to be about 2". The capacity, however, reduced to insignificant levels in the second and third cycle (see Table 4). This indicates that the removal of Fe(CO)₅ by the catalyst is chemical.

The H-Y zeolite (column #2) had a capacity of about 0.19 mmole/gm for Fe(CO)₅ with 3.3" MTZ (see Figure 3 for breakthrough curves) in the first cycle. The capacity of H-Y zeolite for Fe(CO)₅ remained the same in the second and third cycles. This is consistent with earlier observations from a recirculating adsorption apparatus (1). Also, the zeolite capacity matches well with the capacity observed earlier at similar CO₂ partial pressure.

The initial capacity of BPL carbon (column #3) for iron carbonyl was estimated at 0.64 mmole/gm (see Figure 4 for breakthrough curves). It dropped to 0.41 mmole/gm in the second cycle and 0.29 mmole/gm in the third cycle. The decline in BPL carbon's capacity was expected. The capacity also matches well with the capacity observed earlier (1) at similar CO₂ partial pressure.

In cycles 2 and 3, formation of Fe(CO)₅ in the H-Y zeolite was observed, as well as BPL carbon bed when the feed to the bed was free of any Fe(CO)₅ (see results in first hour, Figure 5). Fe(CO)₅ was probably formed on-stream from Fe deposited on adsorbents during regeneration. The regeneration temperature may have been too high, causing decomposition of Fe(CO)₅ and depositing Fe on the adsorbent. No Fe(CO)₅ was formed in the beds during the first cycle. Several low temperature regenerations were attempted. However, the baseline concentration did not change significantly (see Table 5). It was encouraging to observe a significant amount of Fe(CO)₅ leaving the system. It appears that removing the Fe from the two beds was partially successful.

Removal of Carbonyl Sulfide

The Cu/Zn catalyst (column #1) showed significant capacities for COS (0.19 mmole/gm) initially. The MTZ was estimated to be 2.7" (see Figure 6 for breakthrough curve). However, the capacity was practically zero in subsequent cycles, indicating chemical reaction.

Capacities of zeolite (column #2) and BPL carbon (column #3) were insignificant for COS.

The initial capacity of the FCA carbon (column #4) for COS was higher than expected (0.56 mmole/gm). However, its mass transfer zone was also high (see Figure 7). Unexpectedly, the capacity decreased substantially to 0.13 mmole/gm in the second cycle. Probably the adsorption occurred

Figure 2

COOLWATER COAL GAS STUDY - LAB TEST # 1

CYCLE # 1 FOR 53-86 CAT (COLUMN # 1)

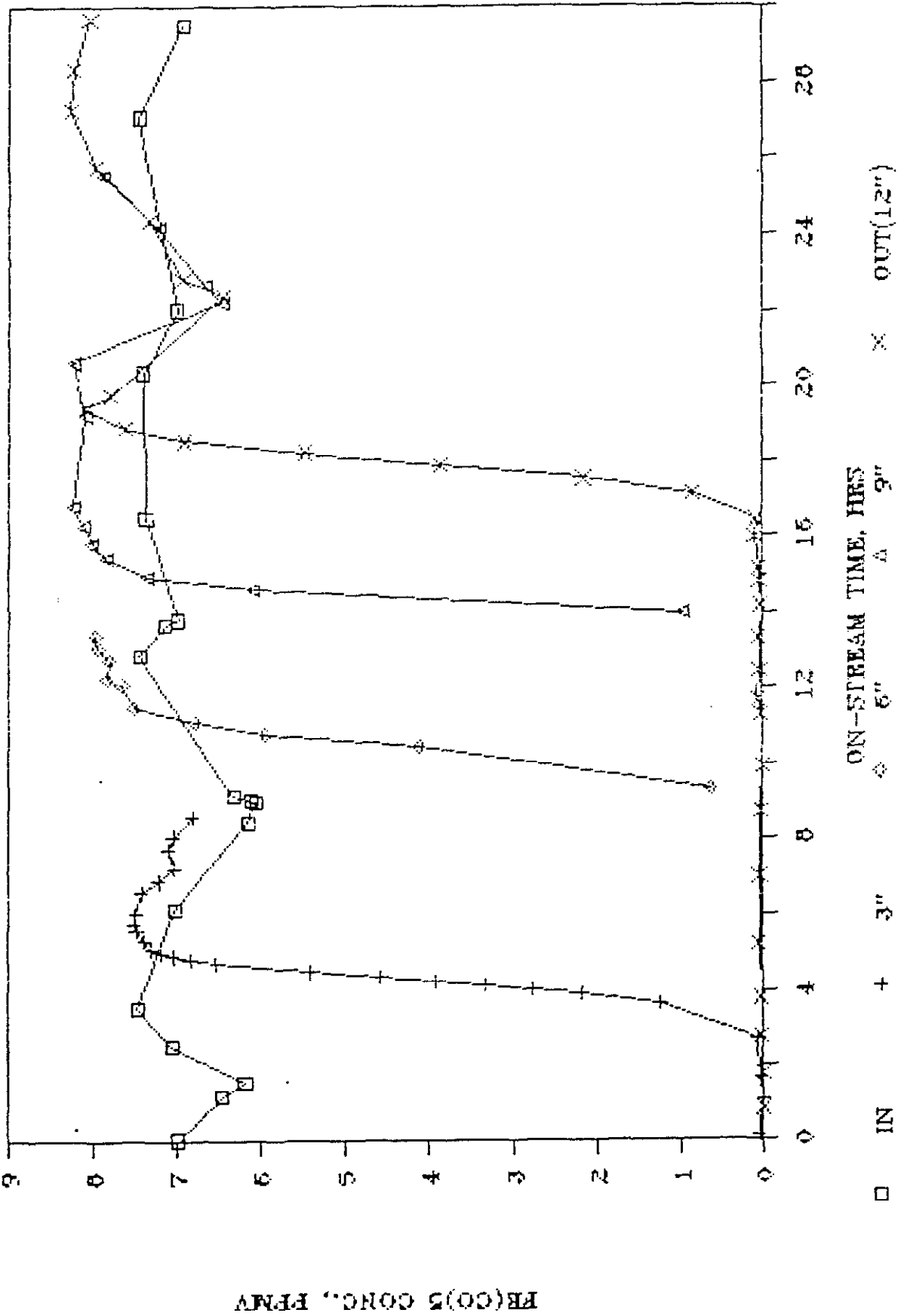


Figure 3

COOLWATER COAL GAS STUDY - LAB TEST # 1

CYCLE # 1 FOR H-Y ZEOLITE (COLUMN # 2)

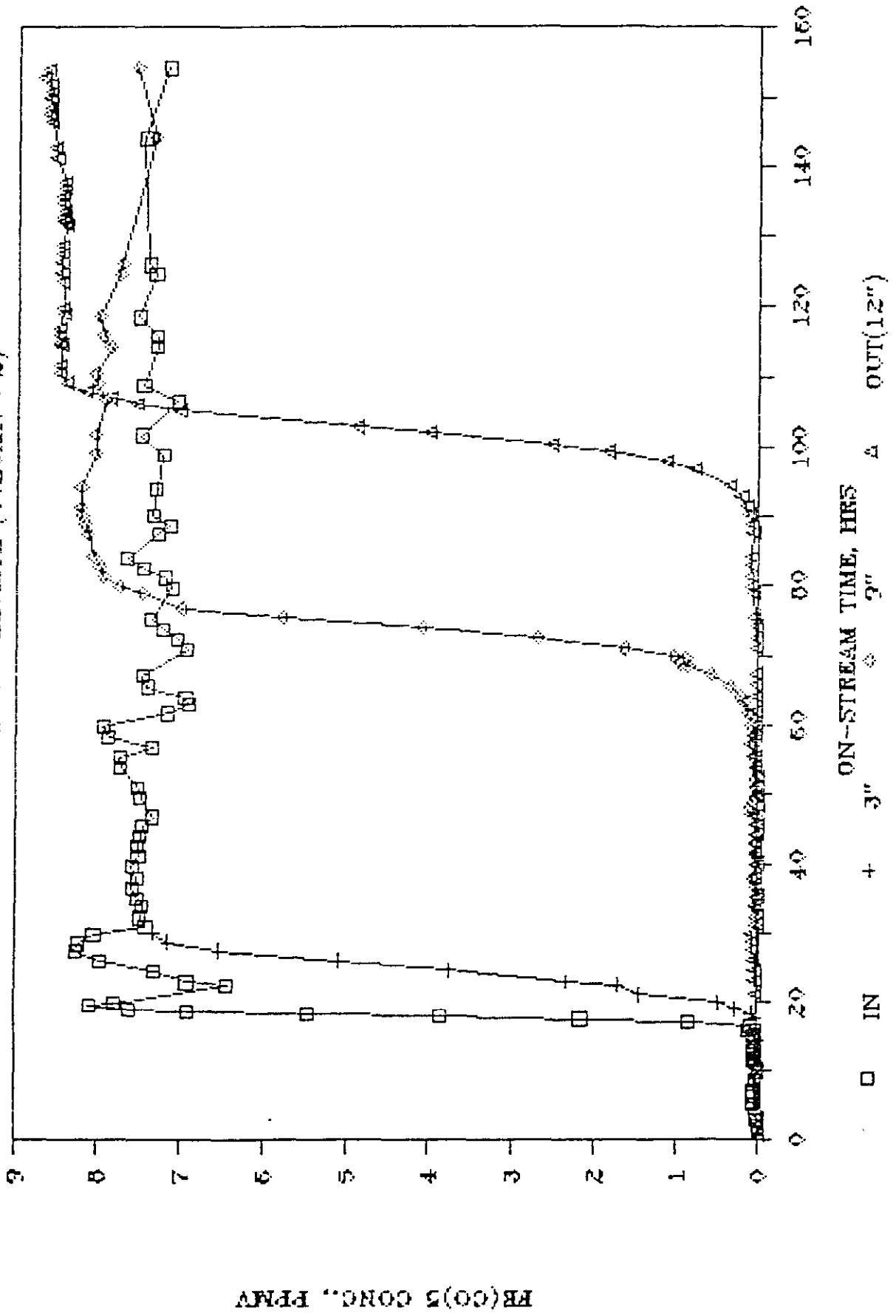


Figure 4

COOLWATER COAL GAS STUDY -- LAB TEST # 1

CYCLE # 1 FOR BPL CARBON (COLUMN # 3)

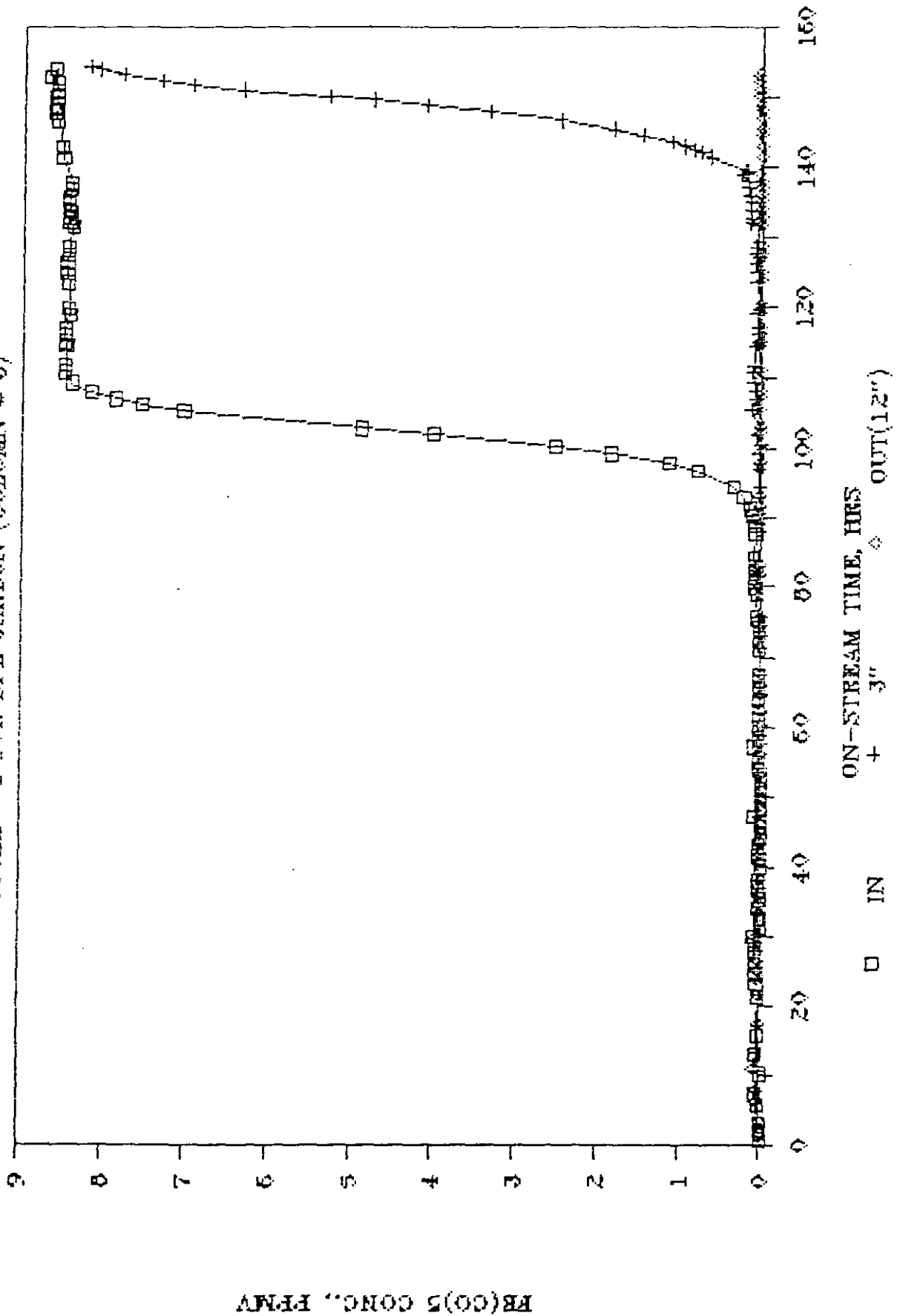


Figure 5

COOLWATER COAL GAS STUDY -- LAB TEST # 1

CYCLE # 3 FOR HPL CARBON (COLUMN # 3)

