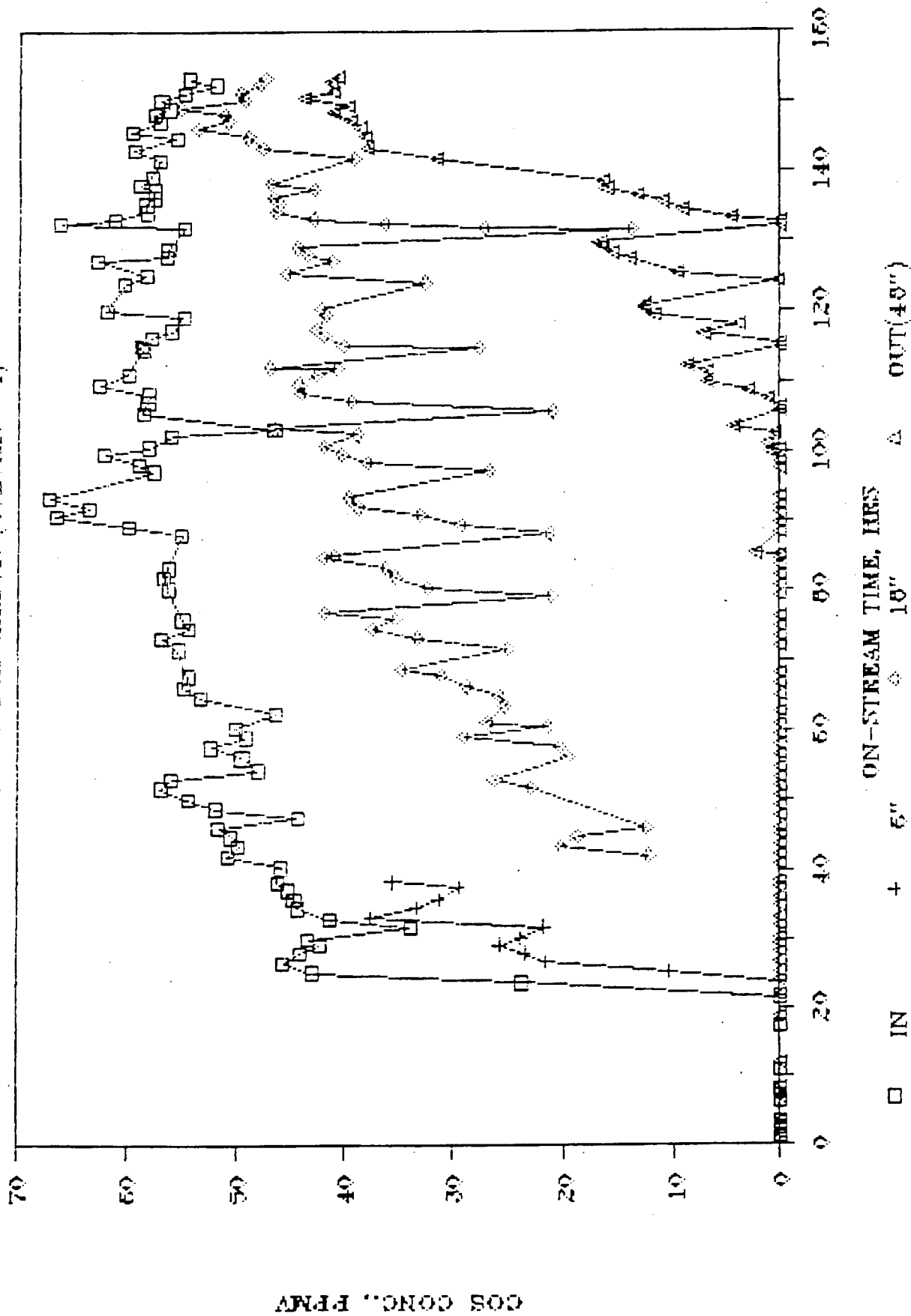


COOLWATER COAL GAS STUDY - LAB TEST # 1

CYCLE # 1 FOR FCS CARBON (COLUMN # 4)

Figure 7



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 4		TO 250 F IN 11 HRS, 10 HRS AT 250 F. 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 2, 3 4	<i>100%</i>	TO 500 F IN 5 HRS. TO 250 F IN 5 HRS, 17 HRS AT 250 F. 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 C, 750 PSIG @ 5,000 GHSV)

