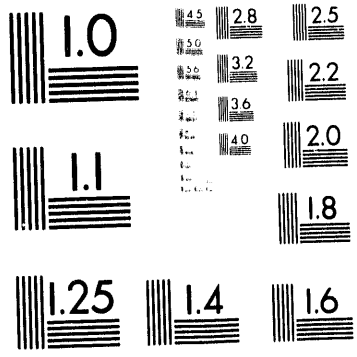
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1 of 2

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DEVELOPMENT OF ALTERNATIVE FUELS FROM COAL DERIVED SYNGAS

Topical Report

Task 2.2: Demonstration of a One-Step Slurry-Phase Process for the Production of Dimethyl Ether/Methanol Mixtures at the LaPorte Alternative Fuels Development Unit

Contractor

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Contents

ACRONYMS AND ABBREVIATIONS

AFDU	Alternative Fuels Development Unit, LaPorte, Texas
Al_2O_3	Alumina
CGCC	Coal Gasification Combined Cycle
CSTR	Continuous Stirred Tank Reactor
CO	Carbon Monoxide
CO_2	Carbon Dioxide
Cu	Copper
DME	Dimethyl Ether
DOE	United States Department of Energy
DVR	Design Verification Review
GC	Gas Chromatograph
°F	temperature unit, degrees Fahrenheit
H_2	Hydrogen
LPDME	Liquid Phase Dimethyl-Ether
LPMEOH	Liquid Phase Methanol
MeOH	Methanol
N_2	Nitrogen
NDG	Nuclear Density Gauge
PFD	Process Flow Diagram
ppm	parts per million, by volume
psig	pressure unit, pound-force per square inch, expressed in gauge

ABSTRACT

This report documents the engineering, modification, and operations efforts of the demonstration of dimethyl-ether/methanol coproduction in a slurry-phase reactor. The demonstration was carried out in a 2 ft diameter bubble column reactor at the U.S. Department of Energy-owned Alternative Fuels Development Unit (AFDU) in LaPorte, Texas, during April and May of 1991.

Several modifications were made to the existing plant to facilitate this demonstration. Old, unused equipment was refurbished and commissioned. New equipment and instrumentation were also purchased and installed. The equipment modifications made it possible to remove the product DME and by-product CO_2 from the reactor effluent.

The coproduction of dimethyl-ether (DME) and methanol (MeOH) was accomplished in the slurry reactor by physically mixing two different catalysts. The catalyst used to produce MeOH from syngas was manufactured by BASF (type S3-86); the catalyst used to convert MeOH to DME was Catapal γ-alumina. The ratio of MeOH to DME catalysts determined the selectivity towards DME.

The AFDU demonstration sought to study the effect of cocatalyst ratio on product selectivity. Three different proportions of DME catalyst were examined: 0, 6.6, and 19.3 wt% alumina. At each catalyst proportion, the plant was operated at two different gas space velocities. Some process variables were maintained at fixed conditions. The most important of these variables included: reactor temperature (482°F), reactor pressure (750 psig), and reactor feed gas composition (35% H_2, 51% CO, 13% CO_2, 1% other, nominal-molar basis).

The results from this demonstration were consistent with expectations based on prior laboratory work. It may be concluded that, given a prior understanding of slurry hydrodynamics, the commercial scale-up of DME technology is relatively straightforward.

1. EXECUTIVE SUMMARY

This report documents the engineering, modification, and operations efforts directed towards the demonstration of dimethylether(DME)/methanol coproduction in a slurry-phase reactor. The demonstration was carried out in a 2 ft diameter bubble column reactor at the U.S. Department of Energy (DOE) owned Alternative Fuels Development Unit (AFDU) in LaPorte, Texas.

This demonstration, conducted during April and May of 1991, was the first under Contract No. DE-AC22-91PC90018, "Development of Alternative Fuels from Coal Derived Syngas" between Air Products and Chemicals, Inc. and the U.S. Department of Energy (DOE), with later participation by the Electric Power Research Institute (EPRI). The engineering and modifications were part of Task 1; the actual demonstration was part of Task 2.

Several modifications were made to the existing plant to facilitate this demonstration. Old, unused equipment was refurbished and commissioned. New equipment and instrumentation were also purchased and installed. The equipment modifications made it possible to remove the product DME and by-product CO_2 from the reactor effluent. This, in turn, allowed the unconverted syngas in the reactor effluent to be recycled, thereby maintaining appropriate circulation rates, as well as maximizing syngas utilization.

The coproduction of DME and methanol (MeOH) was accomplished in the slurry reactor by physically mixing two different solid catalysts. The catalyst used to produce MeOH from syngas was BASF S3-86; the catalyst used to convert MeOH to DME was Catapal γ-alumina. The ratio of MeOH to DME catalysts determined the selectivity towards DME.

The AFDU demonstration sought to study the effect of cocatalyst ratio on product selectivity. Three different proportions of DME catalyst were examined: 0, 6.6, and 19.3 wt% alumina. At each catalyst proportion, the plant was operated at two different gas space velocities. Some process conditions were fixed. The most important of these included: reactor temperature (482°F), reactor pressure (750 psig), and reactor feed gas composition (35% H_2, 51% CO, 13% CO_2, 1% other, nominal-molar basis). As a consequence of the demonstration method, less important process variables such as catalyst concentration in the slurry, and slurry level varied somewhat.

Following plant recommissioning, the MeOH catalyst was activated in-situ with dilute syngas, the usual technique. After completion of catalyst activation, the plant operated for five days at baseline conditions making MeOH. After a few days the test data collection period began. Three data "points" were collected; one at a space velocity (SV) of 5700 sl/kg-hr and two at SV=8900–9100. The MeOH production rate was as expected.

Next, a precalculated portion of MeOH catalyst was withdrawn and an equal portion of alumina (by weight) was added to bring the cocatalyst composition to 6.6 wt% alumina. Four data points were collected: two at SV=5400 and two at SV=8900. The redundant data points were collected to check for performance degradation with time on-stream (there was none). The production of DME met expectations while that of MeOH exceeded expectations somewhat. The selectivity, expressed as the ratio of DME to MeOH, was approximately 2/3 (by mole) at the lower space velocity and 1/3 at the higher space velocity.

Once again, more reactor slurry was withdrawn and an equal portion of alumina (by weight) was added to bring the cocatalyst composition to 19.3 wt% alumina. Three data points were collected at SV=5900, SV=9500, and again at SV=5900. The production of DME fell slightly short of expectations while that of MeOH met expectations. The selectivity, expressed as the ratio of DME to MeOH, ranged between 2.6/1 and 1.8/1 at the lower space velocity and 1.2/1 at the higher space velocity.

The results from this demonstration were consistent with expectations based on prior laboratory work.[1] However, there was evidence that the catalyst-blend has a greater tendency to settle-out than the MeOH catalyst alone. This departure is probably more pronounced at lower gas velocities. Additional work in this area is warranted. It may be concluded that, given a prior understanding of slurry hydrodynamics, the commercial scale-up of DME technology is relatively straightforward.

2. INTRODUCTION

As part of the DOE-sponsored contract "Synthesis of Dimethyl Ether and Alternative Fuels in the Liquid Phase from Coal-Derived Syngas" (Contract No. DE-AC22-90PC89865), the single-step, slurry phase DME synthesis process was developed. This development involved screening of catalyst systems, process variable studies and catalyst life studies—all carried out in two 300 ml stirred autoclave reactors.

Conceived as a spin-off from the Liquid Phase Methanol (LPMEOH) process, the new process significantly improved the syngas conversion efficiency over that of the LPMEOH process. This improvement was achieved by replacing a portion of MeOH catalyst with a dehydration catalyst in the reactor, resulting in the product MeOH being converted to DME, thus avoiding the thermodynamic equilibrium constraint of the MeOH reaction. A preferred catalyst system, consisting of a physical mixture of a MeOH catalyst and a γ-alumina, was identified. An improvement of about 50% in MeOH equivalent productivity was achieved compared to the LPMEOH process. The details of the catalyst development and optimization efforts have been documented elsewhere.[1] Following is an overview of the current state of Air Products' slurry-phase DME efforts.

2.1 CHEMISTRY OF DME SYNTHESIS FROM H_2/CO SYNGAS

DME can be produced from syngas via a two-step reaction mechanism. In the first step syngas is converted to MeOH:

$$2\ H_2 + CO \Longleftrightarrow MeOH \qquad \text{(step 1)}$$

In the second step MeOH is dehydrated to form DME:

$$2\ MeOH \Longleftrightarrow DME + H_2O \qquad \text{(step 2)}$$

Both these steps are reversible and exothermic. At equilibrium, the MeOH production step is favored by higher pressure; the DME step is pressure neutral. Each of these steps is catalyzed by a different material: MeOH is produced using a mixed metal catalyst such as copper-zinc on alumina, while DME is produced using an acid dehydration catalyst such as alumina.

The MeOH catalyst used also exhibits activity towards the water-gas shift reaction:

$$H_2O + CO \Longleftrightarrow CO_2 + H_2 \qquad \text{(step 3)}$$

Shift is necessary to increase the hydrogen availability when processing CO-rich synthesis gases (typical of modern efficient coal gasification).

Multistep processes, which use separate reactors for each step, cannot exploit the potential synergy of the three reactions. If these three reactions are conducted simultaneously, MeOH synthesis drives the forward shift reaction, and DME synthesis drives both the MeOH and shift reactions. Consequently, a one-step process is more flexible and can operate under a wider range of conditions than a multistep process. In addition, multistep processes require separate reactors, heat exchangers, and associated equipment.

The production of DME has many potentially commercial benefits. First, synthesis of DME can lead to higher syngas conversion per pass, improving the flexibility of co-producing power and clean liquid fuels in Coal Gasification Combined Cycle (CGCC) power plants.[2] Second, mixtures of DME and MeOH may have potential in the clean-burning oxygenated fuels transportation market. On-board generation of DME has already been investigated by Karpuk and Cowley[3] as a means of improving MeOH's cold-start characteristics. Finally, and perhaps most importantly, DME is a well-known intermediate in processes for converting synthesis gas to liquid fuels and chemicals.[4,5] Apart from being a precursor in Mobil's MTG process, DME offers potential as a chemical building block to mixed ethers, currently attractive as replacement octane blending agents in the U.S. gasoline pool.