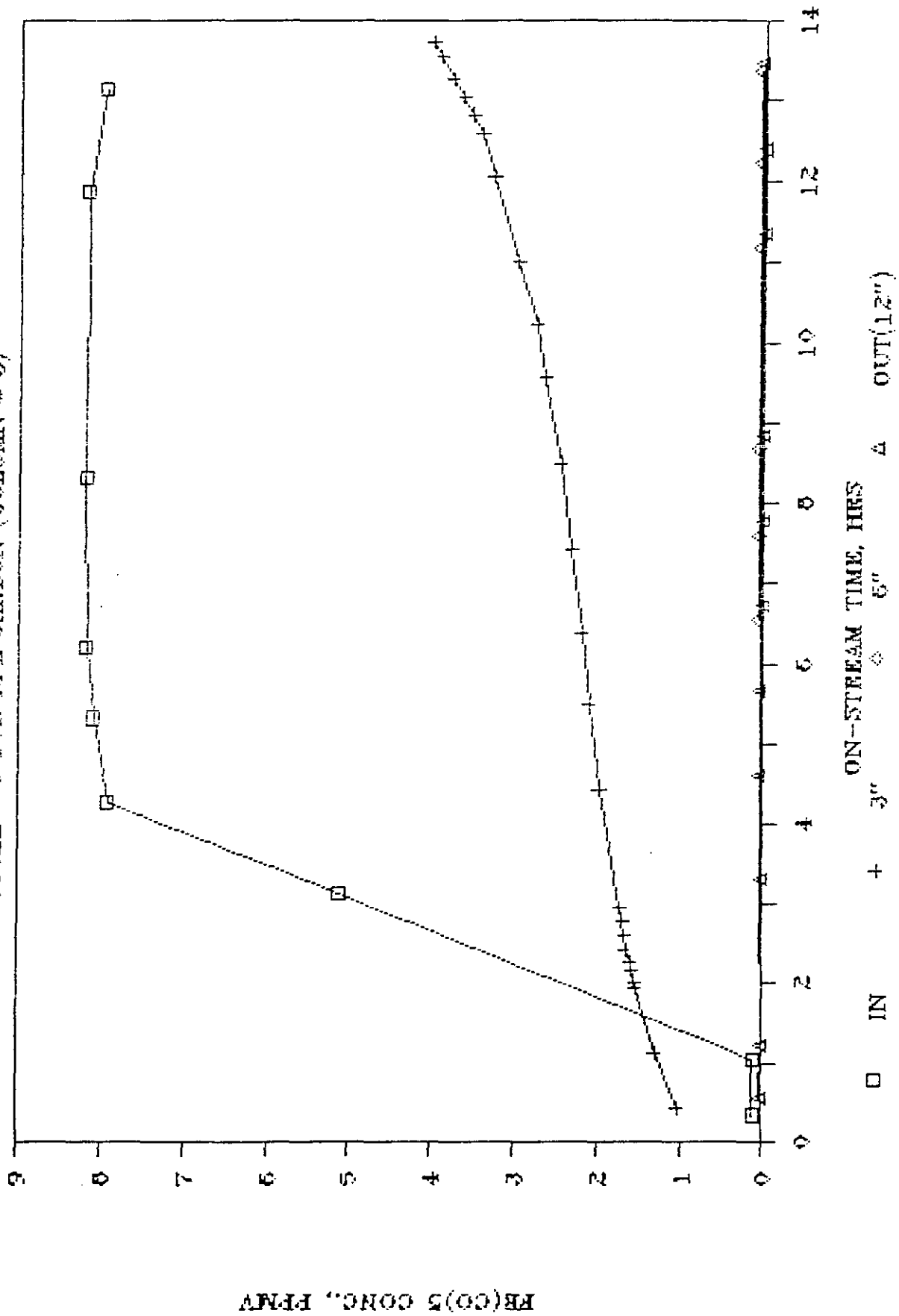


Table 5

COOLWATER COAL GAS CLEAN UP LAB TEST # 1 FE(CO)5 REMOVAL

	H-Y ZEOLITE (COL # 2, 12')	BPL CARBON (COL # 3, 12')
CYCLE 1		
CAP. (MMOLES/GM)	0.19	0.64
MTZ (*)	3.3	1
BASELINE CONC (PPMV)	0.01	0.01
CYCLE 2		
CAP. (MMOLES/GM)	0.19	0.41
MTZ (*)	2.2	1.3
BASELINE CONC (PPMV)	1.5	1.3
CYCLE 3		
CAP. (MMOLES/GM)	0.19	0.29
MTZ (*)	4	3.2
BASELINE CONC (PPMV)	0.6	1.6
CYCLE 4		
BASELINE CONC (PPMV)	0.5	1.9
CYCLE 5		
BASELINE CONC (PPMV)	0.7	1.5

Figure 6

COOLWATER COAL GAS STUDY -- LAB TEST # 1

CYCLE # 1 FOR S3-86 CAT (COLUMN # 1)

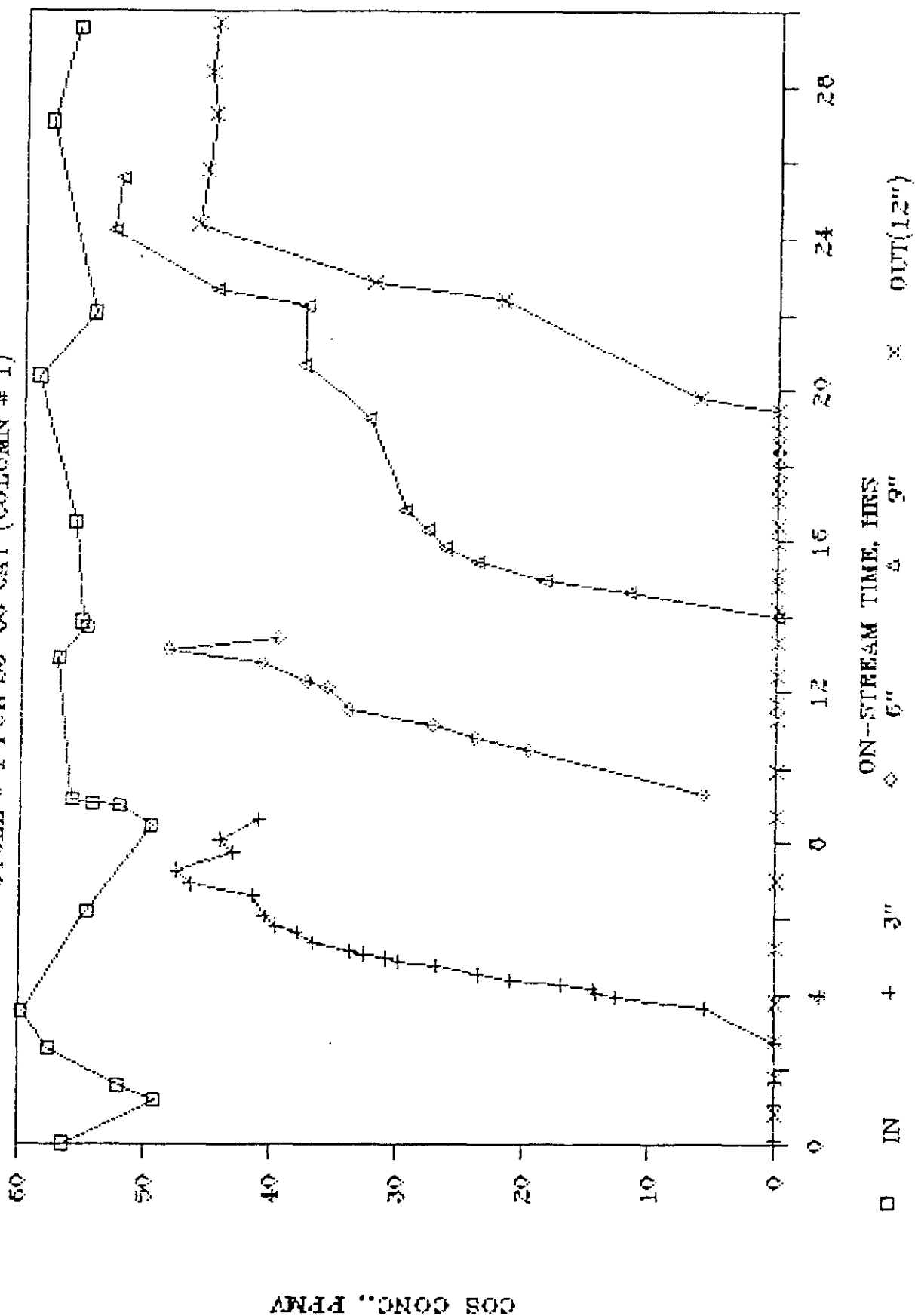
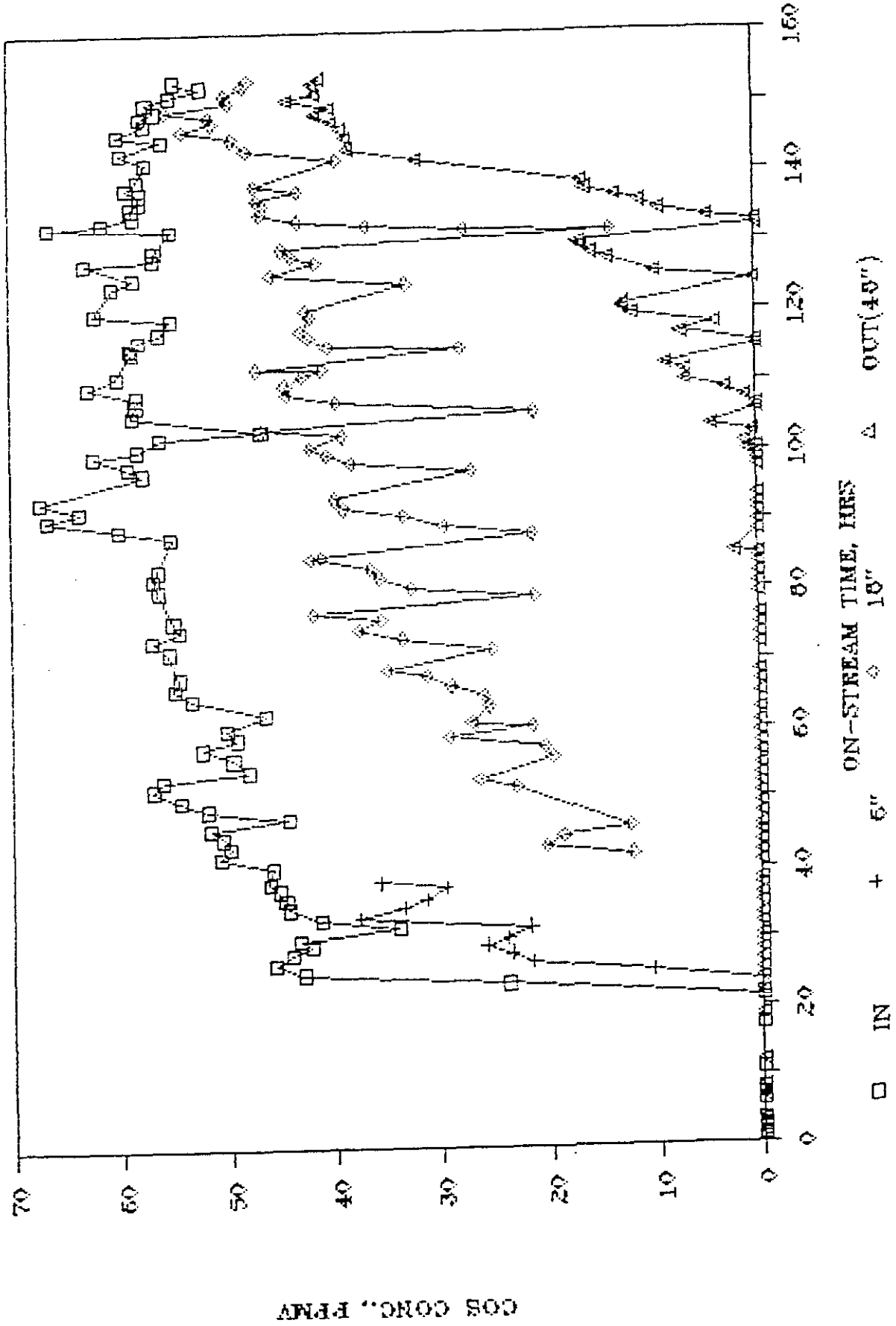


Figure 7

COOLWATER COAL GAS STUDY - LAB TEST # 1

CYCLE # 1 FOR FCA CARBON (COLUMN # 4)



through a slow chemical reaction. This was not evident in the recirculating apparatus with much lower residence/ on-stream time. Even after a longer regeneration, the capacity reduced further to 0.019 mmole/gm in the third cycle. Investigation of different regeneration methods (e.g., use of steam) for FCA carbon, as well as the use of hot ZnO for COS removal is recommended.

Removal of Hydrogen Sulfide

Since the CW gas lost almost all of its original H₂S before the study, about 7 ppm of H₂S were added in the coal gas stream to evaluate the adsorbents for its removal. The Cu/Zn catalyst appeared to be removing H₂S adequately. In 30 hours on-stream with 7 ppm H₂S added, we did not see any H₂S breaking through the sample port closest (3") to the inlet.

Lab Test # 2

In addition to studying Fe(CO)₅ and H₂S removal from the coal gas by adsorption, performance of a methanol catalyst downstream of the adsorbents was also monitored during Lab Test #2. This would confirm the effectiveness of adsorption system. The columns were loaded with fresh adsorbents similar to Lab Test #1, except that the H-Y zeolite and BPL carbon columns were short loaded (0.5 ft) to get quicker cycles (see Table 6). The activation of the Cu/Zn catalyst in column #1 and drying of the zeolite in column #2 were also carried out as in Lab Test #1. The autoclave was loaded with about 50 grams of F21/OE75-43 catalyst powder and 115 grams of Drakeol-10 oil. The catalyst slurry was reduced in the autoclave using 2% H₂ in N₂ at 100 psig with temperature ramping. The cumulative H₂ uptake was about 2.42 scf/lb of catalyst, very close to the expected amount.

Two cycles were completed on the adsorption system. The operating parameters for each adsorption and regeneration are summarized in Table 7. All the adsorptions were conducted at 450 psig inlet pressure (430 psig outlet) and ambient temperature. All regenerations were conducted simultaneously in parallel using 1 lit/min nitrogen counter current (up) flow through each column. Capacity and mass transfer zone results for various adsorbents are given in Table 8.

Removal of Iron Carbonyl

Low temperature regeneration with ramping improved the regeneration of H-Y zeolite and BPL carbon. Less iron was deposited on the adsorbents during regeneration compared to earlier runs. This is evident from the lower baseline Fe(CO)₅ concentration observed during the second cycle (see Table 9). Also, the zeolite at the end of the the second test was found to be non-magnetic. This is an improvement over the first test in which the used zeolite was found to be magnetic due to iron deposit.