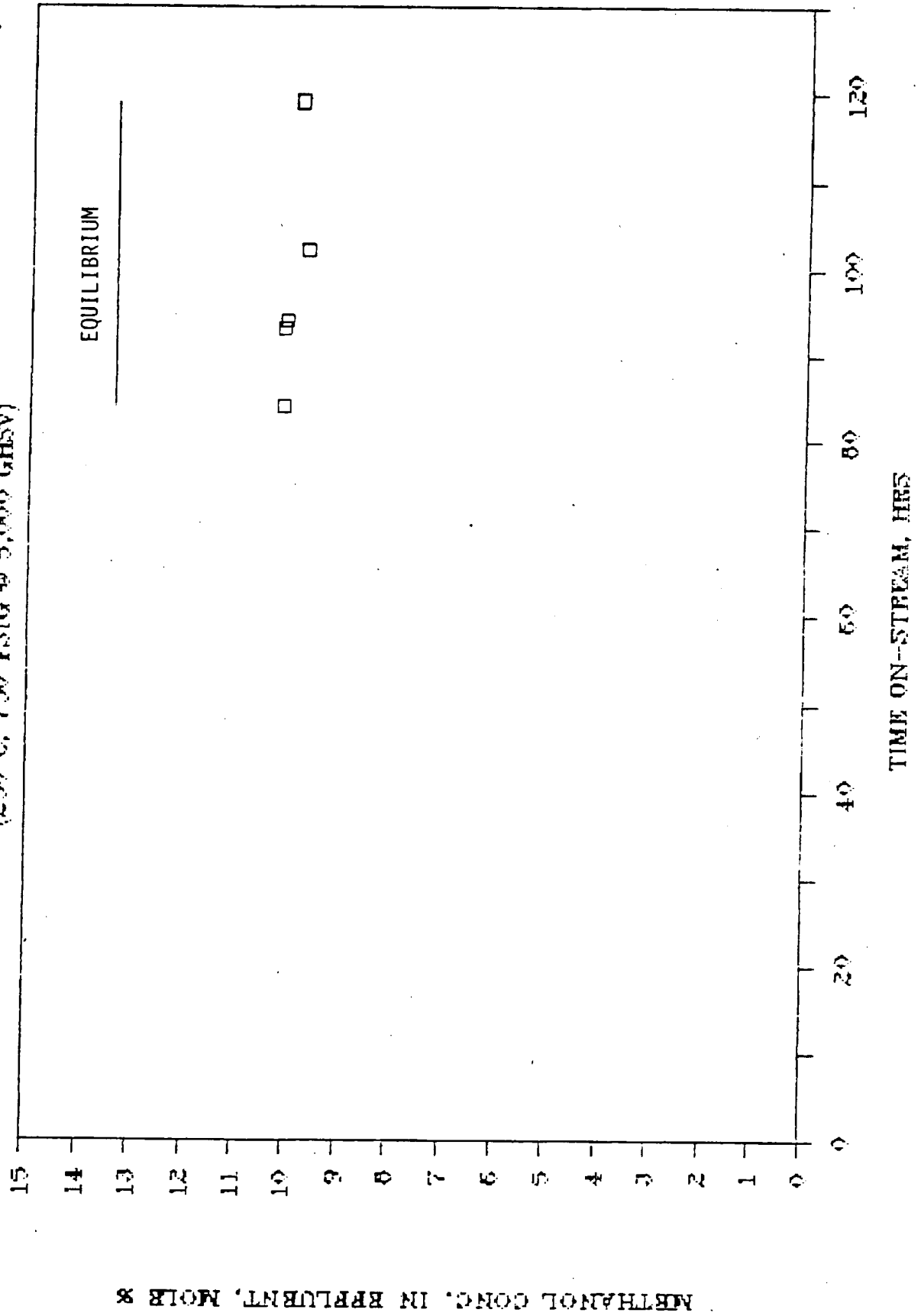


Table 10

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.