2.2 LABORATORY RESEARCH—BASIC PERFORMANCE

For the laboratory work, commercially available catalysts were primarily used, although some novel catalytic materials were also examined. All catalysts were activated according to the manufacturers' recommended procedures. They were slurried in either degassed WITCO 70 or degassed DRAKEOL 10, food grade mineral oils which are primarily C_{18}-C_{31} paraffins. Slurry concentrations varied from 15 to 30 wt% catalyst (based on the total weight of the slurry).

Initial screening studies were carried out on a number of catalyst pairs to identify the system with the greatest activity and mutual physical compatibility.[6] The prototypical catalyst pair discussed here used powdered BASF S3-86 to activate the MeOH and shift steps, and Catapal γ-alumina for the dehydration step.

A variety of process variable scans were conducted to characterize performance. Independent variables included temperature, pressure, space velocity, feed gas composition, and catalyst proportions. The dependent variables included productivity and selectivity. A summary of the range of process variables is included in Tables 2.2-1 and 2.2-2.

TABLE 2.2-1
FEED GAS TYPES STUDIED

TYPE	COMPOSITION (MOLE %)			
	H_2	CO	N_2	CO_2
DOW	41	41	2	16
SHELL	30	66	1	3
TEXACO	35	51	1	13
H_2-RICH	74	15	4	7
BALANCED	50	50	0	0

TABLE 2.2-2
RANGE OF PROCESS VARIABLES

VARIABLE	RANGE
Temperature	482–536 °F (250–280°C)
Pressure	750–1450 psig
Space Velocity	1,500–10,000 sl/kg-hr
Catalyst Proportion	0 - 50 (wt% alumina)

The characteristic behavior of Liquid-Phase DME (LPDME) is contrasted with LPMEOH in Figure 2.2-1, which presents the CO conversion as a function of space velocity. The CO conversion in LPDME is up to twice as high as that in LPMEOH and much higher than the equilibrium conversion achievable from the MeOH reaction alone. Interestingly, the gap between DME equilibrium and the DME performance curve indicates that there is still substantial room for catalyst improvement.

As one would expect, raising the reactor temperature increases the activity of both catalysts. However, the rate of dehydration is more strongly affected by temperature, such that overall, DME selectivity increases. This effect is illustrated in Figure 2.2-2.

Pressure has a pronounced impact on overall productivity. By increasing pressure, the first of the two sequential steps can be driven forward at a greater rate, resulting in increased productivity for both components (see Figure 2.2-3). The response of selectivity to increasing pressure is dependent on space velocity. At lower space velocity, selectivity to DME increases with increasing pressure; at higher space velocity, the reverse is true.

The relative proportions of S3-86 and alumina have a profound impact on process performance (see Figure 2.2-4). As would be expected, increasing the percentage of dehydration catalyst increases selectivity to DME. In addition, at very low proportions of alumina, increasing its relative amount significantly increases the overall per-pass equivalent MeOH productivity (equivalent productivity is defined as productivity of MeOH plus twice the productivity of DME). If one continues to increase the proportion of dehydration catalyst, the incremental increase in productivity slows until a maximum is reached. Beyond this point, continued increases in the alumina proportion result in reduced productivity. The composition which corresponds to the maximum productivity is a function of pressure, temperature, catalyst types, and syngas composition. Commercially, one must consider both selectivity and productivity before deciding on the appropriate catalyst proportion. For the purposes of demonstrating the scale-up in the AFDU, two particular alumina contents were chosen: one at relatively low alumina content (6.6 wt%) to produce methanol as the major component, and the other at a higher alumina content (19.3 wt%) to produce a DME-rich product at the maximum equivalent productivity.

The laboratory screening and process variable studies successfully identified the attractive operating envelope for DME synthesis. A major question which cannot be resolved in mechanically stirred autoclaves is whether the dual-catalyst system will remain homogenized when agitated within a bubble column reactor. Improper mixing and/or stratification of the two catalysts will introduce mass transfer resistance and reduce productivity. Other issues which are appropriate to this technology include catalyst preparation and handling, start-up, and shutdown. Finally, hydrodynamic data such as vapor hold-up and catalyst agglomeration are important.

FIGURE 2.2-1

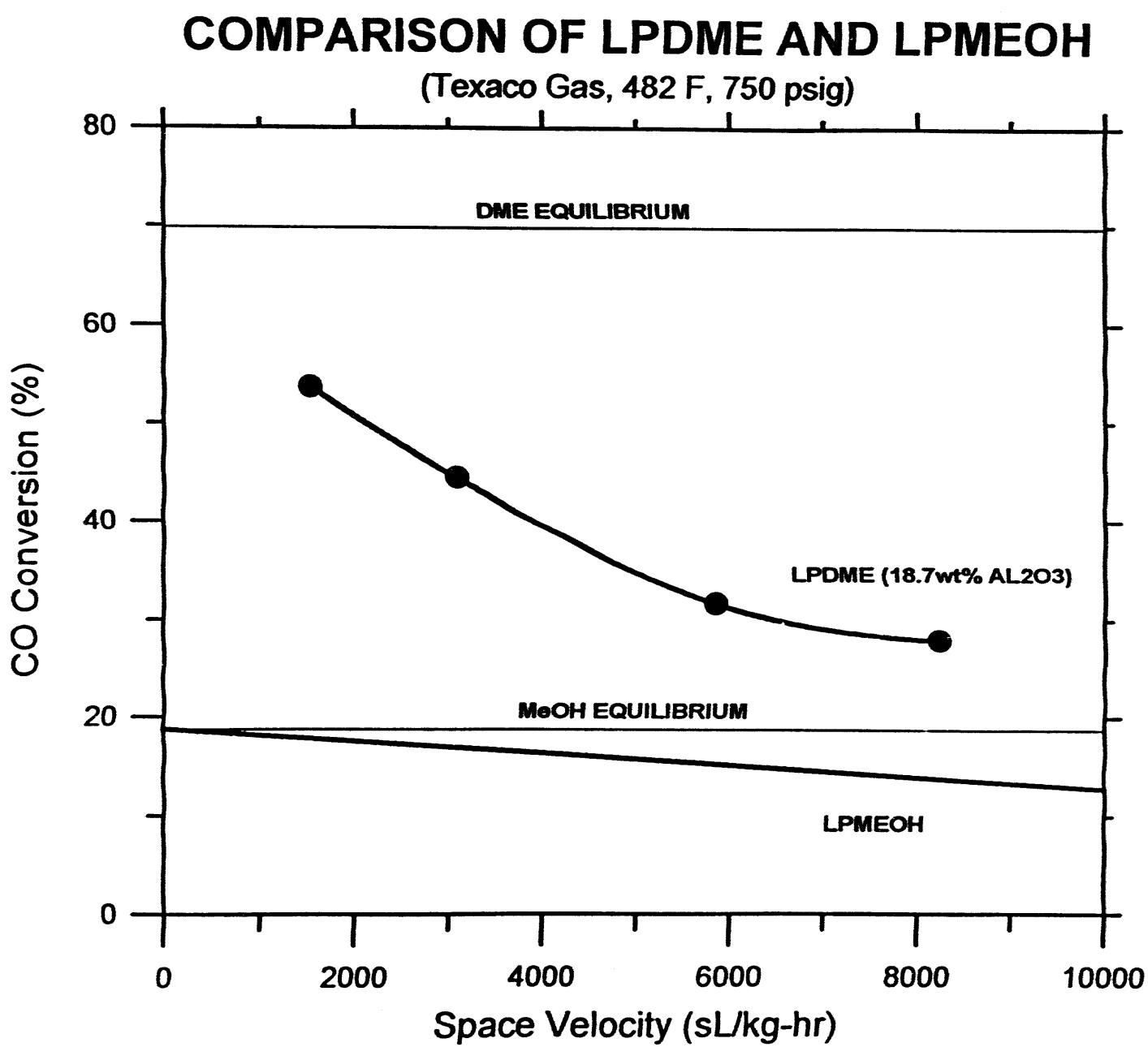

COMPARISON OF LPDME AND LPMEOH
(Texaco Gas, 482 F, 750 psig)
80
60
40
20
0
CO Conversion (%)
DME EQUILIBRIUM
LPDME (18.7wt% AL2O3)
MeOH EQUILIBRIUM
LPMEOH
0
2000
4000
6000
8000
10000
Space Velocity (sL/kg-hr)

FIGURE 2.2-2

EFFECT OF TEMPERATURE ON DME SYNTHESIS

(Texaco Gas, 750 psig, 8100 sL/kg-hr, 18.7% Al2O3)