Removal of Carbonyl Sulfide

This test confirmed non-regenerability of FCA Carbon (for COS) using N₂ at 500°F (see Table 8). The capacity dropped from 0.7 mmole/gm in first cycle to 0.09 mmole/gm in second cycle.

Table 6

COOLWATER COAL GAS CLEAN UP LAB TEST # 2 ADSORPTION BEDS

COLUMN	ADSORBENT	POISON	LENGTH	WEIGHT
1	CU/ZN BASF S3-86 CATALYST	HCL, H2S	1 FT	81 GM
2	LINDE H-Y ZEOLITE	FE(CO)5	0.5 FT	19.7 GM
3	BPL CARBON	NI(CO)4	0.5 FT	15.5 GM
4	FCA CARBON (WITH CU/CR OXIDE)	COS	4 FT	141 GM

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

Table 7

COOLWATER COAL GAS CLEAN UP LAB TEST # 2

RUN NO.	COLUMNS ONLINE	BREAKTHRU INFO	CONDITIONS	COMMENTS
8	1, 2, 3, 4	1, 2, 3, 4	4.4 L/M FOR 95 HRS	+ H2S
8R	2, 3		TO 250 F IN 11 HRS, 10 HRS AT 250 F.	
	4		TO 500 F IN 8 HRS, 13 HRS AT 500 F.	
9	1, 2, 3, 4	1, 2, 3, 4	4.4 L/M FOR 70 HRS	+ H2S
9R	1		TO 500 F IN 5 HRS.	
	2, 3		TO 250 F IN 5 HRS, 17 HRS AT 250 F.	
	4		TO 500 F IN 5 HRS, 17 HRS AT 500 F.	

Table 8

COOLWATER COAL GAS CLEAN UP LAB TEST # 2

POISON	FE(CO)5	FE(CO)5	FE(CO)5	COS	COS
COLUMN #	1	2	3	1	4
LENGTH (*)	12	6	6	12	48
ADSORBENT	S3-86 CAT	H-Y ZEOLITE	BPL CARBON	S3-86 CAT	FCA CARBON
CYCLE 1					
CAP. (MMOLES/GM)	0.02	0.09	0.69	0.20	0.70
MTZ (*)	1.8	4.2	NA	6.9	NA
CYCLE 2					
CAP. (MMOLES/GM)	0	0.14	0.47	0	0.09
MTZ (*)	-	1.7	2.3	-	24

NA - NOT AVAILABLE

Table 9

COOLWATER COAL GAS CLEAN UP LAB TEST # 2 FE(CO)5 REMOVAL

	H-Y ZEOLITE (COL # 2, 6")	BPL CARBON (COL # 3, 6")
CYCLE 1		
CAP. (MMOLES/GM)	0.09	0.69
MTZ (")	4.2	NA
BASELINE CONC (PPMV)	0.1	0.4
CYCLE 2		
CAP. (MMOLES/GM)	0.14	0.47
MTZ (")	1.7	2.3
BASELINE CONC (PPMV)	0.3	0.3

NA - NOT AVAILABLE

Removal of Hydrogen Sulfide

With about 7 ppm H₂S added in the coal gas, no H₂S breakthrough was observed in column #1 (F21/OE75-43 catalyst) during 100 hours of H₂S injection.

Methanol Catalyst Performance

The autoclave was operated at 5000 sl/kg-hr, 750 psig and 250°C for about 120 hours. Initially, a scatter in the product analysis data was observed, probably due to condensation of methanol in a back pressure regulator (BPR). Additional heat tape was installed on the BPR with individual temperature control. Raising the BPR temperature from 60 to 140°C eliminated the problem. The expected methanol concentration of about 10% was observed in the effluent after about 96 hours on-stream (see Figure 8). This is below the thermodynamic equilibrium concentration of 13.4%. Methanol production appeared to be stable.

Field/Lab Tests with Great Plains Coal Gas

Field Test # 1

The objective of this field test was to investigate the removal of methanol catalyst poisons from live coal gas by adsorption and evaluate catalyst performance after the coal gas clean-up. The coal gas clean-up trailer was transported to Great Plains Synfuels Plant, North Dakota and was situated in the plant to receive coal gas from outlet stream of the Rectisol unit.

Catalyst Life Test with Adsorbents On-stream

The adsorption columns were loaded with fresh adsorbents similar to the lab tests with CW coal gas (see Table 10). The H-Y zeolite and BPL carbon columns were short loaded to get quicker cycles. The Cu/Zn catalyst in column #1 was reduced using 2% H₂ in N₂ at 100 psig with temperature ramping. The zeolite in column #2 was dried using N₂ at 500°F for about 12 hours. The autoclave was loaded with about 25 grams of F21/OE75-43 catalyst powder and 100 grams of Drakeol-10 oil. The catalyst slurry was reduced in the autoclave using 2% H₂ in N₂ at 100 psig with temperature ramping.

The first cycle was started up with the autoclave at 10000 sl/kg-hr, 750 psig and 250°C. The adsorption system was operated at 300 psig inlet pressure and 5% higher flow rate than the autoclave (4.38 vs. 4.17 lit/min). The excess flow was vented through a back pressure regulator. GC analysis of the coal gas indicated that the gas had no H₂S or COS (<0.25 ppm). Also, amounts of Fe(CO)₅ and Ni(CO)₄ detected were insignificant (<0.03 ppm). The feed gas had a composition of about 20% CO, 63% H₂, 0.35-0.75% CO₂, and 16.5-18.0% CH₄.

Figure 8

LAB TEST # 2 (COOLWATER COAL GAS)

(250 G, 750 PSIG @ 5,000 GHSV)

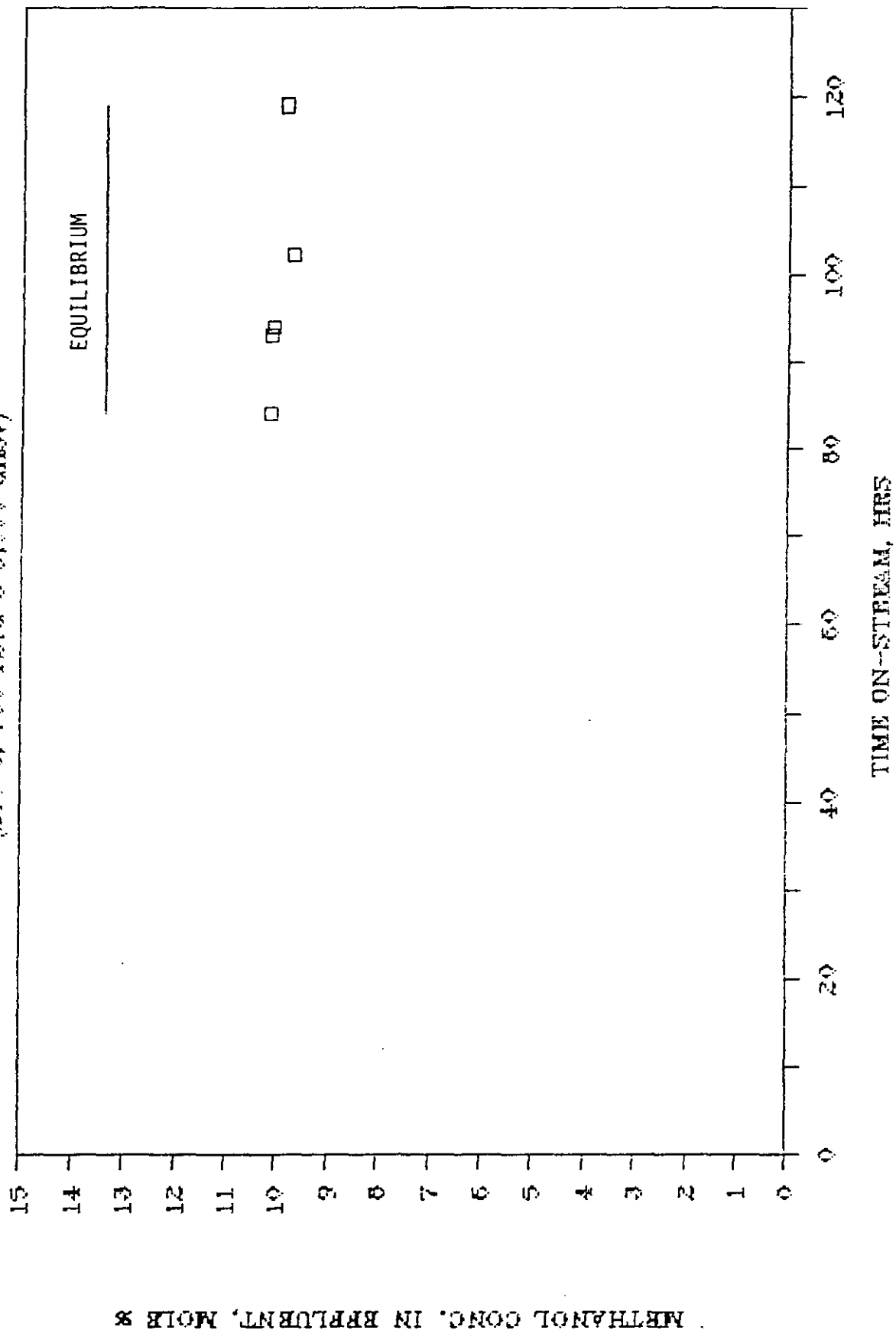


Table 10

GREAT PLAINS COAL GAS STUDY

FIELD TEST # 1

ADSORPTION BEDS

COLUMN	ADSORBENT	POISON	LENGTH	WEIGHT
1	CU/ZN BASF S3-86 CATALYST	HCL, H2S	1 FT	79.8 GM
2	LINDE H-Y ZEOLITE	FE(CO)5	0.5 FT	19.7 GM
3	BPL CARBON	NI(CO)4	0.5 FT	14.8 GM
4	FCA CARBON (WITH CU/CR OXIDE)	COS	4 FT	141.9 GM

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

Methanol concentration in the product effluent is plotted as a function of on-stream time in Figure 9. Methanol concentration dropped substantially from about 8 mole% at the start to about 5.7 mole% after 80 hours. The initial deactivation rate was higher than expected. The activity appeared to stabilize over the next 110 hours. Methanol concentration remained in the 5.3 - 5.7 mole% range, with productivity of about 21 gmole/hr-kg, during this period (see Figure 10). This activity level, however, was lower than the results obtained from the 300 hour old catalyst with synthesized Great Plains gas in the lab. The low CO₂ concentration of the coal gas (see Figure 9) was a concern. Productivity is significantly sensitive to CO₂ concentration in the 0 - 2 mole% range, which may be responsible for low and fluctuating productivity.

A gradual decline in catalyst activity was observed over the next 125 hours (from 190 to 315 hrs on-stream). The deactivation rate was much higher than expected. Methanol concentration in the effluent dropped to about 4.5% after 300 hours. No H₂S, COS, Fe(CO)₅ or Ni(CO)₄ were detected in the feed by on-line GC analysis. Spot checks for Cl⁻, CN⁻, NH₃, and arsenic compounds by wet chemical methods also showed negative responses.

The adsorbents were regenerated after 315 hours on-stream. If the adsorbents were saturated with any unknown poison, this would possibly get some capacity back and temporarily slow down the deactivation of the catalyst. During the regeneration, the effluent was analyzed and one unknown peak (at 2.2 minutes) was observed on the PID set up for sulfur detection. However, this unknown peak was not observed in the feed. Presumably, this unknown species was either concentrated on the adsorbents or formed during regeneration. It could also be ethane, which has a retention time of 1.9 minutes.

Resumption of operation after regeneration was delayed due to detection of ppm levels of H₂S and COS in the feed by our sulfur GC. The analysis by Great Plains did not show any sulfur (<50 ppb). There was no sulfur in the autoclave since the unit was not operating at that time. An unknown peak was observed at about 9.5 minutes in the sulfur GC. This had not appeared before as the chromatogram was usually terminated after 6 minutes (after both H₂S and COS are out). This component was later identified as propane.

Catalyst activity was even lower after restart of the autoclave (about 4% methanol in effluent). Perhaps the presence of some poison at reaction temperature and pressure during three days of shutdown (no flow) deactivated the catalyst. Fluctuations of CO₂ content in the feed increased after regeneration, and methanol concentration dropped significantly at lower CO₂. The catalyst, however, showed signs of deactivation after the CO₂ effect was accounted for. For example, methanol concentration dropped from 4% to 3.6% in about 4-5 days at CO₂ concentration of 0.6% in feed. The effect of CO₂ during the entire test can be seen in Figure 11. Methanol concentration in effluent is plotted as a function of CO₂ concentration in effluent. The data are divided in five segments according to the on-stream time. Lower methanol

Figure 9

FIELD TEST # 1 (GREAT PLAINS COAL GAS)

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

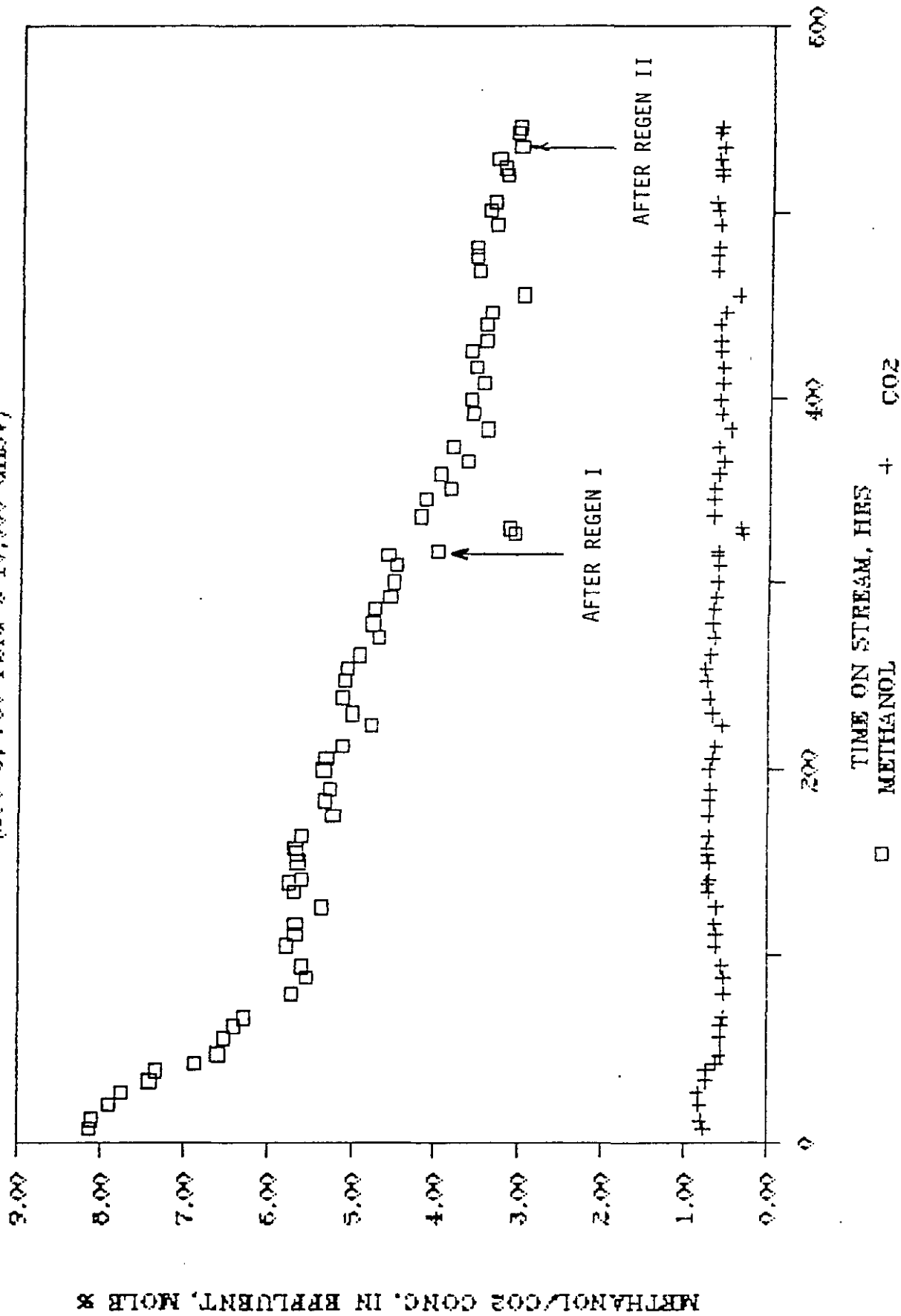


Figure 10

FIELD TEST # 1 (GREAT PLAINS COAL GAS)

