

Task 3.5: Poison Resistant Catalyst Development and Testing

Final Topical Report

**Design and Construction of the Alternative Fuels Field Test Unit
and Liquid Phase Methanol Feedstock and Catalyst Life Testing
at Eastman Chemical Company (Kingsport, TN)**

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1.0 Introduction

1.1 Alternative Fuels Field Test Unit (AFFTU)

The AFFTU is a portable laboratory designed specifically to provide on-site evaluation of potential feedstocks for processes that produce alternative fuels from indigenous raw materials such as coal, natural gas or environmentally disadvantaged carbonaceous feedstocks. Since conversion of these raw materials into feed gas streams can produce a variety of bulk gas compositions, which furthermore can contain a myriad of trace components, it is necessary to evaluate each new feedstock on an individual basis. While it is possible to prepare blended gas mixtures to simulate the bulk composition of a known feedstock, it is neither possible nor cost-effective to simulate adequately the variety of trace chemicals present in that feedstock -- some of which may not even be detected by routine analysis. Additionally, the transient composition of the gas during upsets or routine process changes may have an impact on the proposed process that is not foreseen in standard design. To address these concerns, the AFFTU was constructed with the following experimental capabilities:

1. A state-of-the-art gas chromatograph system to perform semi-continuous monitoring of both bulk composition and the concentration of key trace poisons down to one part per billion (ppb).
2. A 30-mL reactor system that can accept up to two feed streams from the customer, allowing a true life test with the actual gas projected for use in the proposed facility.
3. A manifold of four adsorbent beds, located upstream of the reactor, which permits the testing of adsorbents for the removal of contaminants from the feed stream. The effectiveness of these adsorbents may be evaluated either by analysis of the gas upstream and downstream of the bed (or at an intermediate point within the bed) or by observing the impact of the presence or absence of that bed on the actual stability of the catalyst activity.

To achieve portability, the AFFTU was constructed in a commercial 48-foot trailer. Roughly half of the trailer is dedicated as "office" space, and it contains three personal computers that serve as an interface to the process control and handles data acquisition and analysis. The other half houses the laboratory, which is highly automated and designed for unattended operation. When not in use at a customer's site, the AFFTU is located at Air Products' Iron Run research facility, where it becomes an effective extension of the Alternative Fuels research laboratories.

1.2 Kingsport Testing

A 260 ton-per-day Liquid-Phase Methanol (LPMEOH™) Plant has been constructed and commenced start-up in January 1997 at Eastman Chemicals' Kingsport, Tennessee facility as part of the Department of Energy's Clean Coal Technology program. The objective of this project is to "demonstrate the production of methanol using the LPMEOH™ process in conjunction with an integrated coal gasification facility."¹ Design and construction of the plant is the responsibility of Air Products and Chemicals, Inc.. Start-up inaugurated a four-year demonstration period, under which Eastman Chemical Company will assume operation of the facility.

A highly simplified flow sheet for the Kingsport LPMEOH™ facility is given in Figure 1. Three gas streams are available as feedstocks to the process: “balanced syngas” from Eastman’s coal gasifiers, “makeup CO” from a cold box and “H₂ makeup” from Eastman’s existing methanol unit. The reactor will operate at 250°C and 750 psig. Downstream of the reactor, unreacted syngas will be separated from the products and roughly 90% of it will be recycled.

It is well known that the presence of even trace amounts of certain compounds in the feed gas to a methanol synthesis catalyst can cause unacceptable rates of catalyst deactivation. For this reason, extensive testing of the feed streams at Kingsport was performed during the project design phase. The results of this testing are summarized in Table 1; the full report is provided as Appendix 1. No known catalyst poisons were found in concentrations that would render the Eastman’s feed streams unsuitable as feedstocks to a LPMEOH™ plant. Based on this work, an activated carbon guard bed (see Figure 1) was designed to protect the catalyst against possible contamination by iron or nickel carbonyl in the event of an upset in the gasifiers or syngas purification system.

Table 1 - Summary of Poisons Pretesting

Component	Specification (ppmv)	Measured Concentration (ppmv)
Arsenic, as AsH ₃	0.01	0.027
Halogens (Cl & F)	0.01	~0
HCl	0.01	<1
Fe(CO) ₅	0.01	<0.01
Ni(CO) ₄	0.01	≤0.001
Ammonia	10	<0.023
HCN	0.01	<1
Acetonitrile	?	<0.5
H ₂ S (post Eastman guardbed)	0.03*	0.035±0.024
COS	0.03*	<0.5

*[Note that the 30-ppb specification for COS and H₂S is an arbitrary division between COS and H₂S; the true specification is 60 ppb *total sulfur*.]

The results of the pre-testing of the Kingsport feed streams provided a sound basis for proceeding with the project and designing the guard bed. However, prudent engineering practice required the performance of additional on-site feedstock testing. This testing involved running a bench-scale LPMEOH™ reactor for one month using feed gas directly from Eastman’s piping, while simultaneously monitoring the concentrations of key catalyst poisons. The following factors were involved in this decision:

- The pre-testing provided a picture of the average expected poisons levels in the three feed streams. It did not provide very much information on the frequency and magnitude of upsets or the poisons concentration excursions that might result. Therefore longer term monitoring of the key catalyst poisons would be valuable in confirming that the existing guard bed design was adequate.

- In the case of a few of the potential catalyst poisons (HCN and acetonitrile, for example), the testing method was not sufficiently sensitive to discern whether the concentration of those compounds met the specification. Furthermore, for many of the compounds, the specifications themselves represent *judgments* based on the best available information. Performing an actual life test using the syngas in question provides a reliable measurement of the true impact of these trace compounds on the stability of the catalyst.
- It is possible that an *unknown poison* is present, either continually or during upsets, which has a deleterious effect on the methanol synthesis catalyst.
- The construction of the Kingsport plant represents a leap both in terms of *scale* and *feedstock source*. It is therefore desirable to eliminate the feedstock as a possible variable by demonstrating stable LPMEOH™ reaction activity using Eastman's feed streams.

The AFFTU was taken to Kingsport in May 1996 for six weeks of on-site testing. As a result of this work, the assumption that the Eastman syngas is sufficiently poison-free to sustain stable catalyst activity was confirmed, and additional insights into the identity and concentrations of catalyst poisons in that feedstock were obtained. This report describes the AFFTU and the Kingsport testing.

2.0 Objectives

The AFFTU was designed to provide on-site testing of the quality of synthesis gas feeds for conversion to fuels via liquid phase technologies. The overall objective was to provide an accurate measure of the quality of the syngas via:

1. The capability to run the desired reaction for an extended period using the customer's synthesis gas as feed.
2. State-of-the-art trace gas analysis targeting specific, known catalyst poisons.
3. Highly automated data acquisition and storage.
4. Equipment and operating procedures designed with the safety of the operators and the equipment as the top priority.

The objective of the AFFTU/Kingsport project was to provide long-term testing of two of the three feed streams (i.e., the balanced syngas and makeup CO streams) for the Liquid Phase Methanol demonstration plant at Eastman Chemical Company (Kingsport, TN) for poisons that would cause faster than anticipated catalyst deactivation. Two forms of testing were employed: (1) a life test of the LPMEOH™ reaction in a 300-mL reactor using the actual feed streams and (2) semi-continuous analysis of those same feed streams using gas chromatographs equipped with detectors sensitive to targeted poisons.

3.0 Experimental Methods

3.1 Design of the AFFTU

The AFFTU is a mobile laboratory housed in a tractor trailer. T. A. Dahl was responsible for the design and construction. The project was completed on time and on budget (see Appendix 3). Considerable cost savings were achieved by reusing large portions of the experimental apparatus from the similar system built for the proposed 1989 Clean Coal demonstration project at Beulah, North Dakota. The bulk of the cost of the current system went into upgrading the onboard gas analysis and data acquisition and control systems. These improvements permitted analysis of trace catalyst poisons down to the *one part per billion* levels. These improvements also permitted unattended data acquisition which allowed around-the-clock monitoring of gas concentrations.

The trailer is divided by a wall into two portions: an office area and a laboratory area. The office area houses three personal computers, a sink and counter, and most of the control and data acquisition electronics. The laboratory area houses all of the experimental apparatus and analytical equipment, tools and chemicals storage.

The utility requirements of the AFFTU are minimal, allowing for maximum flexibility in siting. The specific requirements are:

1. 480V-3Ph-60Hz electrical supply (75 kVA, 90A transformer)
2. Potable water
3. Instrument air: 150 psig
4. Instrument nitrogen: 150 psig
5. Municipal drain/sewer for sink

The experimental apparatus (Figures 2 through 11) consists of a feed manifold, adsorption (pretreatment) system and autoclave system. The feed manifold allows the blending of two feed streams (supplied by Eastman), as well as any of several cylinder gases (2% hydrogen in nitrogen is shown in Figure 2). Flows are controlled with mass flow controllers, MFC1 and MFC2. The adsorption system is designed to permit up to four adsorbent beds to be placed in series in the feed stream for selective removal of various catalyst poisons potentially present in the syngas. A compressor is available if adsorption at pressures greater than the supplied feed pressure is desired. A back-pressure regulator (BPR1) maintains the pressure in the adsorption system. The treated feed is sent to a 300-mL stirred autoclave (Autoclave Engineers). This reactor is equipped with a gas-liquid separator, maintained at 145°C, to return any entrained slurry to the reactor. Feed pressure to the reactor may be boosted using compressor COMP2; reactor pressure is set with regulator R5 and is maintained using BPR3. The flow rate is set by mass flow controller MFC3. Typically the flow rate set by MFC1 and MFC2 is least 10% above that of MFC3; this helps to eliminate any pulsations caused by the compressors, while guaranteeing that flow will be maintained. The excess feed vents through BPR2. The reactor effluent is vented through a wet test meter to obtain an accurate measurement of the reactor exit flow.

A list of the specific components of the AFFTU is provided as Appendix 2.

3.2 Onboard Gas Analysis

Analysis of the gas compositions was performed by two Hewlett-Packard 6890 Gas Chromatographs (GCs). These GCs were configured for the specific analyses by Wasson-ECE Instrumentation, and the flow sheets are provided in Figure 12 (a) and (b). GC1 was dedicated to bulk gas analysis and was equipped with two detectors: a thermal conductivity detector (TCD) for analysis of hydrogen, carbon monoxide, carbon dioxide and nitrogen, and a flame ionization detector (FID) for hydrocarbons analysis (primarily methanol for the Kingsport work). GC2 was dedicated to analysis of ppb levels of four poisons: hydrogen sulfide and carbonyl sulfide using a Sulfur Chemiluminescence Detector (Sievers) and nickel and iron carbonyl using an Electron Capture Detector (Hewlett-Packard). The analysis of these metal carbonyls and sulfides was shown to be sensitive down to 1 ppb; that is, a clear and unambiguously integrable peak could be observed at that concentration. Calibration was performed using standards with considerably higher concentrations, and linearity of the detector response was assumed in order to interpolate to concentrations below those used for calibration. Examples of the chromatograms are given in Figure 12 (c) through (f). Details of the GC techniques are provided in Tables 2 and 3.

Table 2 - Gas Chromatograph #1: Bulk Gas Analysis

Detector	A: FID	B: TCD	C: TCD
Components/Analysis	Hydrocarbons	CO, CO ₂ , N ₂	H ₂
Sample Size	0.1 mL	1.0 mL	1.0 mL
Carrier Gas	Helium	Helium	Nitrogen
Detector Temp.	250°C	200°C	50°C
Injector Temp.	200°C	200°C	Not Applicable
Columns	#1) 0.53 mm x 9 cm Wasson KC5 capillary #2) 0.53 mm x 50 m Wasson KC5 capillary	#3) 1/16 in. x 8 ft Wasson Km1 (80/100) #4) 1/16 in. x 10 ft Wasson Km2S (80/100)	#5a) 1/8 in. x 6 ft Wasson K1 (80/100) #5b) 1/8 in. x 7 ft Wasson K2 (80/100) #6) 1/8 in. x 2 ft Wasson K2 (80/100) #7) 1/8 in. x 2 ft Wasson K2 (80/100)
Temp. Program	85°C Isothermal		
Valve Program	0.01 min 0.05 min 0.05 min 0.75 min 0.75 min 2.30 min 2.90 min 4.00 min 5.00 min	Valve 2 ON Valve 1 ON Valve 7 ON Valve 3 ON Valve 7 OFF Valve 1 OFF Valve 4 ON Valve 2 OFF Valve 3 OFF	

| 5.50 min | Valve 4 OFF |

Table 3 - Gas Chromatograph #3: Poisons Analysis

Detector	A: Hewlett-Packard Electron Capture Detector	B: Sievers Instruments, Inc. Sulfur Chemiluminescence Detector
Components/Analysis	Fe(CO) ₅ , Ni(CO) ₄	COS, H ₂ S
Sample Size	1.0 mL	1.0 mL
Carrier Gas	Nitrogen	Helium
Detector Temp.	150°C	Not Applicable
Injector Temp.	100°C	Not Applicable
Columns	#3) 1/8 in. x 10 ft 10% Squalane on Chromosorb W-AW (100/120)	#1) 1/8 in. x 30 in. Wasson K20 (80/100) #2) 1/8 in. x 30 in. Wasson K20 (80/100)
Temp. Program	50°C Isothermal	
Valve Program	0.01 min 0.05 min 4.00 min 4.00 min	Valve 2 ON Valve 1 ON Valve 2 OFF Valve 1 OFF

3.3 Feed Streams

Eastman’s “balanced syngas” stream was connected to the AFFTU primary feed; the company’s “makeup CO” stream was connected to the secondary feed. For most of the AFFTU experiments at Kingsport, a feed mixture of 75% balanced syngas and 25% makeup CO was used. This corresponded to the condition in the demonstration plan that used the highest quantity of makeup CO. This case was chosen since our objective was not to mimic the final plant design, but rather to evaluate the poisons concentrations for both streams.

3.4 Adsorption System Design and Operating Conditions

The adsorption system (see Figures 2 and 6) consists of five beds -- four operating beds and a fifth bed filled with alumina which is used to decompose toxic metal carbonyls desorbed from the other four beds during regeneration. A detailed drawing of one of these beds is given in Figure 11. Each bed is approximately 12 inches long and 0.65 inches inside diameter. Four-foot-long beds are also available, but were not used in the Kingsport testing. Sampling ports are located at three intermediate positions along the bed.

The choice of adsorbents and their position in the pretreatment sequence (Table 4) was based on results from our laboratory and the previous Field Test Unit work in Beulah, ND.^{2,10}

Table 4 - Adsorbents Used for Kingsport Testing

Bed	Adsorbent	Target Contaminant	Weight	Temp.
1	Ground S3-86	H ₂ S, COS	80.71 g	Room
2	LZY-52	Ni(CO) ₄	36 g	Room
3	BPL Carbon	Fe(CO) ₅ , Ni(CO) ₄	29.14 g	Room
4	UCI G-132D	AsH ₃	69.53 g	40°C
5	Alumina	Decomp. Carbonyls	42.8 g	250°C

Bed #1 was packed with the same type of catalyst as was used in the reactor, BASF S3-86. To avoid introducing any undue pressure drop associated with a fine powder, pelletized S3-86 was selected and coarsely ground to the range 35-100 mesh.

The intended adsorbent for Bed #2 was Linde LZY-72, a hydrogen-exchanged zeolite Y. Previous experimentation at Air Products had shown this material to be an effective and partially regenerable sorbent for nickel carbonyl.² However, Linde had no LZY-72 available, so it was agreed that LZY-52, a sodium-exchanged Y, would be tested instead.

The BPL carbon used in Bed #3 is a commercially available microporous carbon from Calgon. This is the same material that will be used in the actual guard bed being installed in the Kingsport LPMEOH™ Demonstration Facility. A smaller extrudate (12x30 mesh) was used in the AFFTU to avoid channeling problems in the bed. This carbon is known to be an effective adsorbent for metal carbonyls and a variety of other trace components; however, it is not expected to be useful for the removal of sulfides.

G-132D, an arsine removal material from UCI, is a mixed copper and zinc oxide that removes arsine via reaction with CuO, forming copper arsenide. To improve the rate of this reaction, the bed was maintained slightly above room temperature in accordance with the manufacturer's recommendations.

The metal carbonyls were decomposed on a bed of Kaiser A-201 alumina heated to 250°C. The function of the alumina is primarily to provide a high surface area on which the decomposition can occur.

3.5 Safety Considerations

The AFFTU was subjected to Air Products' Process Hazards Review protocol. This protocol reviews the equipment and procedures in terms of chemical hygiene/exposure, strategies to handle potential hazards, risk minimization, required training and personal protective equipment, operability and acceptable design practices. An Operational Readiness Inspection (ORI) at Air Products verified that the equipment had been constructed in accordance with the Hazards Review and that all alarms and safety interlocks were calibrated and functioning properly. Details of the design were supplied to Eastman for their review. Once the AFFTU was installed at Kingsport, a second ORI was performed by a combined team of Air Products and Eastman personnel. Minor changes in the tie-in tubing that connected the AFFTU to Eastman's syngas headers were implemented as a result.

4. Results

4.1 Preliminary AFFTU Tests (Run 14987-1)

A preliminary test (“Shakedown Run”) of the AFFTU systems was performed at Air Products’ Iron Run facility (Fogelsville, PA) on April 10-26, 1996. This provided an opportunity to de-bug the data acquisition and control systems, as well as verify that all of the experimental components were functioning properly.

The shakedown run used powdered BASF S3-86 catalyst in the methanol synthesis reactor, employing Texaco-type gas from a tube trailer as feed. Our standard laboratory conditions were used. The resulting product stream concentrations were in line with our experience (Table 5).

Table 5 - Shakedown Run Summary

Catalyst:	30.20 grams BASF S3-86 [453-8264]
Slurry Oil:	119.80 grams Drakeol-10
Reduction:	2% hydrogen in nitrogen; 730 sccm (GHSV=1450 L/kg-hr), 100 psig 100°C-125°C in 2 hours 125°C-150°C in 5 hours 150°C-200°C in 6 hours 200°C hold for 4 hours 200°C-240°C in 4 hours
Feed Gas Composition:	51% CO, 35% H ₂ , 13% CO ₂ and 1% N ₂
Reaction Temperature:	250°C
Reaction Pressure:	750 psig
Reactor Feed:	3085 sccm (GHSV@6000 L/kg-hr)
Ads. System Feed:	3500 sccm (excess vented through BPR2)
Ads. System Pressure:	350 psig
Typical Product:	8.3% methanol, 51.2% CO, 23.8% H ₂ , 13.8% CO ₂ and 1% N ₂
Product Flow:	2570 sccm
Methanol Productivity:	18.8 gmol/kg-hr
Equilibrium Approach:	44%

The four adsorption beds were loaded with the same adsorbents that were eventually used for the Kingsport test (Beds 1-3 were reloaded at the beginning of the Kingsport run). All four beds were kept on line through the entire shakedown run.

The shakedown run yielded the following results:

- The capability of the equipment to sustain an active, stable LPMEOH™ reaction was demonstrated.
- The GC methods were reproducible, and accurate analyses were achieved.
- Several critical problems with the data acquisition software surfaced during the shakedown run. These were corrected, allowing unattended data acquisition to be achieved. Particularly useful was the ability to change sampling ports automatically and to sample from those ports at predetermined times.

- The presence of 10-15 ppm of iron carbonyl and 14 ppb of COS in the tube trailer gas was observed. This underscores the importance of our current procedure for pretreating the gas for our laboratory operations by passing it through a bed of adsorbent carbon.
- The progressive breakthrough of iron carbonyl through Beds #1 and #2 was observed.

4.2 Kingsport Testing (Run 14987-27)

The conditions used in the Kingsport run are given in Table 6, and the chronology of the run is provided in Table 7.

Table 6 - Kingsport Run Summary

Catalyst:	30.02 grams BASF S3-86 [453-8264]
Slurry Oil:	120.12 grams Drakeol-10
Reduction:	2% hydrogen in nitrogen; 754 sccm (GHSV@1500 L/kg-hr), 100 psig 100°C-125°C in 2 hours 125°C-150°C in 5 hours 150°C-200°C in 6 hours 200°C hold for 4 hours 200°C-240°C in 4 hours
Feed Gas Composition:	~42% CO, ~55% H ₂ , 1.5±0.5% CO ₂ and 0.55% N ₂
Reaction Temperature:	250°C
Reaction Pressure:	750 psig
Reactor Feed:	3150 sccm (GHSV@6300 L/kg-hr)
Ads. System Feed:	2666 sccm balanced syngas; ~900 sccm makeup CO (excess vented through BPR2)
Ads. System Pressure:	450 psig
Typical Product:	10% methanol, 45% CO, 42% H ₂ , 2% CO ₂ and 0.75% N ₂
Product Flow:	2350 sccm
Methanol Productivity:	23 gmol/kg-hr
Equilibrium Approach:	20%

Table 7 - Chronology of Kingsport Run

Event	Date & Time	Time Onstream*	Days of Operation**
Beginning of Run	5/15 1440	0	-0.35
Bed #4 Dropped	5/20 830	114	4.4
Bed #2 Dropped	5/21 930	139	5.44
Bed #1 Dropped	5/22 1000	163	6.56
Bed #3 Dropped	5/26 1500	264	10.67
First Gasifier Outage	5/30 1430	360	14.65
Restored	5/31 400	360	15.21
Second Gasifier Outage	6/6 730	503	21.36
Restored	6/10 1000	503	25.47
Run Terminated	6/17 1700	678	32.76

*The cumulative time (in hours) of exposure of the catalyst to feed gas.

**The number of days since the beginning of the experiment. The negative value at the beginning results from differing definitions of when the experiment began. Continuous syngas poisons monitoring (“Days of Operation”) began several hours after the point we adopted as the basis for our “Time Onstream” datum.

4.2.1 Poisons Monitoring Results

Summary

Four materials that are known to poison the S3-86 methanol catalyst were observed during at least portions of the testing period: iron carbonyl, nickel carbonyl, hydrogen sulfide and carbonyl sulfide. No other compounds (other than the bulk components of the feed and product streams) were observed with either the Electron Capture Detector or the Sulfur Chemiluminescence Detector. The packed bed of BASF S3-86 methanol synthesis catalyst was effective for the removal of <20 ppb iron carbonyl, <3 ppb hydrogen sulfide and <20 ppb carbonyl sulfide, but was saturated rapidly by the 10-200 ppb nickel carbonyl initially present in the feed stream. The activated carbon bed (Calgon BPL) was effective for the removal of both iron and nickel carbonyl and the trace hydrogen sulfide in the feed. Carbonyl sulfide was not removed by the BPL carbon. The nickel carbonyl was clearly demonstrated to be an artifact of the fresh tie-in tubing between Eastman’s piping and the AFFTU. Most, if not all, of the iron carbonyl was likely also an artifact of the tie-in. The sulfides are believed to be inherent in Eastman’s syngas.

4.2.1.1 Carbonyl Sulfide

Carbonyl sulfide was observed throughout the testing period. The concentration typically remained between 7 and 15 ppb. During days 1-5, this concentration fluctuated according to a 24-hour cycle, as did the metal carbonyls, reaching a maximum value in the late afternoon. After day 5, these fluctuations disappeared. No satisfactory explanation as to why this component should initially fluctuate regularly in concentration and then later achieve a comparatively steady concentration has been found.

Tripling the flow rate of fresh feed into the AFFTU on day 10 had no effect on the feed concentration of COS, which did not diminish over the course of the testing period. These observations suggest that the COS is truly present in the Eastman syngas.

In the middle of the testing period, Eastman's gasifiers were off for four days (days 22-25). When syngas generation was restored, a significant COS excursion was observed, beginning with a concentration of 190 ppb and falling gradually to 30 ppb over a 10-hour period (see Figure 14). Restoration of gasifier function after an earlier, briefer outage (days 14-15) did not result in such an excursion. The ephemeral nature of these excursions demonstrates the need for long-term on-site testing.

When all four guard beds were in place, the COS was largely removed by Bed #1 (S3-86). Roughly 0.5 ppb of COS passed through this bed, and this level of COS continued essentially unattenuated through the remaining three beds. The sequential removal of Beds 4 and 2 obviously had little impact on the COS concentrations elsewhere in the system. Just prior to the removal of Bed #1 (day 6), samples were taken from the intermediate sampling port 3 in. from the feed end of Bed #1. The concentration was found to be 0.4-0.5 ppb, the same as the exit concentration, indicating that the COS adsorption front had not penetrated one quarter of the way through the S3-86 bed. Removal of Bed #1 left only the BPL carbon bed in place. Feed concentrations of COS of 8-14 ppb passed basically unchanged through this bed.