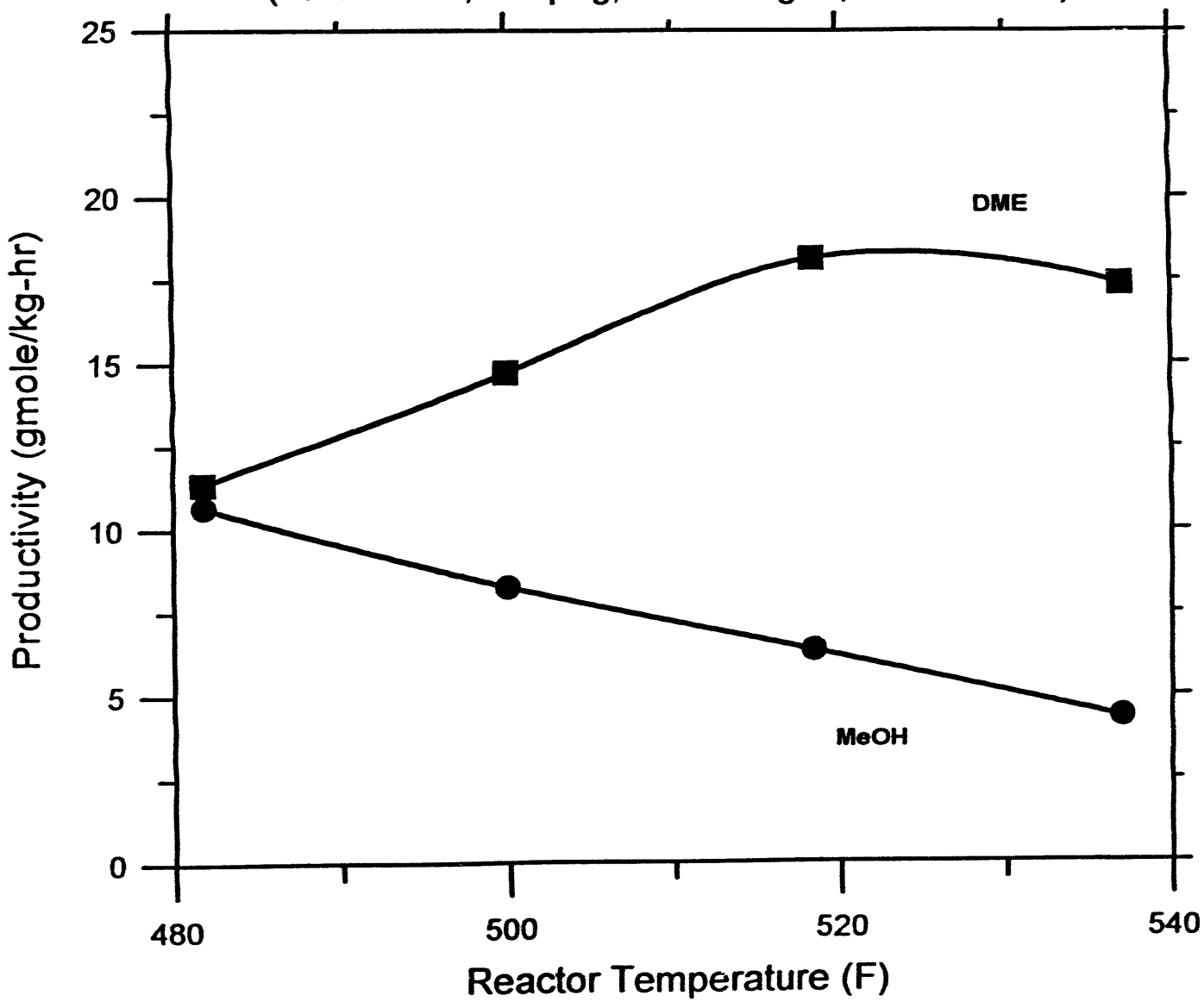


FIGURE 2.2-3

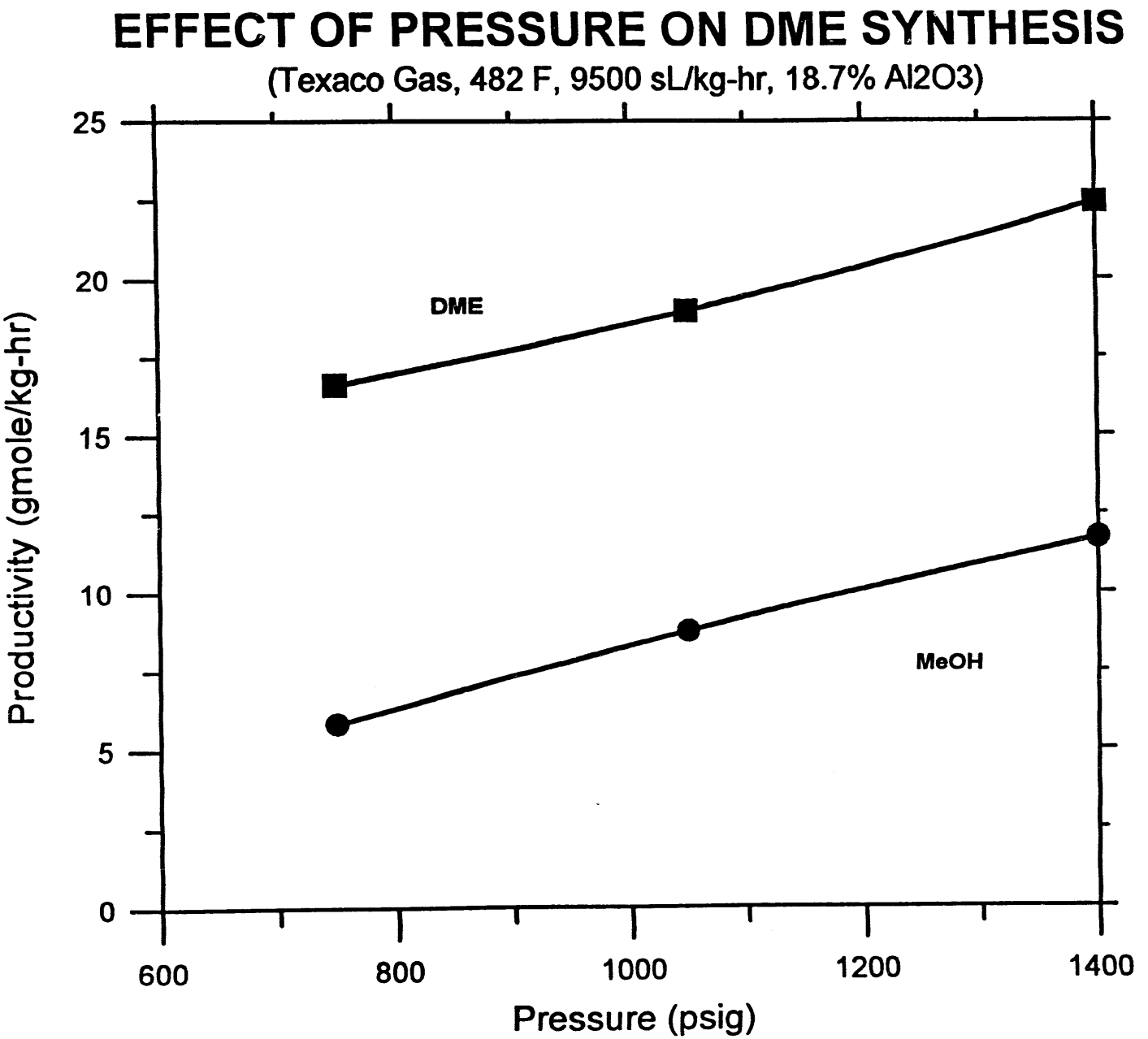
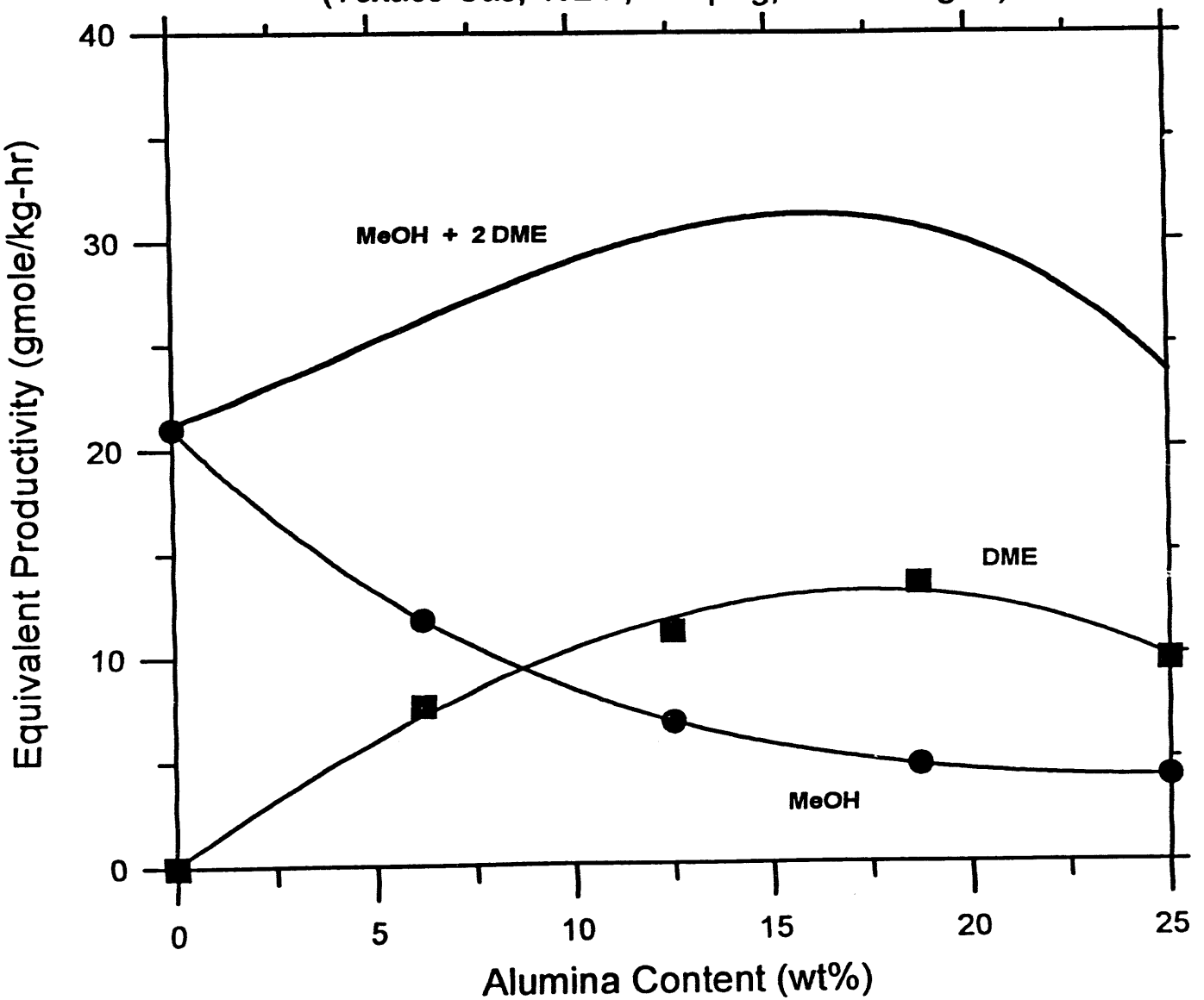

EFFECT OF PRESSURE ON DME SYNTHESIS
(Texaco Gas, 482 F, 9500 sL/kg-hr, 18.7% Al2O3)
Productivity (gmole/kg-hr)
25
20
15
10
5
0
DME
MeOH
600
800
1000
1200
1400
Pressure (psig)

FIGURE 2.2-4

EFFECT OF CATALYST PROPORTION ON DME SYNTHESIS

(Texaco Gas, 482 F, 750 psig, 5900 sL/kg-hr)



Having established the feasibility of the slurry-phase coproduction of DME and MeOH,[1] the next step towards commercialization is to demonstrate that the technology can be scaled-up from mechanically-stirred, bench-scale reactors to bubble column slurry reactors. The results of this scale-up effort are the subject of this report.