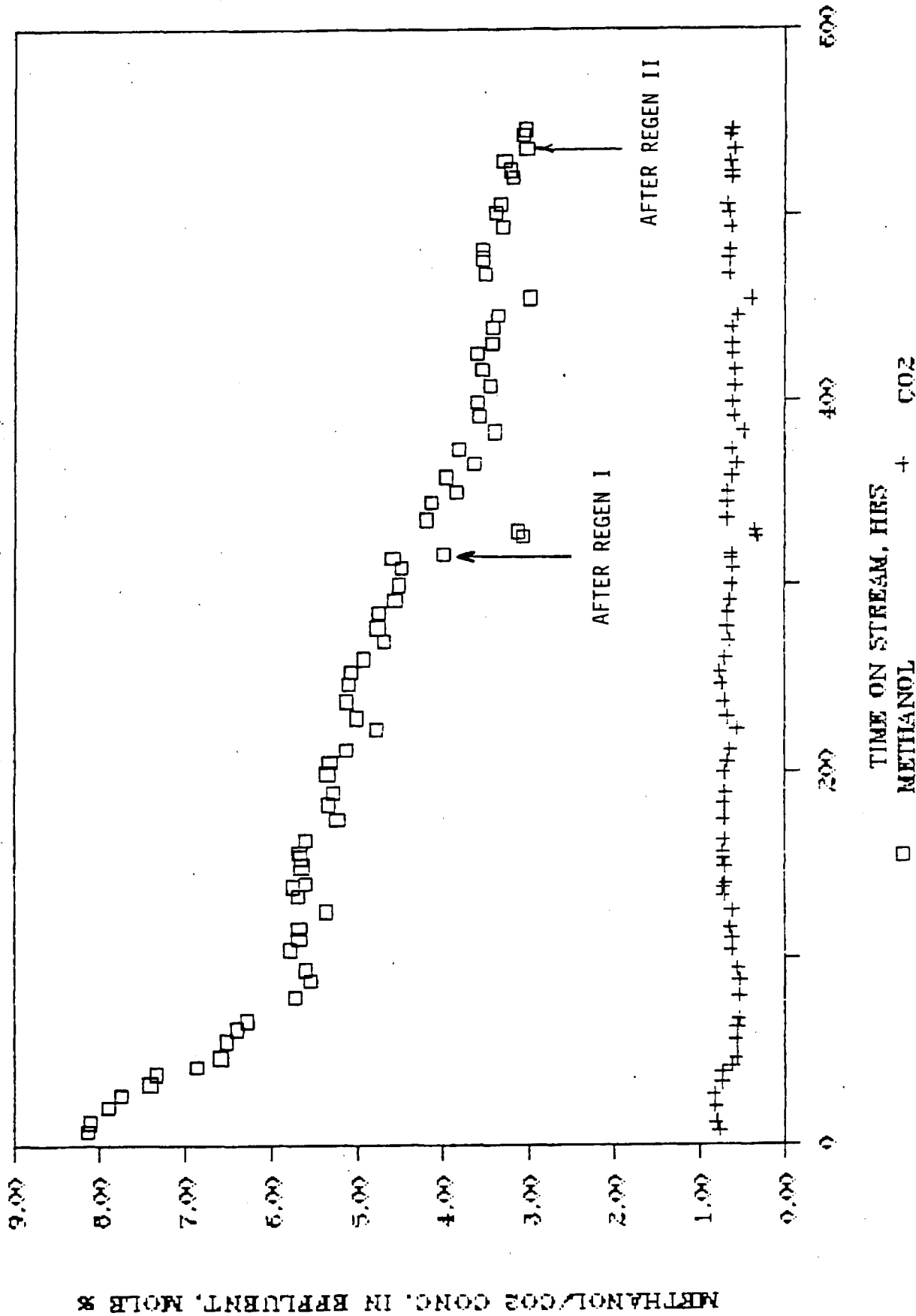
Resumption of operation after regeneration was delayed due to detection of ppm levels of H₂S and COS in the feed by our sulfur GC. The analysis by Great Plains did not show any sulfur (<50 ppb). There was no sulfur in the autoclave since the unit was not operating at that time. An unknown peak was observed 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 @ 19,000 GHSV)



FIELD TEST # 1 (GREAT PLAINS COAL GAS)