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

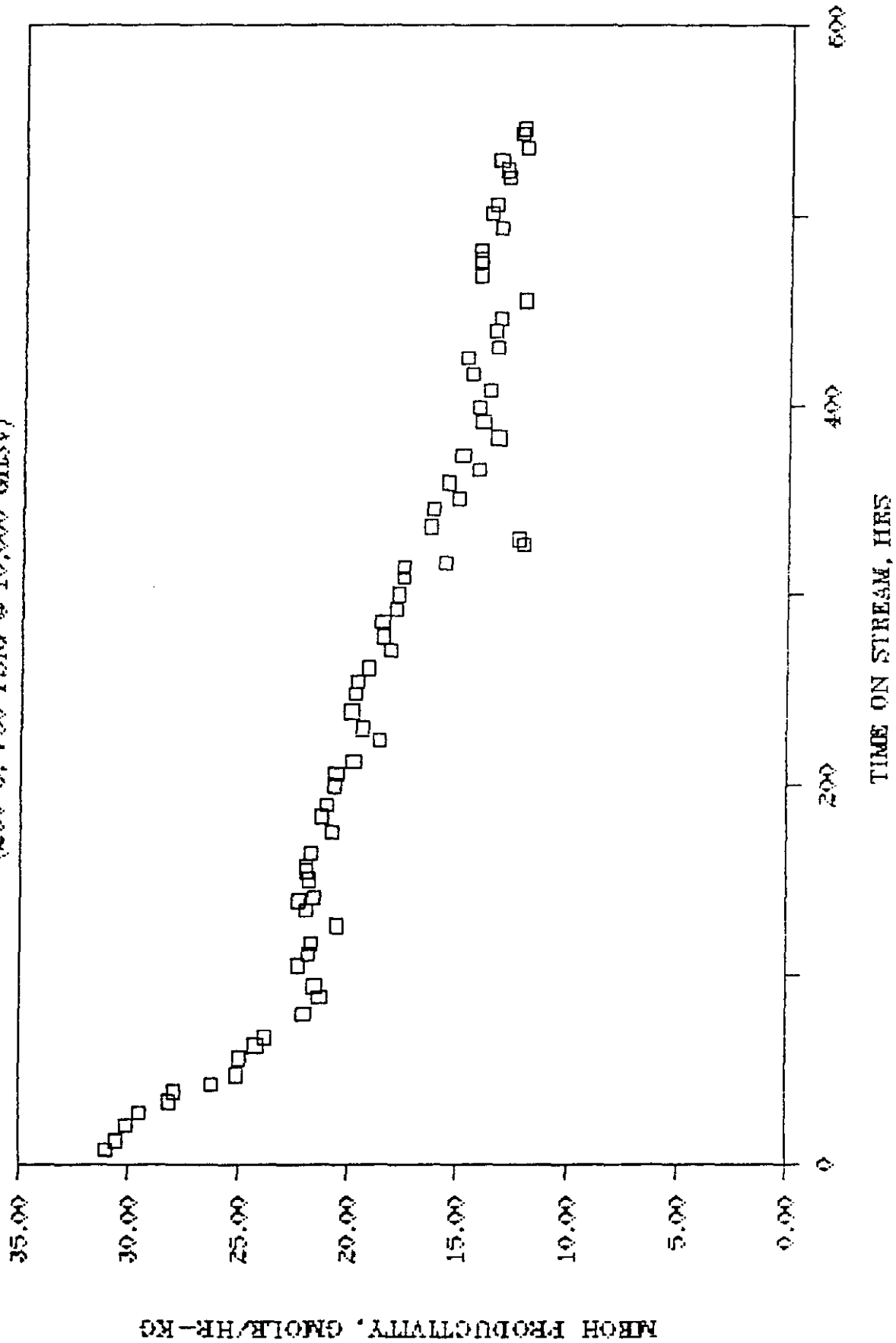
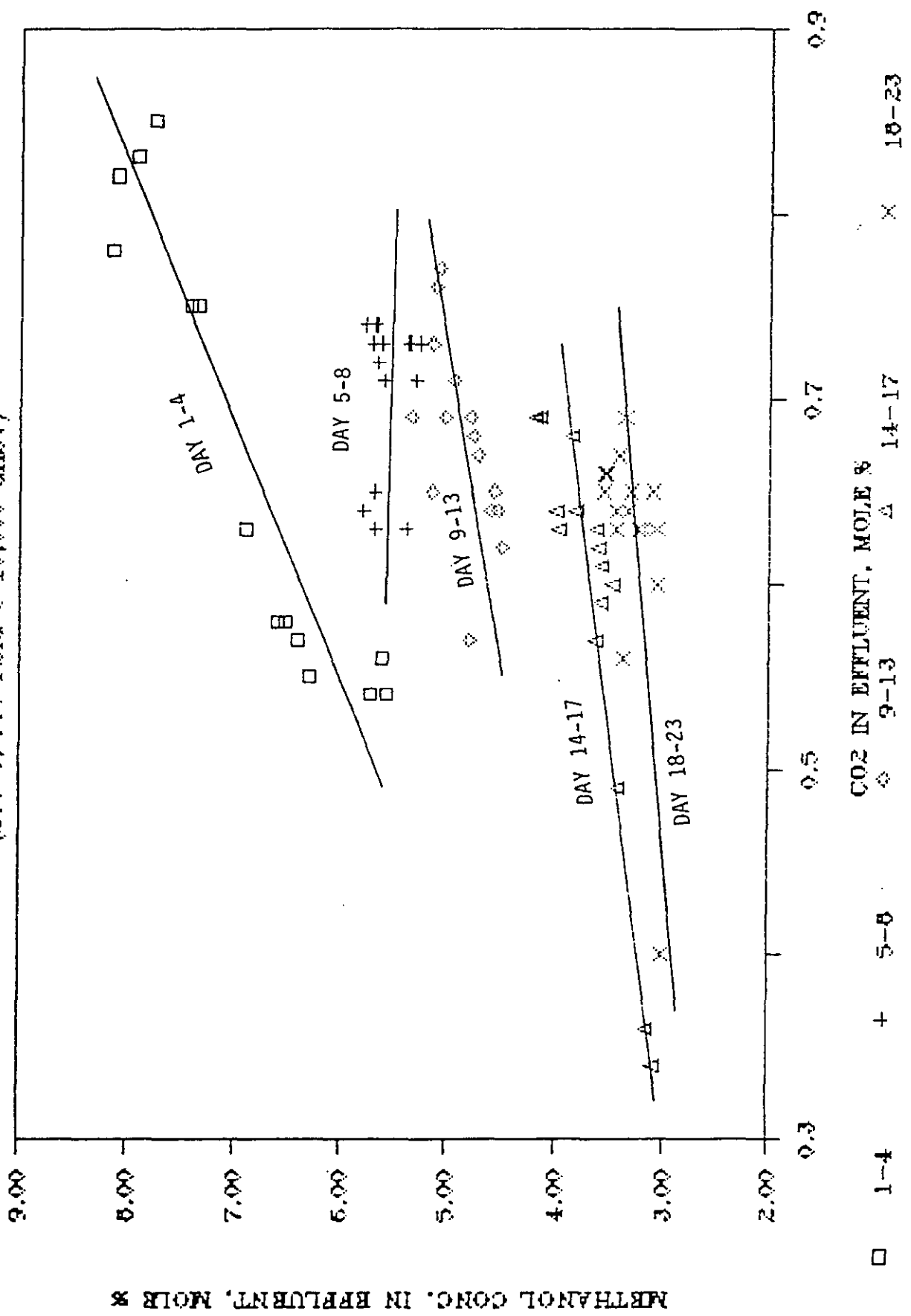


Figure 11

EFFECT OF CO₂ ON METHANOL CONC.

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



concentrations were generally observed at lower CO₂ concentrations in the effluent at a given age of catalyst. However, at a constant CO₂ concentration in effluent, methanol concentration dropped with days on-stream, indicating definite deactivation.

Conversions of CO, H₂, CO₂ and CH₄ during the test are plotted in Figure 12. CO and H₂ conversion steadily decreased during the test. CO₂ conversion started out negative (produced) but soon became positive and increased with time on-stream. CH₄ conversion remained low. Its deviation from zero probably indicates experimental errors.

One reason for catalyst deactivation could be the low CO₂ content (0.35 to 0.75%) in the feed. It is known that a certain amount of CO₂ is needed in the feed to enhance catalyst activity. However, the long term effect due to CO₂ deficiency is not known. The other reason may be that some catalyst poisons escaped the four adsorbents and deactivated the catalyst. Examples are unsaturated hydrocarbons.

Analytical Results on Gas/Catalyst Samples

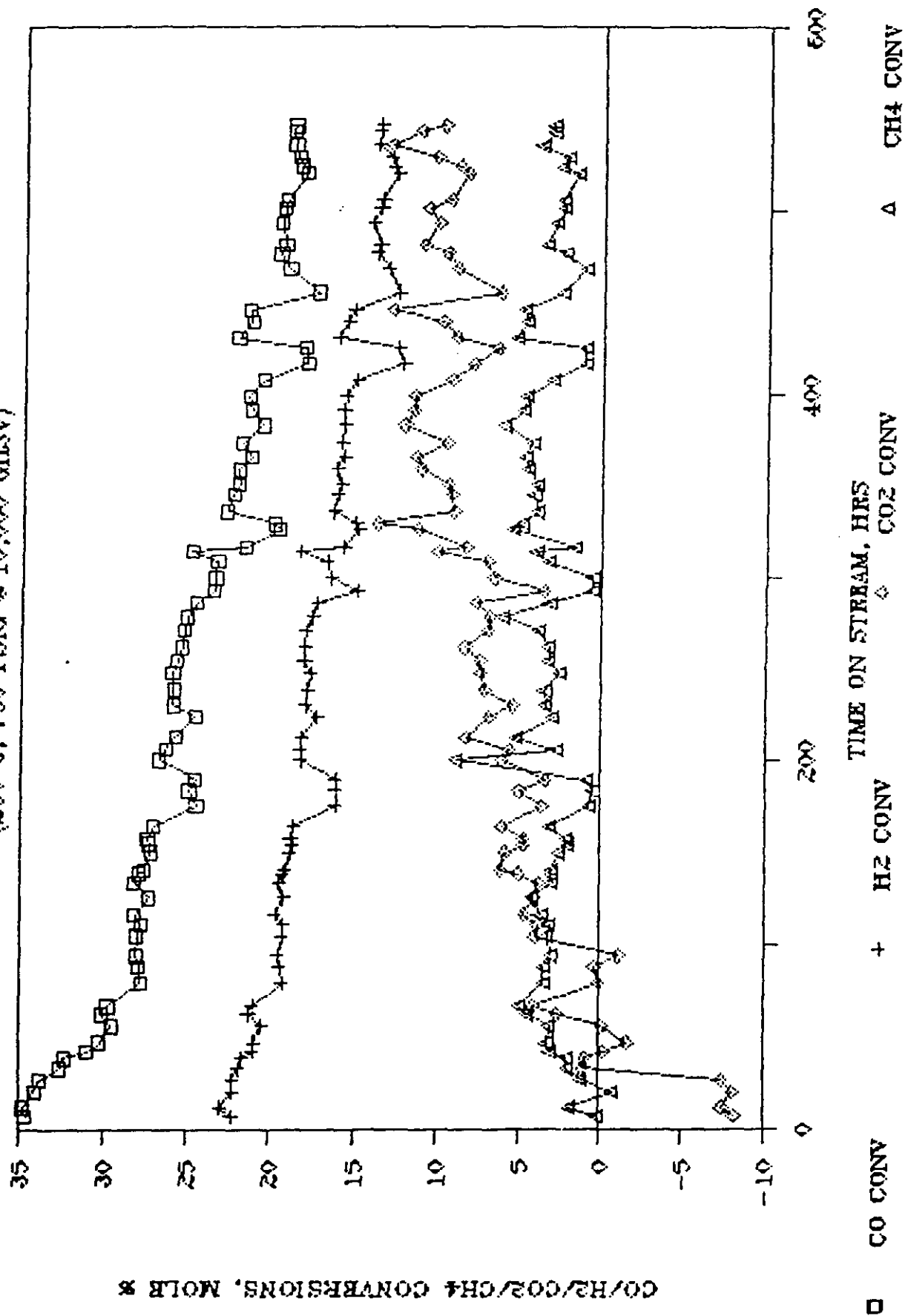
To identify the unknown catalyst poisons, gas samples were taken during both on-stream and regeneration periods with specially made sample devices and shipped to Allentown for GC-MS analysis. GC Analysis at Great Plains (both Air Products and DGC) revealed the presence of ethylene, propylene and acetonitrile in the inlet to the adsorption system during on-stream period and the outlet from the adsorption system during regeneration. The field test was terminated after 545 hours on-stream and the used catalyst and adsorbents were shipped to Allentown for potential catalyst poisons analysis. The GC-MS analysis on gas samples revealed:

- Significant amount of water in the inlet and outlet stream of the adsorption system (about 1000 ppmv).
- Benzene and toluene in both streams (about 6 ppmv total in inlet and 0.06 ppmv in outlet).
- Ethane and propane in both streams (>>6 ppmv).
- Significant acetonitrile (>6 ppmv) in the inlet to the adsorption system and none in outlet.
- Substantial amount of DME and water (>>6 ppmv) in the sample from the regeneration outlet. DME and some of the water were believed to be formed during regeneration from methanol adsorbed during on-stream period.
- Acetonitrile (>6 ppmv) in the regeneration outlet.
- C₃-C₁₁ alkanes (>6 ppmv) in the regeneration outlet.
- Benzene and toluene (about 7 ppmv each) in the regeneration outlet.