3. PROCESS DEVELOPMENT AND AFDU MODIFICATION

Under previous contracts with DOE, Air Products and Chemicals, Inc. has operated a semi-works scale high pressure bubble column reactor at DOE's AFDU in LaPorte, Texas. This facility is capable of processing syngas of virtually any composition. Most recently, the plant demonstrated LPMEOH technology at a maximum production rate of 12 tons/day of MeOH.[7]

As part of the current contract with DOE, modifications have been made to the plant to facilitate the demonstration of DME in the slurry phase. Most notably, unit operations were added to allow product DME and co-product CO_2 to be removed from the reactor effluent (a refrigerated, partial condensation process was used).

3.1 PROCESS DESCRIPTION

A schematic of the AFDU flowsheet is shown in Figure 3.1-1. Hydrogen, CO, and CO_2 are blended and compressed, then mixed with recycle gas to form the desired syngas composition and flow. This reactor feed is preheated, then introduced to the bottom of the slurry reactor. The syngas flows upward through the slurry (catalyst-mix plus mineral oil) and is partially converted to products and by-products. The heat of reaction is absorbed by the oil and then rejected to an internal heat exchanger. The gross reactor effluent is passed through a cyclone to remove catalyst fines, then cooled to condense traces of slurry oil. The resultant vapor is considered to be the net reactor effluent and contains MeOH, DME, CO_2, H_2O, and unreacted reactor feed. This stream is subsequently chilled against cooling water, and introduced to a separator where the bulk of the MeOH and any water is recovered as a liquid. The remaining vapor portion is cooled in a series of heat recovery and refrigerant exchangers, then directed to a second separator where DME and a portion of CO_2 is removed as liquid. The vapor from this separator is rewarmed, compressed, and recycled to the front-end. The DME-bearing liquid is flashed to a lower pressure and vaporized to reject CO_2 and partially concentrate the DME.

Flows and composition are measured at various strategic points in the process (indicated in Figure 3.1-1 by "F, X"). The two key points are reactor feed and reactor effluent. The additional process points are measured to provide information which can be used to resolve the material balance.

The centerpiece of the plant is the reactor (see Figure 3.1-2). The reactor is approximately 28 ft tall and can accommodate 20 ft of slurry; the internal diameter is 22.5 inches. A nuclear density gauge (NDG) is used to determine level and measure vapor holdup. Scans of the reactor are made at predetermined positions, as indicated. The reactor is equipped with an internal heat exchanger which maintains reactor temperature.

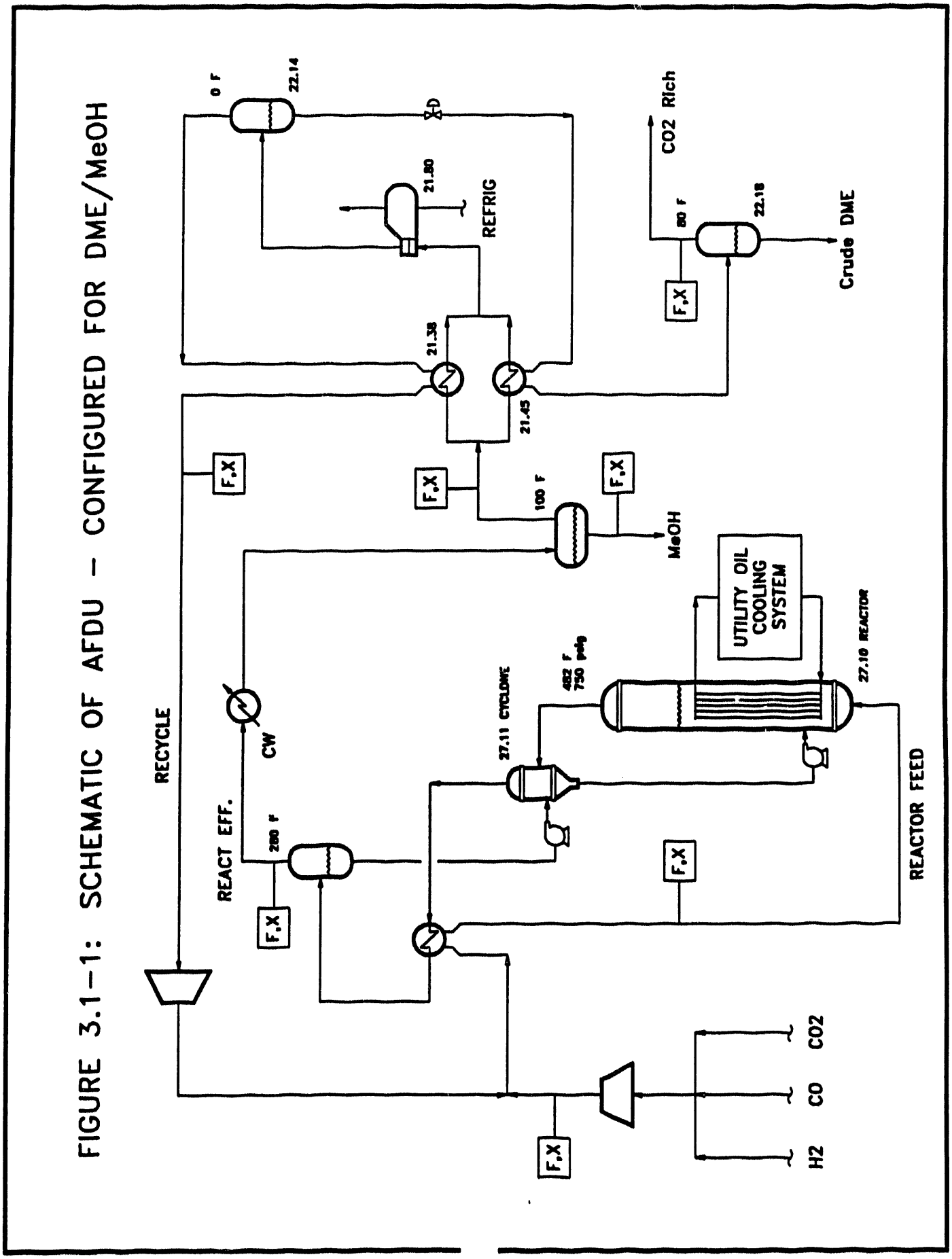
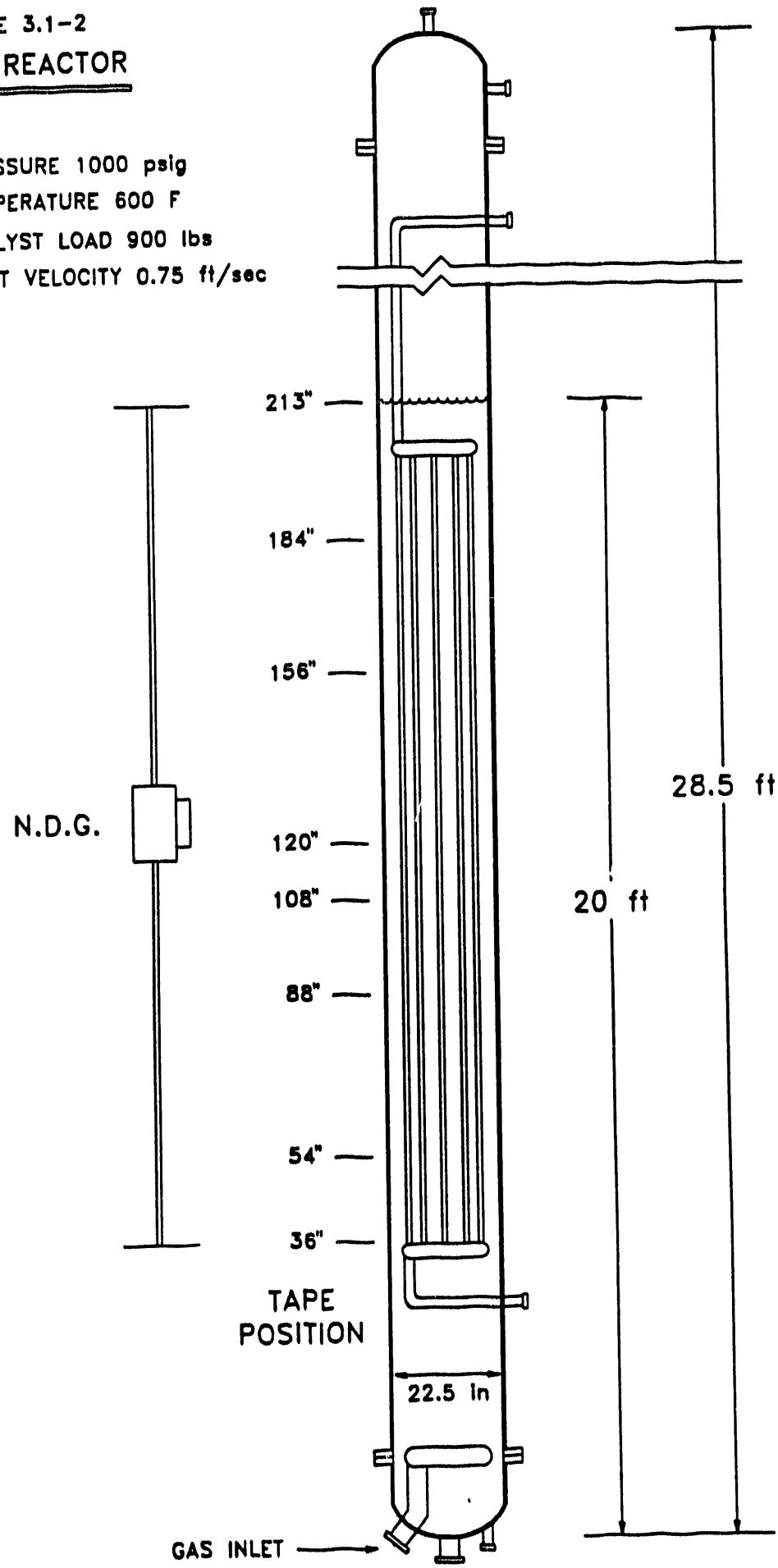