The presence of (typically) 5-20 ppb COS in our mixture of 75% balanced syngas and 25% makeup CO was unexpected based on the pre-testing results, which had indicated that most of the 10-60 ppb total sulfur in the balanced syngas was in the form of H₂S. However, as discussed in Section 4.2.3, the reactor data show that at these levels, COS does not significantly affect catalyst stability.

4.2.1.2 Hydrogen Sulfide

Analysis of ppb levels of hydrogen sulfide is difficult due to the tendency of H₂S to react with process tubing. This reaction is reversible; therefore saturating the tubing walls with sulfide ("pickling") is, at best, a temporary solution. Our approach was to use sulfide-resistant silico-steel tubing for as much of the analytical lines as practical and to attempt to maintain the system in a "pickled" state. The fact that no hydrogen sulfide was initially observed at Kingsport (see Figure 15) and that eventually H₂S was observed approaching a level of roughly 3-4 ppb suggests that the system was initially not pickled, and gradually approached a pickled state, which permitted H₂S to reach the sulfur detector. We need to consider not only the analytical tubing, but also the entire length of fresh stainless steel used to tie the AFFTU to Eastman's syngas headers.

On day 9, catalyst poisons analysis was interrupted for 4 hours while calibration of the metal carbonyls detector was performed. During this period, H₂S-free carbonyl standard was directed through the analytical system, and the pickling was lost. When the feedstock analysis was resumed later that day, no H₂S was detected. This underscores the difficulty of the ppb H₂S analysis. H₂S concentrations in the range of 1-3 ppb were observed intermittently thereafter, through the second gasifier outage (day 21).

After the second outage, hydrogen sulfide was detected fairly rapidly and leveled off in a concentration range of 2.5-6 ppb, spiking once to 29 ppb. It appears that the actual concentration of hydrogen sulfide in the Eastman syngas after the second outage was somewhat higher than during the previous portion of the run.

To summarize, in spite of the analytical challenges, we are comfortable that the actual hydrogen sulfide concentration in the Eastman gas was generally in the 2-4 ppb range prior to the second gasifier outage and in the 2.5-6 ppb range after it. These results are notably different from the pre-testing report (Table 1), which specified 10-60 ppb of total sulfur, essentially completely in the form of hydrogen sulfide.³

There are several possible explanations for this discrepancy:

1. The pre-test for hydrogen sulfide also detected COS.
2. Hydrogen sulfide is converted to COS in the AFFTU tie-in and/or analytical tubing.
3. The amount of hydrogen sulfide in Eastman's gas can vary considerably.

The trace amounts of hydrogen sulfide we detected in the trailer feed were readily removed by Bed #1, the crushed S3-86 pellets. When this bed was removed, the BPL carbon likewise was successful in removing all traces of hydrogen sulfide from the reactor feed. This is attributed to the low inlet H₂S concentration, since previous work has shown that BPL carbon is not a particularly effective material for H₂S removal.⁴

4.2.1.3 Nickel Carbonyl

Nickel carbonyl was observed in the trailer feed over much of the six weeks of work in Kingsport. Both the iron and nickel carbonyl levels demonstrated a strong 24-hour cycle that followed ambient temperature (Figure 16a).⁵ The highest concentrations were almost always observed in late afternoon and were typically five times higher than the minimum concentrations. This observation is consistent with the kinetically limited formation of these poisons as the syngas flows through iron- and nickel-containing process lines and equipment. It has been shown that the formation of both of these catalyst poisons is reasonably sensitive to temperature in this temperature range.⁶ This correlation is clearly seen in Figure 16c.

The presence of nickel carbonyl in the AFFTU feed was shown to be an artifact of the tie-in between Eastman's piping and the AFFTU. This conclusion is based on the following observations:

1. Nickel carbonyl concentrations, initially in the 100-300 ppb range, eventually dwindled to undetectably low levels. This is consistent with the progressive removal of nickel from the source of the artifact (valve lubricant, for example).
2. Tripling the flow rate of gas through the tie-in tubing (on day 10 and thereafter) caused an immediate drop in the nickel carbonyl concentration (to undetectable levels; see Figure 16a-16c). Because day 10 was comparatively cool, the concentration of nickel carbonyl before the flow rate was tripled was already quite low. By the end of day 11, the concentration of nickel carbonyl was similar to that before the tripling of the flow. However, the ambient temperature on that day was considerably higher; in Figure 16c, this temperature difference is accounted for, and the impact of tripling the flow is more clearly seen.

3. Temporarily stopping the flow caused a buildup in nickel carbonyl in the tie-in line, indicating that this poison is formed there. This was clearly observed when flow was resumed on three occasions: first, during the initial testing of the gas (before the period shown in Figure 13); second, during the restart after the first gasifier outage (day 15); and finally after the second gasifier outage, when nickel carbonyl was briefly observed long after it had disappeared from normal onstream sampling.

The comparatively high concentrations of nickel carbonyl observed when syngas was first fed to the trailer rapidly saturated Bed #1 (S3-86). Three days later, nickel carbonyl broke through Bed #2 (LZY-52). Bed #3 (BPL carbon) was also found to be effective in removing all of the 5-60 ppb of nickel carbonyl still present in the AFFTU feed over the following eight days until this bed was taken out.

4.2.1.4 Iron Carbonyl

Iron carbonyl was observed throughout the six weeks of testing. Concentrations were generally in the range of 4-20 ppb before the flow through the tie-in was tripled, and 1-4 ppb when tripled flow was used (see Figures 13 and 16a-c). This change in concentration leads to the hypothesis that the presence of iron carbonyl is an artifact of the tie-in and not representative of the Eastman syngas itself. This hypothesis is supported by the observation, already described for nickel carbonyl, that particularly high iron carbonyl levels were measured whenever flow was restarted through the tie-in lines, indicating that this material accumulates when flow is stopped. However, two observations prevent us from stating definitively that all the iron carbonyl was an artifact. First, unlike nickel carbonyl, the concentration of iron carbonyl remained steady throughout the run. This means that if iron carbonyl was being generated in the tie-in tubing, the source of iron was not as limited as that of nickel. Second, the instantaneous drop in iron carbonyl concentration upon tripling of the feed was only 35% (from 5.1 to 3.3 ppb), quite far from a proportional decrease. This certainly could be explained by the fact that increasing the flow rate in the tie-in tubing results in a higher rate of iron carbonyl formation, either because of improved mass transfer to/from the tubing wall⁷ or because of LeChâtelier's principle (per Equation 1). In the limiting case in which the formation of iron carbonyl was extremely fast, an equilibrium concentration of iron carbonyl would be expected, regardless of the flow rate through the tie-in lines. Nevertheless, the other limiting case, in which the rate of iron carbonyl formation is very slow, must also be considered. In this case, tripling the flow rate should result in a proportional decrease in the part of the overall measured iron carbonyl concentration that is an artifact. Under this assumption, 2.5 ppb of the iron carbonyl must be present in Eastman's syngas upstream of the tie-in lines.



Iron carbonyl was strongly adsorbed by S3-86. During the first 6 days of operation, the S3-86 adsorbent bed (Bed #1) was in place, and no iron carbonyl was found to penetrate even 3 in. into the 12-in. bed.

4.2.2 Methanol Productivity Results

4.2.2.1 General Comments

The overall productivity history of the life test is shown in Figure 17. The FID was recalibrated at 260 hours on stream, resulting in the two curves shown.

The data were analyzed by our standard reaction model. The results of this analysis and all the measured bulk gas data are given in Appendix 5. Fugacities were estimated with Air Products' proprietary thermodynamics package, which uses the modified Redlich-Kwong equation of state. The resulting k_M history is given in Figure 18.

During the initial 50 hours on stream, fairly rapid loss of catalytic activity was observed. This is typical behavior for methanol production runs using this catalyst. After this initial period, activity decline was gradual and fairly steady. Several abrupt productivity losses (for example, at roughly 370, 390, 500, 540 and 660 hours on stream) are not reflected in the k_M because, as explained in the following section, these productivity fluctuations were due to changes in the feed CO_2 content and not to changes in the actual activity of the catalyst.

4.2.2.2 Carbon Dioxide Effects

The results given in Figures 18 and 19 show convincingly that many of the irregularities in reactor methanol productivity observed over the course of the life test were due to fluctuations in the CO_2 content of Eastman's syngas stream. This kinetic model not only takes into account the dependence of the methanol synthesis rate on the fugacities of CO and H_2 , but also contains a correction term that accounts for the dependency on CO_2 . When the k_M from this model is plotted as a function of time on stream, many of the productivity fluctuations are smoothed out. The most obvious example of this is the loss in productivity observed after the second gasifier outage. It is apparent that the catalyst did not deactivate appreciably during the four days of the outage; rather, it was low CO_2 concentrations in the post-outage syngas that were responsible for the low productivity.

The reason that these comparatively small fluctuations in CO_2 concentration have an unusually large impact on the reactor productivity is that although the rate is essentially independent of CO_2 level at CO_2 concentrations above 7%, below 5% CO_2 the rate decreases rapidly with falling CO_2 levels. Fortunately, even if these fluctuations are typical, they should not have a significant impact on the performance of the Kingsport plant, since the recycle is expected to raise the reactor product CO_2 levels to the 7-10% range. For a few of the planned test cases in the demonstration plan, recycle ratios may be sufficiently low to cause these variations in CO_2 to have an reasonable impact. The concentration of CO_2 in Eastman's feed and, particularly, in the reactor effluent, must be taken into account when the performance of the Kingsport plant is evaluated.

4.2.2.3 Analysis of Deactivation Rates

Past experimentation in the laboratory using syngas free of contaminants provided the basis for evaluating the stability of the methanol synthesis activity. This data are given in Table 8.

Table 8 - Typical Clean-Feed LPMEOHä Activity and Stability

Gas Type	CO	H ₂	CO ₂	k _M Deactivation Rate	Productivity Deactivation Rate
“Shell”	66	30	3	-0.042 %/hr	-0.0039 %/hr
“Texaco”	51	35	13	-0.045 %/hr	-0.019 %/hr
“Eastman”	39	50	9	-0.053 %/hr	-0.024 %/hr

Figure 20 shows the slopes (obtained by linear regression) of various portions of the productivity history. Because the change in carbon dioxide concentration after the second gasifier outage caused a significant drop in productivity, several cases that ignore the data after this point were considered. For the same reason, the rate constant data were more useful in evaluating the stability of the catalyst. This analysis is given in Figure 21; the data from Figures 20 and 21 are summarized in Table 9. A comparison of these results with the baseline data in Table 8 leads to the conclusion that the Eastman syngas did not contain any compounds that adversely affected the stability of the methanol synthesis catalyst when compared to operation using laboratory syngas. Note that the feed mixture used in the Kingsport testing (42% CO, 55% H₂ and 2% CO₂) was not identical to any of the standard mixes shown in Table 8. However, the interpretation of the results of the testing was straightforward because the observed deactivation rates were lower than any of the baseline cases given in Table 8. The lone exception to this was the productivity loss during the period after the last guard bed was removed (0.035%/hr). The rate constant declined 0.038%/hr during that period, showing that the catalyst was at least as stable as the baseline cases and that the apparently higher productivity deactivation rate was due to changes in the feed gas composition.

Table 9 - Kingsport Test Stability Data

Description	Period	k _M Deactivation Rate	Productivity Deactivation Rate
Whole Test	0-672 Hours	-0.038 %/hr	
No Guard Beds	264-672 Hours	-0.038 %/hr	-0.035 %/hr
COS Exposure	163-264 Hours	-0.001 %/hr	+0.014 %/hr
After Initial Drop	50-672 Hours	-0.031 %/hr	
No Guard Beds and Before Second Outage	264-500 Hours		-0.017 %/hr
After Initial Drop and Before Second Outage	50-500 Hours		-0.011 %/hr

One unexpected finding in the poisons analysis was the presence of 5-20 ppb of carbonyl sulfide in the trailer feed. As a consequence of this observation, the period of time in which the AFFTU was operated with Bed #3 alone was extended. This bed, which contained BPL carbon, selectively removes metal carbonyls, but allows carbonyl sulfide to pass through. Extending this stage to 100 hours permitted an assessment of the stability of the catalyst in the presence of 5-20 ppb COS without introducing any ambiguities due to the presence of iron and nickel carbonyl. As can be seen in Figures 20 and 21, the reaction was very stable during this period; in fact, the slope of the productivity was actually positive during this time. The k_M data show that the true activity did diminish very slightly and

that the productivity increase was a reflection of the increasing CO₂ content of the feed over this time frame. We conclude that COS at these levels does not have a measurable impact on the stability of the S3-86.⁸

4.2.3 Analytical Results

At the end of the life test, the four guard beds were purged individually with nitrogen for 15 minutes each. Bed #1 received an additional post-treatment: overnight passivation with 2% oxygen in nitrogen to reoxidize the copper. After these treatments, samples were taken from each end (feed and product) of the four guard beds.

The post-reaction slurry was removed from the autoclave, and a total of 92 grams was recovered. Since a few grams were lost during the transfer, a good estimate is that 95 grams of the original 150 grams of slurry remained in the autoclave at the end of the reaction. Separate weights of oil and catalyst were not measured; however, it is likely that most of the lost weight was due to oil losses.⁹ The slurry was allowed to settle, the oil was then decanted and the remaining catalyst was washed with cyclohexane.

Samples of the spent slurry oil and catalyst, together with samples from the top and bottom of each adsorbent bed, were sent to Air Products' analytical group. The desired outcomes of this analysis were to:

- Assess any physical or chemical changes that may have occurred to the catalyst that could help determine the nature of the gradual deactivation over the course of the experiment or the more abrupt deactivation seen during the second gasifier outage.
- Determine whether degradation of the Drakeol-10 slurry oil could be responsible for the gradual loss of methanol productivity.
- Provide additional information on the distribution of adsorbed poisons on the adsorbent beds and the utility of those beds for the removal of specific poisons.

4.2.3.1 Analysis of Spent Oil

A sample of the spent oil was analyzed by infrared, Raman and UV/Vis spectroscopy. A sample of fresh oil and a sample of oil from a 435-hour run previously performed in the laboratory were also analyzed for comparison.

The results (Figures 22-24) showed that the three oils were essentially identical under both infrared and Raman spectroscopy. The UV/Vis spectra, which are more sensitive to unsaturation, clearly show the growth of peaks in the 200-300 nm region. These peaks are indicative of unsaturation or conjugated unsaturation. Thus it appears that although the oil remained basically unchanged throughout the run, there was some development of unsaturation, presumably through cracking of the hydrocarbon chains. Another possibility is that small amounts of unsaturated hydrocarbons were formed as by-products of the methanol synthesis reaction, and traces of these remained in the oil. In either case, it seems unlikely that this small amount of change in the slurry medium could have caused the gradual deactivation of the S3-86.

4.2.3.2 XRD Analysis of Spent Catalyst

X-Ray Diffraction analysis of the spent catalyst was carried out to determine whether the crystallite size of the copper had grown appreciably during the run. During the two Great Plains (Beulah, ND) Coal Gas tests, a relationship was noted between deactivation of the S3-86 and crystallite growth.¹⁰ The first test showed significant deactivation, and the Cu crystallites grew from an initial size of roughly 100Å to 400Å over the 550-hour run. In the second trial, stable activity was seen, and the final Cu crystallite size was 140Å (400 hours on stream). Thus, it appears that the deactivation of the catalyst can be correlated with, though not necessarily attributed to, the growth of the copper crystallites.

The diffraction pattern for the spent catalyst sample is shown in Figure 25. Peaks for Cu and ZnO, as well as a third phase (perhaps CuO), were observed. The crystallite size of copper was calculated to be 179.4 (+/- 3.5)Å using the Scherrer equation with alumina as an external standard.

The general conclusion in comparing the Kingsport catalyst to the one from Great Plains is that roughly twice as much crystallite growth was observed over twice as long a run. It is consistent that both runs underwent comparatively slow deactivation, while the Great Plains run, which deactivated quickly, also showed much faster copper crystallite growth.

4.2.3.3 Elemental Analysis of Spent Catalyst and Guard Beds

All of these samples were subjected to elemental analysis by ICP-AES (Inductively Coupled Plasma Atomic Emission Spectroscopy) and/or ETA-AAS (Electrothermal Atomization Atomic Adsorption Spectroscopy). The complete report from F. A. Lucrezi is given in Appendix 4 and is summarized below in Table 10, which also includes information about the amount of time on stream each bed experienced.

Table 10 - Elemental Analysis of Catalyst and Guard Bed Samples (in ppm)

Sample	Iron	Nickel	Arsenic	Sulfur	Chloride	Onstream Time, hrs
Catalyst	172 [408]*	58 [408]	184 [408]	<=660 [509]	5570 [678]	678
S3-86 Feed	118 [163]	<10 [163]	<100 [163]	<=360 [163]	<=740 [163]	163
S3-86 Product	88	<10	<50	<=170	<=360	
LZY-52 Feed	242 [0]	<=19 [262]	<50 [139]	<=330 [0]	<=810 [?]	139
LZY-52 Product	261	<=22	<50	<=130	<=650	
BPL Feed	4390 [101]	120 [262]	299 [264]	4960 [101]	1050 [101+]	264
BPL Product	4480	39	<50	3740	<=740	
G132D Feed	1240 [0]	<=20 [0]	<50 [0]	<=420 [0]	<=360 [?]	114
G132D Product	1190	<=24	<50	<=390	<=750	

*Numbers in []s indicate the number of hours which that bed was exposed to levels of each contaminant roughly equal to that present in the raw feed gas.

The following comments and observations apply:

- When Bed #1 was taken out of the feed stream, iron carbonyl was not detected even 3 in. into it. The baseline iron content of S3-86 was typically 70 ppm. The feed end iron level of 118 ppm was consistent with the average exposure of 12 ppb over a 163-hour period.
- The BPL carbon, which was very effective in removing iron carbonyl, contained such a high background level of iron that the gradient of adsorbed iron carbonyl was not observed.
- Adsorption of nickel carbonyl onto the S3-86 bed was not observed, consistent with the rapid breakthrough of this component. However, 58 ppm of nickel was found on the S3-86 from the slurry. It may be that the reaction of $\text{Ni}(\text{CO})_4$ with S3-86 is slow at room temperature, but not at 250°C.
- A clear nickel gradient was observed on the BPL carbon, which showed excellent ability to remove this poison.
- The presence of arsenic, which was anticipated based on the preliminary feedstock testing, was confirmed. Only the BPL carbon showed a clear affinity for this component. The G-132D, although designed for arsine removal, was downstream of the BPL carbon and was taken out of the feed stream first; it was therefore never exposed to this compound. The higher loading was observed at the feed end of the BPL bed (299 ppm) compared with the S3-86 in the slurry and in Bed #1, in spite of the greater exposure of both of these samples to arsenic. This observation reinforces the hypothesis that the S3-86 is not a particularly active arsenic scavenger.
- Assuming that all the arsenic entering the carbon bed was captured by the first 20 grams of adsorbent, one obtains an estimated average arsenic concentration of 40 ppb in the syngas mixture. This is comparable to the pre-guardbed value of 27 ppb reported in the preliminary gas testing. The expected low levels of arsine were therefore confirmed and the guard bed should be able to remove them. Furthermore, when all the guard beds were removed, this level of arsine did not lead to an observable increase in the rate of catalyst deactivation.
- The sulfur data were consistent with our GC observations. The fact that sulfur was obviously adsorbed onto Bed #2, in spite of the fact that this bed was never exposed to the full feed levels of COS, substantiates the observation (made via GC) that Bed #1 was not 100% effective in removing COS.
- The most striking information provided by the analysis was the high chloride concentration measured on the post-slurry catalyst (0.56%). In spite of this, stable catalyst activity was observed over the course of the life test; therefore, we concluded that this loading of chloride does not measurably impact the catalyst's performance. The comparatively low levels seen on the S3-86 from Bed #1 indicate that the high concentration found on the catalyst in the reactor is not a baseline level. Both Beds #1 and #3 appear to have had some affinity for the chloride; however, it appears that the S3-86 in the slurry at 250°C was a much more effective sink for this contaminant. Regarding chloride, the preliminary report (Appendix 1) states "No additional amount detected on spent catalyst surface

vs. fresh catalyst. No further analysis performed”, and supported this observation with FT-IR data indicating <1 ppm chlorine. However, the catalyst limit was given as 0.01 ppm. A rough estimate of the average chloride content of the feed gas mixture based on the final loading and 678 hours of total exposure was 0.88 ppm. It is certainly possible that this reflects one or more excursions in the chloride content and that the average value is not meaningful.

5.0 Conclusions

1. The AFFTU was constructed on schedule and at the budgeted cost.
2. The capabilities of the AFFTU to perform on-site evaluation of catalyst performance and stability coupled with state-of-the-art gas chromatography for ppb level analysis of sulfides and metal carbonyls were demonstrated.
3. Stable LPMEOH™ catalyst activity was demonstrated over a 28-day life test using the actual syngas feed that will be used at the Kingsport LPMEOH™ Demonstration facility. During the final 420 hours of the test, the syngas was fed to the reactor without any pretreatment; the stable catalyst activity observed during this period confirmed that no catalyst poisons were present in the syngas at sufficient concentrations to measurably impact the catalyst performance.
4. Onboard gas analysis revealed the presence of iron and nickel carbonyl, hydrogen sulfide and carbonyl sulfide in the AFFTU feed. The nickel carbonyl was shown to be an artifact of the tie-in tubing; the iron carbonyl was also at least partially, if not totally, an artifact. All four compounds were present at levels comfortably below the specifications set by Air Products’ process engineering.
5. Chemical analysis of the spent catalyst and guard beds revealed the presence of arsenic and chloride. Neither of these was present in high enough concentrations to measurably increase the rate of catalyst deactivation.
6. When Eastman’s gasifiers were restarted after a shutdown, levels of both trace poisons and the bulk gases increased significantly from the steady-state level. It has been recommended for plant operation that these analyses be performed before the LPMEOH™ reactor is placed back on stream after an upset.
7. The carbon dioxide concentration in Eastman’s syngas was found to fluctuate in the range of 1 to 2%. In the once-through design of the AFFTU reactor system, these fluctuations resulted in obvious changes in methanol productivity. The recycle stream in the actual LPMEOH™ demonstration plant will keep carbon dioxide levels high enough that these fluctuations should not have any impact.

Overall, the design and fabrication of the AFFTU was very successful. In addition to meeting the technical requirements and the constraints of schedule and cost, the AFFTU design was approved by

both Air Products' and Eastman's safety teams. During the work at Kingsport, the AFFTU proved to be a safe and easily operated laboratory and also provided a comfortable working environment. An obvious improvement in operability compared with the previous Field Test Trailer was seen, a result of the improved analytical and data handling equipment.

The Kingsport testing was likewise a success and provided positive results. This testing confirmed that the Eastman syngas meets process engineering's specifications and is capable of being used as a feed to the LPMEOH™ reaction with no measurable decrease in catalyst stability compared with laboratory data. Further insights were gained into the nature of the poisons in the Eastman syngas and the possibility of potential concentration excursions with gasifier restart.

6.0 Recommendations

Several recommendations were made to Air Products' process engineering group as a result of this work. The confirmation that Eastman's syngas yielded stable catalyst activity substantiated the decision to design the plant with a single carbon guard bed to handle traces of metal carbonyls that might be present during upsets. Two other recommendations were to:

1. Monitor poisons and bulk gas concentrations before putting the LPMEOH™ Demonstration Facility back on stream after gasifier outages.
2. Scrutinize the data collected during the four-year demonstration plan to ensure that carbon dioxide fluctuations do not impact the data, leading to false conclusions.

7.0 Current Status of the AFFTU

The AFFTU has been returned to Air Products' Iron Run site in Fogelsville, PA, where it serves as an extension of the Alternative Fuels II research facilities. This equipment remains available for use in evaluating future Liquid Phase Technology sites, providing analytical or start-up support for existing facilities or for qualifying new catalysts using on-site syngas.

8.0 Acknowledgments

G. M. Muraro, B. A. Toseland and X. D. Peng each spent a week on site at Kingsport, providing backup to T. A. Dahl and assistance and/or guidance with the experimental work. From our Process Engineering group, V. E. Stein, B. L. Bhatt and C. M. Chen provided valuable technical suggestions and guidance. Barry Street of Eastman Chemical was of inestimable help in making arrangements for the installation of the AFFTU and in supporting the project while the AFFTU was on site.