Figure 12

FIELD TEST # 1 (GREAT PLAINS COAL GAS)

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



The water in the streams was unexpected and could deactivate the catalyst if it entered the reactor in liquid form with impurities, such as dissolved sulfur compounds. Benzene, toluene, ethane, and propane, in the quantities discovered, were not believed to be detrimental to the catalyst. Acetonitrile was a possible catalyst poison, but it was successfully picked up by the adsorption system when the samples were taken. Various analyses of the spent catalyst showed:

- Substantial crystallite size growth (from about 100 Å to 400 Å Cu, using XRD analysis).
- Significant Fe pickup (from about 50 ppm to 400 ppm, using both XRF and AA analysis).
- Some Ni pickup by AA (from 20 ppm to 120 ppm); however, none indicated by XRF.

The crystallite growth showed damage to the catalyst. The Fe and Ni pickup have been fatal to the catalyst in the past.

Lab Test # 1

Catalyst Life Test with Synthesized GP Gas

A test was conducted in Air Products' laboratory in Allentown to check if lack of sufficient CO₂ in the feed was responsible for the catalyst deactivation in the Great Plains test. This test was conducted in the 300 cc unit #1 (not in the trailer pilot unit). This unit has been previously used for methanol synthesis work. The details of this unit are available in a hazards review document (5). Synthesized Great Plains feed (63% H₂, 20% CO, 16.5% CH₄ and 0.5% CO₂) without any poisons was used for the test. The autoclave was loaded with about 15 grams of F21/OE75-43 catalyst powder and 130 grams of Drakeol-10 oil. The catalyst slurry was reduced in the autoclave using 2% H₂ in N₂ at 100 psig with temperature ramping. The cumulative H₂ uptake was about 2.41 scf/lb of catalyst, close to the expected number.

The autoclave was started up at 10,000 sl/kg-hr, 750 psig and 250°C. The methanol concentration observed in the product effluent is plotted as a function of on-stream time in Figure 13. The catalyst appeared stable over 400 hours on-stream. Methanol productivity after 400 hrs was much higher compared to Field Test #1 (27 gmole/hr-kg vs. 14 gmole/kg-hr; see Figure 14). It is clear that a low amount of CO₂ in the feed does not result in unstable catalyst activity. Conversions of CO, H₂, CO₂ and CH₄ during the test are plotted in Figures 15 and 16. CO and H₂ conversion remained constant during the test. CO₂ conversion started out negative (produced) but soon became positive and increased with time on-stream. CH₄ conversion remained low and probably represented experimental error.

Figure 13

FIELD/LAB TESTS WITH GP COAL GAS

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

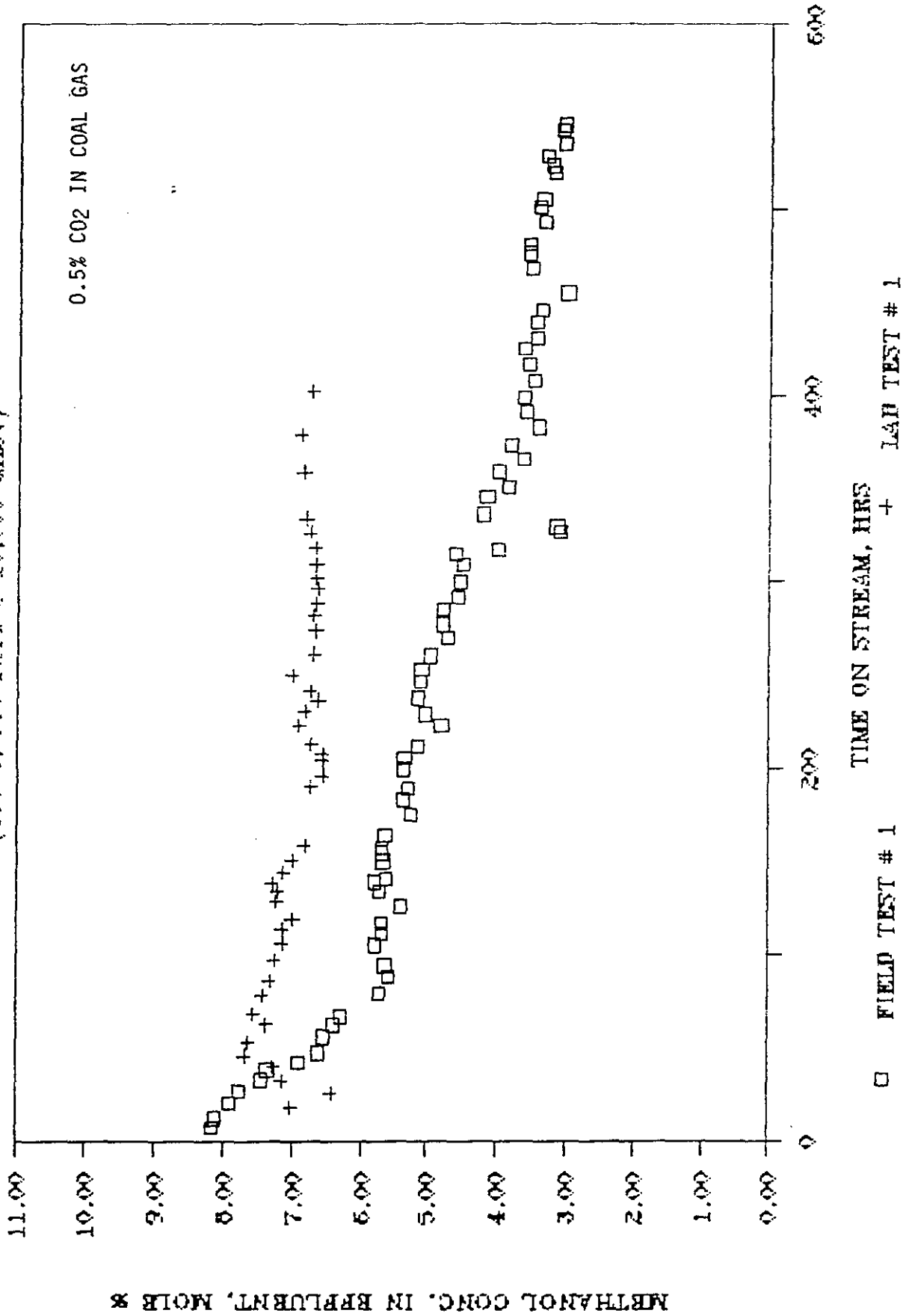


Figure 14

FIELD/LAB TEST WITH GP COAL GAS

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

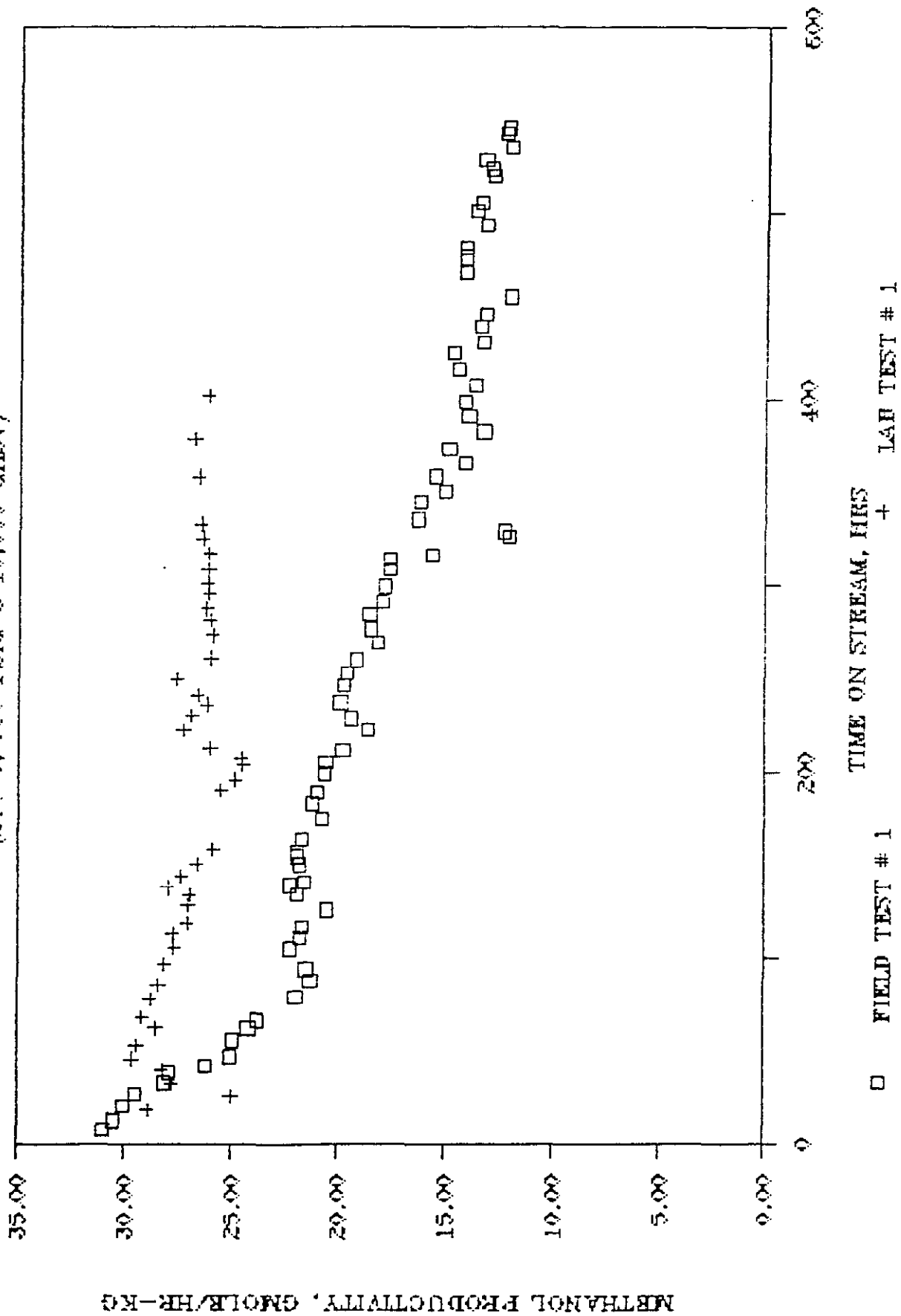


Figure 15

LAB TEST # 1 (SYNTHESIZED GP COAL GAS)