FIGURE 3.1-1: SCHEMATIC OF AFDU - CONFIGURED FOR DME/MeOH
0 F
22.14
21.80
REFRIG
CO2 Rich
80 F
22.18
Crude DME
F,X
21.38
21.45
100 F
MeOH
RECYCLE
CW
REACT EFF.
280 F
27.11 CYCLONE
452 F
750 psig
UTILITY OIL
COOLING
SYSTEM
27.10 REACTOR
REACTOR FEED
CO2
CO
H2

FIGURE 3.1-2

27.10 REACTOR

MAXIMUM PRESSURE 1000 psig
MAXIMUM TEMPERATURE 600 F
TYPICAL CATALYST LOAD 900 lbs
MAXIMUM INLET VELOCITY 0.75 ft/sec



3.2 PROJECT EXECUTION

The plant, as it existed to demonstrate LPMEOH technology, had no capability to remove CO_2 or DME from the reactor effluent. As a result, new and modified equipment was designed and installed. A list of the major items added is summarized below:

ITEM	TYPE OF EQUIPMENT	STATUS	DESIGN P (psig) shell	tube
21.38	Shell & Tube Exchanger	reactivated	1000	1000
21.45 A&B	Hairpin Exchangers	new	1000	1000
21.80	Kettle Evaporator	new	667	1000
22.14	High Pressure Separator	modified	1000	n/a
22.18	Low Pressure Separator	modified	1000	n/a
28.40	DME Storage Tank	new	250	n/a

The 21.38 was an existing exchanger which had been previously out of service. The 22.14 and 22.18 were used in 1983 as catalyst guard beds and had been removed from the unit. These two vessels were modified to accommodate feed nozzles and liquid level instrumentation.

The 21.45 A&B hairpin exchangers and the 21.80 evaporator were purchased under the current contract. The 21.80 evaporator was designed to utilize an existing liquid CO_2 supply to provide refrigeration but also be capable of handling low-pressure freon or propane as a refrigerant in the future. Finally, the 28.40 storage tank was purchased to temporarily store any DME which would be produced during the subsequent operation.

The initial flowsheet development and major equipment sizing was performed under a previous contract.[8] The detailed flowsheet development and piping, valve, and instrumentation design were carried out under the current contract.

The instrumentation and piping associated with the new/modified equipment is not itemized here but is displayed in the detailed process flow diagram (PFD) in Figure 3.2-1 (essentially, all valves and instrumentation on the right half of the PFD are new).

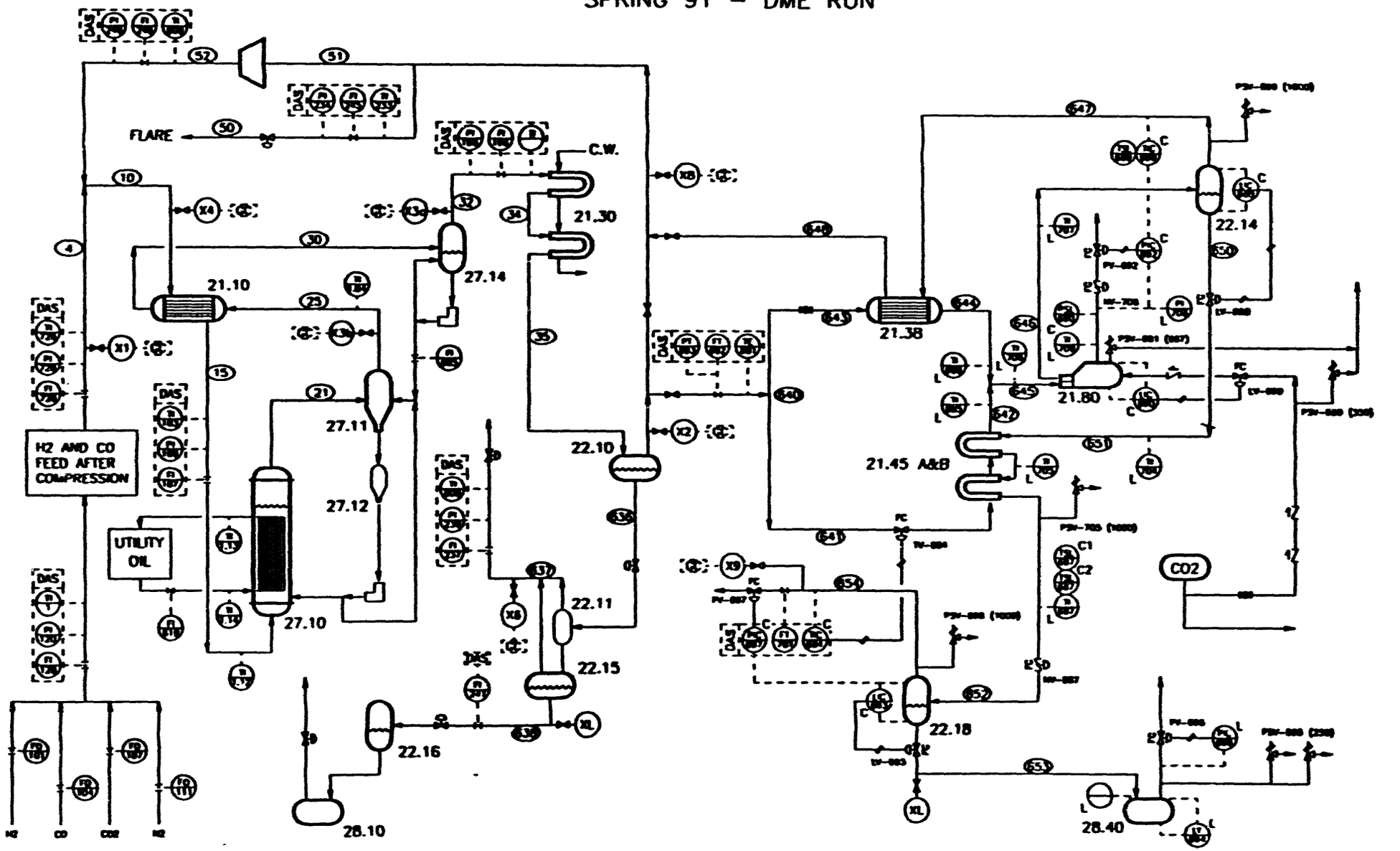
The majority of the design and procurement effort was completed by January 1991. In February, the final flowsheet review, called the Design Verification Review (DVR), was completed. The documentation of this review meeting provides a good summary of the potential hazards which were identified and the steps that were required to address them. The DVR document has been attached as Appendix A.

On-site construction began in January 1991. By early April, the new equipment and instrumentation had been installed. The final plant check-out was completed in April along with the reactivation of the data acquisition computers and the analytical devices.

FIGURE 3.2-1

ALT. FUELS DEVELOPMENT UNIT

SPRING 91 – DME RUN



4. DEMONSTRATION AT THE AFDU

Operations were carried out at the LaPorte facility between 29 April and 17 May 1991 to demonstrate the coproduction of DME and MeOH in a slurry reactor. The approach was to blend in dehydration catalyst (alumina) with the MeOH catalyst to produce DME and thereby drive the equilibrium-limited MeOH reaction farther forward, resulting in higher syngas conversion.

Daily reports were issued during the course of the run. A reproduction of the run chronology is attached as Appendix B. Highlights of the five major tasks are presented here:

- Calibrate instruments, recommission the data computer, check for system cleanliness (Shakedown)
- Activate MeOH catalyst (Run AF-A1)
- Baseline MeOH production with BASF S3-86 catalyst (Run AF-R1)
- MeOH/DME production with 93.4% MeOH catalyst and 6.6% dehydration catalyst, Catapal γ-alumina (Run AF-R2)
- MeOH/DME production with 80.7% MeOH catalyst and 19.3% dehydration catalyst (Run AF-R3)

4.1 SHAKEDOWN

Because the facility was inactive during the previous two years, all instrumentation was fully recalibrated. In addition, the Gas Chromatographs (GCs) and data acquisition computer were reactivated. Some of the electronic equipment associated with the data computer was replaced.

The nuclear density gauge used to determine liquid level and vapor holdup in the reactor was calibrated on 25 and 29 April. The initial calibration was suspect, so a recalibration was also performed following the run on 20 May. Details of the calibration effort are found in Appendix C.

As an integral part of shakedown activities, syngas is circulated through the plant to remove iron and nickel carbonyls, known MeOH catalyst poisons. Analysis of the syngas was performed to detect carbonyls as well as chlorides and sulfides. Documentation of these analyses is attached as Appendix D. To summarize the findings—all poison levels were quite low.

4.2 CATALYST ACTIVATION

The activation of the MeOH catalyst was undertaken using dilute syngas (3.5 vol% in N_2). This operation, referred to as Run AF-A1, was developed in work completed under a previous DOE contract (DE-AC22-87PC90005).[7] Total specific uptake of H_2 + CO (SCF/lb catalyst) was lower than expectations (based on total contained copper-oxide in the catalyst) but the subsequently high catalyst productivity met that of laboratory catalysts, so activation was undoubtedly successful. Improved measurements of the low flow of H_2 and CO used during activation are required. Details of the activation can be found in Appendix E.

4.3 SYNGAS CONVERSION DEMONSTRATIONS

There were two major objectives for the run: 1) demonstrate the concept of enhanced syngas conversion, and 2) map system performance with variation in catalyst proportion.

Although there were a large number of independent process variables open for investigation, it was elected to fix feed composition, reactor temperature and pressure, and total catalyst load. Catalyst proportion (ratio), superficial inlet velocity, and slurry level were allowed to vary.

Fixed Process Variables

A Texaco-type reactor feed was used throughout: 35% H_2, 51% CO, 13% CO_2, and 1% N_2. This gas simulates the once-through operation that was used extensively in previous LPMEOH work. While operating in the DME-mode, some DME survived in the recycled gas and showed up in the reactor feed (approximately 1%). To compensate, the CO_2 content in the feed gas was reduced.