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- ¹ Estimating Scope Report, Kingsport Liquid Phase Methanol Demonstration Facility, Rev. 0 (1 August 1994).
- ² “Liquid phase methanol LaPorte PDU: Modification, operation, and support studies. Task 3.4, Adsorbent evaluation for removal of catalyst poisons from synthesis gas.”, Topical Report No. DOE/PC/90005-T34, (28 September 1990).
- ³ This pre-testing sulfide data was provided by Eastman’s analytical group. They measure the concentration of hydrogen sulfide using an online technique involving reaction with lead acetate (Tracor Atlas Lead Acetate Tape/Reflectance); they also periodically measured the concentration of H₂S when the sample was first passed over a catalyst to convert all sulfur to H₂S. Because there was little or no difference between these two measurements, they concluded that most of the sulfur was present as H₂S.
- ⁴ R. J. Grant, M. Manes and S. B. Smith, “Adsorption of Normal Paraffins and Sulfur Compounds on Activated Carbon”, *AIChE Journal*, 8(3) (1962).
- ⁵ The temperature data presented in Figure 16 was recorded using a thermocouple located inside the AFFTU; the external temperature was not recorded. However this temperature does reflect the external temperature although the amplitude of the temperature fluctuations is not as large.
- ⁶ (a) R. L. Montgomery, “Engineering-Support Services for the DOE/GRI Coal-Gasification Research Program: Metal-Carbonyl Formation in Coal-Gasification Processes”, (April 1981). (b) H. Inouye and J. H. DeVan, “Formation of Iron Carbonyl Between a 1/2 Pct Mo Steel and High-Pressure Gases Containing Carbon Monoxide”, *J. Materials for Energy Systems*, 52(1), (1979). Reference (b) also gives data showing the reduced nickel carbonyl concentrations which result from increasing flow rate through an experimental system.
- ⁷ The flow in the tie-in tubing, both before and after tripling of the flow, is laminar. The Reynolds number is estimated to be 250 and 750 for the respective cases.
- ⁸ The fact that the slope of the k_M data was less negative during the period when COS was present than during the time immediately before, when no known poisons were permitted to reach the catalyst, should not be interpreted as an indication that COS stabilizes the catalyst activity! In fact, this results from (a) data scatter and the relatively small number of points acquired, (b) inability of the model to completely account for changes in CO₂ and (c) residual impact of the initial hyperactivity/deactivation which appears to persist well beyond the initial 50 hours on stream.
- ⁹ The subsequent run in the AFFTU (Run 14987-54, also a LPMEOH™ experiment) showed a similar weight loss. After this run, the temperature of the gas-liquid separator was lowered from 145°C to 140°C and much better oil retention was observed.
- ¹⁰ “Liquid phase methanol LaPorte process development unit: Modification, operation, and support studies. Task 3.8, Catalyst poisons field demonstration.”, Topical Report No. DOE/PC/90005-T38, (9 Nov 1990).

Appendix 1: Summary of Kingsport Pretesting

Methanol Feed Contaminants: Summary of Analytical Results (rev. 4/28/95)

Component	Catalyst Limit (ppmv)	Analytical Method Used	Sampling Technique	Sample Date	ppmv in Syngas Feed, pre-G.Bed	ppmv in CO Makeup	ppmv in H ₂ Makeup	Comments
Acetylene	5	GC-FID	Offline gas	8/5/94	< 0.5 (Note 2)	< 0.5 (Note 2)	< 0.5 (Note 2)	
		GC-FID	Offline gas	2/94	< 1 (Note 2)	< 1 (Note 2)	< 1 (Note 2)	
Arsenic, as AsH ₃	0.01 ?	HGA-AAS	Charcoal tube	8/5/94	0.027	< 0.001	< 0.001	Eastman syngas guard bed
		ICP-AES	Acid scrub	4/94	< 0.04	N/A	< 0.04	
		TOF-SIMS	Spent catalyst	1993	Significant amount of AsO ₂ ⁻ detected on spent catalyst surface vs. fresh catalyst.			
Halogens (Cl & F)	0.01	TOF-SIMS	Spent catalyst	1993	No additional amount detected on spent catalyst surface vs. fresh catalyst. No further analysis performed.			
HCl		FT-IR	Offline gas	2/94	< 1	< 1	< 1	
Iron, as Fe(CO) ₅	0.01	ICP-AES	Acid scrub	12/94	< 0.01	< 0.01	< 0.01	APCI guard bed for upset
		F-AAS	Offline gas	8/5/94	< 0.01	< 0.01	< 0.01	
		ICP-AES	Acid scrub	4/94	< 0.025	N/A	< 0.025	
		F-AAS	Charcoal tube	8/5/94	< 0.05	< 0.04	< 0.07	
		TOF-SIMS	Spent catalyst	1993	Slightly more Fe ⁺ detected on spent catalyst surface vs. fresh catalyst.			
Nickel, as Ni(CO) ₄	0.01	ICP-AES	Charcoal tube	8/5/94	≤ 0.001	< 0.001	< 0.002	APCI guard bed for upset
		ICP-AES	Acid scrub	12/94	< 0.01	< 0.01	< 0.01	
		ICP-AES	Acid scrub	4/94	< 0.025	N/A	< 0.025	
		TOF-SIMS	Spent catalyst	1993	No additional amount of Ni ⁺ detected on spent catalyst surface vs. fresh catalyst.			
Nitrogen compounds Ammonia	10	ion chromatography	Acid scrub	3/94	< 0.23	N/A	< 0.23	
		FT-IR	Offline gas	2/94	< 1	< 1	< 1	
HCN	0.01	FT-IR	Offline gas	2/94	< 1	< 1	< 1	Need more sensitive analysis and/or portable test trailer.
		ion chromatography	Caustic scrub	3/94	< 5	< 2.5	< 7.5	
		TOF-SIMS	Spent catalyst	1993	No additional amount of CN ⁻ detected on spent catalyst surface vs. fresh catalyst.			

Component	Catalyst Limit (ppmv)	Analytical Method Used	Sampling Technique	Sample Date	ppmv in Syngas Feed, pre-G.Bed	ppmv in CO Makeup	ppmv in H ₂ Makeup	Comments
Amines		GC-NPD	Offline gas	8/5/94	<0.5	<0.5	<0.5	
		GC-FID	Offline gas	2/94	<0.5	<0.5	<0.5	
		TOF-SIMS	Spent catalyst	1993	Increased amount of amine-type species detected on spent catalyst surface vs. fresh catalyst.			
Acetonitrile	?	GC-FID	Offline gas	8/5/94	<1	<1	<1	Technical risk. See HCN.
		GC-FID	Offline gas	2/94	<0.5	<0.5	<0.5	
NO _x	0.1	FT-IR	Offline gas	2/94	<1	<1	<1	
		TOF-SIMS	Spent catalyst	1993	No additional amount of NO ₃ ⁻ detected on spent catalyst surface vs. fresh catalyst. (Note 2)			
Oxygen	1500	trace O2 analyzer	Online gas	1/95	100 to 200	N/A	N/A	Levels in syngas & H2 makeup unusually high & may be in error
		GC-TCD	Offline gas	8/5/94	4000	800	71400	
Sulfur, total	0.06	TOF-SIMS	Spent catalyst	1993	No additional amount of SO ₃ ⁻ detected on spent catalyst surface vs. fresh catalyst.			
H ₂ S (pre-Guard Bed)		Tracor Atlas lead-acetate tape/reflectance	Online gas	3/2/94 to 8/10/94	0.061±0.031	Note 2	Note 2	
		ion chromatography	Caustic scrub	3/94	<4	<2	<6	
H ₂ S (post-Guard Bed)	0.03	Tracor Atlas lead-acetate tape/reflectance	Offline gas	3/2/94 to 8/10/94	0.035±0.024	Note 2	Note 2	Eastman syngas guard bed.
COS	0.03	GC-FPD	Offline gas	8/5/94	<0.5	<0.5 (Note 2)	<0.5 (Note 2)	EMN data shows that nearly all sulfur is in form of H ₂ S. EMN guard bed will not remove COS ambient temp.
Unsat. hydrocarbons (olefins, aromatics)	300	GC-FID	Offline gas	8/5/94	<1	<1	<1	
		GC-FID	Offline gas	2/94	<1	<1	<1.8	

Component	Catalyst Limit (ppmv)	Analytical Method Used	Sampling Technique	Sample Date	ppmv in Syngas Feed, pre-G.Bed	ppmv in CO Makeup	ppmv in H₂ Makeup	Comments
Antimony		ICP-AES	Acid scrub	12/94	< 0.025	< 0.025	< 0.025	
		ICP-AES	Acid scrub	4/94	< 0.025	N/A	< 0.025	
Barium		TOF-SIMS	Spent catalyst	1993	None detected on spent catalyst surface.			
Beryllium		ICP-AES	Acid scrub	12/94	< 0.025	< 0.025	< 0.025	
		ICP-AES	Acid scrub	4/94	< 0.025	N/A	< 0.025	
		TOF-SIMS	Spent catalyst	1993	None detected on spent catalyst surface.			
Boron		TOF-SIMS	Spent catalyst	1993	None detected on spent catalyst surface.			
Cadmium		N/A						
Calcium		TOF-SIMS	Spent catalyst	1993	Slightly more detected on spent catalyst surface vs. fresh catalyst.			
Chromium		ICP-AES	Acid scrub	4/94	< 0.025	N/A	N/A	
		TOF-SIMS	Spent catalyst	1993	None detected on spent catalyst surface.			
Cobalt		TOF-SIMS	Spent catalyst	1993	None detected on spent catalyst surface.			
Lead		N/A						
Manganese		N/A						
Mercury		Cold Vapor AAS	Acid scrub	12/94	< 0.01	< 0.01	< 0.01	
		Cold Vapor AAS	Acid scrub	4/94	< 0.025	N/A	< 0.025	
Phosphorus		N/A						
Potassium	absent	TOF-SIMS	Spent catalyst	1993	Slightly more detected on spent catalyst surface vs. fresh catalyst.			
Radionuclides		N/A						
Selenium		ICP-AES	Acid scrub	12/94	< 0.15	< 0.15	< 0.15	
		ICP-AES	Acid scrub	4/94	< 0.15	N/A	< 0.15	
		TOF-SIMS	Spent catalyst	1993	None detected on spent catalyst surface.			

Component	Catalyst Limit (ppmv)	Analytical Method Used	Sampling Technique	Sample Date	ppmv in Syngas Feed, pre-G.Bed	ppmv in CO Makeup	ppmv in H₂ Makeup	Comments
Silver		TOF-SIMS	Spent catalyst	1993	None detected on spent catalyst surface.			
Sodium	absent	TOF-SIMS	Spent catalyst	1993	Slightly more detected on spent catalyst surface vs. fresh catalyst.			
Thallium		TOF-SIMS	Spent catalyst	1993	None detected on spent catalyst surface.			
Vanadium	absent	ICP-AES	Acid scrub	12/94	< 0.025	< 0.025	< 0.025	

Notes:

1. In general, the lower detectable limit is dependent on the amount of gas sampled, the sampling procedure, the final analytical instrument, and the amount of interfering species. The notation "< X" is used to indicate that the analyte was not detected at the lower detectable limit of X.
2. Not expected to be present and no further analysis performed.

Abbreviations:

N/A: Not Analyzed

F-AAS: Flame Atomic Absorption Spectroscopy

FT-IR: Fourier Transform - Infrared Spectroscopy

GC-FID: Gas Chromatography - Flame Ionization Detector

GC-FPD: Gas Chromatography - Flame Photometric Detector

GC-NPD: Gas Chromatography - Nitrogen-Phosphorus Detector

GC-TCD: Gas Chromatography - Thermal Conductivity Detector

HGA-AAS: Heated Graphite Atomization Atomic Absorption Spectroscopy

ICP-AES: Inductively Coupled Plasma Atomic Emission Spectroscopy

TOF-SIMS: Time-of-Flight Secondary Ion Mass Spectrometry

Appendix 2: AFFTU Parts & Components List

Comp.	Part No./Supplier	Type	Pressure	Temp °C	Seals	Location
V(M1)1	SS-1KS6/Whitey	Shutoff	3000	21		Dock 3
V1	SS-43S6/Whitey	Ball Valve	3000	65	TFE	1° Feed
V2	SS-1KS4/Whitey	Shutoff	3000	93	KEL-F	1° Feed
V3	SS-43S6/Whitey	Ball	3000	65	TFE	1° Feed
V4	SS-43S6/Whitey	Ball	3000	65	TFE	1° Feed
V5	SS-1KS4/Whitey	Shutoff	3000	93	KEL-F	1° Feed
V6	SS-43S6/Whitey	Ball	3000	65	TFE	1° Feed
V7	SS-1KS4/Whitey	Shutoff	3000	93	KEL-F	1° Feed
V8	SS-1KS4/Whitey	Shutoff	3000	93	KEL-F	1° Feed
V9	SS-43S6/Whitey	Ball	3000	65	TFE	1° Feed
V10	SS-1KS4/Whitey	Shutoff	3000	93	KEL-F	1° Feed
V11	SS-1KS4/Whitey	Shutoff	3000	93	KEL-F	1° Feed
V12	SS-4P4T/Nupro	Plug	3000	204	Viton	1° Feed
V13	SS-4P4T/Nupro	Plug	3000	204	Viton	1° Feed
V14	SS-4P4T/Nupro	Plug	3000	204	Viton	Adsorption
V15	6V-71B4TG/Autoclave	Shutoff	3000	316	Teflon Glass	Adsorption
V16	SS-1VS4/Whitey	Shutoff	3000	232	TFE	Adsorption
V17	SS-4P4T/Nupro	Plug	3000	204	Viton	Adsorption
V18	SS-ORS2/Whitey	Regulating	3000	232	TFE	Adsorption
V19	SS-4P4T/Nupro	Plug	3000	204	Viton	Adsorption
V20	6V-71B4TG/Autoclave	Shutoff	11500	316	Teflon Glass	Adsorption
V21	SS-1VS4/Whitey	Shutoff	3000	232	TFE	Adsorption
V22	SS-4P4T/Nupro	Plug	3000	204	Viton	Adsorption
V23	SS-ORS2/Whitey	Regulating	3000	232	TFE	Adsorption
V24	SS-4P4T/Nupro	Plug	3000	204	Viton	Adsorption
V25	6V-71B4TG/Autoclave	Shutoff	11500	316	Teflon Glass	Adsorption
V26	SS-1VS4/Whitey	Shutoff	3000	232	TFE	Adsorption
V27	SS-4P4T/Nupro	Plug	3000	204	Viton	Adsorption
V28	SS-ORS2/Whitey	Regulating	3000	232	TFE	Adsorption
V29	SS-4P4T/Nupro	Plug	3000	204	Viton	Adsorption
V30	6V-71B4TG/Autoclave	Shutoff	11500	316	Teflon Glass	Adsorption
V31	SS-1VS4/Whitey	Shutoff	3000	232	TFE	Adsorption
V32	SS-4P4T/Nupro	Plug	3000	204	Viton	Adsorption
V33	SS-ORS2/Whitey	Regulating	3000	232	TFE	Adsorption
V34	SS-ORS2/Whitey	Regulating	3000	232	TFE	Adsorption
V35	SS-ORS2/Whitey	Regulating	3000	232	TFE	Adsorption

Comp.	Part No./Supplier	Type	Pressure	Temp °C	Seals	Location
V36	SS-4P4T/Nupro	Plug	3000	204	Viton	Adsorption
V37	SS-4P4T/Nupro	Plug	3000	204	Viton	Adsorption
V38	SS-4P4T/Nupro	Plug	3000	204	Viton	Adsorption
V39	SS-1KS4/Whitey	Shutoff	3000	93	KEL-F	Adsorption
V40	SS-1KS6/4/Whitey	Shutoff	3000	93	KEL-F	Reduction
V41	SS-1KS6/4/Whitey	Shutoff	3000	93	KEL-F	Reduction
V42	SS-OKS2/Whitey	Shutoff	3000	93	KEL-F	Reduction
V43	SS-OKS2/Whitey	Shutoff	3000	93	KEL-F	Reduction
V44	SS-OKS2/Whitey	Shutoff	3000	93	KEL-F	Reduction
V45	SS-ORS2/Whitey	Regulating	3000	232	TFE	Trailer
V46	SS-ORS2/Whitey	Regulating	3000	232	TFE	Trailer
V47	SS-ORS2/Whitey	Regulating	3000	232	TFE	Trailer
V48	SS-ORS2/Whitey	Regulating	3000	232	TFE	Trailer
V49	SS1S4/Whitey	Vee	3000	232	TFE	Adsorption
V49A	SS-43S4/Whitey	Ball	3000	65	TFE	Adsorption
V50	SS-OKS2/Whitey	Shutoff	3000	93	KEL-F	2° Feed
V52	SS-OKS2/Whitey	Shutoff	3000	93	KEL-F	2° Feed
V52A	SS-OKS2/Whitey	Shutoff	3000	93	KEL-F	2° Feed
V53	SS-1KS4/Whitey	Shutoff	3000	93	KEL-F	Autoclave
V54	SS-4P4T/Nupro	Plug	3000	204	Viton	Autoclave
V55	SS-1KS4/Whitey	Shutoff	3000	93	KEL-F	Autoclave
V56	SS-1KS4/Whitey	Shutoff	3000	93	KEL-F	Autoclave
V57	SS-1KS4/Whitey	Shutoff	3000	93	KEL-F	Autoclave
V58	SS-4P4T/Nupro	Plug	3000	204	Viton	Autoclave
V59	SS-4P4T/Nupro	Plug	3000	204	Viton	Autoclave
V60	SS-1KS4/Whitey	Shutoff	3000	93	KEL-F	Autoclave
V61	SS-1KS4/Whitey	Shutoff	3000	93	KEL-F	Autoclave
V62	SS-2P4T/Nupro	Plug	3000	204	Viton	Autoclave
V63	SS-OKS2/Whitey	Shutoff	3000	93	KEL-F	Autoclave
V64	SS-OKS2/Whitey	Shutoff	3000	93	KEL-F	Autoclave
V65	SS-2P4T/Nupro	Plug	3000	204	Viton	Autoclave
V66	6V-7B4TG/Autoclave	Shutoff	11500	316	Teflon Glass	Autoclave
V67	SS-1KS4/Whitey	Shutoff	3000	93	KEL-F	Autoclave
V68	SS-OKS2/Whitey	Shutoff	3000	93	KEL-F	Autoclave
V69	SS-1VS4/Whitey	Shutoff	3000	232	TFE	Autoclave
V70	SS-OKS2/Whitey	Shutoff	3000	93	KEL-F	Reduction
V70A	SS-OKS2/Whitey	Shutoff	3000	93	KEL-F	Autoclave

Comp.	Part No./Supplier	Type	Pressure	Temp °C	Seals	Location
V71	SS-ORM2/Whitey	Regulator	3000	232	TFE	Autoclave
V73	SS-4P4& / Nupro	Plug	3000	204	Viton	2° Feed
V74	SS-1KM4S4 / Whitey	Shutoff	5000	93	KEL-F	2° Feed
V75	SS-4P4& / Nupro	Plug	3000	204	Viton	2° Feed
V(N)1	B18KS8/Whitey	Shutoff	3000	93	TFE	Nitrogen
V(N)2	B18KS8/Whitey	Shutoff	3000	93	TFE	Nitrogen
V(N)3	B1KS4/Whitey	Shutoff	3000	93	TFE	Nitrogen
V(N)4	B1KS4/Whitey	Shutoff	3000	93	TFE	Nitrogen
V(N)4	SS-4P4T/Nupro	Plug	3000	204	Viton	Nitrogen
V(A)1	B18KS8/Whitey	Shutoff	3000	93	TFE	Inst. Air
V(A)2	B1KS4/Whitey	Shutoff	3000	93	TFE	Inst. Air
V(A)3	B18KS8/Whitey	Shutoff	3000	93	TFE	Inst. Air
GV1	SS-OKS2/Whitey	Shutoff	3000	93	TFE	Gas Manifold
GV2	SS-OKS2/Whitey	Shutoff	3000	93	TFE	Gas Manifold
GV3	SS-OKS2/Whitey	Shutoff	3000	93	TFE	Gas Manifold
GV4	SS-OKS2/Whitey	Shutoff	3000	93	TFE	Gas Manifold
GV5	SS-OKS2/Whitey	Shutoff	3000	93	TFE	Gas Manifold
GV6	SS-OKS2/Whitey	Shutoff	3000	93	TFE	Gas Manifold
GV7	SS-OKS2/Whitey	Shutoff	3000	93	TFE	Gas Manifold
GV8	SS-OKS2/Whitey	Shutoff	3000	93	TFE	Gas Manifold
GV9	SS-OKS2/Whitey	Shutoff	3000	93	TFE	Gas Manifold
GV10	SS-OKS2/Whitey	Shutoff	3000	93	TFE	Gas Manifold
GV11	SS-OKS2/Whitey	Shutoff	3000	93	TFE	Gas Manifold
GV12	SS-OKS2/Whitey	Shutoff	3000	93	TFE	Gas Manifold
GV13	SS-OKS2/Whitey	Shutoff	3000	93	TFE	Gas Manifold
GV14	SS-OKS2/Whitey	Shutoff	3000	93	TFE	Gas Manifold
GV15	SS-OKS2/Whitey	Shutoff	3000	93	TFE	Gas Manifold
GV16	SS-OKS2/Whitey	Shutoff	3000	93	TFE	Gas Manifold
GV17	SS-OKS2/Whitey	Shutoff	3000	93	TFE	Gas Manifold
GV18	SS-OKS2/Whitey	Shutoff	3000	93	TFE	Gas Manifold
GV19	SS-ORS2/Whitey	Regulating	3000	232	TFE	Gas Manifold
GV20	SS-OKS2/Whitey	Shutoff	3000	93	TFE	Gas Manifold
GV21	SS-ORS2/Whitey	Regulating	3000	232	TFE	Gas Manifold
GV22	SS-OKS2/Whitey	Shutoff	3000	93	TFE	Gas Manifold
GV23	SS-ORS2/Whitey	Regulating	3000	232	TFE	Gas Manifold
GV23A	SS-OKS2/Whitey	Shutoff	3000	93	TFE	Autoclave

Comp.	Part No./Supplier	Type	Pressure	Temp °C	Seals	Location
GV24	SS-ORS2/Whitey	Regulating	3000	232	TFE	Gas Manifold
GV25	SS-OKS2/Whitey	Shutoff	3000	93	TFE	Gas Manifold
GV26	SS-1KS4/Whitey	Shutoff	3000	93	Kel-F	Gas Manifold
P1	QM 0-2000/McDaniel Controls Inc.	SS	2000			1° Feed
P2	QM 0-2000/McDaniel Controls Inc.	SS	2000			1° Feed
P3	QM 0-2000/McDaniel Controls Inc.	SS	2000			1° Feed
P4	QM 0-2000/McDaniel Controls Inc.	SS	2000			1° Feed
P5	QM 0-2000/McDaniel Controls Inc.	SS	2000			1° Feed
P6	QM 0-2000/McDaniel Controls Inc.	SS	2000			1° Feed
P7	KMP AB 1207/McDaniel Controls Inc.	SS	2000			1° Feed
P8		SS	2000			1° Feed
P9	QM 0-2000/McDaniel Controls Inc.	SS	2000			Adsorption
P10	QM 0-2000/McDaniel Controls Inc.	SS	2000			Adsorption
P11	QM 0-2000/McDaniel Controls Inc.	SS	2000			Adsorption
P12	QM 0-2000/McDaniel Controls Inc.	SS	2000			Adsorption
P13	QM 0-2000/McDaniel Controls Inc.	SS	2000			Adsorption
P14	QM 0-2000/McDaniel Controls Inc.	SS	2000			Adsorption
P15	QM 0-2000/McDaniel Controls Inc.	SS	2000			Adsorption
P16	QM 0-2000/McDaniel Controls Inc.	SS	2000			Adsorption
P17	KMP AB 429/McDaniel Controls Inc.	SS	3000			Reduction
P18	McDaniel Controls Inc.	SS	2000			Reduction
P19	US Gauge		0-3000			2° Feed
P20	US Gauge		0-3000			2° Feed
P21	232.30/Wika	F. Flange	2000	21		Autoclave
P22	232.30/Wika	F. Flange	2000	21		Autoclave
P23	KMU/McDaniel Controls	U-Clamp	2000	21		Autoclave
P24	KMU/McDaniel Controls	U-Clamp	2000	21		Autoclave
P25	QM McDaniel Controls		2000	21		Autoclave
P26	QM McDaniel Controls		2000	21		Autoclave
P27	QM McDaniel Controls		2000	21		Autoclave
P28	QM McDaniel Controls		2000	21		Autoclave
P29			30	21		Autoclave
P30						2° Feed
P(N)1	Wika 316 SS		0-200			Nitrogen
P(N)2	Wika 316 SS		0-200			Nitrogen
P(A)1	US Gauge		0-160			Inst. Air