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

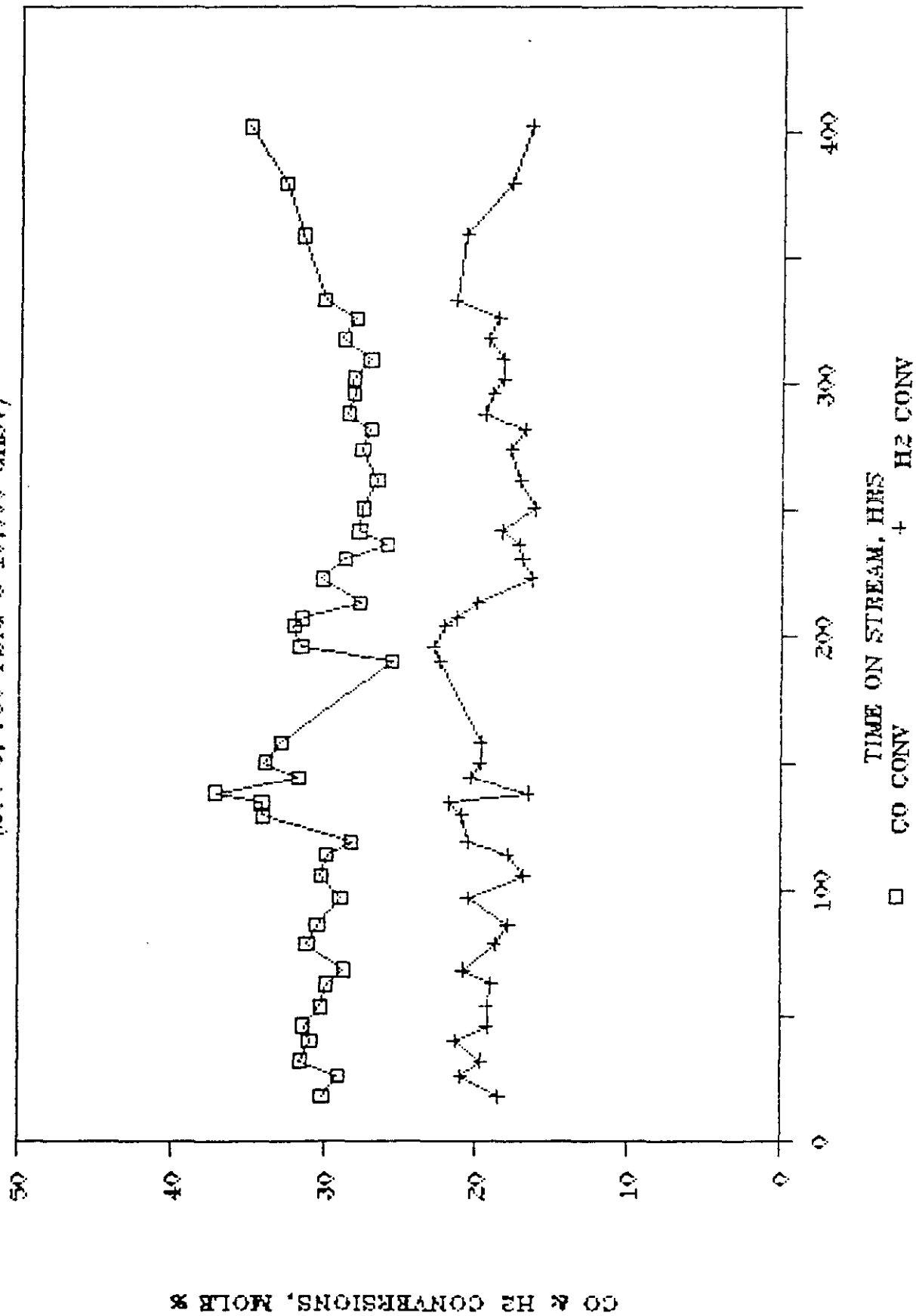
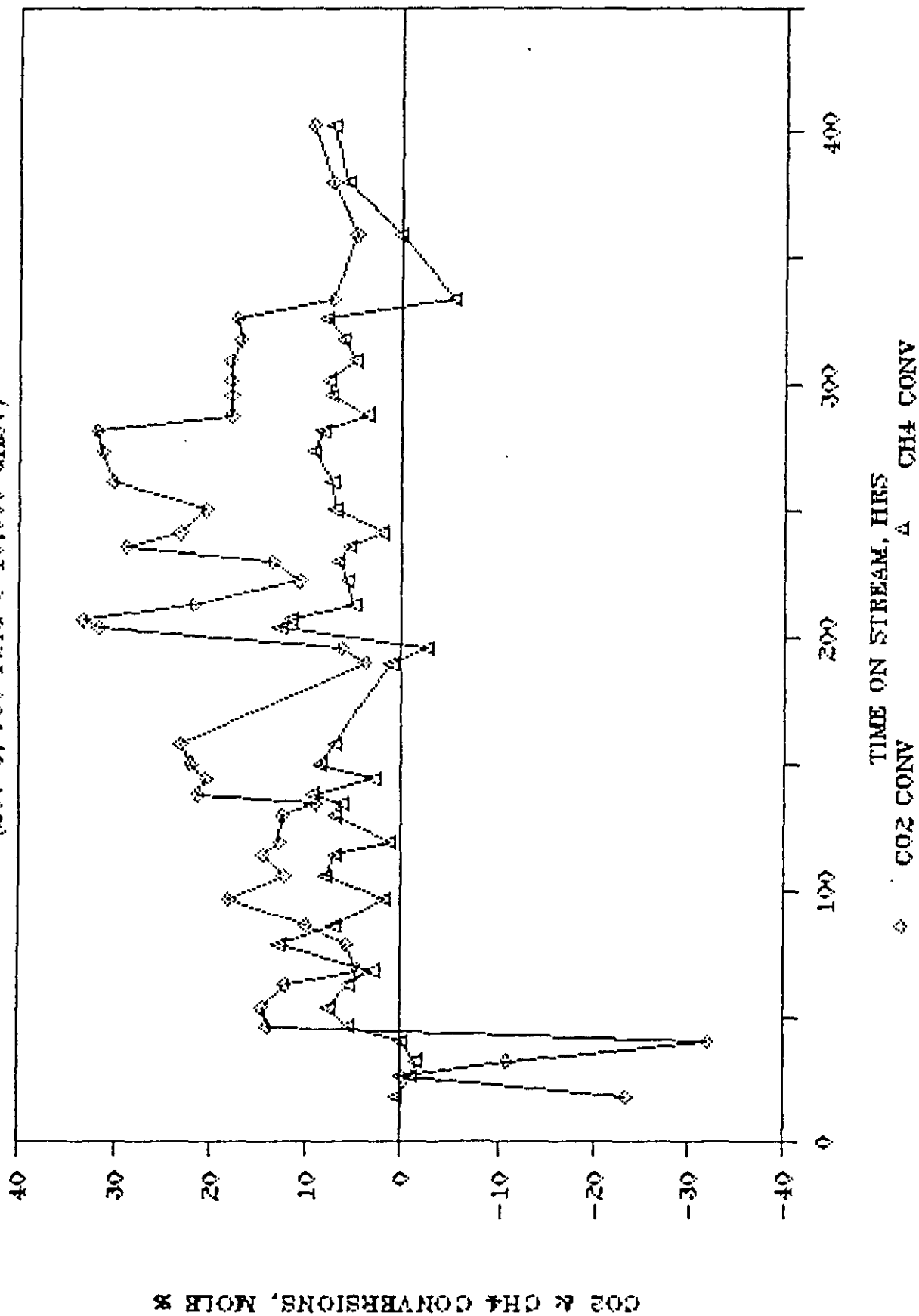


Figure 16

LAB TEST # 1 (SYNTHESIZED GP COAL GAS)

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



Effect of CO₂ on Catalyst Activity

Experiments were conducted to quantify the advantage of higher CO₂ 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% CO₂. It reaches a maximum of about 9.8 mole% at around 5% CO₂, and then decreases slightly with higher CO₂ concentration. The maximum productivity of about 38 gmole/hr-kg was obtained at 5% CO₂, which is about 40% higher than 27 gmole/hr-kg obtained at the 0.5% CO₂ (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 CO₂ 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 H₂S injection system to inject CO₂ into the feed. According to the lab test, low CO₂ does not cause catalyst deactivation. However, additional CO₂ enhances catalyst activity. Also, it may maintain a certain oxidation level and reduce catalyst susceptibility to poisons. Another benefit of CO₂ 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)₅ 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

CO₂ ADDITION TO SYNTHESIZED GP COAL GAS

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

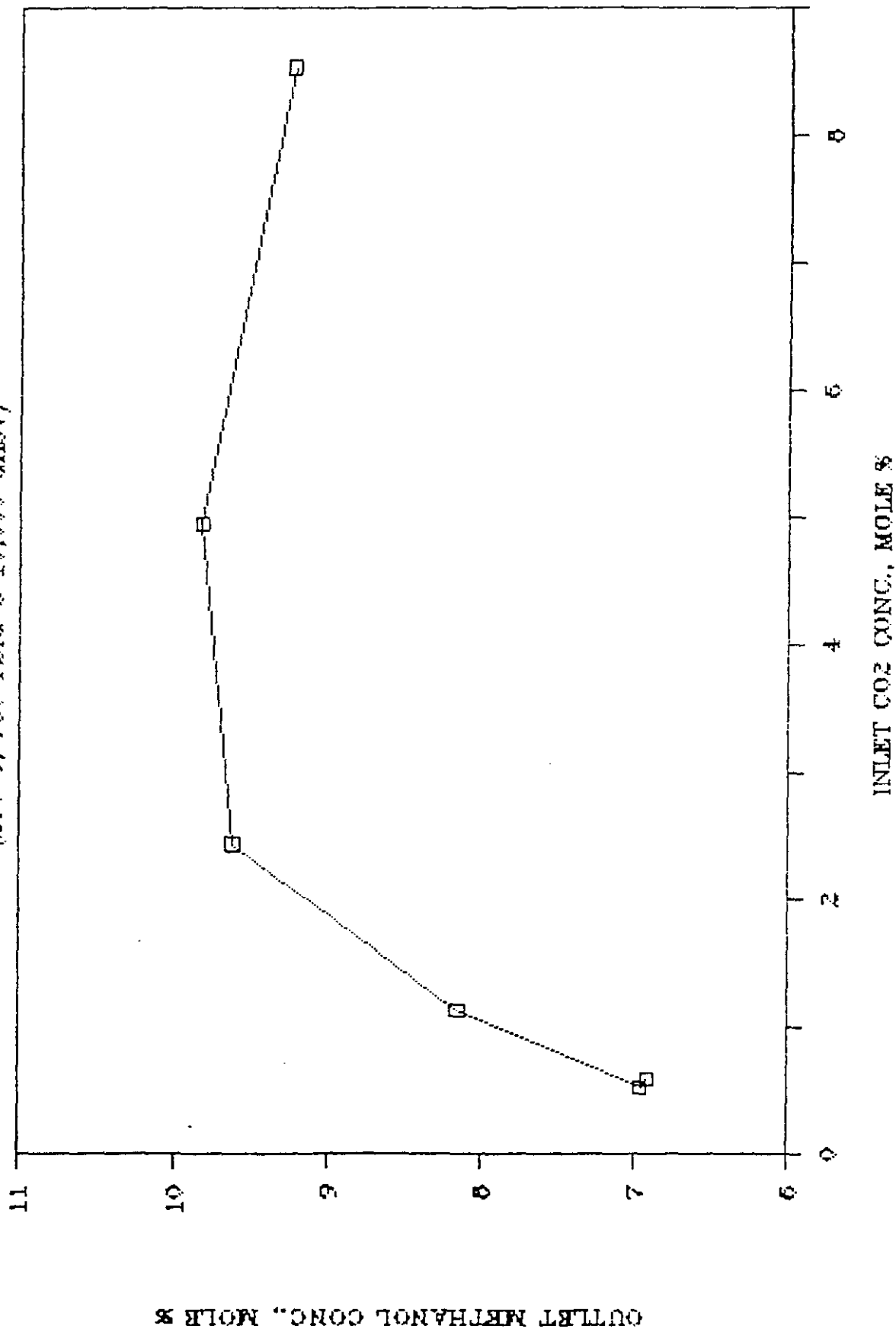
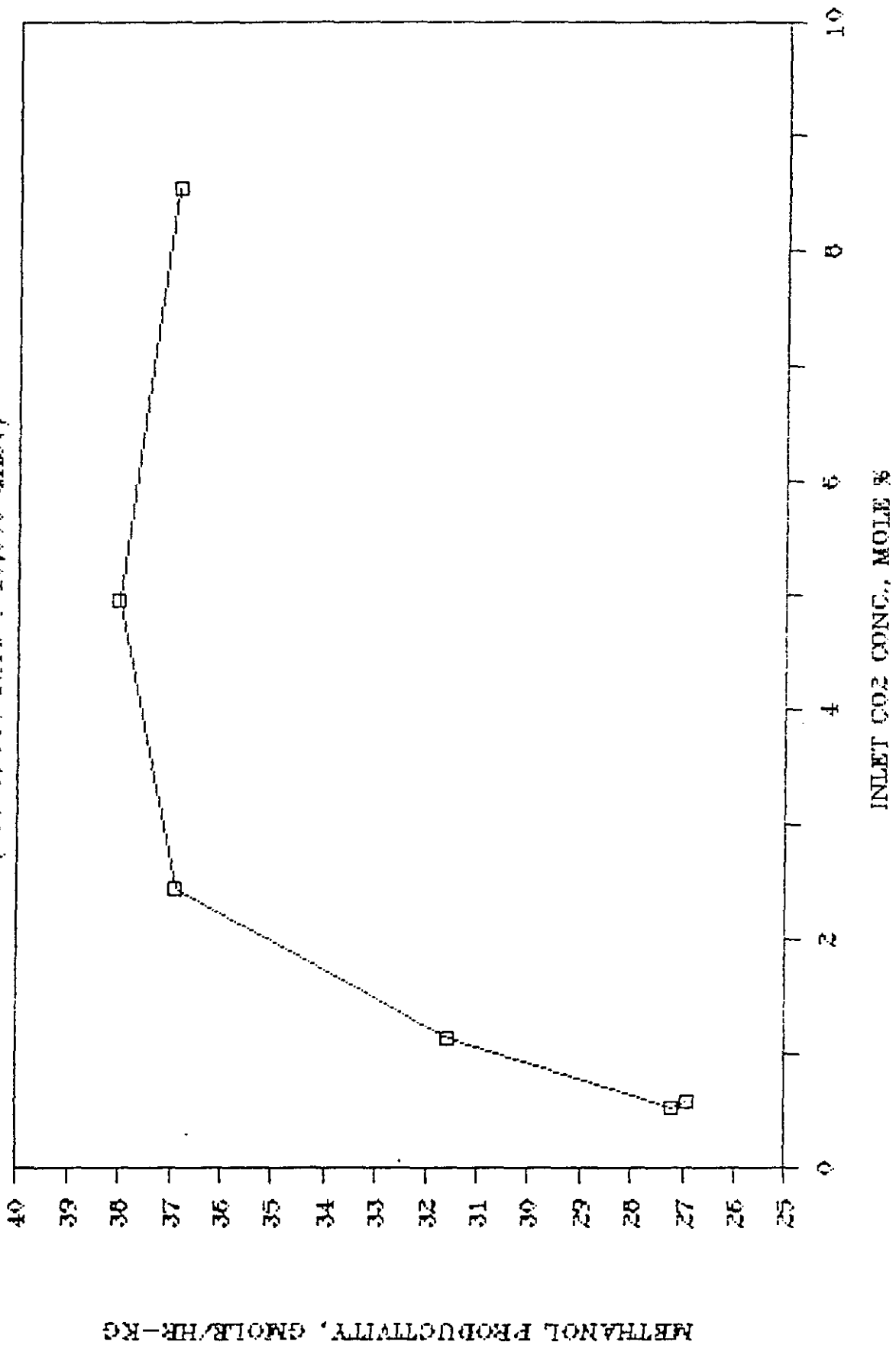


Figure 18

CO₂ 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% H₂ in N₂ at 100 psig with temperature ramping. The molecular sieve in column #1 and the zeolite in column #3 were dried using N₂ 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% H₂ in N₂ 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 H₂S, COS, or Fe(CO)₅ were detected in the feed. Initially, some Ni(CO)₄ (in the range of 10-30 ppb) was detected in the system. After cleaning the suspected section right before the autoclave, the Ni(CO)₄ gradually diminished.

The autoclave was then started up at 10,000 sl/kg-hr, 250°C and 750 psig. The feed gas, with CO₂ added, had a composition of about 19.5% CO, 60% H₂, 5% CO₂, and 15.5% CH₄. 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% CO₂ 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, CO₂ 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 CO₂ in the feed.