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

Figure 10

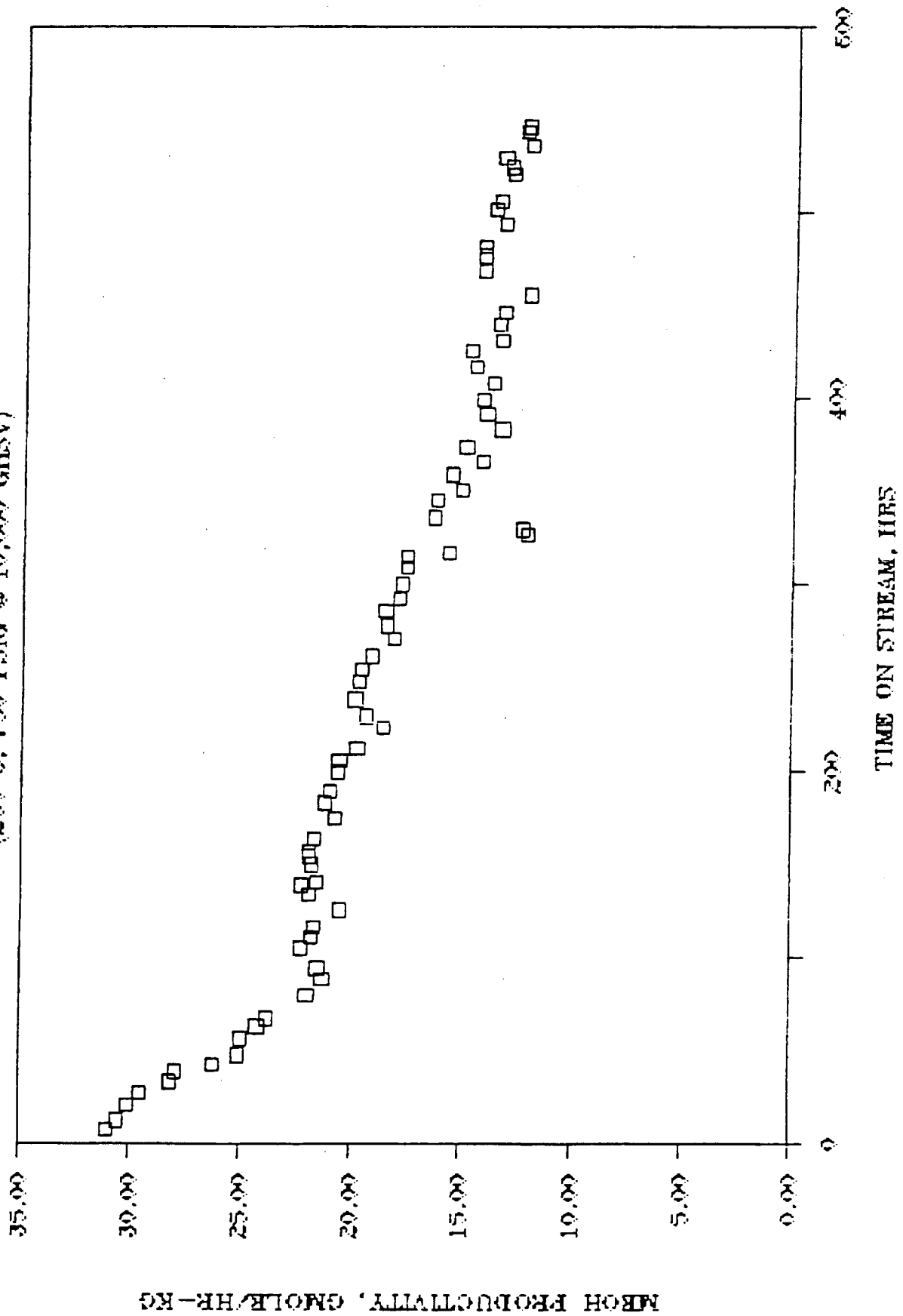
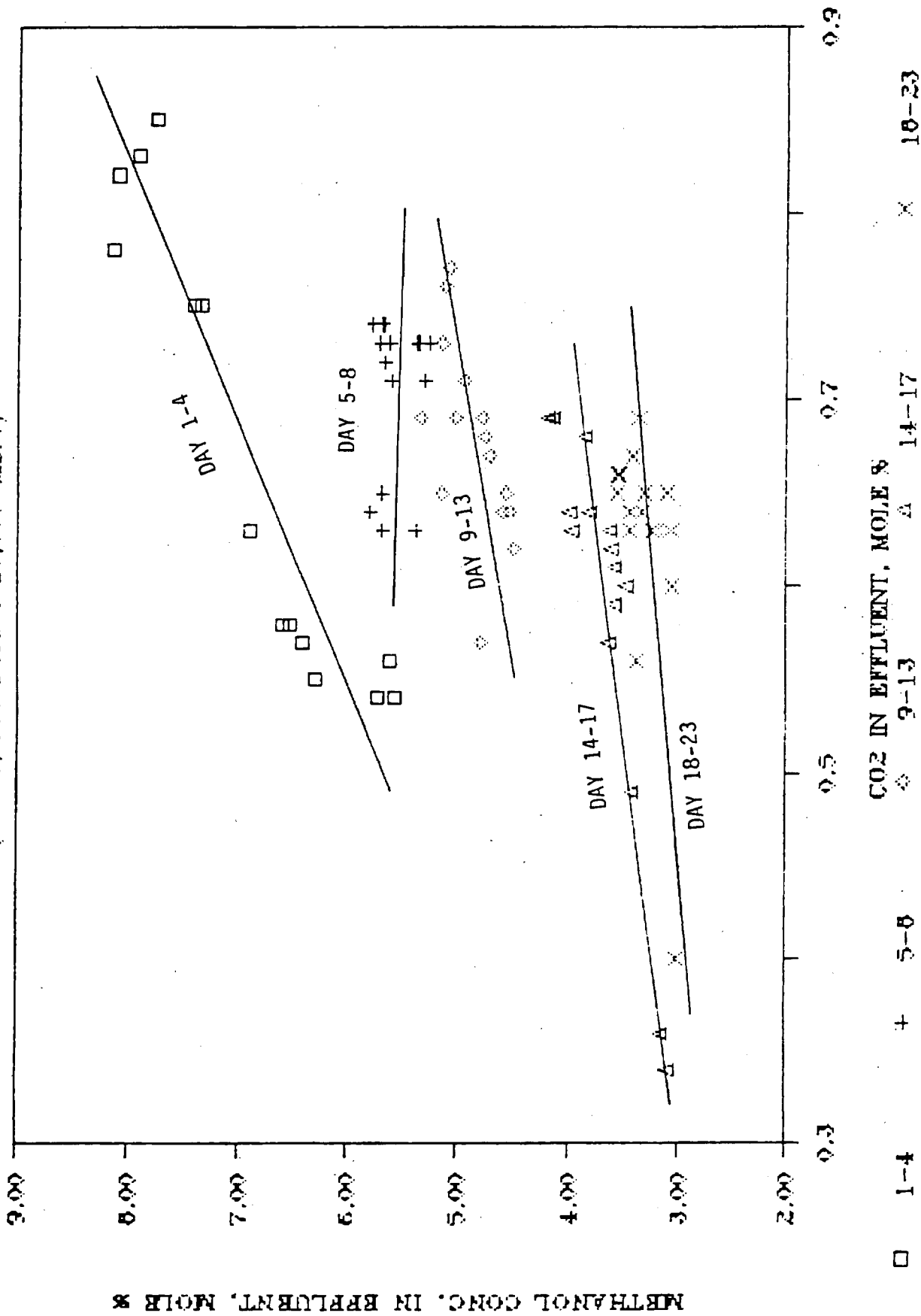