Throughout the run, the reactor was maintained at 482°F and 750 psig. The total catalyst charge was intended to be constant but, in fact, varied between 450 and 485 lbs.

Adjustable Process Variables

Three catalyst proportions were examined: 0, 6.6, and 19.3 wt% alumina. The 0% case served to establish the baseline performance of the MeOH catalyst. The 6.6 and 19.3% cases represent methanol-rich and DME-rich production modes.

At each catalyst proportion, two inlet gas velocities were studied: 0.24 and 0.37 ft/sec. This translates into space velocities of 5,700 and 9,100 sl/kg-hr (nominal). The reactor level was maintained at 75 or 100% of maximum.

Run Conditions

Ten process conditions were investigated during this demonstration as shown in Table 4.3-1.

TABLE 4.3-1
PROCESS CONDITIONS/DESIGNATIONS

RUN #	Wt% Dehydration Catalyst	Space Velocity (sl/kg-hr)	Slurry Level (%)
AF-R1.1	0.0	5,700	75
AF-R1.2	0.0	8,900	100
AF-R1.3	0.0	9,100	81 - 70
AF-R2.1	6.6	5,400	100
AF-R2.2	6.6	8,800	100
AF-R2.3	6.6	5,500	75
AF-R2.4	6.6	9,000	87 - 79
AF-R3.1	19.3	5,900	100
AF-R3.2	19.3	9,500	100
AF-R3.3	19.3	5,900	75

AF-R1 Operations

Following the MeOH catalyst activation, syngas rates were increased to the conditions corresponding to Run AF-R1.1. Initially, there appeared to be a temperature stratification in the reactor (the bottom was 8°F hotter than the top). The temperature stratification persisted, so rates were increased to a point midway between R1.1 and R1.2. The temperature stratification was reduced significantly as mixing improved, provided by the increased gas velocity. This intermediate condition held and by 07:00 on 2 May, the plant had lined-out sufficiently so that a 4-hour period of data collection was undertaken. The productivity of the MeOH catalyst was determined to be about 30 gmoles/hr-kg catalyst (oxide); the corresponding autoclave condition would result in a productivity of 25. The high productivity experienced during this period was due to a number of factors, the two most important being the inherent "hyperactivity" of fresh catalyst and the fact that the AFDU reactor behaves as multiple Continuous Stirred Tank Reactors (CSTRs) in series. At this point it was concluded that the catalyst activation had been successful and operations could continue.

Still concerned that the slurry was not completely homogenized, the rates were further increased to the R1.2 condition. This state was maintained while hyperactivity declined and productivity stabilized. By 03:00 on 3 May the MeOH production had stabilized and the first data collection period began. The reactor slurry level was at 100%.

At 13:00 on 5 May the R1.2 data period was entered and rates were reduced to the R1.1 condition. As a consequence of this lower gas velocity, the slurry level dropped to 75%. The plant quickly lined-out at the new condition and the R1.1 data collection period began at 21:00 on 5 May.

At 17:00 on 6 May the R1.1 data period ended and the rates were increased to correspond to R1.2 (slurry level was at approximately 100%). The primary objective at this point was to thicken the slurry by driving oil out of the reactor (at higher gas throughput the oil loss is increased). By 07:30 on 7 May the slurry level had fallen to 70%. Though the level had continued to decline, MeOH productivity was stable and

a supplemental data period, R1.3, was recorded. Methanol productivity for R1.2 and R1.3 was virtually identical, which indicated no loss of activity with time-on-stream. This point marked the end of the AF-R1 series of operations.

Nearly 10,000 gallons of MeOH product were collected during this campaign. Approximately 7,000 gallons of "typical LaPorte MeOH" were loaded on a trailer and sent to off-site storage.

The composition of the MeOH product was measured every 12 hours and was steady throughout operations. Individual measurements can be found in Table F1 in Appendix F. The average composition is reported below:

Component	Concentration (wt%)
methanol	96.800
ethanol	0.645
propanols	0.244
butanols	0.176
pentanols	0.132
methyl formate	1.084
methyl acetate	0.159
dimethyl ether	0.030
water	0.504
mineral oil	0.226

AF-R2 Operations

While AF-R1 operations were underway, alumina had been charged to the prep tank and heated in oil under N_2 purge to drive off water. When R1 operations were completed and the reactor had been cooled to 250°F, a portion of reactor slurry was withdrawn into a drum (designated drum S1). The remainder of the reactor slurry was transferred into the prep tank and mixed with the (now dry) alumina slurry. After several hours of agitation the prep tank slurry was transferred back to the reactor.

The quantity of oil used to slurry and dry the alumina was greater than that driven-off during the thickening procedure and that drained into drum S1. Therefore, further heating under N_2 flow was required to vaporize the excess oil.

At 11:00 on 8 May the plant was back at pressure and under syngas. The first data period, AF-R2.1, began at 00:00 on 9 May and was completed at 17:00 on 9 May. The selectivity towards DME declined somewhat during this period. The rates were then increased and at 09:00 on 10 May the R2.2 data period began. Production and selectivity were stable during this data period. Productivity towards DME was as expected, while that towards MeOH was greater than anticipated. The molar selectivity, DME/MeOH, was 1/2.9. Equivalent productivity exceeded that of MeOH-only by 24%.

At 12:00 on 11 May the R2.2 data period ended and rates were reduced to the R2.3 condition (a R2.1 repeat). Once again productivity and selectivity were steady. Also as before, productivity towards DME was as expected, while that towards MeOH was greater than anticipated. The molar selectivity, DME/MeOH, had increased to 1/1.8. Equivalent productivity exceeded that of MeOH-only by 11%.

At 16:00 on 12 May the R2.3 data period ended and rates were increased to the R2.2 condition. The primary objective was to thicken the slurry as was done previously. Conditions were stable even though slurry level was falling, so an additional data period, R2.4, was recorded. The results were virtually identical to those recorded during R2.2.

The redundant data points allowed for a check on performance degradation with time on stream—there was none.

AF-R3 Operations

While the AF-R2 operations were winding down, more alumina had been charged to the prep tank and heated in oil under nitrogen purge to drive off water. When the R2 operations were completed and the reactor had been cooled to 250°F, a portion of reactor slurry was withdrawn into a second drum (designated drum S2). The remainder of the reactor slurry was transferred into the prep tank and mixed with the (now dry) alumina slurry. After several hours of agitation the prep tank slurry was transferred back to the reactor.

This time it was not necessary to drive off excess oil and operation under syngas was quickly established. At 00:00 on 14 May the data period for Run R3.1 began. During this period DME selectivity declined as experienced during Run R2.1. Given the quantity of catalyst that should have been in the reactor, overall productivity fell short of expectations. The reason for this observation became clear following the run.

Post-run inspection of the reactor revealed that some catalyst had settled in the bottom head (below the inlet gas sparger). It has been postulated that this catalyst settled because the inlet gas velocities were relatively low compared to those used in previous demonstrations. Furthermore, it is expected that much of this catalyst settled out early on in the last run condition and did not participate in the reaction. Elemental analysis of this material showed it to be high in alumina, which supports the theory that settling occurred during R3 operations and not during previous campaigns. (Refer to Appendix F for a detailed discussion of the catalyst inventory calculations.) These calculations indicate that about 9% of the reactor catalyst had settled out. This "loss" of catalyst resulted in an increased space velocity (in reality).

Given the understanding that space velocities were now higher, productivity during R3.1 was in line with expectations. Productivity towards DME was as expected, while that towards MeOH was slightly greater than anticipated. The molar selectivity, DME/MeOH, was 2.6/1. Equivalent productivity exceeded that of MeOH-only by well over 30%.

At 16:00 on 14 May the R3.1 data period ended and the rates were increased. The reactor level had been at 100% during the previous run, so rates had to be increased gradually while oil was allowed to boil off. At 06:00 on 15 May the higher rates had been attained, the plant was operating steadily, and the R3.2 data period began. Productivity towards DME was slightly less than expected, while that towards MeOH was as anticipated. The molar selectivity, DME/MeOH, was 1.2/1. Equivalent productivity was virtually the same as that of MeOH-only.

At 08:00 on 16 May the R3.2 data period had concluded and rates were quickly dropped to those required for R3.3 (R3.1 repeat). At 12:00 on 16 May the R3.3 data period began and concluded at 09:00 on 17 May. Productivity towards DME was a little less than expected and had declined from R3.1; productivity towards MeOH was as expected. The molar selectivity, DME/MeOH, had fallen to 1.8/1, and equivalent productivity exceeded that of MeOH-only by over 28%.

The reactor level during R3.3 was 75% while that of R3.1 was 100%. There had been concern that the reduction in productivity between these two runs was a consequence of operating at the lower level (one might view this as a reduction in the number of effective CSTRs). To address this issue the reactor level was increased to 100% at the end of R3.3, and between 10:00 and 14:00 on 17 May plant operation was monitored. There was no significant change in the composition of the reactor effluent. It was concluded from this observation that the difference between R3.1 and R3.3 was not a consequence of operating at the reduced level.

At 14:00 on 17 May operations concluded and plant shutdown began.

4.4 RESULTS

The detailed material balance for each operating case is contained in Appendix G. These material balances contain compositions and flows at selected points in the plant—the two most important being the reactor-feed and reactor-out. Also included in these tables are elemental and molar balances at key process locations.

On average, the overall plant elemental balance closed to within 1.5%, which is quite good. The material closure of DME was excellent—the DME reportedly produced in the reactor agreed with the DME measured in the plant exit streams to within 0.2% on average. The material closure of MeOH was less outstanding but averaged 3.1%. The lack of closure with methanol suggests some inaccuracies in measured flow and compositions. One may view this lack of closure as representing uncertainty in the catalyst productivity, which averaged only 1.9% when DME and MeOH were considered together.