After on-stream time of about 280 hours, CO₂ 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

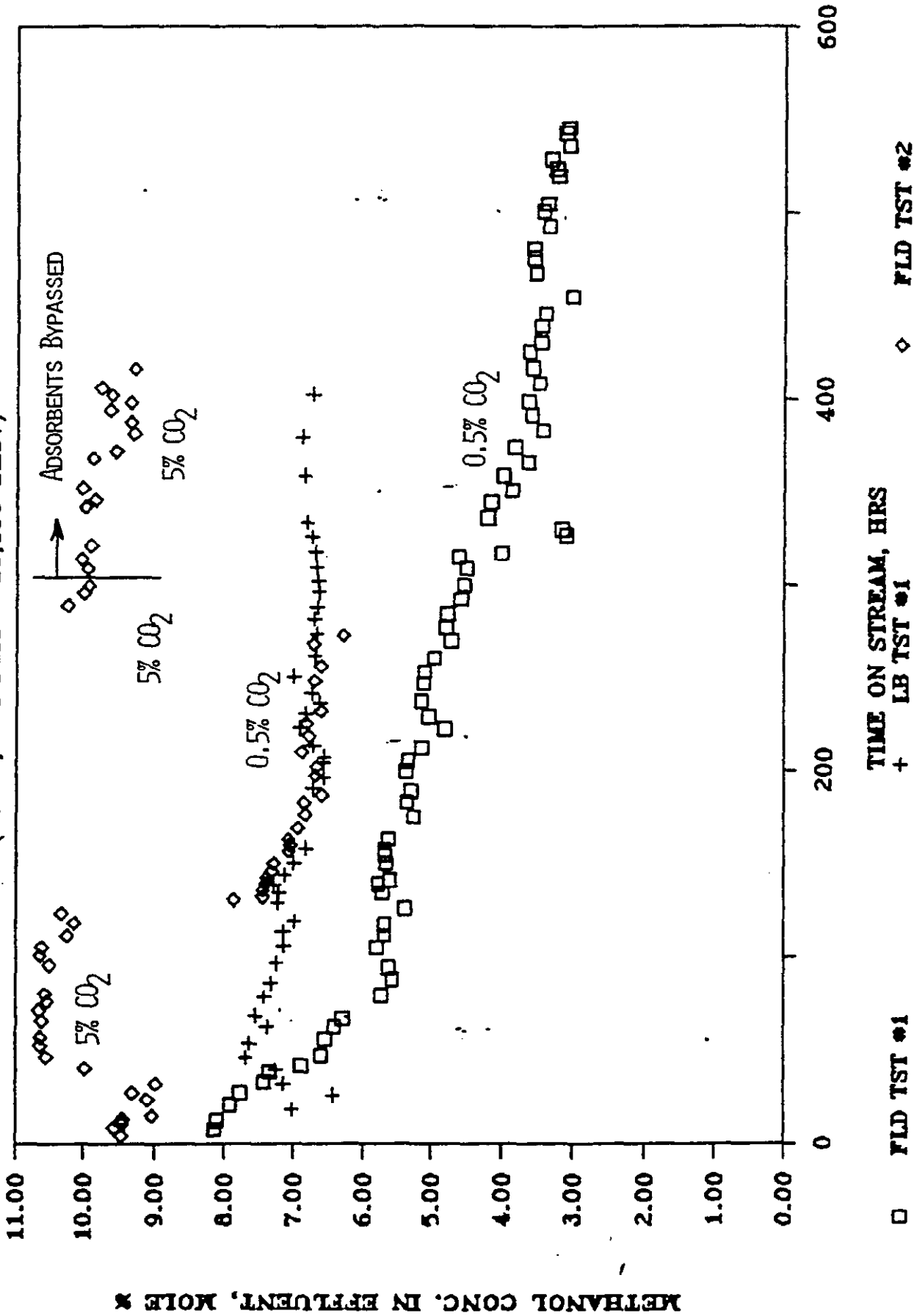
COLUMN	ADSORBENT	POISON	LENGTH	WEIGHT
1	LINDE MOLECULAR SIEVE 3A	H ₂ O	4 FT	186 GM
2	CU/ZN BASF S3-86 CATALYST	HCL, H ₂ S	1.2 FT	90.8 GM
3	LINDE H-Y ZEOLITE	FE(CO)5	1.2 FT	44.5 GM
4	BPL CARBON	NI(CO)4	1.2 FT	33.8 GM
4	FCA CARBON (WITH CU/CR OXIDE)	COS	3 FT	107.1 GM

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

Figure 19

FIELD/LAB TESTS WITH GP COAL GAS

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

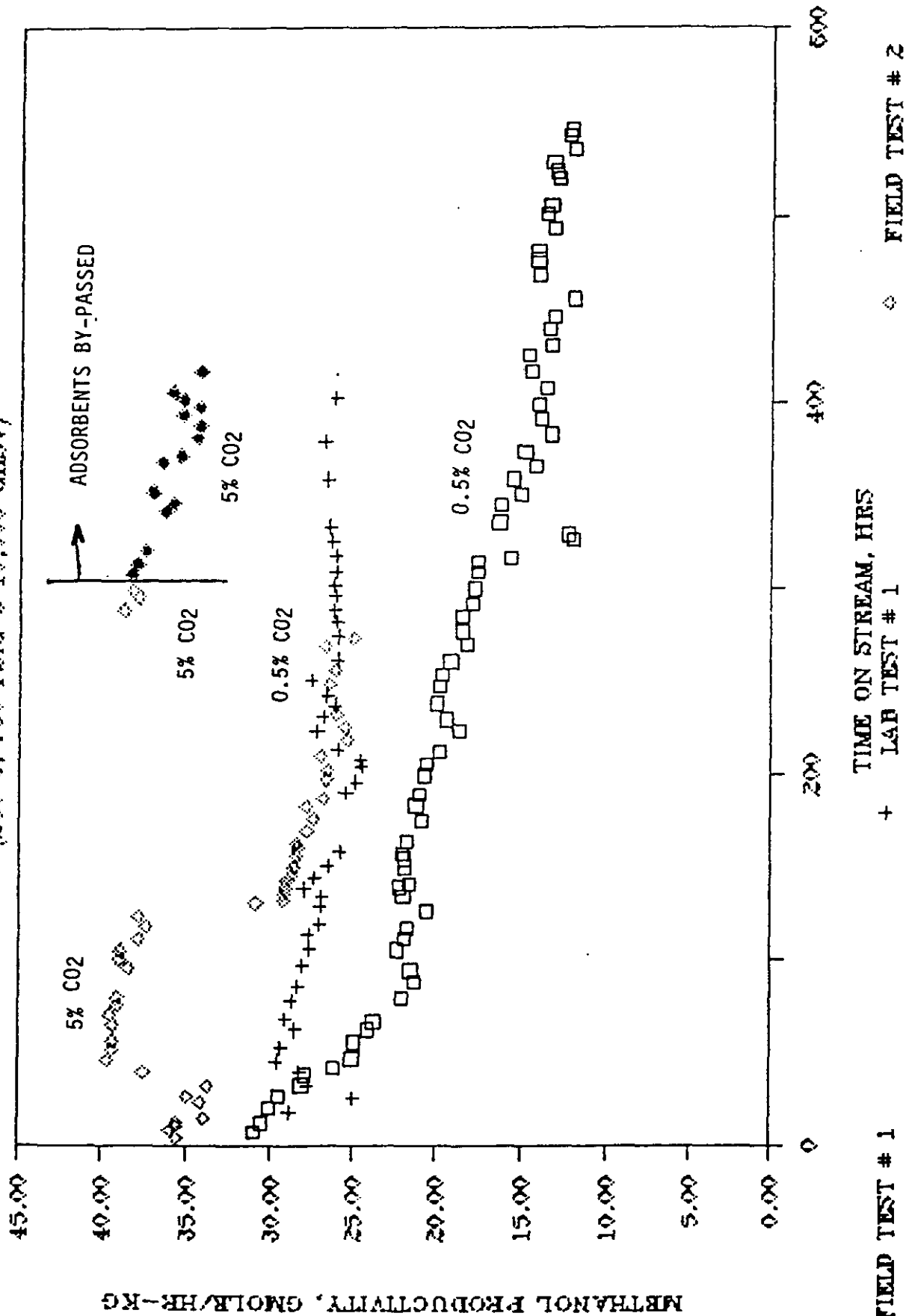


ADSORBENTS REGENERATED EVERY 72 HOURS

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 CO₂ level from 0.5% to 5% in the feed increased methanol productivity about 40%.

Conversions of CO, H₂, CO₂ and CH₄ during the test are plotted in Figure 21. CO and H₂ conversion remained stable at a constant CO₂ level. CO₂ conversion was small at 5% CO₂ and negative at 0.5% CO₂. CH₄ conversion was close to zero as expected.

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

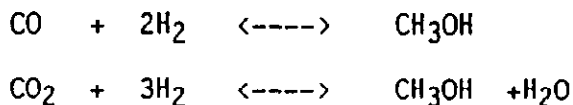
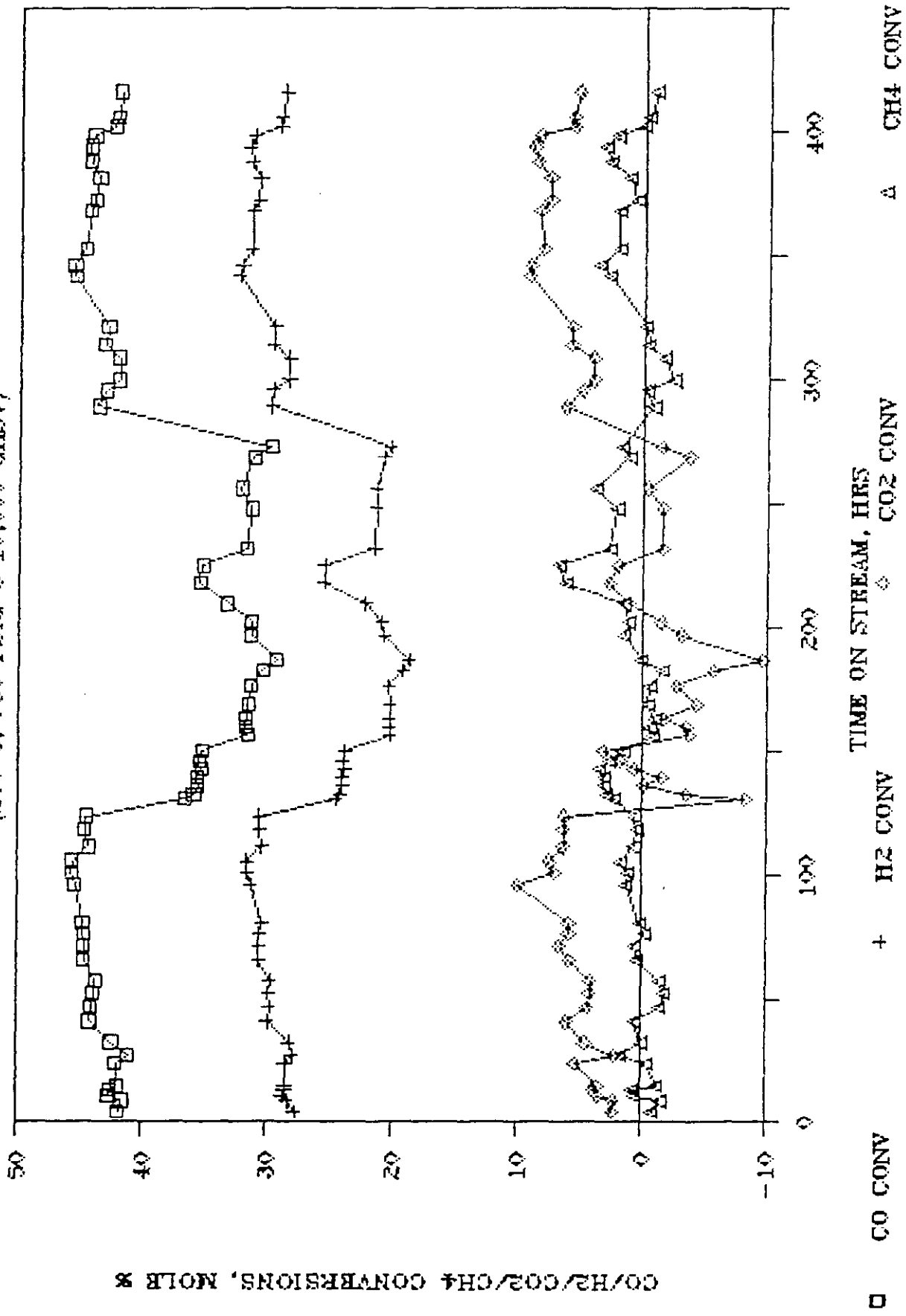


Figure 21

FIELD TEST # 2 (GREAT PLAINS COAL GAS)

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



CO/H2/CO2/CH4 CONVERSIONS, MOLE %

TIME ON STREAM, HRS

□ CO CONV

+ H2 CONV

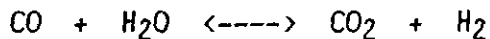
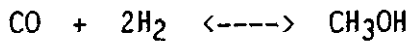
◇ CO2 CONV

△ CH4 CONV

Ratios of H₂ consumed to CO + CO₂ consumed as well as CH₃OH produced to CO + CO₂ consumed were calculated for the three tests. If no other reaction occurred, the H₂ consumed/CO+CO₂ consumed ratio would be slightly higher than 2. The CH₃OH produced/CO+CO₂ 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 H₂ consumed/CO+CO₂ consumed ratio was 2.16 (highest) and the CH₃OH produced/CO+CO₂ 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_{meoh}	=	methanol productivity
K_f	=	rate constant
f_x	=	fugacity of component x
K_{eq}	=	methanol equilibrium constant
k_0	=	pre-exponential factor
T	=	reactor temperature

The effect of CO₂ content on methanol productivity is empirically accounted for by correlating k_0 with the CO₂ 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% CO₂ 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.