Figure 11

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

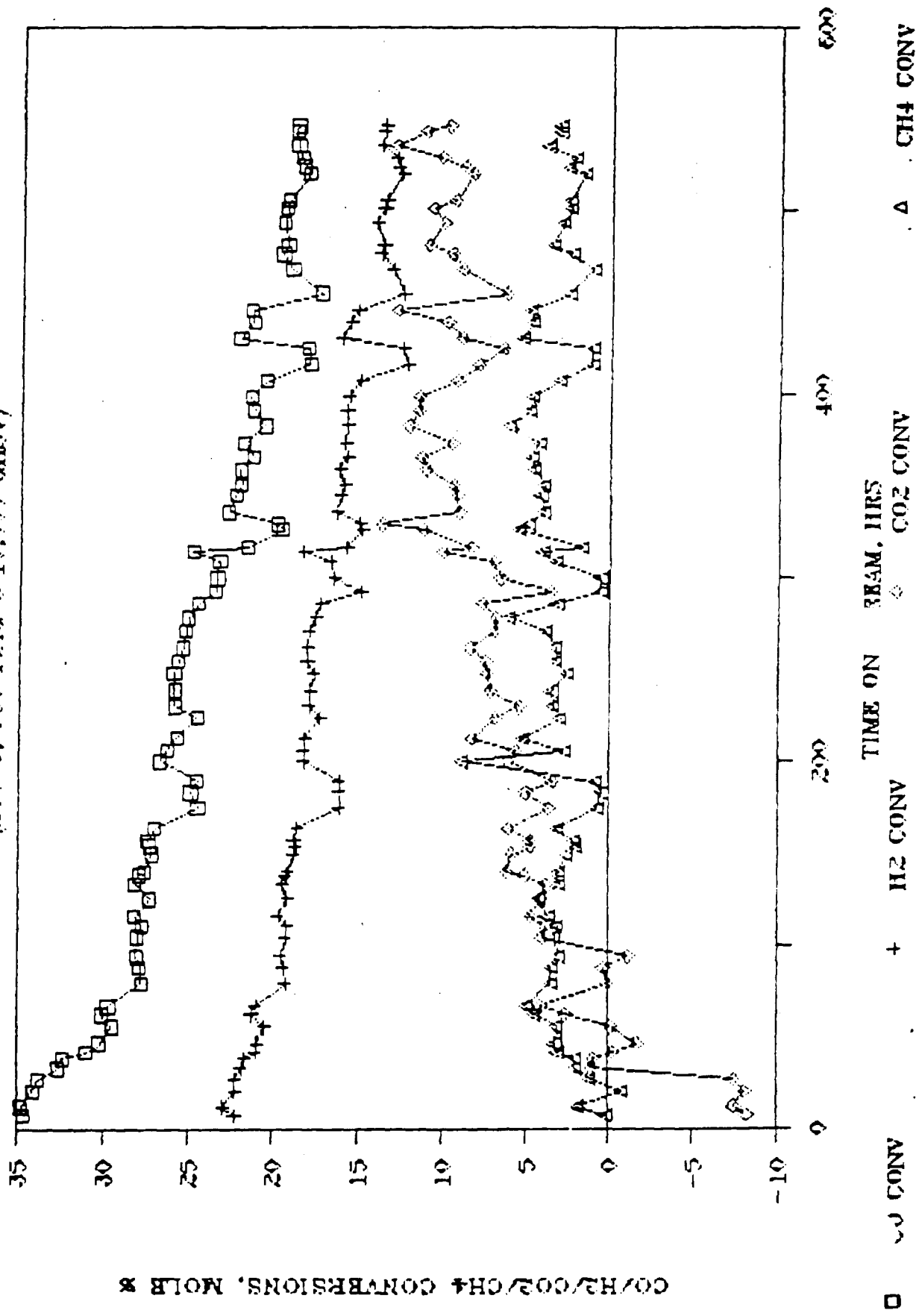
To identify the unknown catalyst poisons, gas samples were taken during both on-stream and regeneration periods with specially made sample devices and shipped to Allentown for GC-MS analysis. GC Analysis at Great Plains (both Air Products and DGC) revealed the presence of ethylene, propylene and acetonitrile 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)