A summary of the material balance results from Appendix G is presented in Table 4.4-1. Most of the information is self explanatory (refer to the nomenclature section of Appendix G for definitions). Some items will be expanded upon here. The items referring to production, productivity, and conversion are based on what is happening across the reactor. For example, DME and MeOH "Makes" do not reflect losses in the purge gases and the like. Also note that the slurry concentrations varied between 25 wt% and 37 wt% catalyst, depending on the run. Based on previous experience with the unit, the variation in catalyst concentration within this range is not expected to affect productivity by introducing a "mass transfer resistance".

Finally, it should be noted that DME was contained in the feed to the reactor. This was expected since the "cold-end" was not designed to fully remove DME. As expected, the presence of DME in the feed gas reduces the reactor productivity. One should consider this if a direct scale-up of the data is attempted.

Plots of the MeOH and DME concentrations in the reactor effluent are attached as Figures F2 (AF-R1), F3 (AF-R2), and F4 (AF-R3) in Appendix F. These figures show that the measured DME and MeOH concentrations were fairly steady, though subject to some fluctuations. Also contained in Appendix F are measured liquid compositions (Tables F1, F2, F3), measured vapor composition of the flash gas (Table F4), measured vapor composition of the DME purge gas (Table F5), and measured liquid production in the day tank (Figure F5).

TABLE 4.4-1

SUMMARY OF RESULTS

Run Number	AF-R1.1	AF-R1.2	AF-R1.3	AF-R2.1	AF-R2.2	AF-R2.3	AF-R2.4	AF-R3.1	AF-R3.2	AF-R3.3
Balance Period										
Start Date	5/5 20:00	5/3 3:00	5/6 21:00	5/9 0:00	5/10 9:00	5/11 16:00	5/12 20:00	5/14 0:00	5/15 6:00	5/16 12:00
End date	5/6 17:00	5/5 13:00	5/7 6:00	5/9 17:00	5/11 12:00	5/12 16:00	5/13 4:00	5/14 16:00	5/16 8:00	5/17 9:00
Time on Stream	108 to 129	43 to 101	133 to 142	184 to 201	217 to 244	248 to 272	276 to 284	304 to 320	334 to 360	364 to 385
Temperature (°F)	480	480	481	481	481	481	481	482	482	482
Pressure (psig)	750	750	751	751	750	751	750	750	752	752
Space Velocity (sL/hr-kg oxide)	5711	8866	9137	5409	8817	5503	8986	5934	9445	5951
Catalyst Proportion (% Al2O3)	0.0	0.0	0.0	6.6	6.6	6.6	6.6	19.3	19.3	19.3
Reactor Level (inches on Tape)	154	210	170 to 140	210	210	153	182 to 162	210	213	156
Catalyst Weight (lb)	479.40	479.40	479.40	484.60	484.60	484.60	484.60	449.30	449.30	449.30
Slurry Concentration (wt %)	30.7	30.3	34.2 to 37.0	n/a	30.0	30.0	32.4 to 34.3	24.8	28.3	29.5
Inlet Superficial Velocity (ft/sec)	0.24	0.37	0.38	0.23	0.37	0.23	0.38	0.23	0.37	0.23
Outlet Superficial Velocity (ft/sec)	0.20	0.31	0.32	0.18	0.30	0.18	0.31	0.18	0.31	0.19
Gas Holdup (vol %)	33.2	47.7	46.9 to 44.7	n/a	46.4	31.1	45.3 to 43.8	35.1	46.0	31.8
CO Conversion (%)	18.1	16.8	16.4	28.6	21.7	26.8	20.9	31.0	20.6	28.2
Syngas Conversion (%)	31.4	29.0	28.2	39.0	31.7	37.6	30.8	38.6	26.8	35.7
Eq. Productivity (gmoles/hr-kg)	21.77	32.02	33.01	27.11	36.06	26.37	35.69	29.99	33.37	27.86
MeOH Make (Ton/day)	4.01	5.90	6.08	2.08	3.95	2.30	4.04	0.84	1.73	1.04
DME Make (Ton/day)	0.00	0.00	0.00	2.13	1.98	1.87	1.87	3.12	2.90	2.71
Reactor Inlet Composition (mole%)										
Hydrogen	35.50	35.35	34.65	35.38	35.52	35.03	35.66	35.60	35.91	35.76
Carbon Monoxide	50.80	50.83	51.02	51.35	51.18	51.63	51.64	51.39	50.68	51.19
Carbon Dioxide	13.13	12.93	13.33	11.51	11.42	11.75	10.92	11.08	11.35	11.45
Nitrogen + Methane	0.57	0.71	0.83	0.68	0.64	0.55	0.57	0.80	0.51	0.43
Methanol	0.00	0.16	0.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dimethyl Ether	0.00	0.00	0.00	1.07	1.23	1.06	1.22	1.12	1.54	1.14
Reactor Outlet Composition (mole%)										
Hydrogen	21.53	22.65	22.40	20.92	23.40	20.79	23.78	23.08	27.30	24.12
Carbon Monoxide	50.77	50.71	50.71	47.30	49.03	48.22	49.78	45.58	47.56	46.23
Carbon Dioxide	16.34	15.67	15.88	19.05	16.19	18.71	15.46	19.99	16.34	19.31
Nitrogen + Methane	0.68	0.85	0.98	0.92	0.78	0.67	0.69	1.11	0.51	0.57
Water	0.08	0.10	0.10	0.14	0.14	0.13	0.04	0.30	0.29	0.29
Methanol	10.42	9.89	9.81	5.96	6.59	6.42	6.58	2.35	2.81	2.84
Other Oxygenates	0.19	0.14	0.12	0.07	0.06	0.07	0.06	0.06	0.01	0.02
Dimethyl Ether	0.00	0.00	0.00	5.64	3.81	4.99	3.61	7.54	5.09	6.61

The first campaign (AF-R1) established the base-line productivity of the methanol catalyst. This series of operations also served as a means of training the new personnel in plant operation and data acquisition. Catalyst productivity, although only modestly sensitive to catalyst activity at these space velocities, was as expected. The operation of the plant was really no different than previous operations.[7]

The second campaign (AF-R2) demonstrated the concept of the enhanced syngas conversion which results by adding a relatively small quantity of dehydration catalyst to the methanol catalyst. At equivalent space velocity, productivity increased by 22% (lower space velocity) and 11% (higher space velocity) by replacing approximately 7% of the methanol catalyst with dehydration catalyst. Equivalent productivity was on-target although the selectivity towards MeOH was higher than expected. Even though the run time was only 88 hours, there was no indication of catalyst deactivation at this level of dehydration catalyst loading.

The final campaign (AF-R3) was to demonstrate a higher level of DME make. At low space velocity the improvement in productivity is about 32%, however, at the higher equivalent space velocity, productivity was about the same as all-MeOH. The operation at roughly 20% dehydration catalyst fell short of expectations in two areas. First, the selectivity towards DME was less than expected and declined with time-on-stream. Second, the catalyst settling was totally unexpected and could not have been anticipated from results in the mechanically stirred autoclaves. There is also some indication of catalyst deactivation, which was expected from previous laboratory work.[9]

The trends observed with respect to dehydration catalyst loading were as expected. Increasing the relative amount of dehydration catalyst initially increases the overall productivity by removing methanol from the system and thereby eliminating the equilibrium constraint of the syngas-to-methanol reaction step. However, the productivity gain diminishes if the concentration of dehydration catalyst is increased beyond a certain level. This is illustrated in Figures 4.4-1 and 4.4-2. These figures compare the individual productivities as a function of alumina content at the lower (4.4-1) and higher (4.4-2) space velocities. In each plot a prediction of performance is shown to illustrate expected productivity. Expected performance was calculated at a representative space velocity using a kinetic model (this model was based on the laboratory autoclave data and assumes the LaPorte reactor acts as 2 CSTRs in series, an assumption based on previous experience).[7]

Figures 4.4-1 and 4.4-2 aptly summarize the results of the entire operation and demonstrate that the laboratory work can be successfully scaled-up. Even though the selectivity and productivity were not *exactly* as predicted, they were close enough that in-the-field modifications could be effective. In particular, the selectivity towards DME could be easily adjusted by making slight changes to the relative proportion of dehydration catalyst.

Gas holdup data are presented in Figure 4.4-3 and compared with predictive curves derived from previous LPMEOH experience. The predictive curves are fits of holdup data taken previously for MeOH-only.[7,10] It is observed that the holdup at 0.3 ft/sec linear velocity agrees well with prediction while at the lower velocity the holdup is slightly lower. It is interesting to note that there is no discernible change in holdup with the different alumina proportions.

FIGURE 4.4-1

PRODUCTIVITIES IN BUBBLE COLUMN AT SV=5700 sL/kg-hr

(Texaco Gas, 482 F, 750 psig. Solid lines are predictions)