Comp.	Part No./Supplier	Type	Pressure	Temp °C	Seals	Location
P(A)2	US Gauge		0-160			Inst. Air
P(A)3	US Gauge		0-200			Inst. Air
CV1 3/8	SS6C/Nupro	Check		21	Viton	Dock 3
CV2 1/4	SS4C 1/3 /Nupro	Check		21	Viton	1° Feed
CV3 1/8	SS2C 1/3 /Nupro	Check		21	Viton	Reduction
CV4 1/4	SS4C 1/3 /Nupro	Check		21	Viton	1° Feed
CV5	SS4C 1/3 /Nupro	Check		21	Viton	Nitrogen
CV6	SS4C 1/3 /Nupro	Check		21	Viton	Adsorption
CV7	SS4C 1/3 /Nupro	Check		21	Viton	Adsorption
CV8	SS4C 1/3 /Nupro	Check		21	Viton	Adsorption
CV9	SS4C 1/3 /Nupro	Check		21	Viton	Adsorption
CV10	SS4C 1/3 /Nupro	Check		21	Viton	Adsorption
CV11	SS4C 1/3 /Nupro	Check		21	Viton	Adsorption
CV12	SS4C 1/3 /Nupro	Check		21	Viton	Adsorption
CV13	SS4C 1/3 /Nupro	Check		21	Viton	Adsorption
CV14	SS4C 1/3 /Nupro	Check		21	Viton	Adsorption
CV15	SS 2C 1/3 Nupro	Check		21	Viton	2° Feed
CV15A	SS 2C 1/3 Nupro	Check		21	Viton	2° Feed
CV16	SS-4C 1/3/Nupro	Check	3000	21	Viton	Autoclave
CV17	SS-2C 1/3/Nupro	Check	3000	21	Viton	Autoclave
CV18	SS-2C 1/3/Nupro	Check	3000	21	Viton	Autoclave
CV19	SS-4C 1/3/Nupro	Check	3000	21	Viton	Autoclave
CV(N)1	B 8C 1/3 /Nupro	Check		21	Buna "N"	Nitrogen
CV(N)2	B 8C 1/Nupro	Check	1	21	Buna "N"	Nitrogen
CV(A)1	B 8C 1/Nupro	Check	1	21	Buna "N"	Inst. Air
R1	26-1025-24-007/Tescom	Pressure Reducing	1500-10	74	Buna "N"	1° Feed
R2	26-1025-24-007/Tescom	Pressure Reducing	1500-10	74	Buna "N"	1° Feed
R3	E11-8-N115H/APCI	Pressure Reducing	3000-2000	74	Buna "N"	Reduction
R4	Tescom/26-1025-24-007	Pressure Reducing	10000in/1500out	74	Buna "N"	2° Feed
R5	26-1027-24-007/Tescom	Reducing	10000/500	74	Buna "N"	Autoclave
R6	26-1025-24-007/Tescom	Reducing	10000/1500	74	Buna "N"	Autoclave
N(R1)	2Z328A/Speed Air	Pressure Reducing	250-0	175		Nitrogen
A(R1)	Norgren 11-002-603	Pressure Reducing	400 in125 out	175		Inst. Air
A(R2)	Norgren 11-002-603	Reducing	125/0	175		Inst. Air
RV1	SS-4R3A1/Nupro	Relief	1300			1° Feed
RV2	SS-4R3A1/Nupro	Relief	1300			1° Feed
RV3		Relief				Adsorption

Comp.	Part No./Supplier	Type	Pressure	Temp °C	Seals	Location
RV4	SS-4R3A1/Nupro	Relief	1300			Reduction
RV5	SS-4R3A1/Nupro	Relief	1300 set	70°F		2° Feed
RV6	SS-4R3A1/Nupro	Relief	1700 set	121	Viton	Autoclave
RV7	SS-4R3A1/Nupro	Relief	1300	121	Viton	Autoclave
RV8	SS-4R3A1/Nupro	Relief	1300	121	Viton	Autoclave
RV9	SS-4CPA4-3/Nupro	Relief	5	149	Buna "N"	Autoclave
N(RV)1	SS-4CPA2150/Nupro	Relief	200			Nitrogen
A(RV)1	B 4CPA2150/Nupro	Relief	100?			Inst. Air
GRV1	SS-4CPA2-50	Relief	100			Gas Manifold
GRV2	SS-4CPA2-50	Relief	100			Gas Manifold
GRV3	SS-4CPA2-50	Relief	100			Gas Manifold
GRV4	SS-4CPA2-50	Relief	100			Gas Manifold
GRV5	SS-4CA-50/Nupro	Relief	100			Gas Manifold
GRV6	SS-4R3A1/Nupro	Relief	1700			Gas Manifold
GRV7	SS-4CA-150/Nupro	Relief	200			Gas Manifold
GRV8	SS-2C-10/Nupro	Relief	10			Gas Manifold
F(A)1	2E764A/Speed Air		150	52	Buna "N"	Inst. Air
F1	SS-6F-90/Nupro	Filter	2500	482	Silver Plated 316SS	1° Feed
F2	SS-4TF-2/Nupro	Filter	6000	482		1° Feed
F3	SS-2F-7/Nupro	Filter	3000	21	316 SS	2° Feed
F4	SS-4F-90/Nupro	Filter	3000	900	316 SS	Autoclave
F5	SS-2F-7/Nupro	Filter	3000	900	316 SS	Autoclave
S1A	8262A215/Stainless Asco	Normally Closed	2200	104	Buna "N"	1° Feed
S1B	8262A215/Stainless Asco	Normally Closed	2200	104	Buna "N"	1° Feed
S2A	8262A215/Stainless Asco	Normally Closed	2200	104	Buna "N"	2° Feed
S2B	8262A215/Stainless Asco	Normally Closed	2200	104	Buna "N"	2° Feed
S3	8262A215/Stainless Asco	Normally Closed	2200	104	Buna "N"	1° Feed
S4	8262A215/Asco	Normally Closed	2200	104	Buna "N"	2° Feed
S5	8262A215/Asco	Normally Closed	2200	104	Buna "N"	Autoclave
S(A)1	8262C232/Brass Asco	Normally Closed	2200	104	Buna "N"	Inst. Air
S(A)2	8262C232/Asco	Normally Closed	2200	104	Buna "N"	Inst. Air
S(G)1	82C2C98/Asco	Normally Shut	1900	60	SS	GC System
S(G)2	82C2C98/Asco	Normally Shut	1900	60	SS	GC System
PS1	J6-612 303 SS/United Electric	Pressure Switch	5000			1° Feed
PS2	J6-612303SS/United Electric	Pressure Switch	5000, set 1600			Autoclave
GP1	JPN/McDaniel Controls Inc.	SS	0-3000			Gas Manifold

Comp.	Part No./Supplier	Type	Pressure	Temp °C	Seals	Location
GP2	JPF/McDaniel Controls Inc.	SS	200			Gas Manifold
GP3	JPN/McDaniel Controls Inc.	SS	3000			Gas Manifold
GP4	JPF/McDaniel Controls Inc.	SS	200			Gas Manifold
GP5	JPN/McDaniel Controls Inc.	SS	3000			Gas Manifold
GP6	JPF/McDaniel Controls Inc.	SS	200			Gas Manifold
GP7	JPN/McDaniel Controls Inc.	SS	3000			Gas Manifold
GP8	JPF/McDaniel Controls Inc.	SS	200			Gas Manifold
GP9	KNP AB1129/McDaniel Controls Inc.	SS	3000			Gas Manifold
GP10	McDaniel Controls Inc.	SS	200			Gas Manifold
GP11	KNP AB1129/McDaniel Controls Inc.	SS	3000			Gas Manifold
GP12	McDaniel Controls Inc.	SS	200			Gas Manifold
GP13	KNP AB1129/McDaniel Controls Inc.	SS	3000			Gas Manifold
GP14	McDaniel Controls Inc.	SS	200			Gas Manifold
GR1	E12-JN145D/APCI	Pressure Reducing			KEL-F/Teflon	Gas Manifold
GR2	E12-JN145D/APCI	Pressure Reducing			KEL-F/Teflon	Gas Manifold
GR3	E12-JN145D/APCI	Pressure Reducing			KEL-F/Teflon	Gas Manifold
GR4	E12-JN145D/APCI	Pressure Reducing			KEL-F/Teflon	Gas Manifold
GR5	CRR215-9014-1/Circle Seal	Pressure Reducing	3000/180			Gas Manifold
GR6	CRR215-9014-1/Circle Seal	Pressure Reducing	3000/180			Gas Manifold
GR7	CRR215-9014-1/Circle Seal	Pressure Reducing	3000/200			Gas Manifold
C1	304L-HDF8-1gal/Whitey	Sample Cylinder	1800	21	316SS	1° Feed
C2	304L-HDF8-1gal/Whitey	Sample Cylinder	1800	21	316 SS	Autoclave
C3	304L-HDF8-1gal/Whitey	Sample Cylinder	1800	21	316 SS	Autoclave
C4	304L-HDF2-1 liter/Whitey	Sample Cylinder	1800	21	316 SS	Autoclave
C5	304L-DHF4-150cc/Whitey	Sample Cylinder	1800	21	316 SS	Gas Manifold
C6	304L-HDF4-500cc/Whitey	Sample Cylinder	1800	21	316 SS	Autoclave
BPR1	26-1725-24-043/Tescom	Back Pressure	10-1500	75	Teflon	Adsorption
BPR2	26-1727-24-043/Tescom	Back Pressure	10/500	74	Buna "N"	Autoclave
BPR3	26-1725-24-043/Tescom	Back Pressure	10/1500	74	Buna "N"	Autoclave
RD1	A232/Fike	Rupture Disk	2036	200	316 SS	Autoclave
G(NV)1	SS-2SG/Nupro	Fine Metering Valve	2000	204	Viton	Adsorption
G(NV)2	SS-2SG/Nupro	Fine Metering Valve	2000	204	Viton	Adsorption
G(NV)3	SS-2SG/Nupro	Fine Metering Valve	2000	204	Viton	GC System
G(NV)4	SS-2SG/Nupro	Fine Metering Valve	2000	204	Viton	GC System
EFV1	EFV-125-S PSO KZ/Chem-Tec Equ.	XS FLOW Valve				1° Feed
EFV2	EFV-125-S PSO KZ/Chem-Tec Equ.	XS FLOW Valve				2° Feed

Comp.	Part No./Supplier	Type	Pressure	Temp °C	Seals	Location
EFV3	6L-E4AB / Nupro	XS Flow Valve	3000			Gas Manifold
PT9	WIKA	P-Transducer				Adsorption
PT14	WIKA	P-Transducer				WTM#1
PT27	WIKA	P-Transducer				Autoclave
PT28	WIKA	P-Transducer				Autoclave
PT29	WIKA	P-Transducer				WTM#2

Appendix 3: AFFTU Budget

Vendor		Budget	Actual
Trailer		\$48,314.00	\$61,526.67
	Trailer	\$9,000.00	\$7,500.00
	Inspection	incl.	\$1,500.00
	Conversion	\$39,314.00	\$15,414.00
	Floor Bastian	incl.	\$1,000.00
	Delivery	incl.	\$75.00
	Ventilation, etc. H. T. Lyons	incl.	\$25,489.00
	Counters Seislove	incl.	\$930.00
	E. Door, etc. APCI	incl.	\$1,645.00
[1]	Steps&Tie-Down H. T. Lyons	\$0.00	\$6,910.00
	Comp. Tables	\$0.00	\$300.00
	GC Stand	incl.	\$450.07
	Water Util. Granger	incl.	\$313.60
GC System		\$100,675.00	\$101,569.80
	2 @ HP6890 GCs Hewlett-Packard	\$34,350.00	\$32,870.00
	HP Detectors Hewlett-Packard	incl.	incl.
	Packed Inlets Hewlett-Packard	incl.	incl.
	Capillary Hewlett-Packard	incl.	incl.
	SCD Sievers	\$17,900.00	\$18,299.00
	GC System Integ. Wasson/ECE	\$31,980.00	\$31,980.00
	TurboChrom Perkin-Elmer	\$9,645.00	\$9,880.00
	Tubing Supelco	\$200.00	\$420.00
	AT-1 Cap. Col. Alltech	\$0.00	\$657.00
	Cables Hewlett-Packard	\$0.00	\$463.80
	APCI Support APCI	\$6,800.00	\$7,000.00
Equipment & Control		\$110,000.00	\$90,061.70
[2]	PLC & Software Allen-Bradley	\$60,000.00	\$27,977.00
	Wiring (PLC) APCI	incl.	\$3,920.00
	Wiring (Gen'l) APCI	\$22,758.00	\$23,693.00
	Programming APCI	\$18,000.00	\$21,600.00
	P_Transducers WIKA	incl.	\$2,162.70
	Encoders Gurley	incl.	\$818.00
	Valco Repairs Valco	\$500.00	\$644.00
	Thermocouples	\$221.65	\$230.00
	Valves & Fittings AV&F	incl.	\$3,500.00
	Supplies/Gases APCI	incl.	\$2,000.00
	Visual Basic Stream Int'l	\$0.00	\$100.00
	Regulators Tescom	\$0.00	\$3,417.00
TOTALS		\$258,989.00	\$253,158.17

[1] Not in original scope. Township inspector required permanent stairs and additional tie-downs before issuing an occupancy permit.

[2] The budgeted \$60,000 was an early estimate, and included any additional hardware and supplies which might be necessary for the automation of the data acquisition and process control.

Appendix 4: Analysis of Spent Catalyst from Kingsport Test

Analysis Report



To: Andy Wang Dept./Loc.: GEG/Iron Run
From: Fred Lucrezi Dept./Ext.: CRSD/15025
Date: 28 August 1996 Lab Name: Spectroscopy
Subject: Washed Methanol Catalyst; Zeolite; Activated Carbon; CuO Catalyst;
Sample No.: 038642

c: E. T. Sydlik; FAL/lb

SUMMARY: One sample of washed methanol catalyst; two samples of copper catalyst (feed and product); two samples of zeolite catalyst (feed and product); two samples of activated carbon catalyst (feed and product); and two samples of copper catalyst with silica (feed and product) were analyzed for iron, nickel, manganese, arsenic, chloride, and sulfur.

ANALYTICAL PROCEDURES: For the washed methanol catalyst, copper catalysts, and activated carbon catalyst samples, ~0.2 grams were weighed into a 500-cc flask and digested with a combination HNO₃, H₂SO₄, and HCl acid digest. The zeolite catalyst samples were digested with a combination HNO₃, HCl, HF, and H₃BO₃ acid digest. These procedures were used for the preparation of the samples for all of the metals except sulfur and chloride. For sulfur and chloride, all of the samples were digested by a KOH fusion, followed by solubilization with HNO₃. All analyses were performed by ICP-AES for the metals (except arsenic, which was analyzed by ETA-AAS) and by ion selective electrode for chloride.

RESULTS AND DISCUSSION

RESULTS: {all in parts per million (ppm) by weight}

Sample #	Sample ID	:::Iron:::	:Nickel:	Manganese	Arsenic	:Sulfur:	Chloride
38642.01	14987-27	172	58	<10	184	<=660	5570
38642.02	Bed #1 Feed	118	<10	<10	<100	<=360	<=740
38642.03	Bed #1 Product	87.9	<10	<10	<50	<=170	<=360
38642.04	Bed #2 Feed	242	<=19	<10	<50	<=330	<=810
38642.05	Bed #2 Product	261	<=22	<10	<50	<=130	<=650
38642.06	Bed #3 Feed	4390	120	41.2	299	4960	1050
38642.07	Bed #3 Product	4480	39	40.6	<50	3740	<=740
38642.08	Bed #4 Feed	1240	<=20	<10	<50	<=420	<=360
38642.09	Bed #4 Product	1190	<=24	<10	<50	<=390	<=750

“< is less than”

“<= is less than or equal to”

Limits of detection may be improved upon with additional work.

Appendix 5: Kingsport Data & Rate Analysis

Pt	TOS(hr)	P(psig)	T(C)	sccm		Feed CO2	H2	CM	CD	N2	Methanol L1	Synth.	MeOH	MEOH
				Vin	Vout							Equil Approach (%)	Equiv rate (gmol/kg-hr)	rate const
A	2.83	751.4	250	2996	2335	1.517	38.25	44.162	2.475	0.89	12.5294	30.63	26.09	2.39
B	6.58	752	249	2996	2348	1.499	39.599	44.919	2.357	0.751	12.4759	26.78	26.12	2.25
C	10.5	752.6	250	2996	2375	1.483	39.902	45.272	2.25	0.742	12.322	27.00	26.10	2.29
D	19.33	751.8	250	2996	2378	1.525	39.983	45.021	2.271	0.737	12.1278	26.71	25.72	2.24
E	25.5	750	250	2996	2420	1.483	40.358	45.131	2.121	0.727	11.3376	24.69	24.47	2.13
F	31.5	750	249	2996	2432	1.528	40.552	45.216	2.103	0.718	11.1045	22.90	24.08	2.05
G	37.5	750.8	249	2996	2435	1.535	40.739	45.003	2.131	0.715	11.3469	23.22	24.64	2.09
GB	43.5	746.4	250	2996	2450	1.561	40.843	44.972	2.125	0.71	11.1288	24.04	24.31	2.10
H	49.5	744.6	250	2996	2475	1.538	41.174	44.973	2.003	0.707	10.6137	22.75	23.42	2.04
J	52.13	744.8	249	2996	2488	1.538	40.85	44.934	1.994	0.702	10.3492	21.58	22.96	1.98
K	58.13	746	250	2996	2475	1.493	41.338	44.868	2.018	0.7	10.6223	22.55	23.44	2.02
L	64.13	746.6	249	2996	2470	1.547	41.248	44.77	2.075	0.725	10.6503	21.73	23.46	1.98
M	70.17	746.6	249	2996	2499	1.475	41.847	44.621	1.969	0.747	10.3935	20.72	23.16	1.96
N	76.13	744.6	250	2996	2510	1.479	41.765	44.541	1.948	0.696	10.4569	22.03	23.40	2.03
O	82.13	751.2	250	2996	2485	1.605	41.158	44.957	2.119	0.697	10.4448	22.00	23.14	1.92
P	88.13	752.8	249	2996	2482	1.65	41.044	44.86	2.194	0.7	10.7406	21.67	23.77	1.94
Q	94.13	751.2	250	2996	2510	1.545	41.58	44.773	2.068	0.703	10.4932	21.75	23.49	1.96
R	100.13	752	249	2996	2535	1.55	41.809	44.766	2.039	0.703	10.1299	19.87	22.90	1.87
S	106.13	751.6	249	2996	2521	1.551	41.555	44.951	2.074	0.7	10.107	20.00	22.72	1.85
T	112.13	752	249	2996	2521	1.582	41.58	44.571	2.095	1.074	10.1787	20.29	22.88	1.86
U	118.13	750.6	249	2996	2550	1.616	41.426	45.075	2.126	0.776	10.0911	20.10	22.95	1.85
V	124.13	749.4	249	2996	2557.76	1.602	42.063	44.668	1.996	0.7	9.7547	19.13	22.25	1.82
W	130.88	750.4	249	2996	2543.76	1.551	41.433	44.72	2.028	1.117	9.8618	19.86	22.37	1.85
X	136.23	751.6	249	2996	2544.84	1.591	41.7	44.583	2.068	0.698	10.128	20.07	22.98	1.87
Y	142.25	749.4	250	2996	2555.94	1.62	41.43	45.08	2.13	0.78	10.0543	21.00	22.92	1.87
Z	148.13	750.4	249	2996	2550	1.525	41.894	44.546	1.988	0.693	9.8234	19.41	22.34	1.84
AA	154.13	750.4	249	2996	2551	1.566	41.661	44.746	2.027	0.698	10.0807	20.02	22.93	1.89
AB	160.13	752	250	2996	2545	1.57	41.471	44.775	2.035	0.7	10.2312	21.30	23.22	1.94
AC	166.13	747.6	250	2996	2546	1.545	41.652	45.098	2.01	0.697	9.9283985	20.64	22.54	1.88
AD	172.25	747.6	249	2996	2510	1.56	43.273	41.786	2.068	0.568	9.8081937	19.57	21.95	1.78
AE	178.25	750.8	249	2996	2520	1.615	42.875	41.944	2.12	0.702	10.113966	20.25	22.73	1.84
AF	184.25	751.2	249	2996	2520	1.66	42.907	41.968	2.175	0.74	10.386034	20.70	23.34	1.88
AG	190.25	750.8	249	3200	2559	1.634	43.348	41.95	2.275	0.675	10.074767	19.74	22.99	1.78
AH	196.25	746	250	3200	2599.06	1.602	43.805	41.36	2.09	0.668	9.8389199	20.34	22.80	1.86

Pt	TOS(hr)	P(psig)	T(C)	sccm		Feed CO2	H2	CM	CD	N2	Methanol	Synth.	MeOH	MEOH
				Vin	Vout						L1	Equil Approach (%)	Equiv rate (gmol/kg-hr)	rate const
AI	202.25	750	249	3200	2551.63	1.638	43.491	41.856	2.116	0.672	9.9554935	19.49	22.65	1.81
AJ	208.25	750	249	3150	2547.61	1.678	43.538	41.735	2.165	0.665	10.124209	19.82	23.00	1.82
AK	214.25	745.8	250	3150	2572.8	1.643	44.385	41.328	2.135	0.698	9.9261639	20.03	22.77	1.81
AL	220.25	744.4	249	3150	2586	1.64	44.338	41.403	2.123	0.8	9.640689	18.72	22.23	1.75
AM	226.25	746.2	249	3150	2557	1.675	44.125	41.693	2.138	0.75	9.9320298	19.20	22.65	1.79
AN	232.25	745	250	3150	2565.6	1.678	44.005	41.835	2.163	0.715	9.8860335	20.08	22.62	1.80
AO	244.25	746.4	249	3200	2570	1.65	44.13	41.47	2.13	0.69	10.06797	19.54	23.07	1.83
AP	250.25	746.2	249	3200	2560.83	1.63	43.86	41.96	2.26	0.76	10.232123	19.85	23.37	1.81
AQ	256.25	745.6	249	3200	2554.23	1.69	43.64	41.51	2.17	0.8	10.124302	20.10	23.06	1.84
AR	263	744.4	250	3200	2560.21	1.663	43.447	41.5	2.151	0.679	10.13622	21.29	23.14	1.89
AS	268	745.6	249	3150	2576	1.554	43.883	41.778	2.077	0.675	9.9088454	19.35	22.76	1.83
AT	274	745.4	249	3200	2569	1.629	44.306	41.599	2.104	0.68	10.171788	19.57	23.30	1.86
AU	280	745	249	3200	2580	1.673	44.165	41.558	2.138	0.68	10.131937	19.66	23.31	1.85
AV	286.25	742.6	250	3175	2581.33	1.628	43.82	41.8	2.12	0.675	9.8120112	20.26	22.59	1.83
AW	292.25	743.8	249	3200	2596.03	1.614	44.083	41.795	2.068	0.673	9.6428305	18.78	22.32	1.78
AX	298.25	744.4	250	3100	2543	1.598	43.838	41.578	2.062	0.669	9.7678771	20.16	22.15	1.81
AY	304.25	744.6	250	3150	2580.46	1.616	43.456	41.833	2.096	0.668	9.8213222	20.47	22.60	1.85
AZ	310.25	746	250	3150	2580.38	1.8	43.408	41.869	2.088	0.931	9.6478585	20.09	22.20	1.81
BA	316.25	746.4	249	3200	2582.23	1.913	43.1	41.683	2.423	0.675	9.8332402	19.89	22.64	1.72
BB	322.88	746.2	249	3200	2599.72	1.74	43.19	41.68	2.28	0.67	9.939013	20.02	23.04	1.80
BC	328.25	746	250	3175	2577.14	1.78	43.49	41.51	2.27	0.67	9.9775605	20.83	22.93	1.81
BD	335.25	746.2	249	3200	2604.5	1.651	43.716	41.79	2.146	0.673	9.798324	19.25	22.76	1.80
BE	340.25	746	249	3200	2603.26	1.666	43.815	41.709	2.185	0.668	9.5140596	18.68	22.09	1.72
BF	347.25	746.8	249	3200	2587.57	1.73	43.78	41.5	2.2	0.67	9.7743017	19.25	22.55	1.77
BG	352.25	747.2	249	3200	2584.11	1.74	43.13	42.13	2.21	0.67	9.7439479	19.44	22.45	1.76
BH	358	747.2	249	3125	2578.39	1.722	43.464	42.056	2.268	0.79	9.7219739	19.15	22.35	1.72
BI	365.5	754.2	250	3100	2525.98	1.9	41.98	42.51	2.59	0.75	10.381471	22.07	23.38	1.77
BJ	368.5	750.8	249	3157.74	2533.16	1.995	42.549	42.112	2.558	0.698	10.158473	20.54	22.95	1.71
BK	374.5	753.2	249	3157.74	2528.56	1.97	42.59	42.217	2.53	0.679	10.330074	20.64	23.29	1.74
BL	380.5	752	250	3157.74	2530.39	1.8	43.123	42.208	2.348	0.67	10.472253	21.42	23.63	1.84
BM	386.5	747.6	250	3157.74	2542.21	1.785	43.352	42.313	2.325	0.676	10.130912	20.75	22.97	1.78
BN	392.5	746.2	249	3157.74	2591.66	1.51	44.11	42.5	1.96	0.67	9.2147114	17.54	21.30	1.71
BO	398.5	746.6	249	3157.74	2582.43	1.54	43.67	42.92	1.96	0.7	9.2710428	17.80	21.35	1.72
BP	404.5	747.4	249	3157.74	2579.22	1.58	43.71	42.6	2.01	0.66	9.6867784	18.62	22.28	1.79