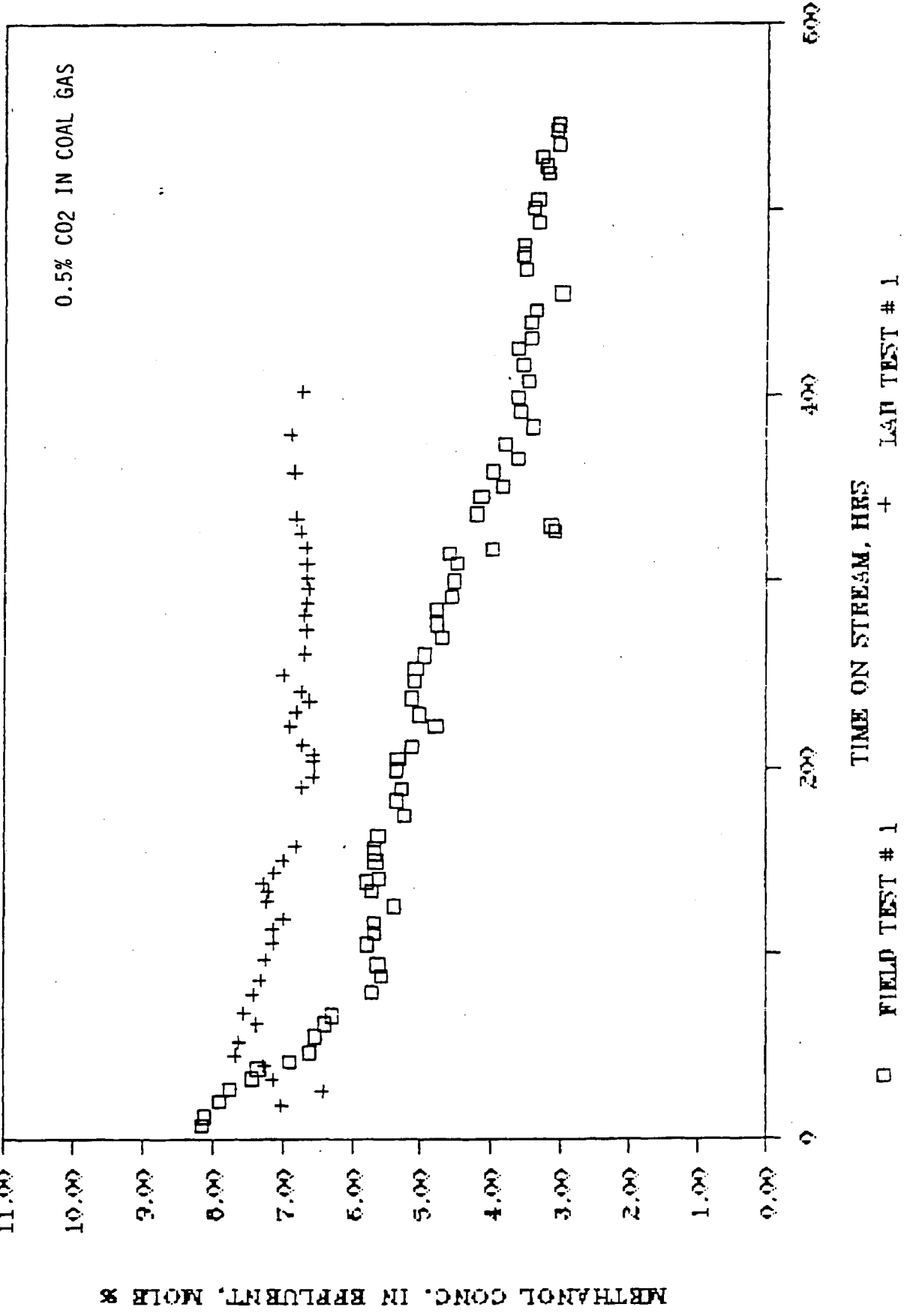


Figure 14

FIELD/LAB TEST WITH GP COAL GAS

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