Figure 22

FIELD TEST # 1 (GREAT PLAINS COAL GAS)

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

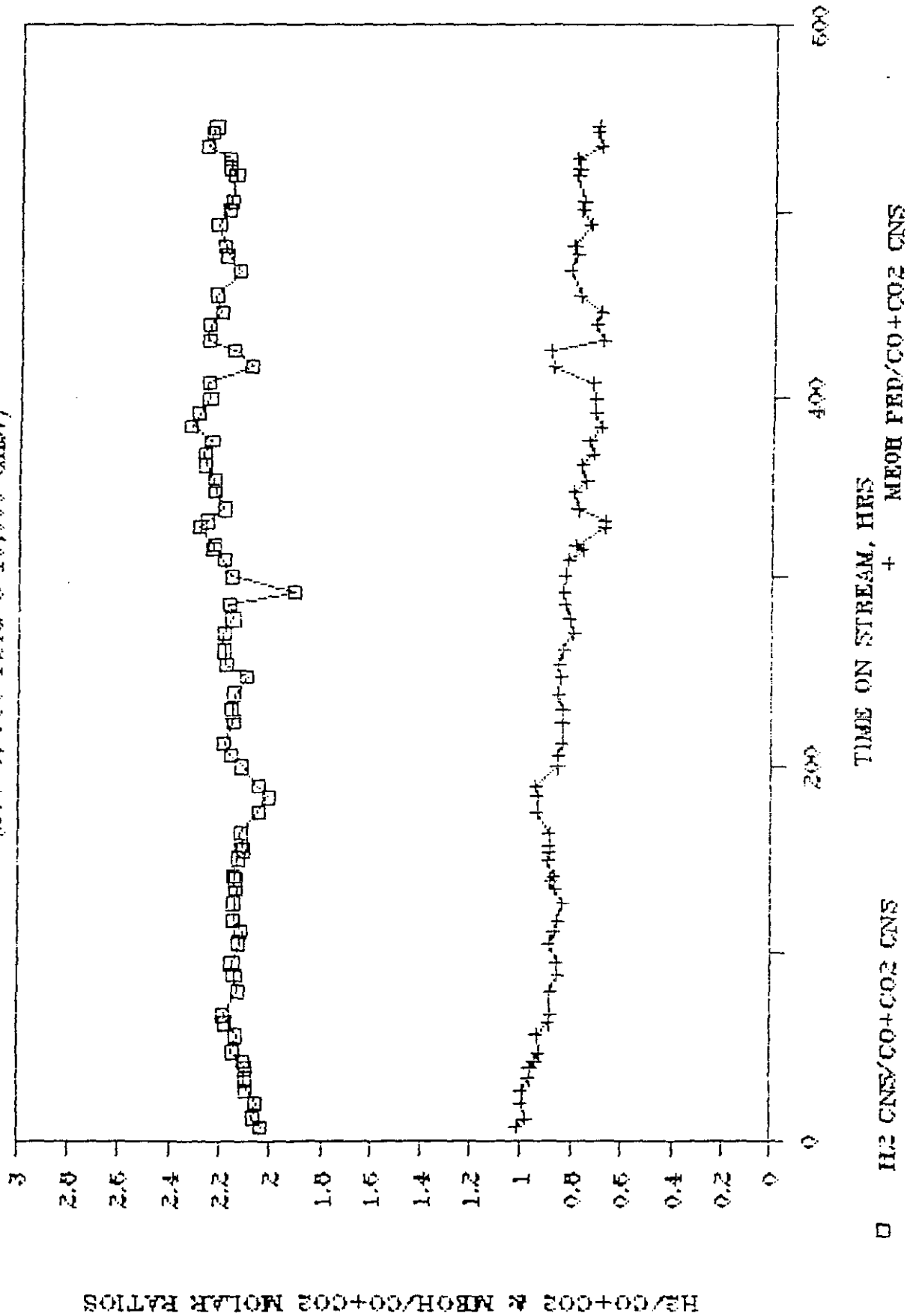


Figure 23

LAB TEST # 1 (SYNTHESIZED GP COAL GAS)

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

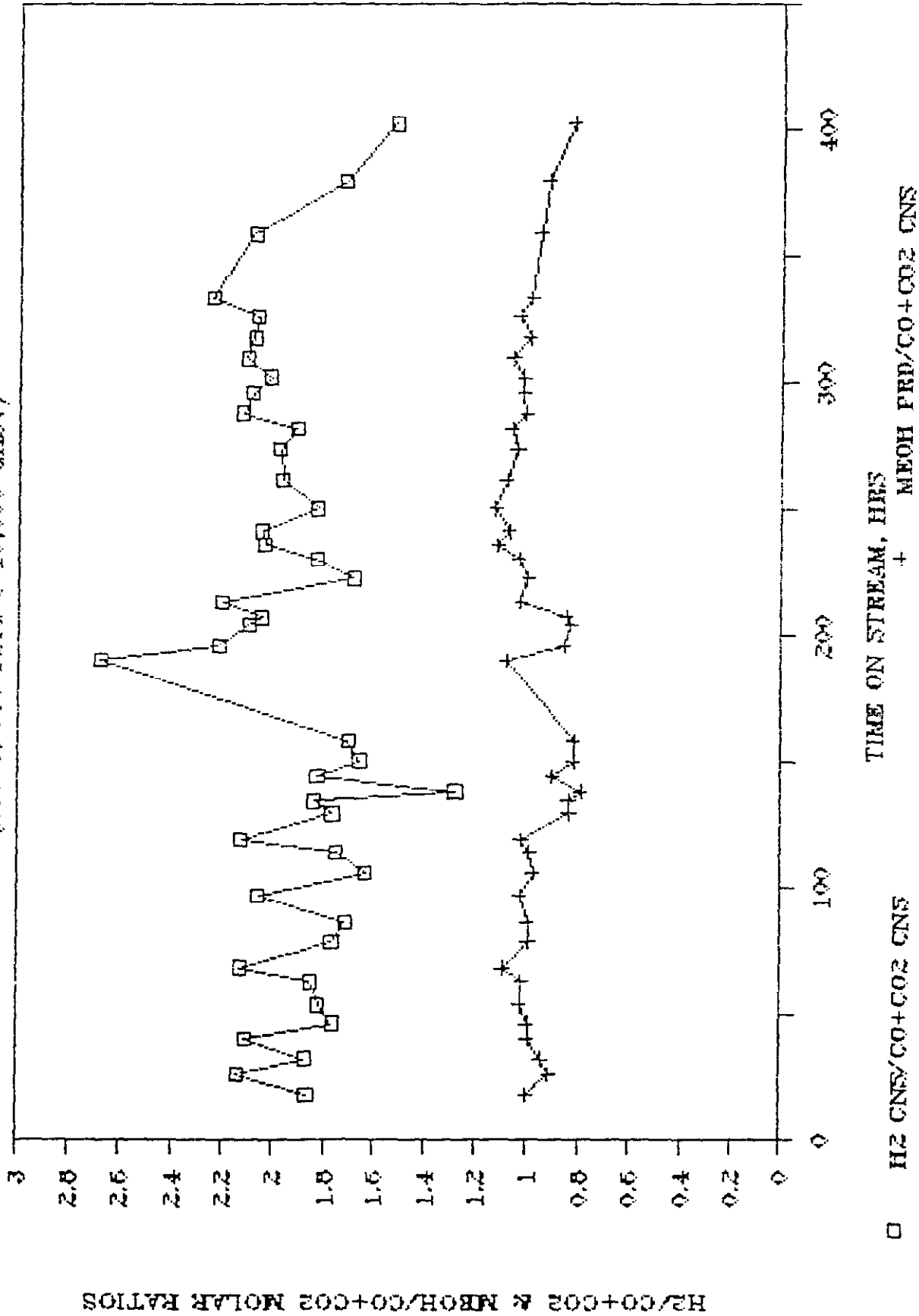


Figure 24

FIELD TEST # 2 (GREAT PLAINS COAL GAS)

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

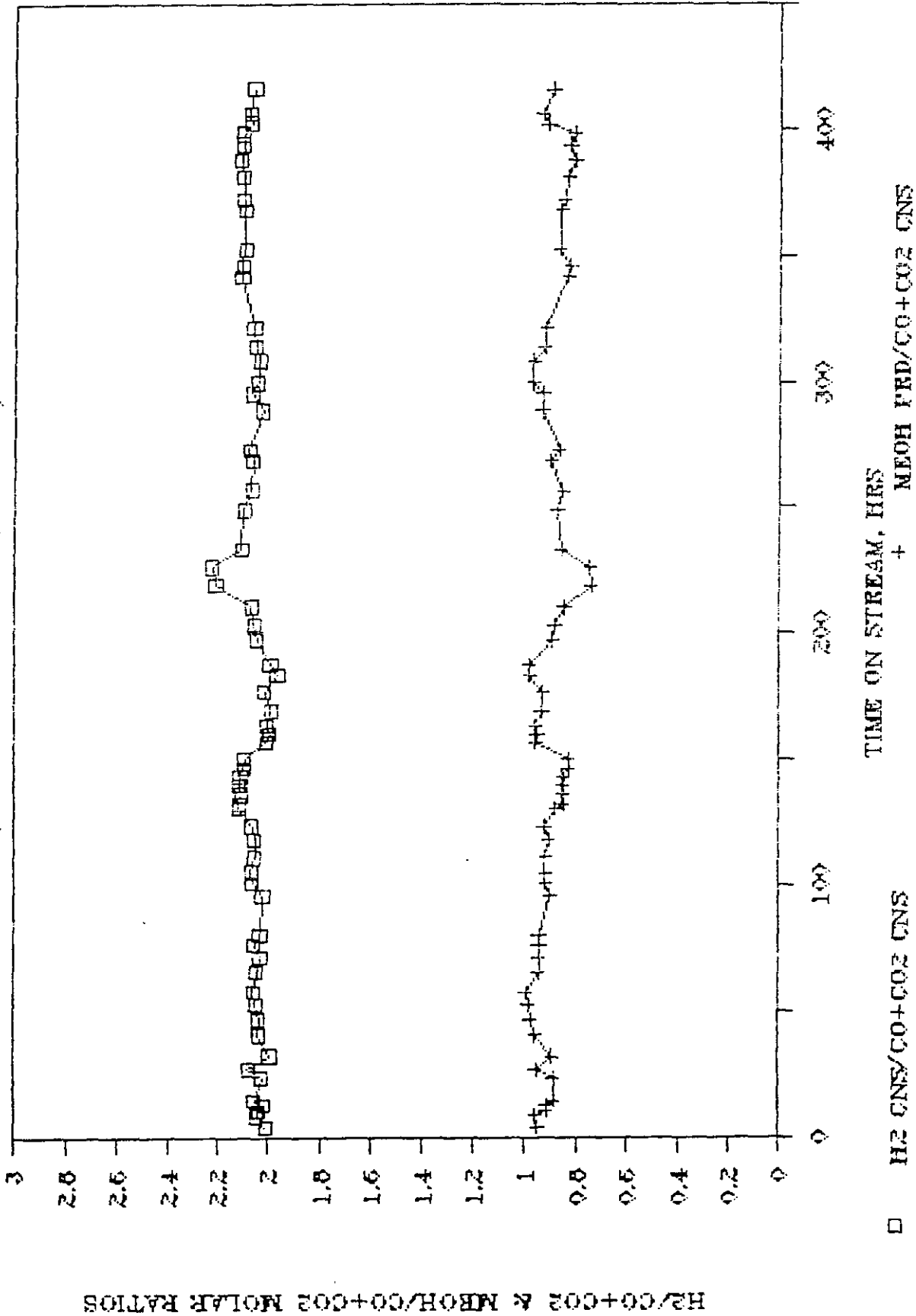


Table 12

METHANOL SYNTHESIS FROM GP COAL GAS AVERAGE MOLAR RATIOS

CH₃OH PRODUCED/
CO+CO₂ CONSUMED

H₂ CONSUMED/
CO+CO₂ CONSUMED

TEST

0.83

2.16

FIELD TEST # 1

0.98

1.94

LAB TEST # 1

0.91

2.06

FIELD TEST # 2

0.87

2.09

FIELD TEST # 2
(ADSORBENTS BYPASSED)

CH₃OH

CO + 2H₂ ----->

REACTIONS:

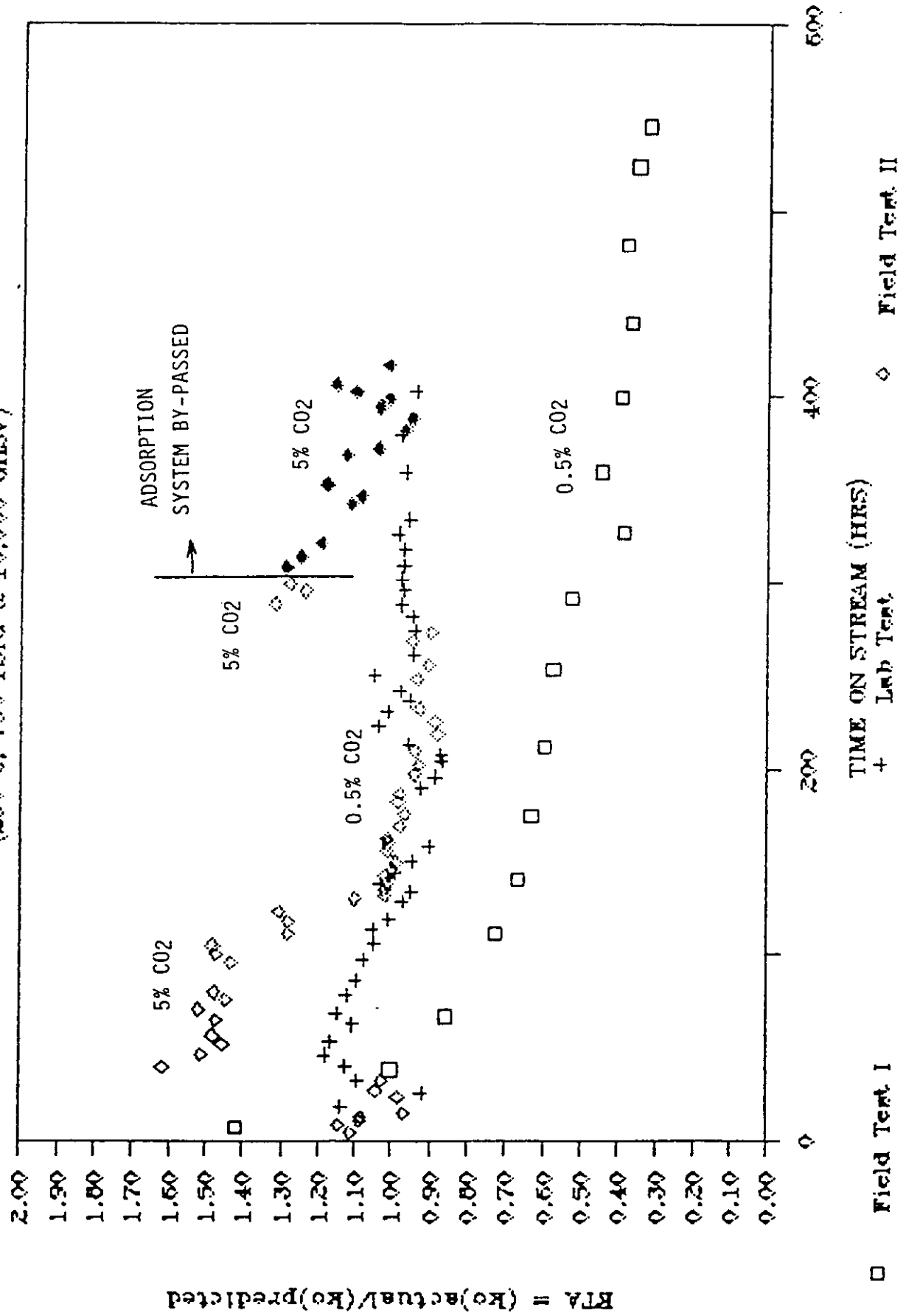
CH₃OH + H₂O

CO₂ + 3H₂ ----->

Figure 25

ETA VS. TIME ON STREAM

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



$$RTA = (k_o)_{actual} / (k_o)_{predicted}$$

□ Field Test I

+ Lab Test

◇ Field Test II

- At 5% CO₂ level in feed, the eta was greater than "1". This indicates the model underpredicts the CO₂ 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, H₂S or CN⁻ 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 (ADSORBENTS BYPASSED)	6.0

NOTE:

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

where (Eta) = ko (actual) / ko (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 H_2S adequately. With about 7 ppm of H_2S added in the coal gas stream, no breakthrough was observed during 100 hours of H_2S 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 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 CO₂ content of the feed to 5% by CO₂ 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.

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