Pt	TOS(hr)	P(psig)	T(C)	sccm		Feed CO2	H2	CM	CD	N2	Methanol	Synth.	MeOH	MEOH
				Vin	Vout						L1	Equil Approach (%)	Equiv rate (gmol/kg-hr)	rate const
BQ	410.5	746.6	250	3157.74	2586.54	1.564	44.069	42.158	2.038	0.669	9.5512104	19.14	22.03	1.77
BR	416.5	746.8	249	3157.74	2602.82	1.525	43.818	42.529	1.934	0.667	9.2391061	17.77	21.44	1.74
BS	422.5	746.8	250	3157.74	2589.29	1.559	43.6	42.598	1.971	0.851	9.355959	18.96	21.60	1.77
BT	429.5	747	249	3157.74	2597.2	1.568	43.66	42.462	1.988	0.674	9.5247672	18.44	22.06	1.78
BU	435.5	746.8	250	3157.74	2598.7	1.583	43.656	42.399	2.012	0.67	9.6479516	19.56	22.36	1.82
BV	441.5	747.8	249	3157.74	2595.55	1.52	43.56	42.69	1.93	0.66	9.0759777	17.56	21.01	1.70
BW	447.5	747.8	249	3157.74	2595.55	1.59	43.88	42.28	1.94	0.66	9.2984171	17.89	21.52	1.75
BX	453.5	747.8	249	3157.74	2595.55	1.61	43.6	42.19	2.04	0.66	9.5315642	18.58	22.06	1.77
BY	459.5	747	249	3157.74	2612.98	1.602	43.403	42.588	2.054	0.663	9.4280261	18.42	21.97	1.75
BZ	465.5	747	249	3157.74	2580.5	1.63	44.43	41.78	2.057	0.66	9.4713222	18.02	21.79	1.71
CA	471.5	747	249	3157.74	2602.05	1.63	44.31	41.85	2.04	0.67	9.5597765	18.25	22.18	1.76
CB	477.5	747	249	3157.74	2593.78	1.86	43.41	42.17	2.3	0.67	9.9770019	19.62	23.08	1.78
CC	483.5	747	249	3157.74	2593.78	1.77	43.68	42.43	2.24	0.67	9.6507449	18.67	22.32	1.71
CD	489.5	746	249	3157.74	2601.47	1.72	43.724	42.533	2.172	0.694	9.2459032	17.90	21.45	1.65
CE	495.5	745.8	249	3157.74	2587.01	1.752	43.515	42.618	2.207	0.694	9.5255121	18.56	21.97	1.70
CF	501.5	745.8	249	3157.74	2588.56	1.746	43.666	42.479	2.179	0.693	9.755959	18.92	22.52	1.76
CG	512.18	750.4	249	3177.8	2657.28	1.498	44.076	41.675	1.672	1.699	8.2960894	16.08	19.66	1.68
CH	517.93	750.4	249	3177.8	2658.1	1.207	44.116	43.191	1.577	0.71	8.388175	15.59	19.88	1.71
CI	523.15	750.4	249	3177.8	2651.1	1.261	44.195	43.032	1.588	0.693	8.4371508	15.68	19.95	1.72
CJ	529.43	750	249	3178.14	2656.54	1.32	43.84	43.51	1.57	0.68	8.2091248	15.36	19.45	1.68
CK	535.18	750.4	249	3178.14	2673.85	1.22	43.75	43.582	1.57	0.67	8.0706704	15.13	19.24	1.66
CL	541	750	249	3178.14	2664.9	1.324	44.157	43.341	1.574	0.662	8.1631285	15.12	19.40	1.66
CM	547.2	750.8	249	3178.14	2645.72	1.497	43.817	42.908	1.891	0.664	8.7420857	16.52	20.62	1.65
CN	553	750.4	250	3178.14	2636.31	1.572	44.097	42.554	1.932	0.673	8.8115456	17.34	20.71	1.66
CO	559.48	750.8	249	3178.14	2630.57	1.822	44.015	42.279	2.16	0.677	8.7879888	16.70	20.61	1.55
CP	565.23	750.8	249	3178.14	2623.31	1.762	44.014	42.086	2.25	0.688	8.9565177	17.08	20.95	1.56
CQ	571.25	751.6	249	3178.14	2625.18	1.915	44.116	41.975	2.219	0.681	8.9468343	16.99	20.94	1.56
CR	577.27	750	249	3178.14	2630.04	1.77	44.075	42.164	2.221	0.68	8.8798883	16.90	20.83	1.56
CS	583.27	747.2	249	3178.14	2634.56	2	43.62	42.42	2.45	0.66	8.6972998	16.94	20.43	1.47
CT	589.55	749.6	249	3178.14	2633.59	1.74	44.69	42.08	2.04	0.66	8.6136872	16.04	20.23	1.55
CU	595.03	750.2	250	3178.14	2632.17	1.81	43.87	42.31	2.25	0.67	8.8231844	17.65	20.71	1.55
CV	601.32	747.4	250	3178.14	2632.34	1.788	44	42.44	2.26	0.67	8.7442272	17.48	20.53	1.53
CW	607.07	746.2	249	3178.14	2642.64	1.782	43.731	42.425	2.315	0.675	8.6893855	16.89	20.48	1.51
CX	613.33	746.8	249	3178.14	2624.65	1.875	43.789	42.342	2.257	0.669	8.8783985	17.20	20.78	1.56

Pt	TOS(hr)	P(psig)	T(C)	sccm		Feed CO2	H2	CM	CD	N2	Methanol		Synth.	MeOH	MEOH	
				Vin	Vout						Approach	Equil	Equiv	rate	const	
											L1	(%)	(gmol/kg-hr)			
CY	619.35	749.8	249	3178.14	2623.51	1.824	43.708	42.222	2.306	0.673	9.0965549	17.56	21.28	1.58		
CZ	625.37	746.6	250	3178.14	2627.52	1.8	43.73	42.63	2.27	0.67	8.8067039	17.77	20.63	1.55		
DA	631.12	745.4	250	3178.14	2652.26	1.722	44.36	42.3	2.15	0.67	8.472067	16.85	20.04	1.52		
DB	637	749.8	249	3178.14	2636.72	1.797	44.131	42.192	2.21	0.665	8.7957169	16.71	20.68	1.54		
DC	643.4	745.4	249	3178.14	2677.3	1.29	44.11	42.92	1.85	0.66	8.4828678	16.09	20.25	1.64		
DD	649.4	747.2	250	3178.14	2679.31	1.226	45.095	43.019	1.534	0.659	7.8678771	14.88	18.80	1.62		
DE	655.4	747.2	250	3178.14	2699.14	1.3	45.039	42.894	1.604	0.662	7.781378	14.80	18.73	1.58		
DF	661.95	750.2	249	3178.14	2666.07	1.466	44.414	43.026	1.819	0.667	8.1809125	15.08	19.45	1.55		
DG	667.45	750.4	249	3178.14	2661.65	1.5	44.405	42.776	1.852	0.664	8.3452514	15.46	19.81	1.57		
DH	673.2	750.4	249	3178.14	2670.75	1.5	44.49	42.7	1.93	0.67	8.3317505	15.41	19.84	1.54		

Figure 1: Simplified Kingsport LPMeOH Flowsheet

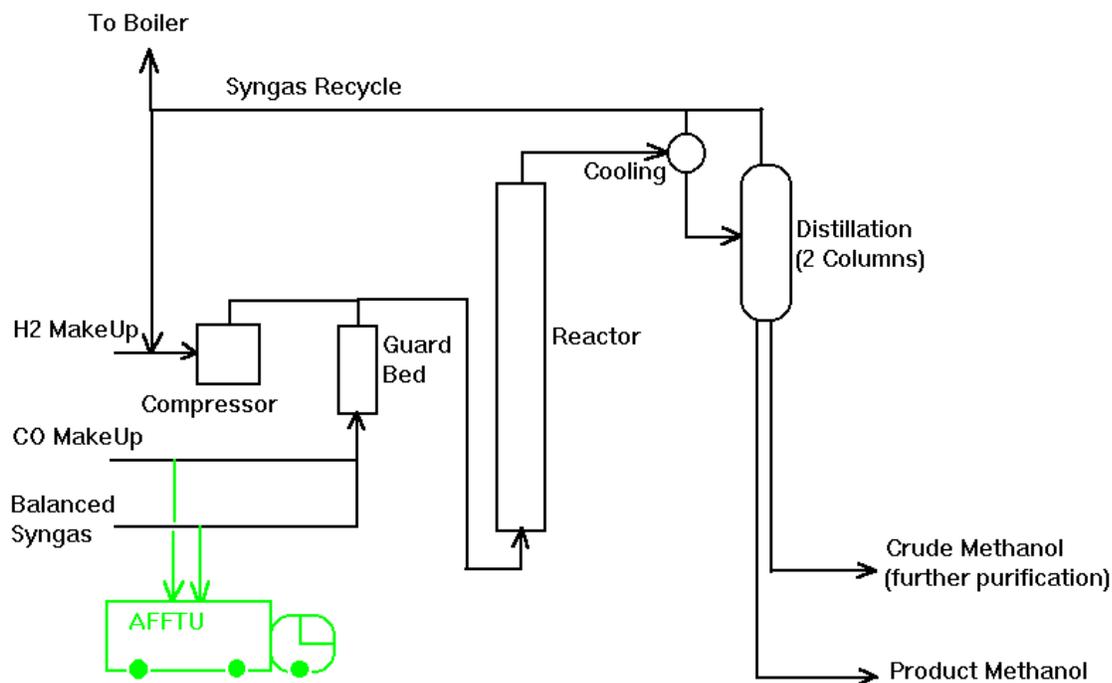
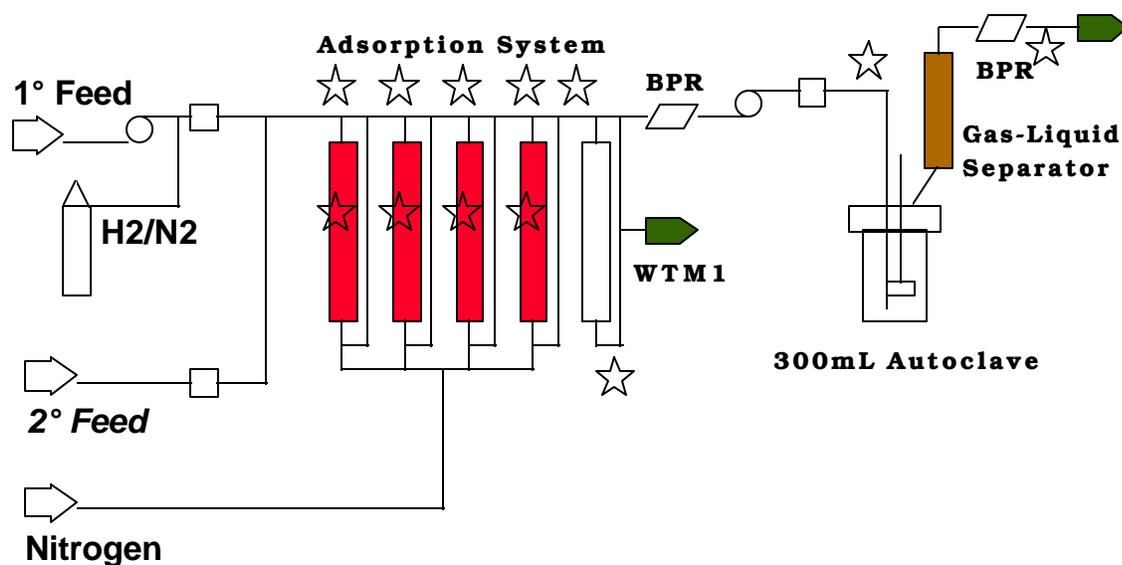