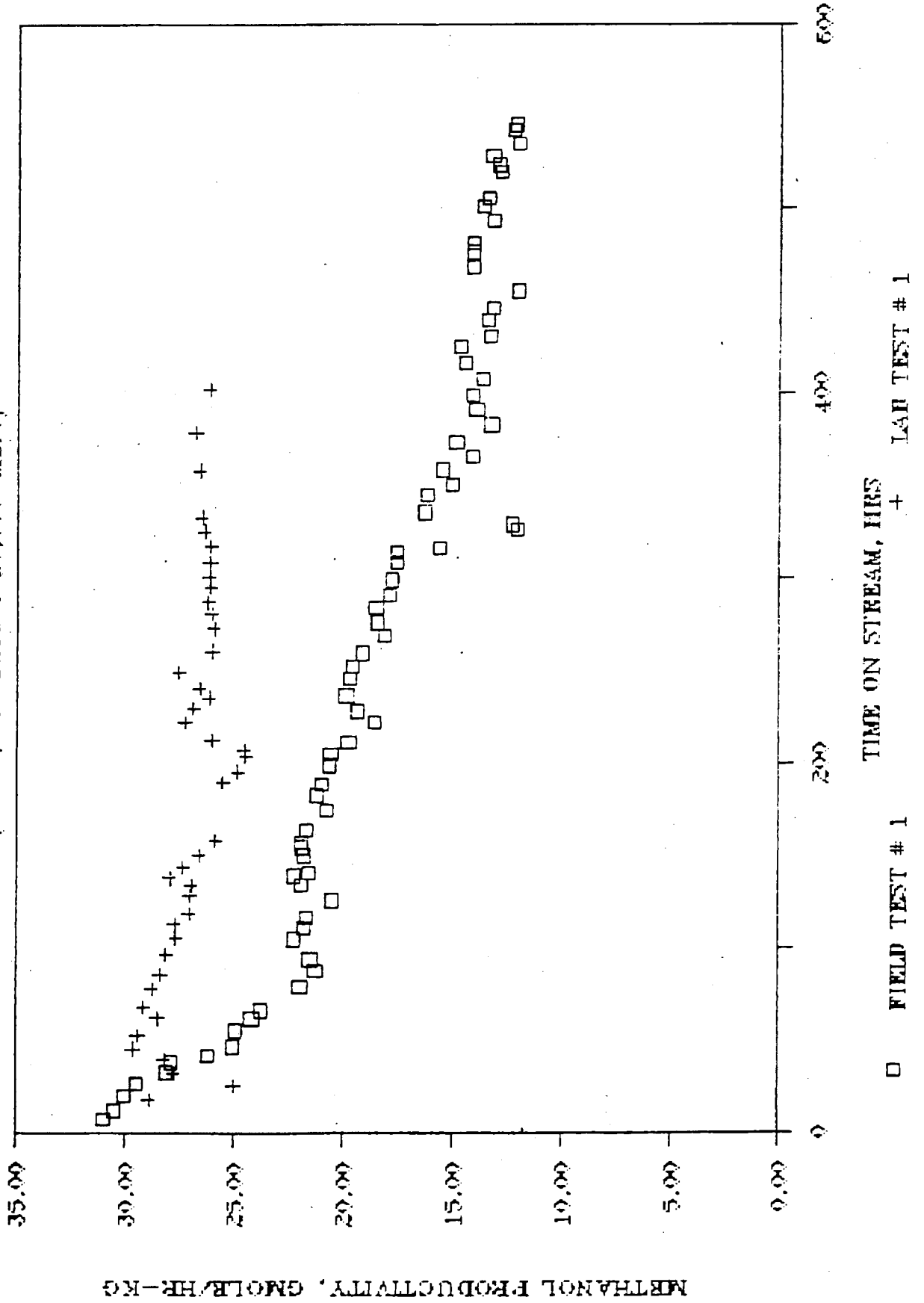


Figure 15

LAB TEST # 1 (SYNTHESIZED GP COAL GAS)

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

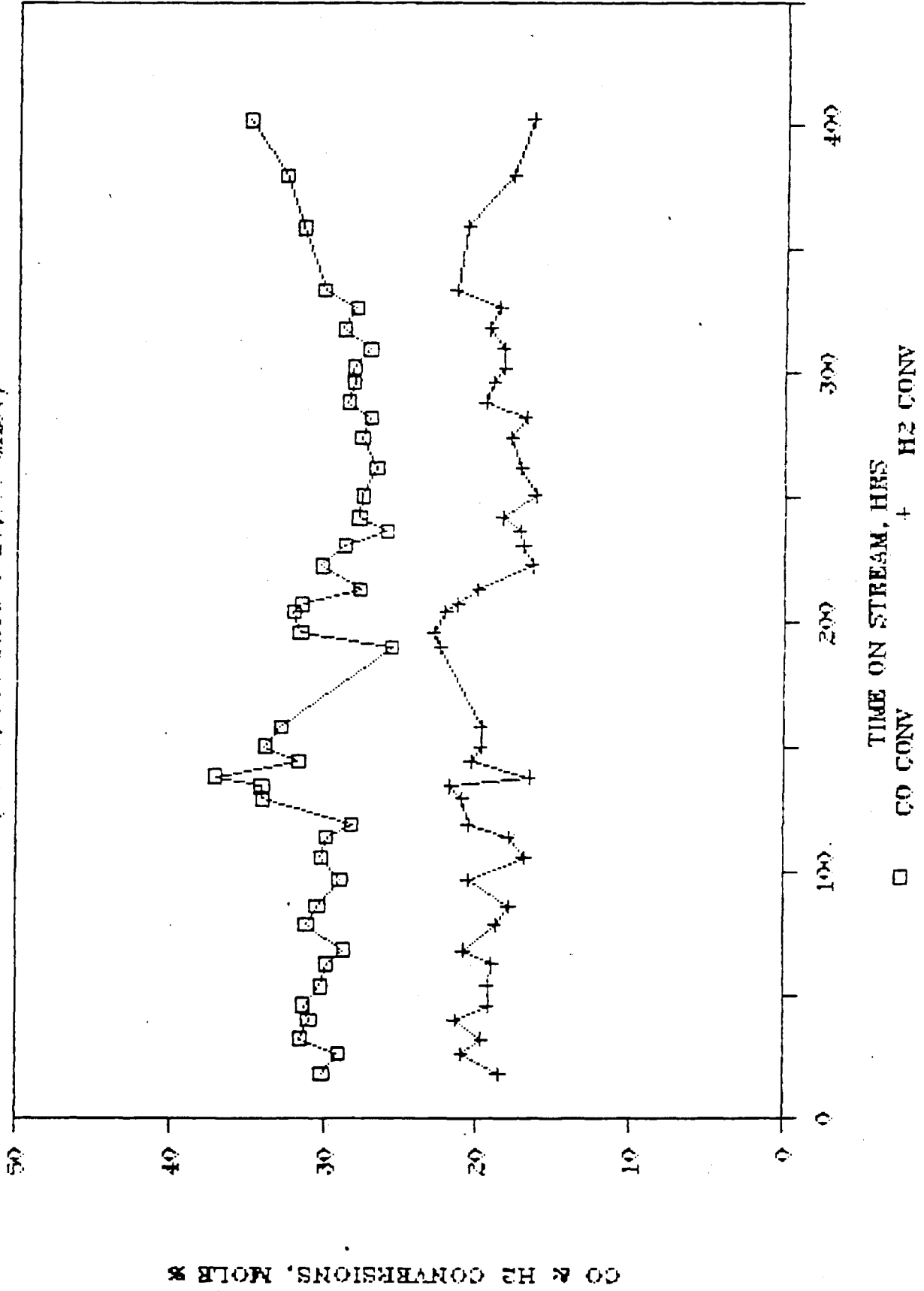


Figure 16

LAB TEST # 1 (SYNTHESIZED GP COAL GAS)

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