Figure 2: Simplified Overview of AFFTU Experimental Apparatus



Stars represent GC sampling points; squares represent mass flow controllers

Figure 3: AFFTU Layout

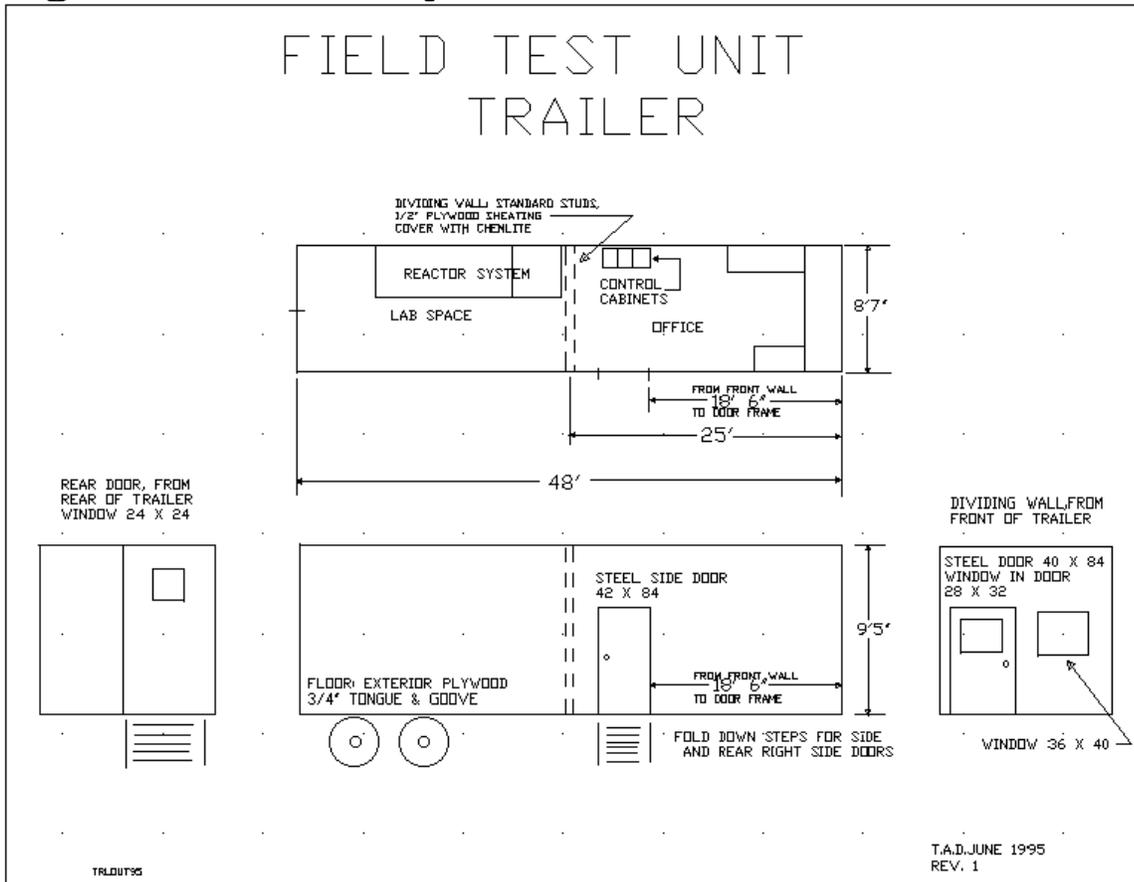


Figure 4: AFFTU Office Area

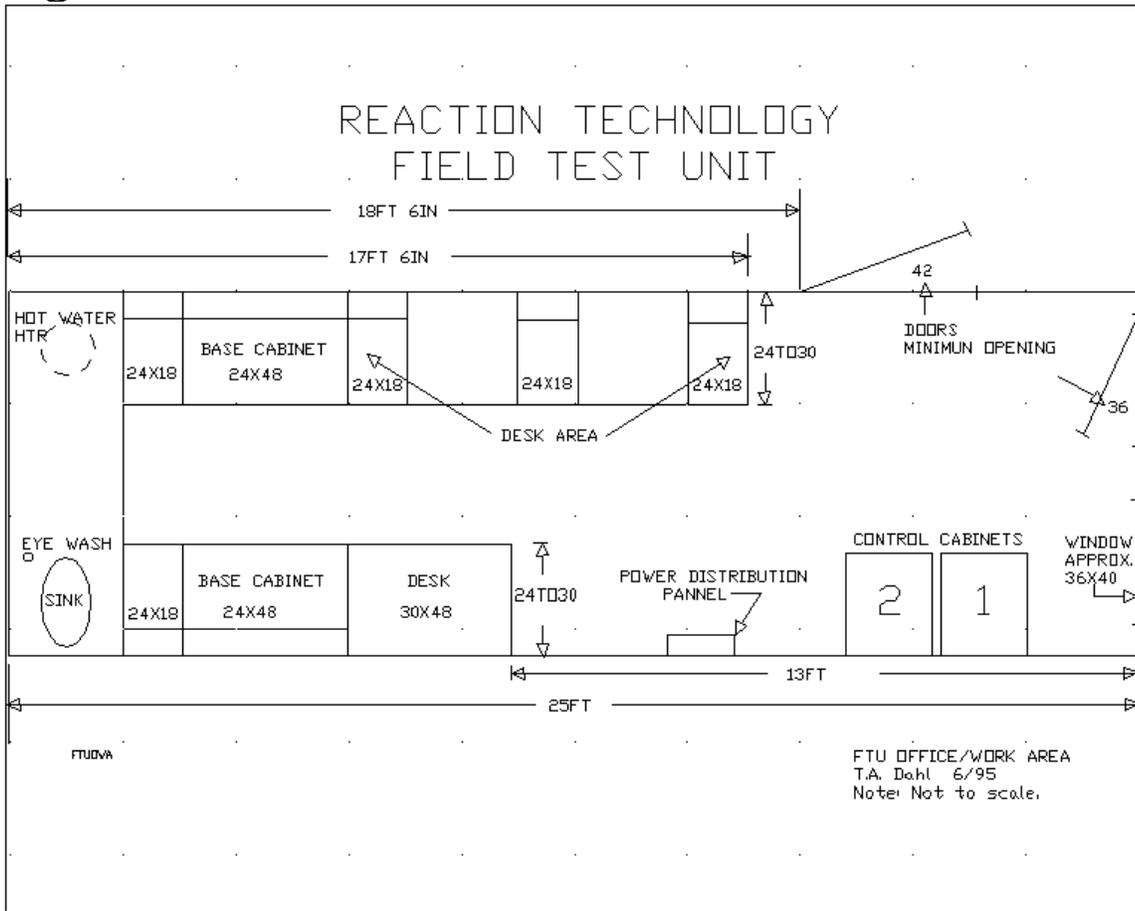


Figure 5: AFFTU Gas Feed System

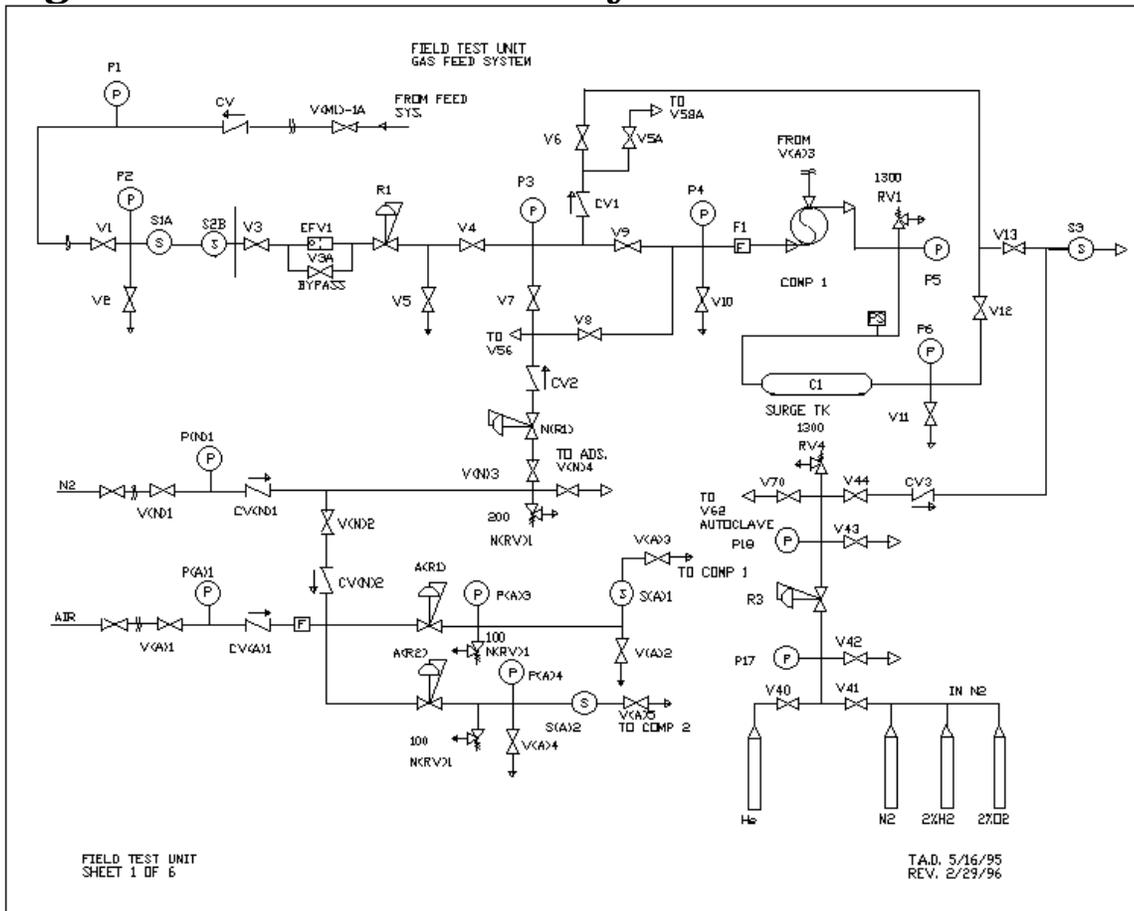


Figure 6: AFFTU Adsorption System

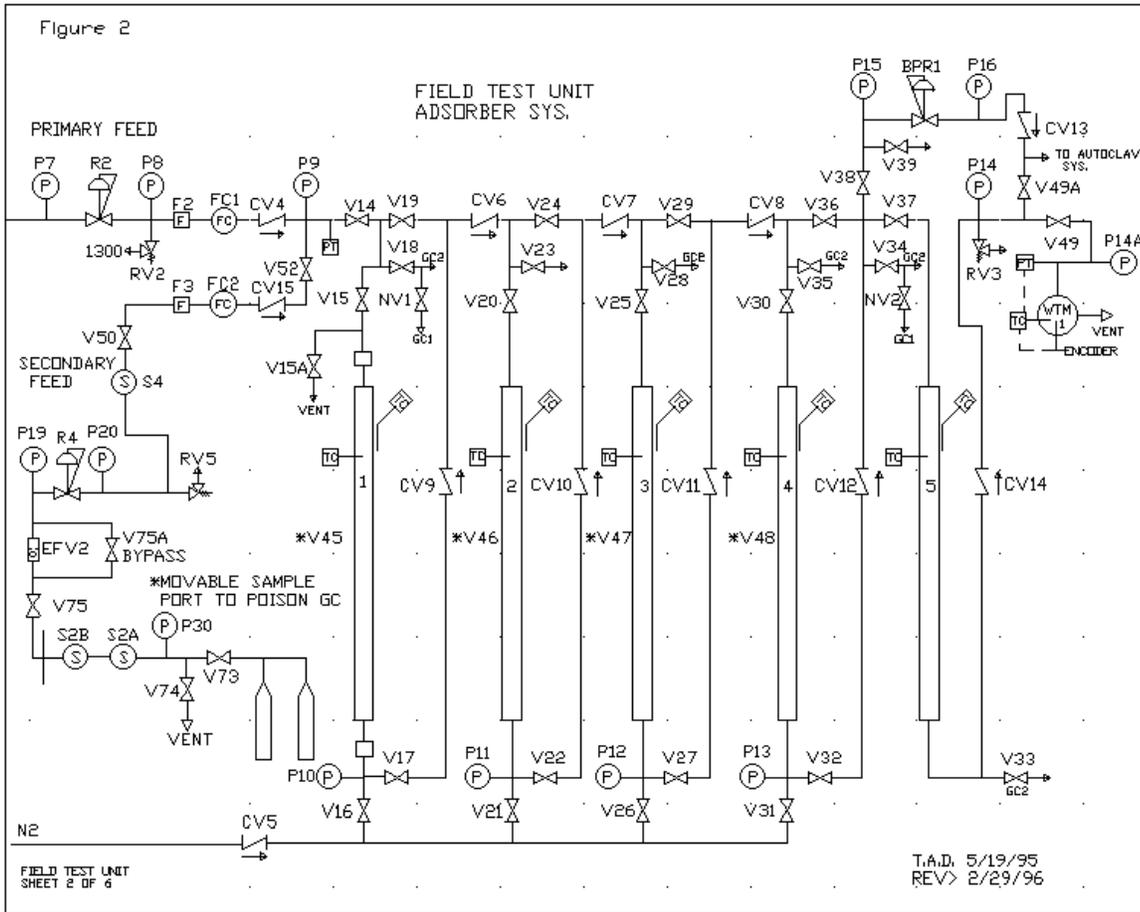


Figure 7: AFFTU Autoclave System

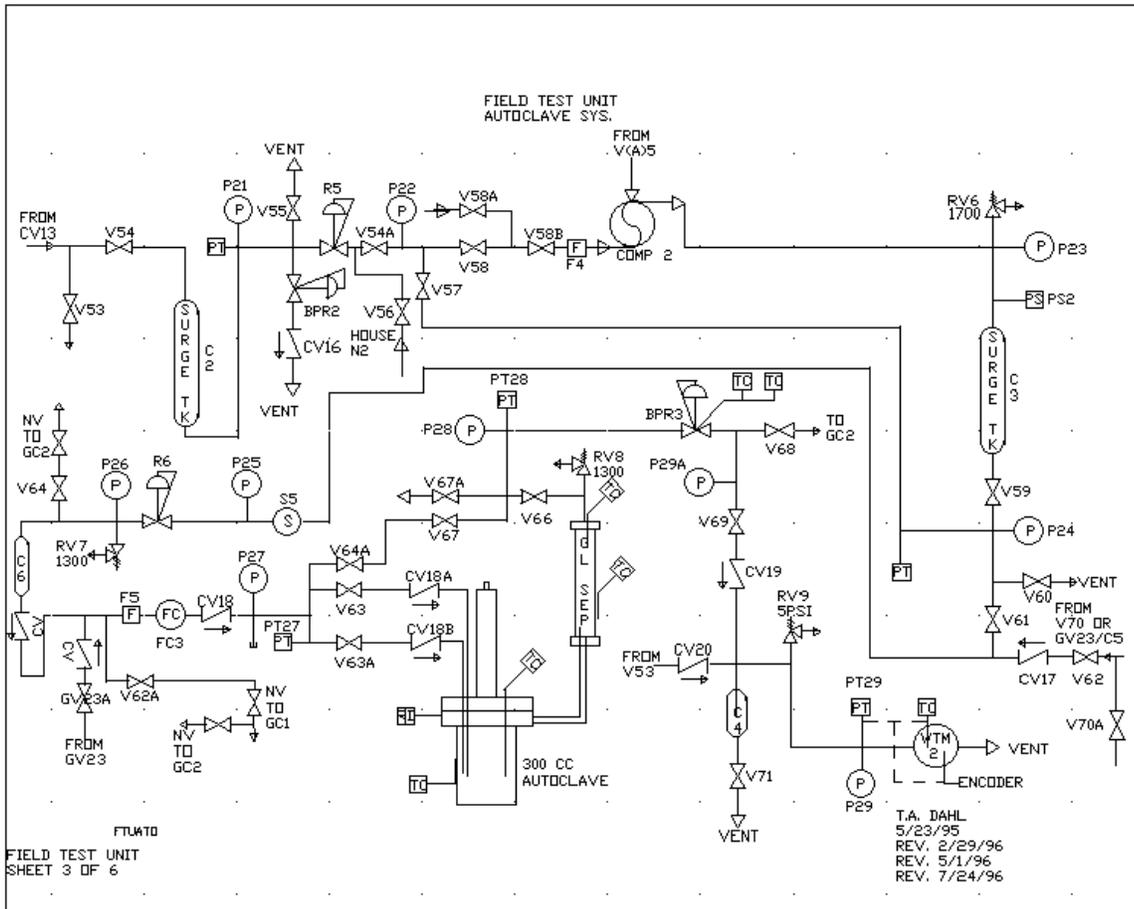


Figure 8: AFFTU GC Gas Manifold

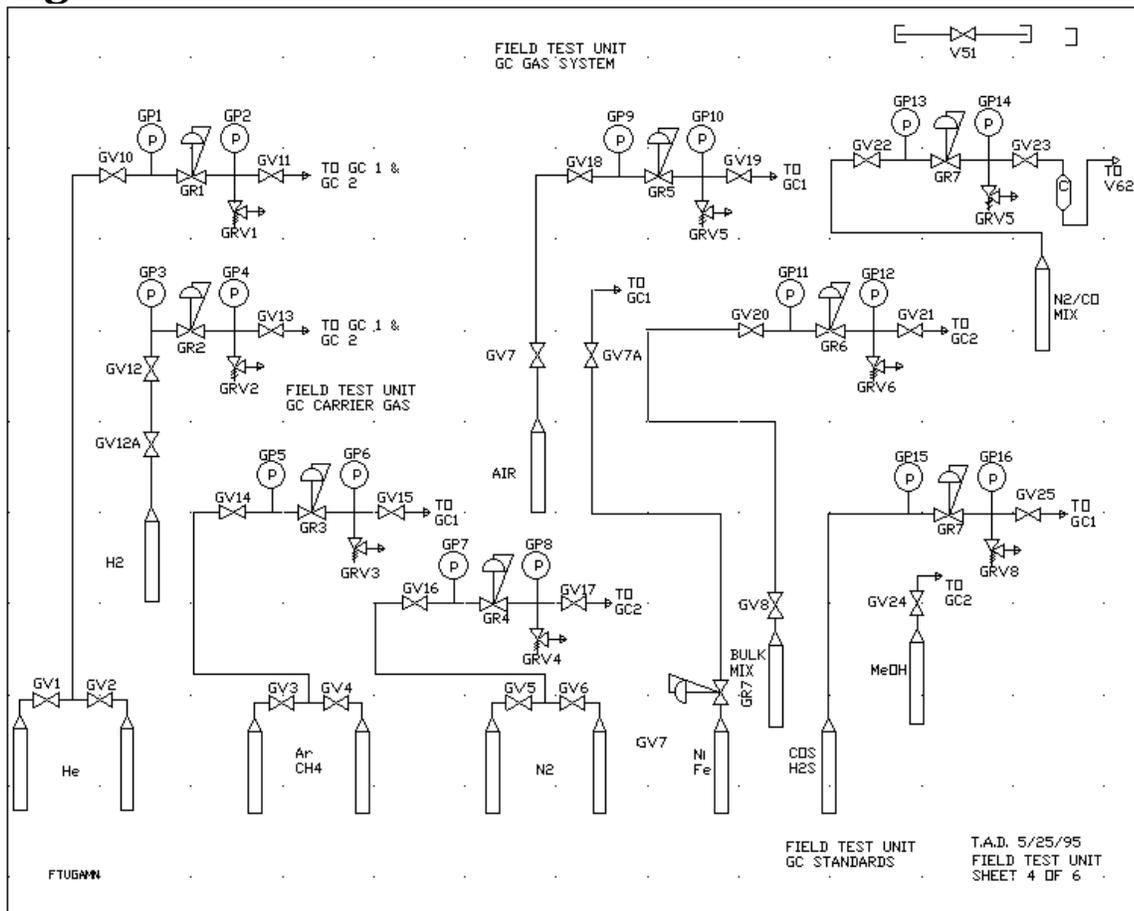


Figure 9: AFFTU Poisons GC Sampling System

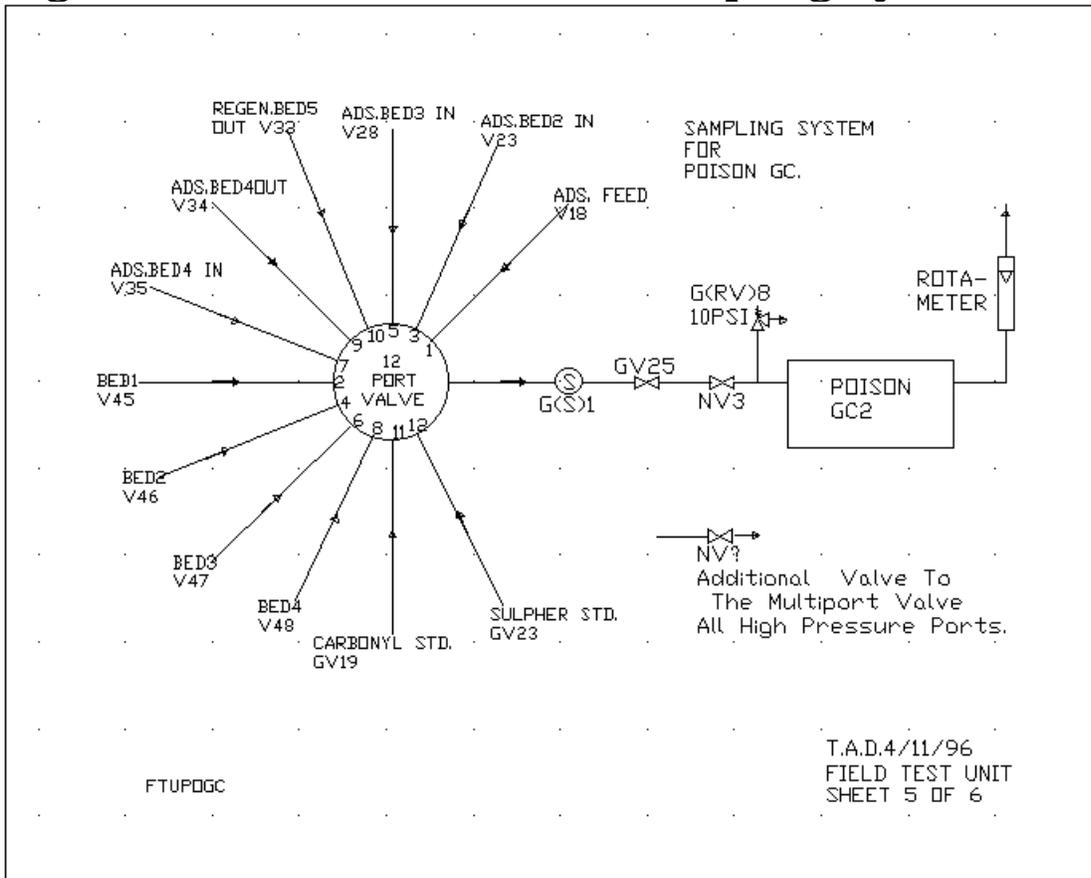


Figure 10: AFFTU Bulk GC Sampling System

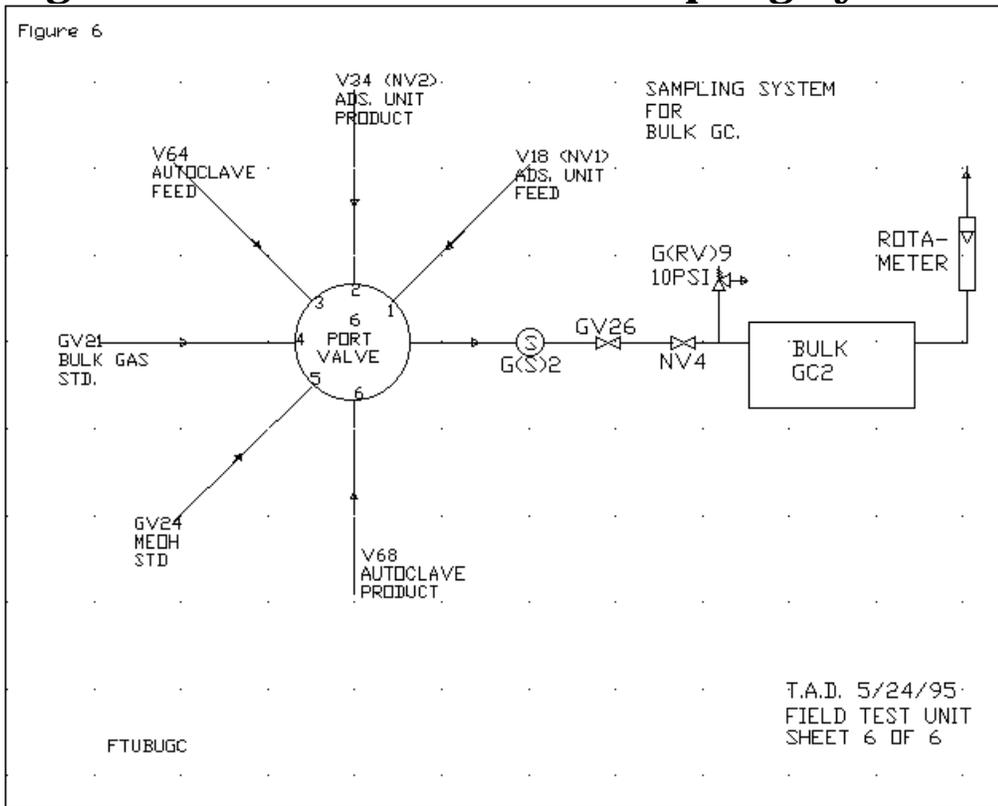


Figure 11: Detail of Adsorption Bed Design

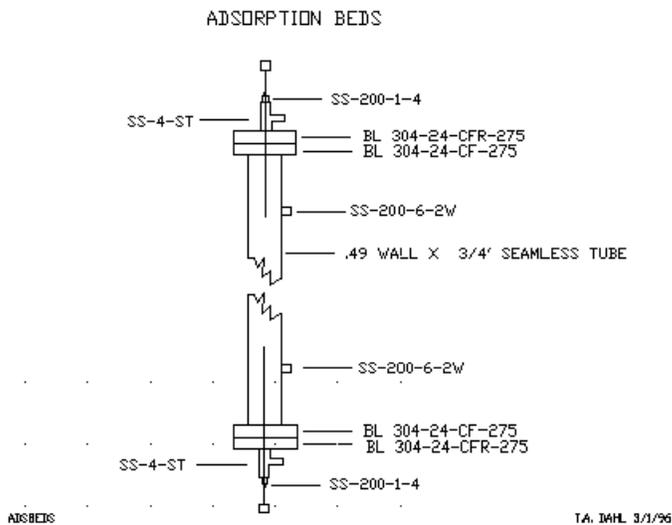


Figure 12a: Bulk GC Configuration

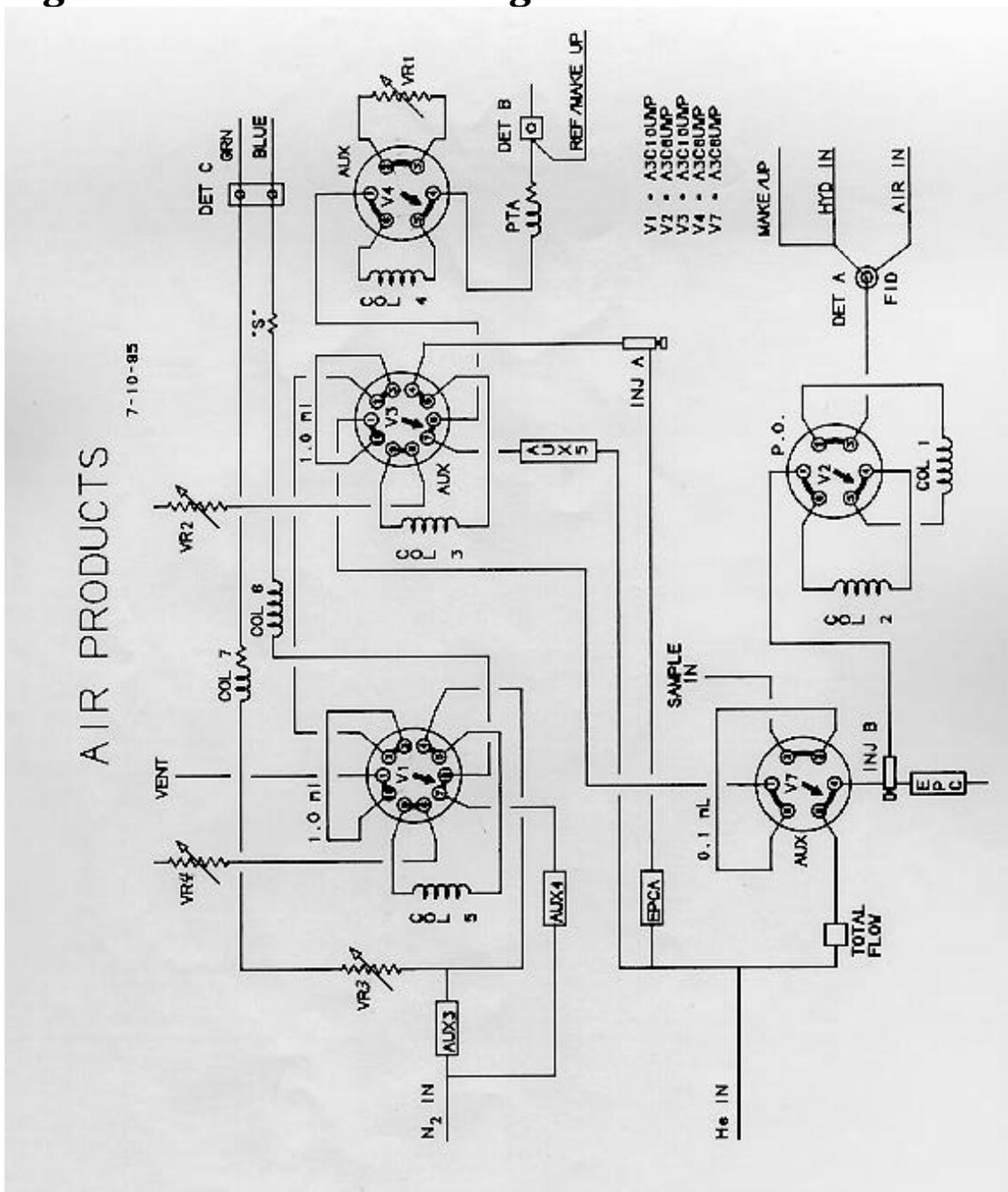


Figure 12b: Poisons GC Configuration

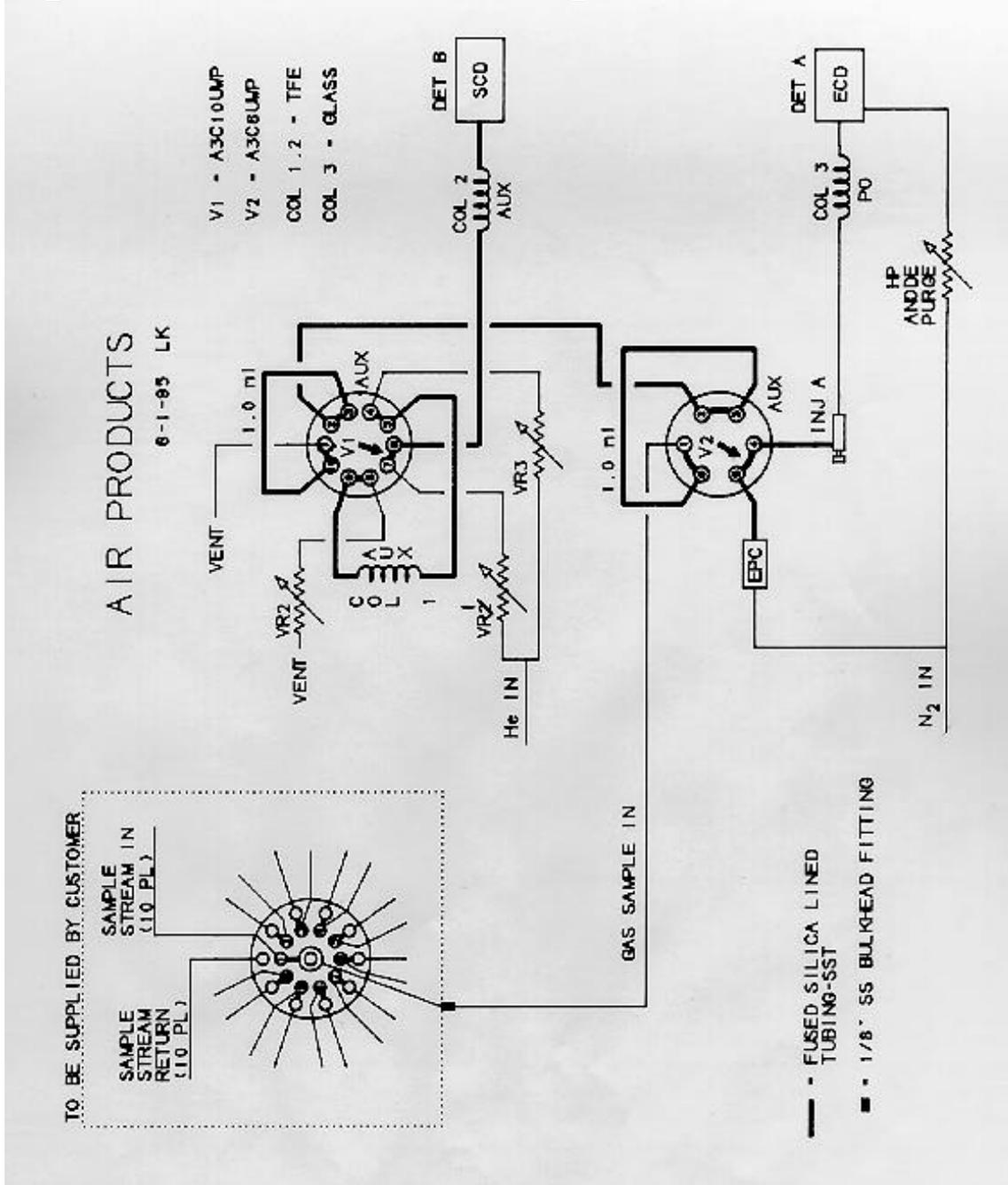


Figure 12c: Typical FID Chromatogram

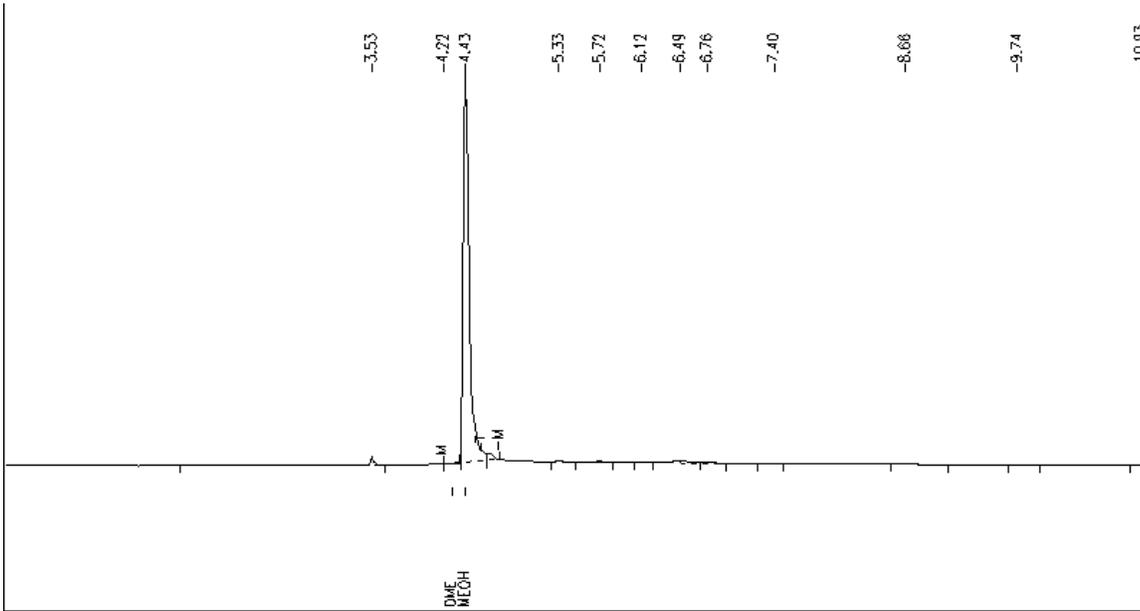


Figure 12d: Typical TCD Chromatogram

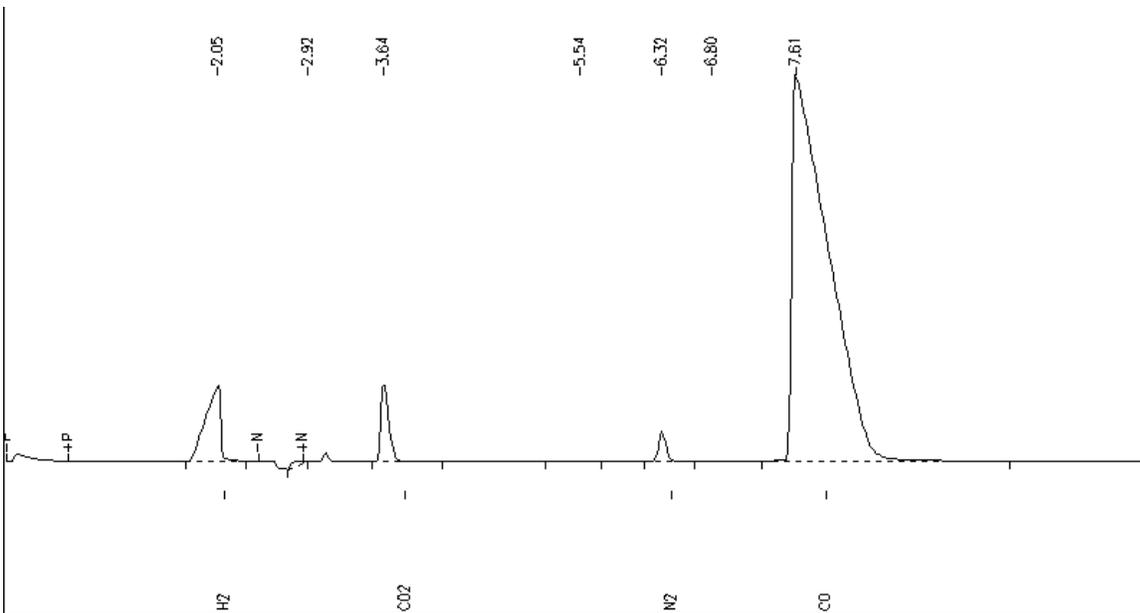


Figure 12e: Typical ECD Chromatogram

40 ppb Ni(CO)₄; 7 ppb Fe(CO)₅

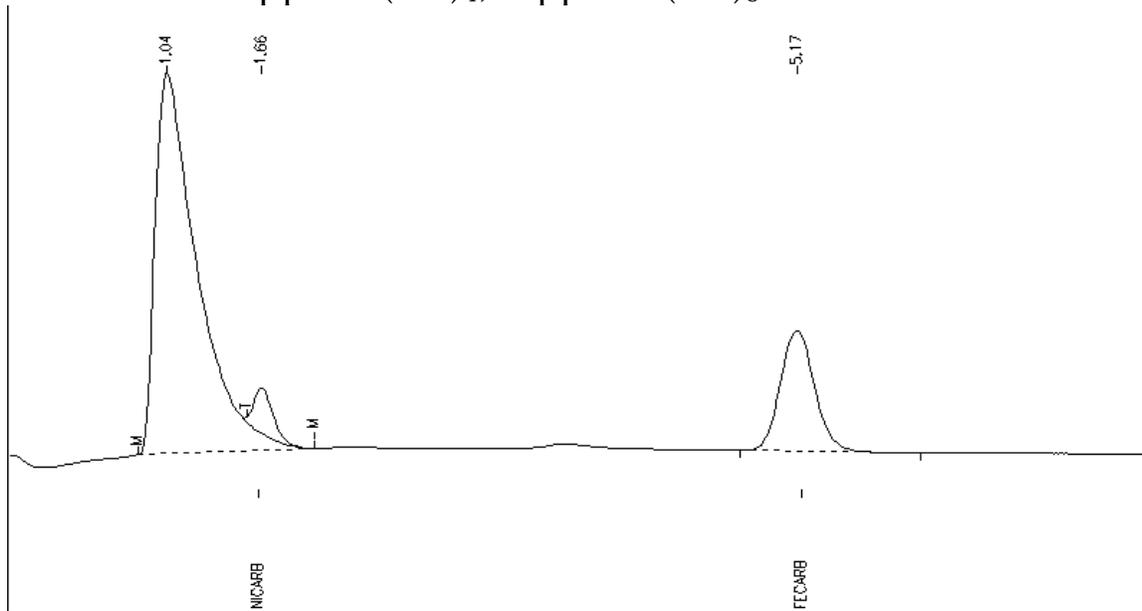
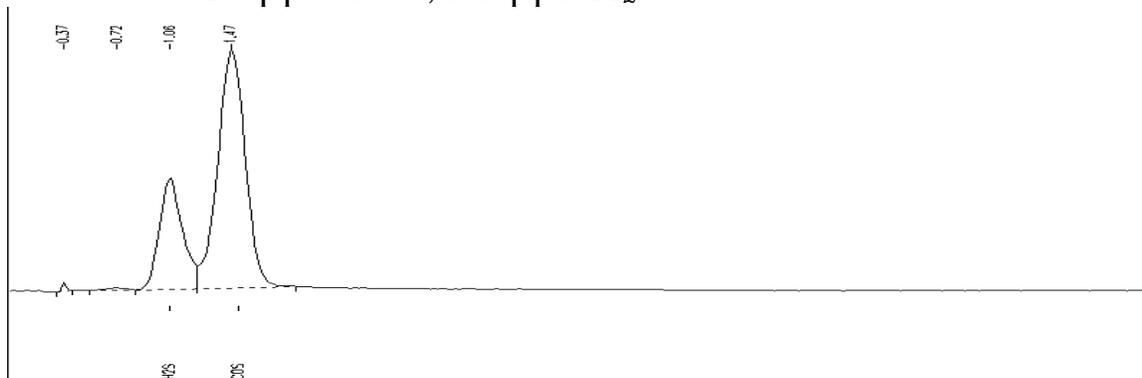


Figure 12f: Typical SCD Chromatograms

40 ppb COS; 29 ppb H₂S



More typical: 8 ppb COS; <1 ppb H₂S (different scale)

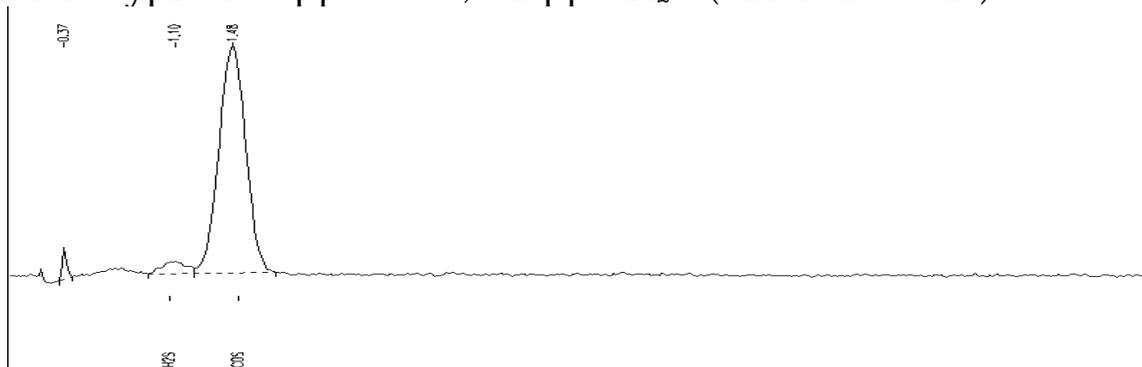


Figure 13: Full Trailer Feed Poisons History

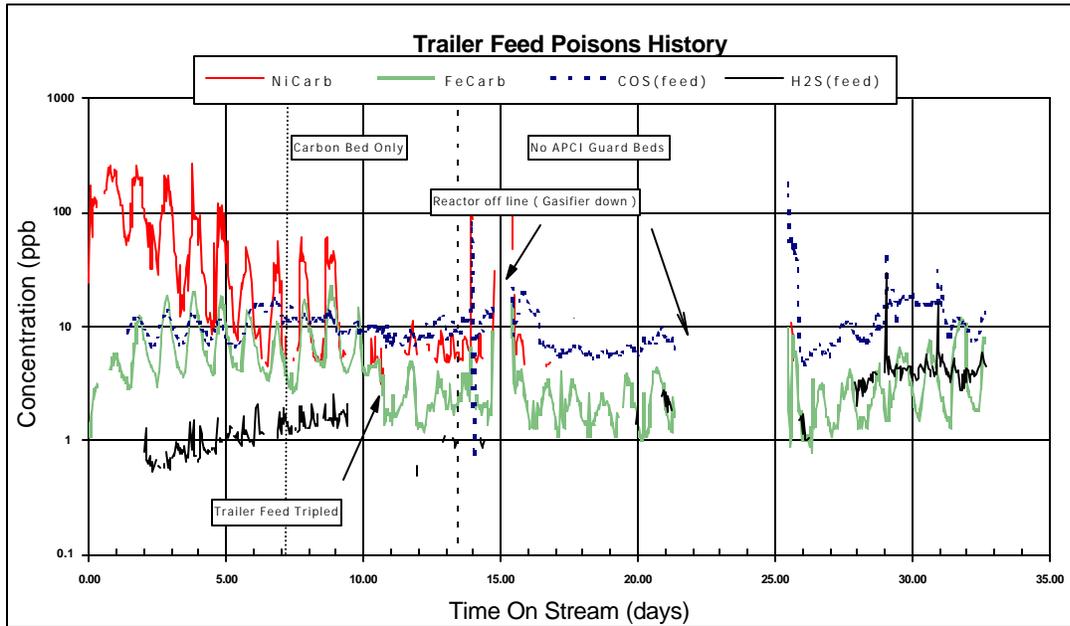


Figure 14: Trailer Feed Poisons History For First Day After Gasifier Restart

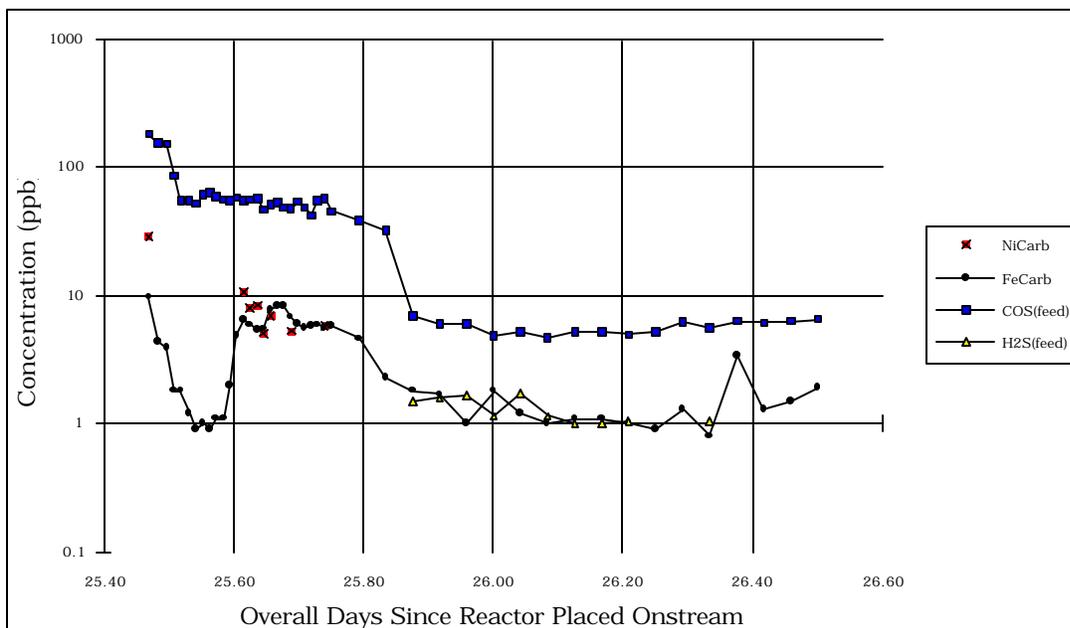


Figure 15: Hydrogen Sulfide History

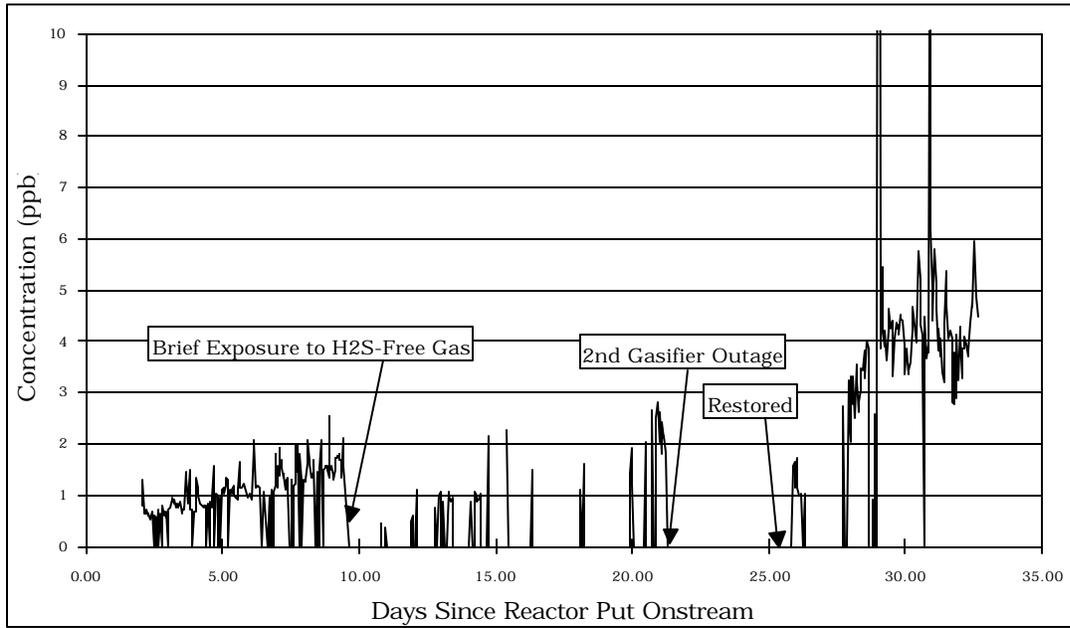


Figure 16a: Concentration Fluctuations and Ambient Temperature

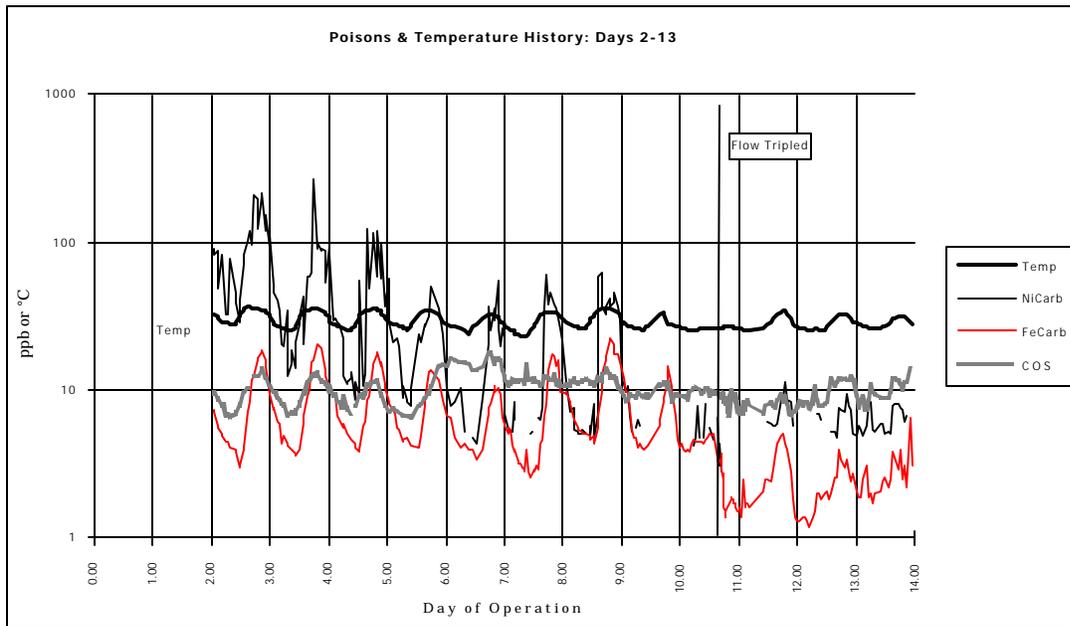


Figure 16b: Effect of Tripling Trailer Feed Flow On Poisons Concentrations

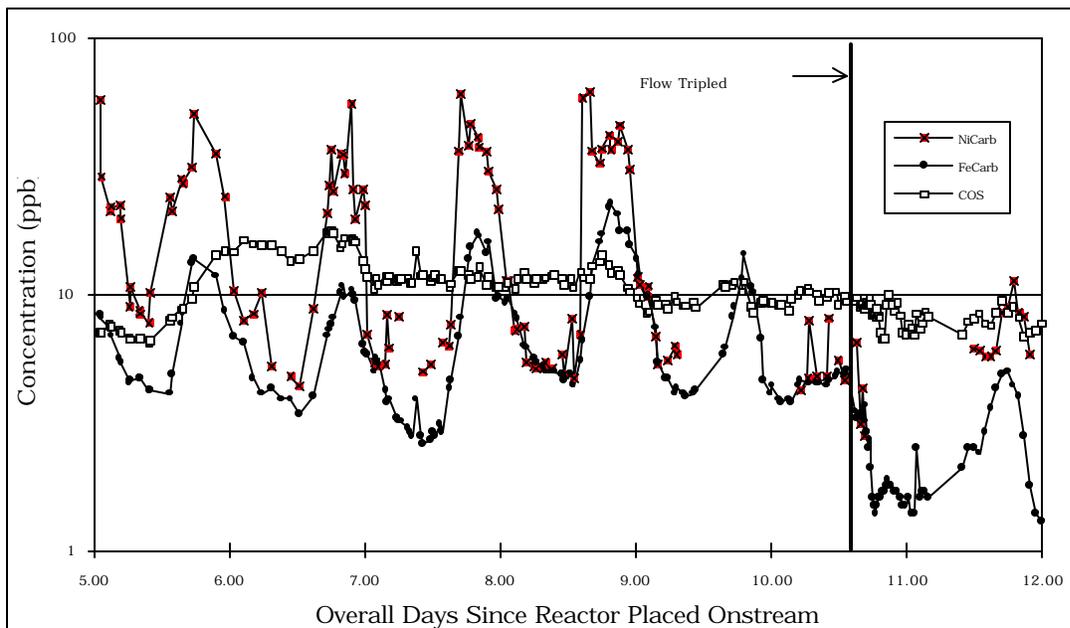


Figure 16c: Correlation of the Daily Maximum Carbonyl Concentrations with the Daily Temperature

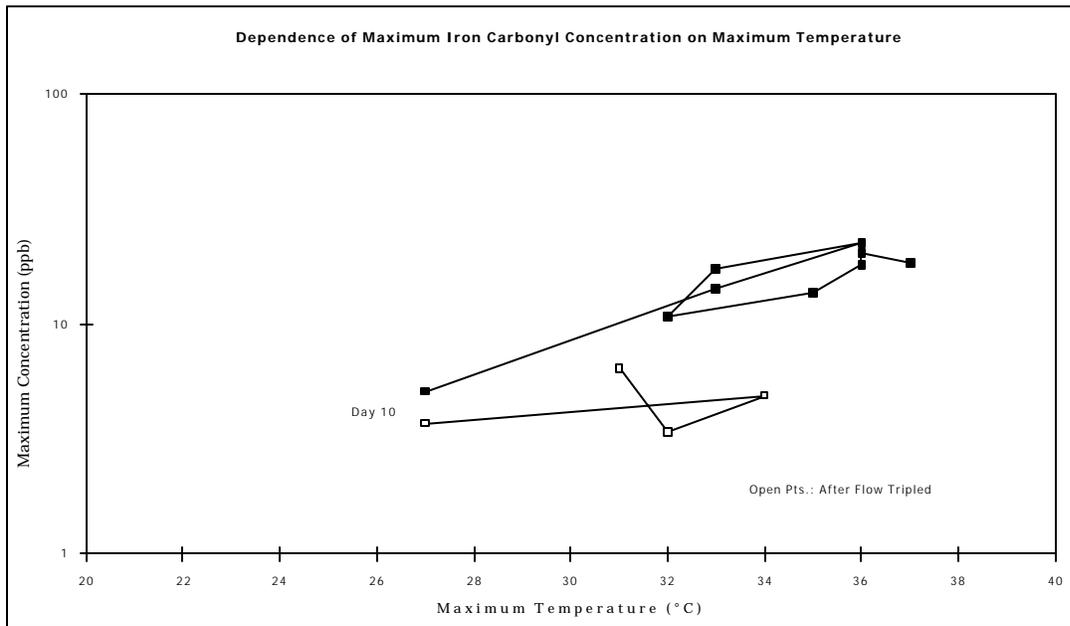
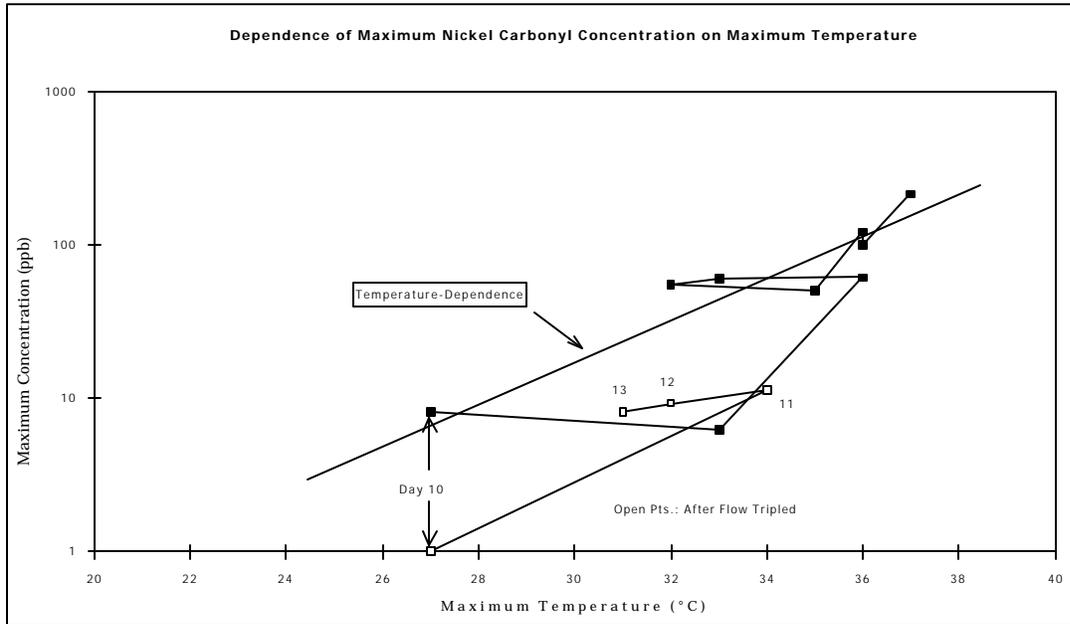


Figure 17: Productivity History

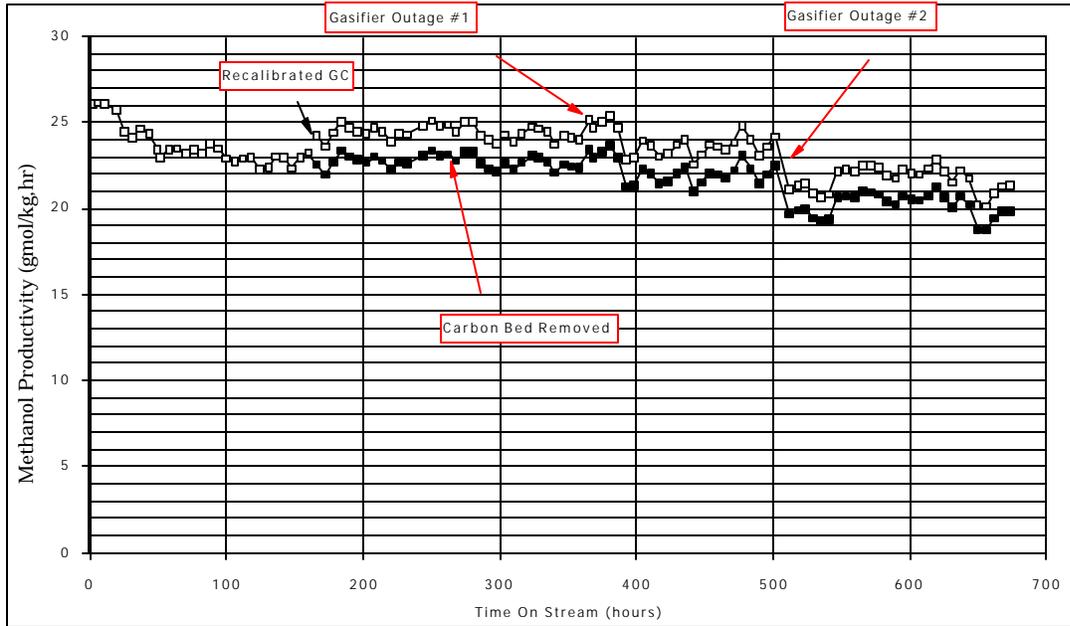


Figure 18: Comparison of k_M and Productivity Histories

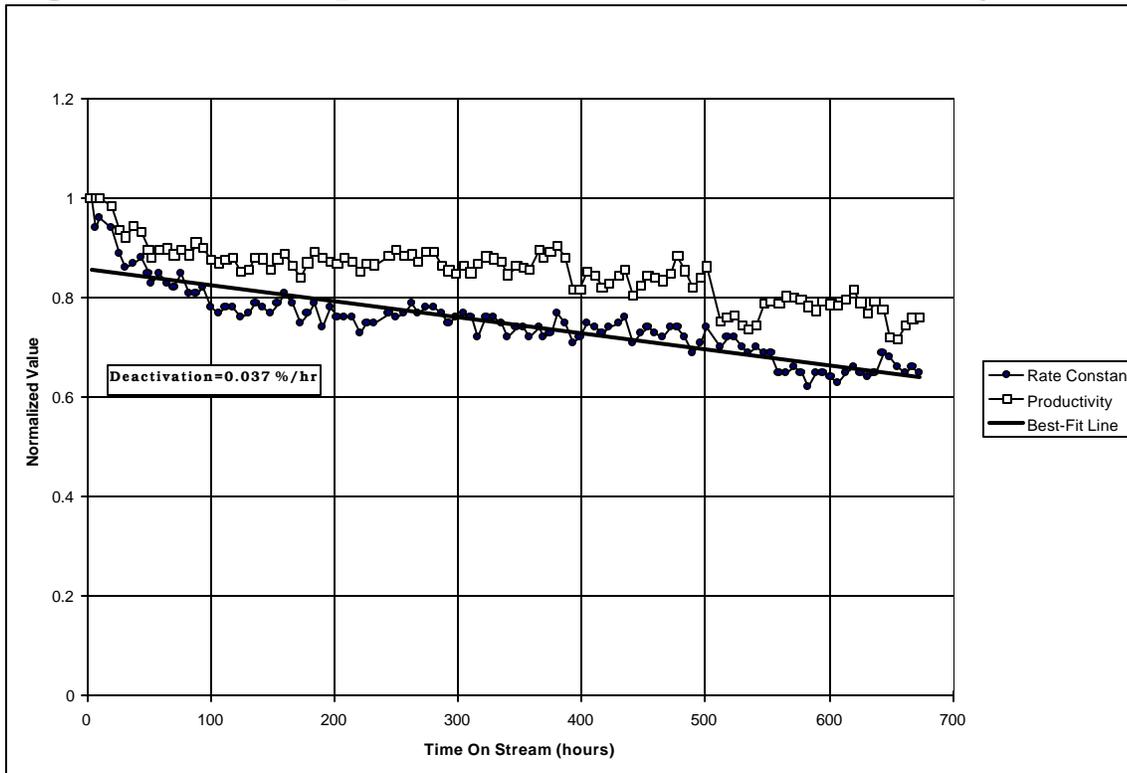


Figure 19: Correlation of Productivity Deviations with Carbon Dioxide Concentrations

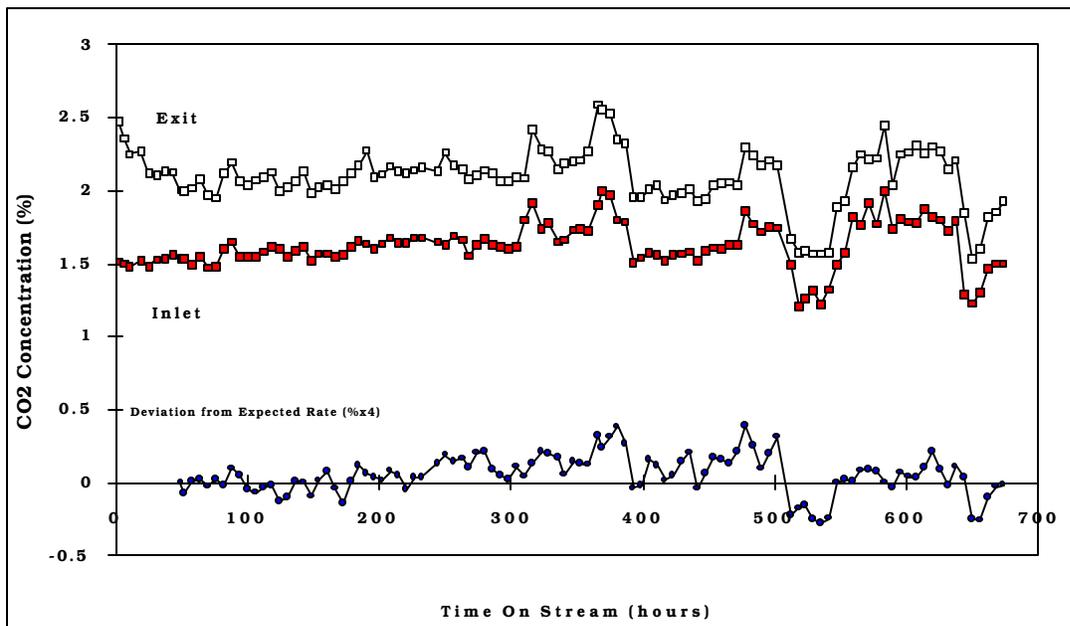


Figure 20: Analysis of Productivity Data

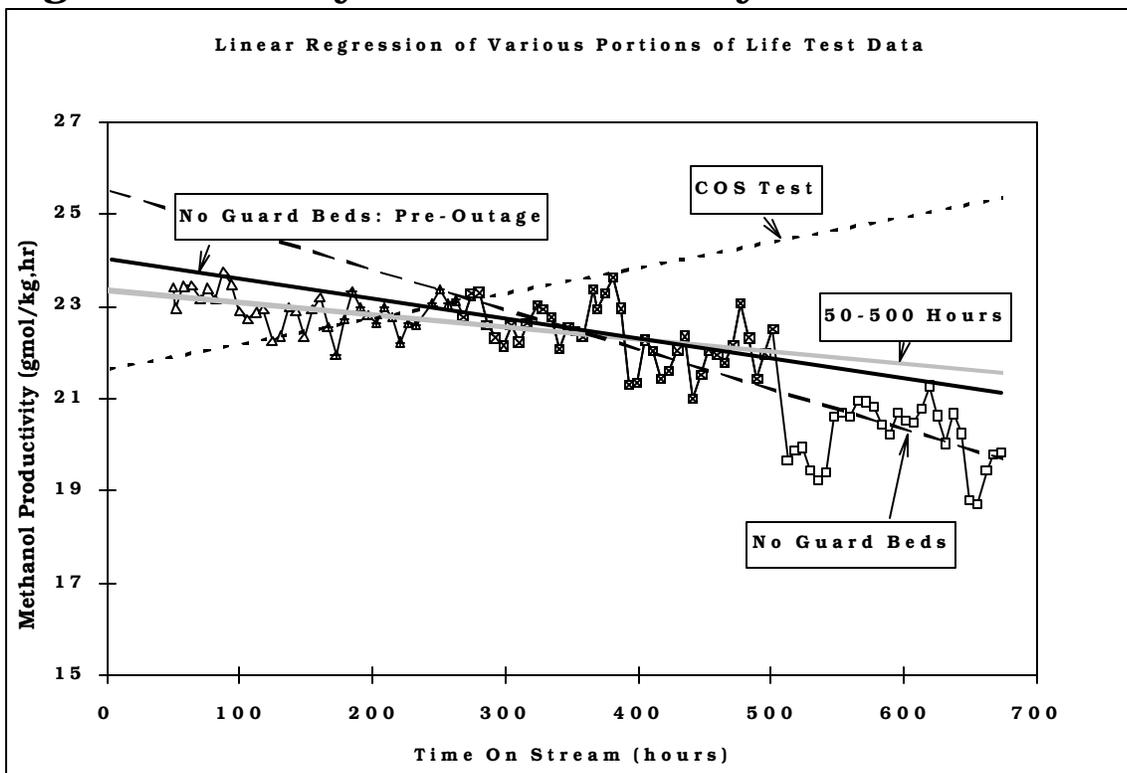


Figure 21: Analysis of Rate Constant Data

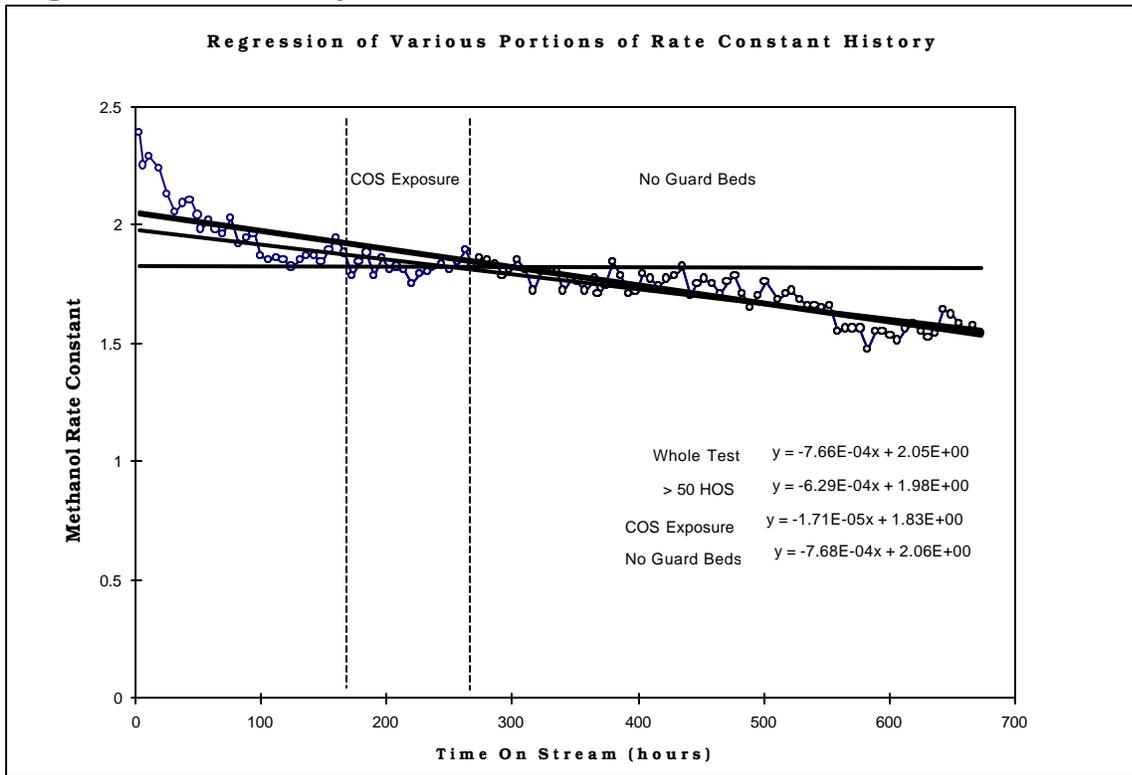


Figure 22: Infrared Spectra of Slurry Oils

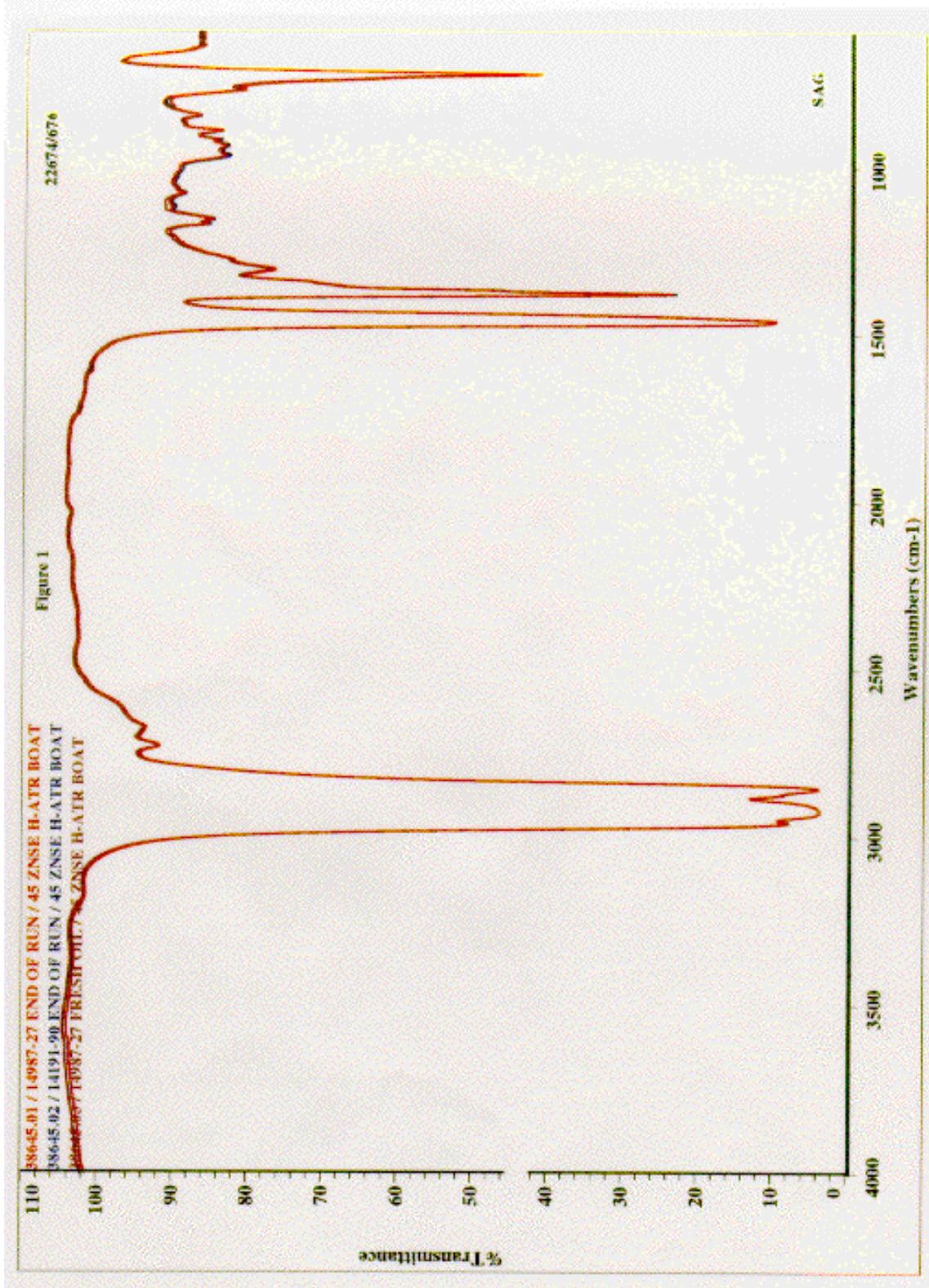


Figure 23: Raman Spectra of Slurry Oils

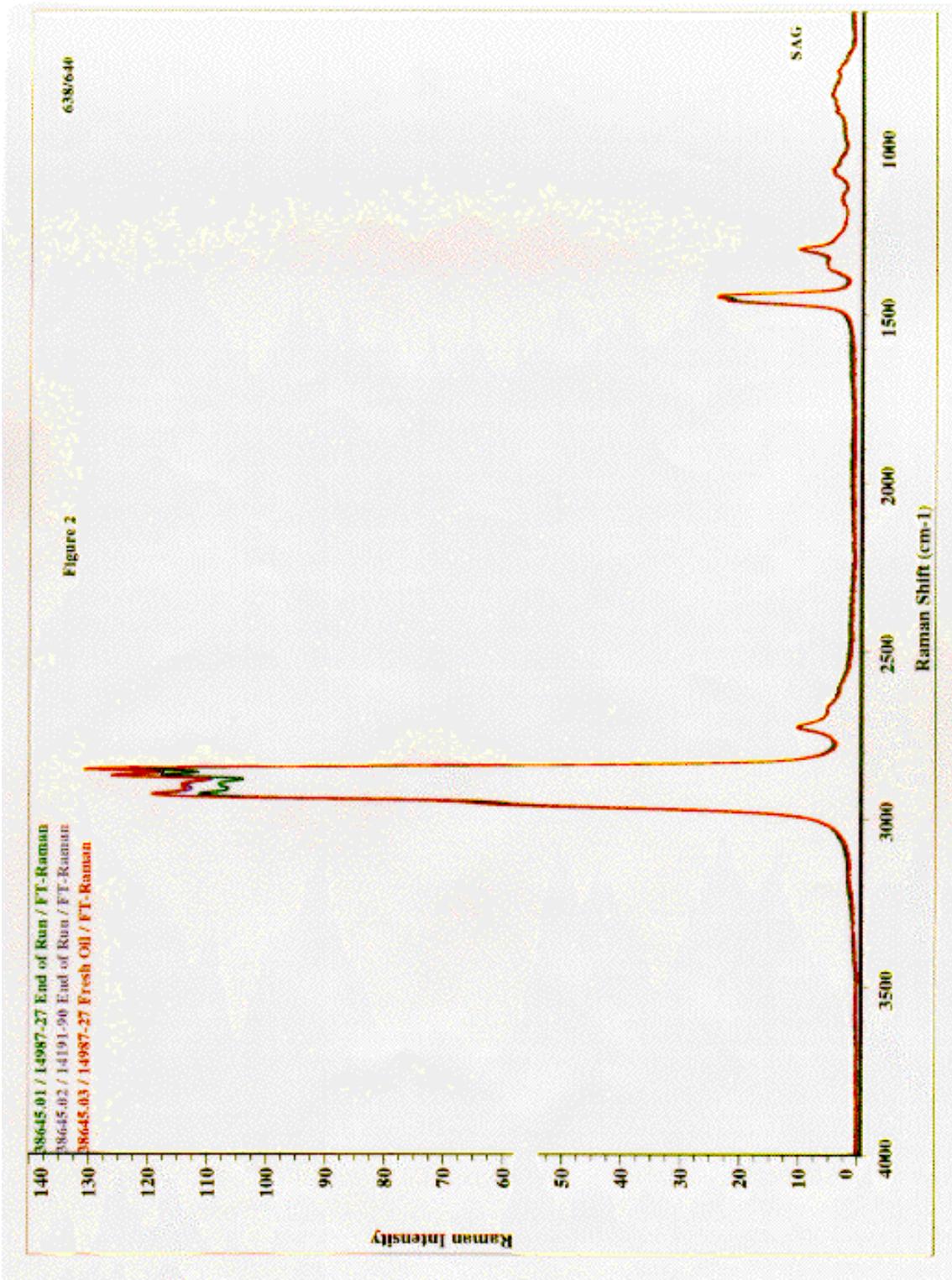


Figure 24: UV/Vis Spectra of Slurry Oils

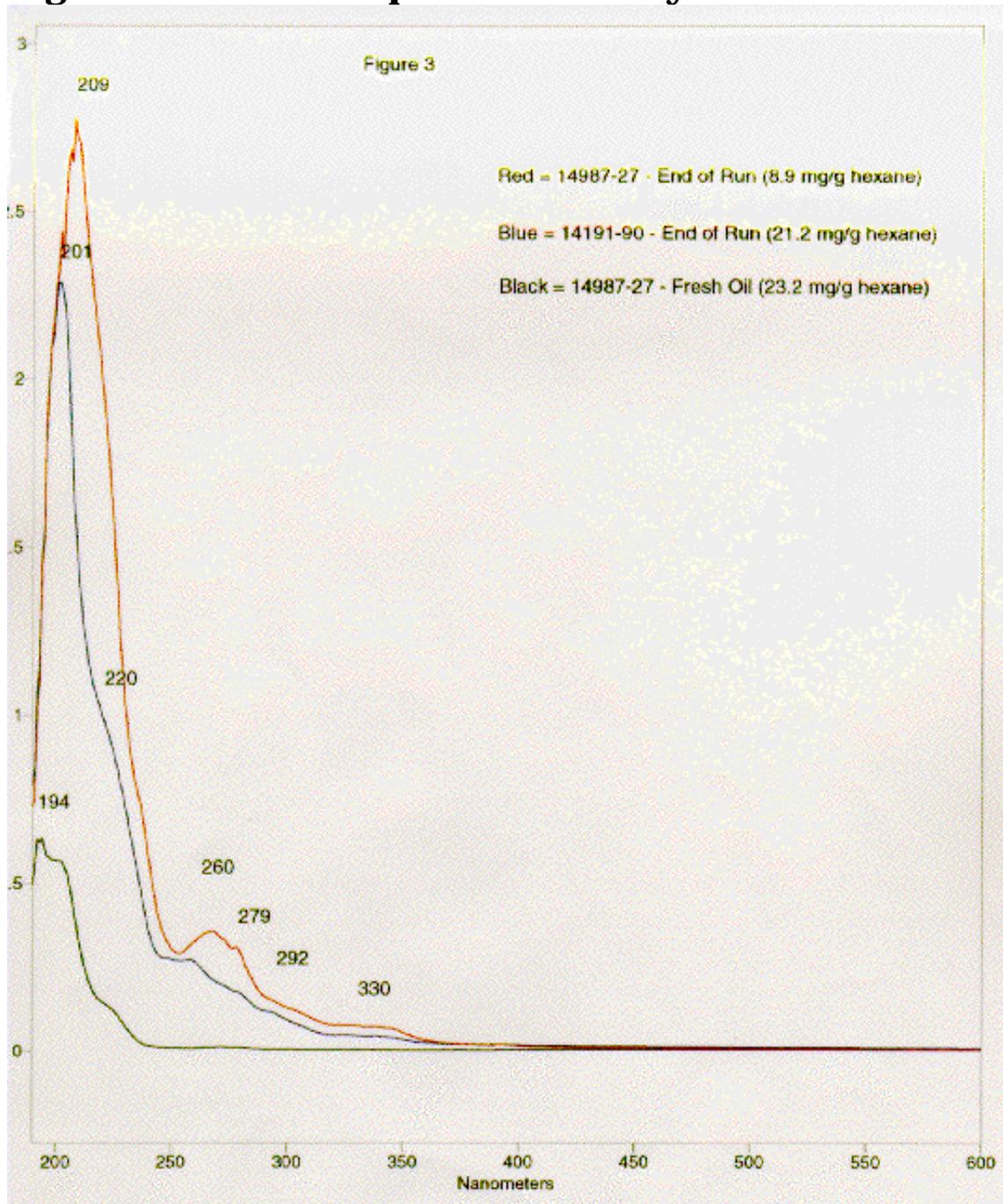


Figure 25: X-Ray Diffraction Pattern of Spent Catalyst from Kingsport Test