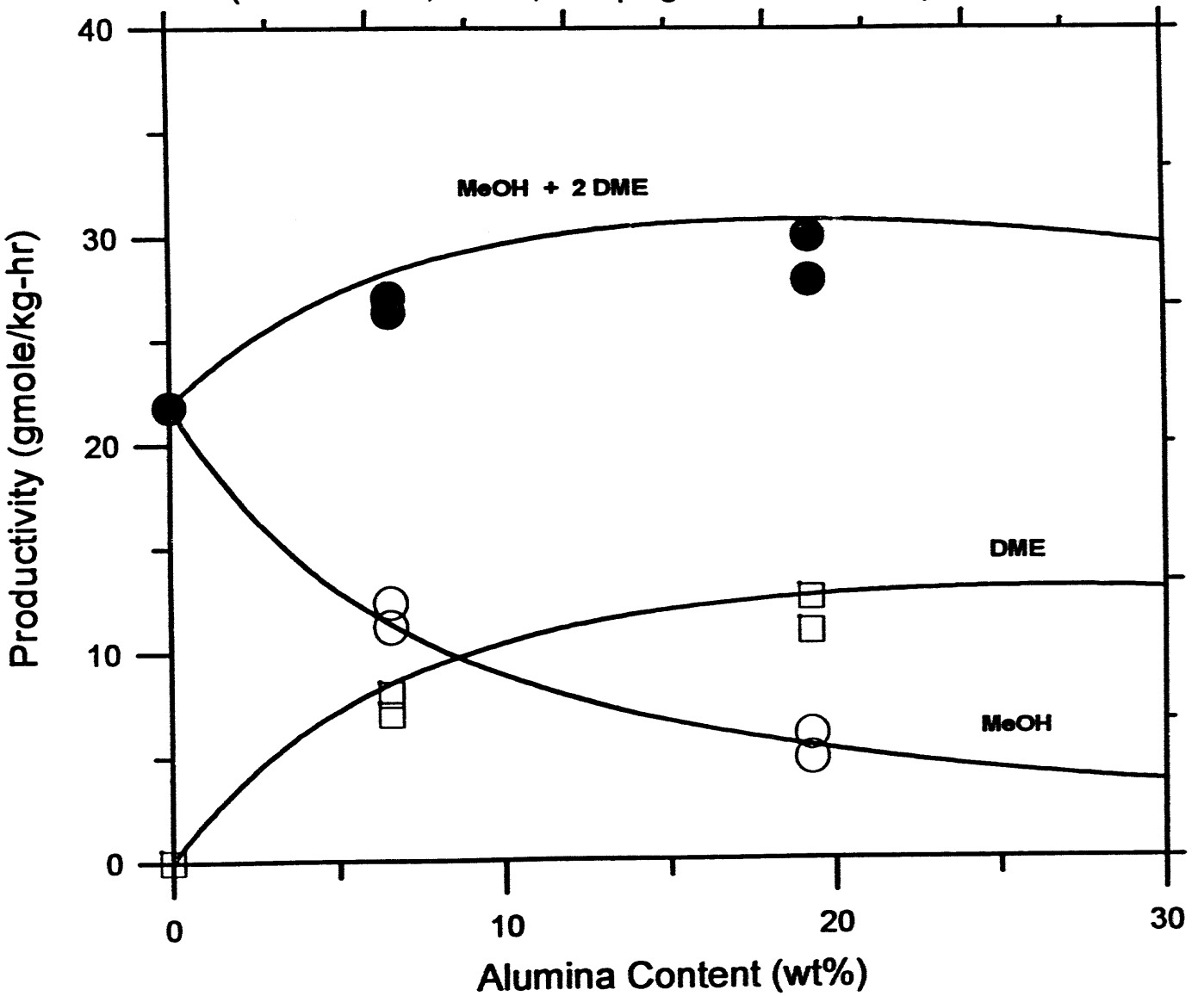


FIGURE 4.4-2

PRODUCTIVITIES IN BUBBLE COLUMN AT SV=9100 sL/kg-hr

(Texaco Gas, 482 F, 750 psig. Solid lines are predictions)

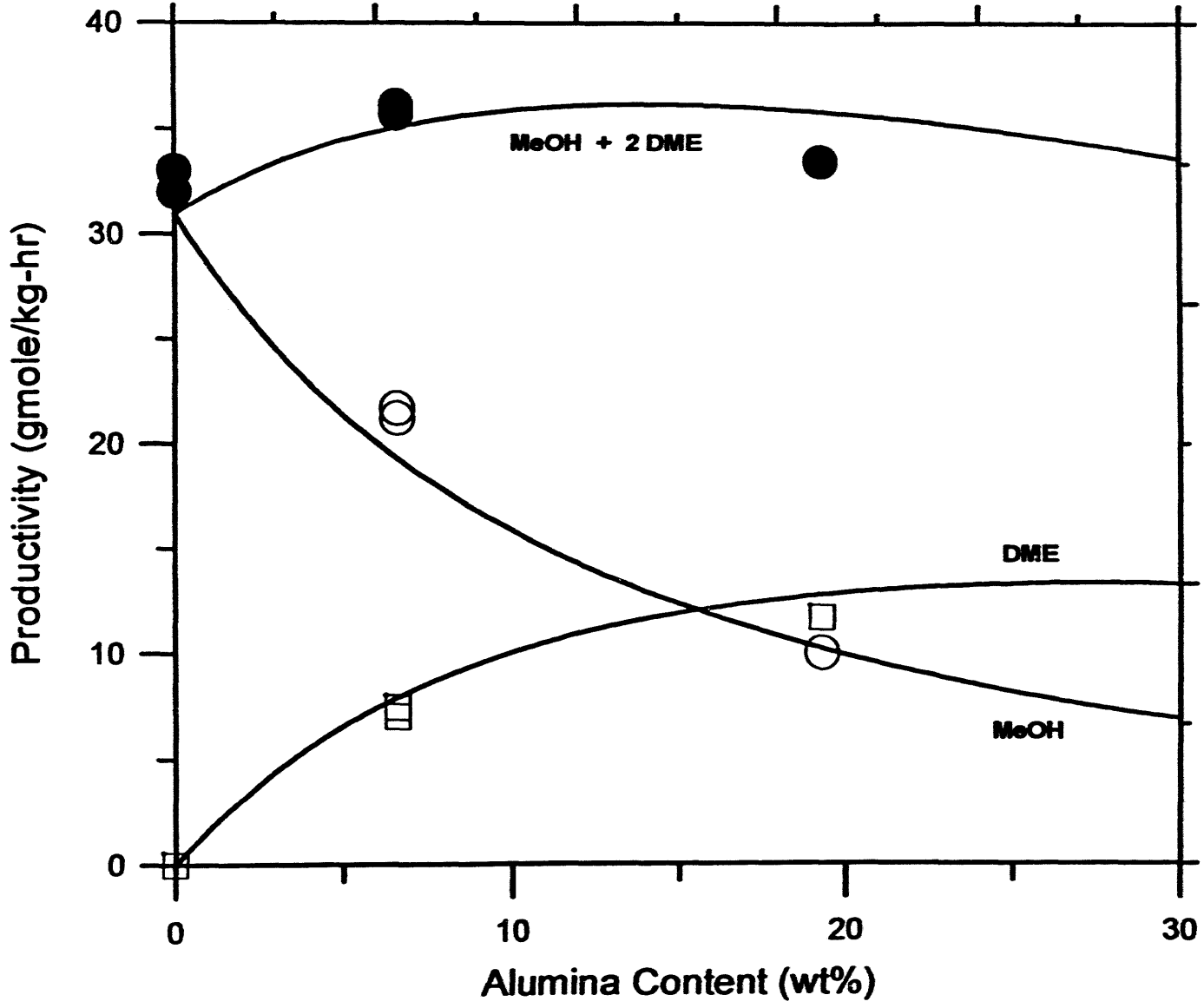
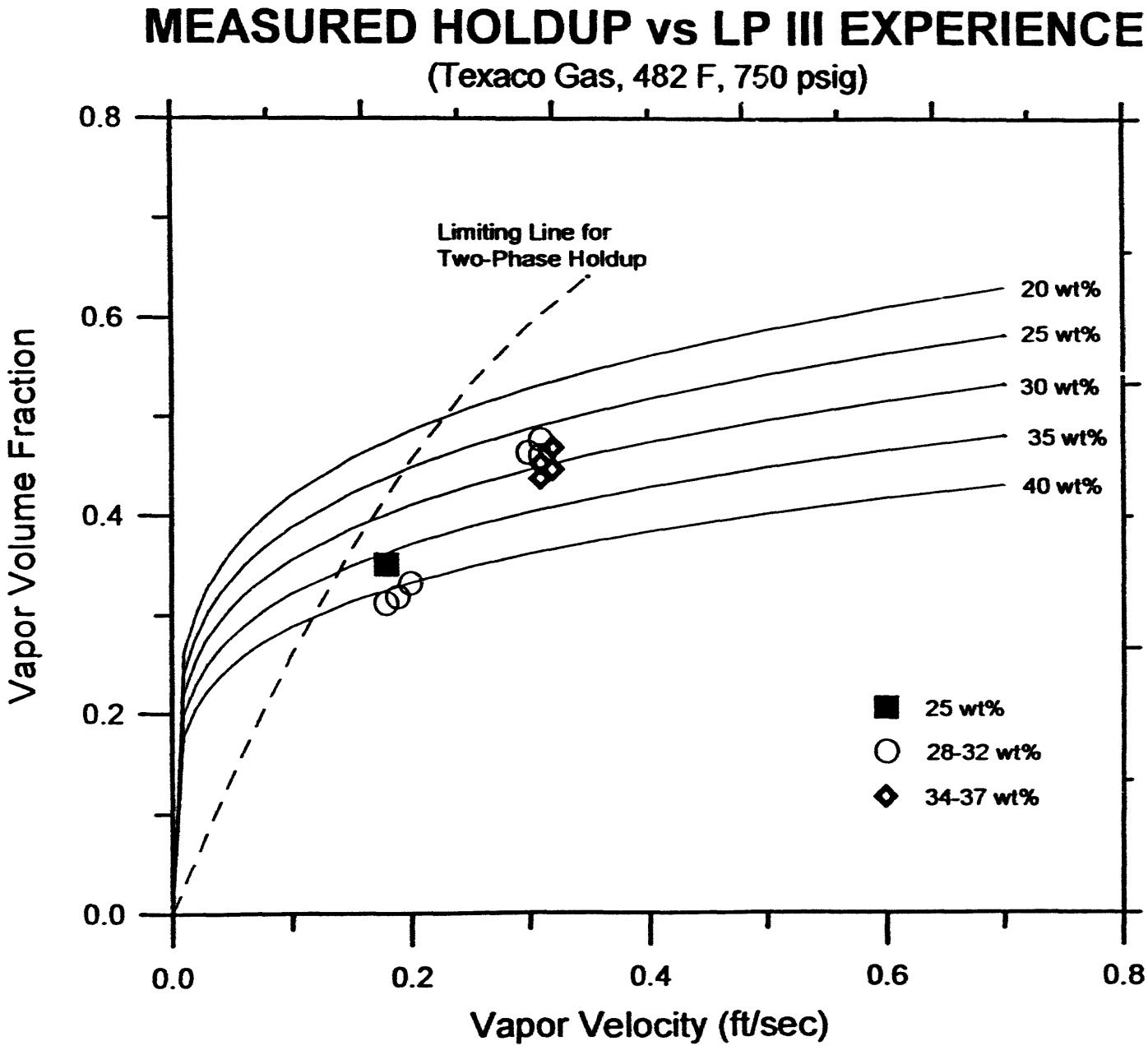


FIGURE 4.4-3


MEASURED HOLDUP vs LP III EXPERIENCE
(Texaco Gas, 482 F, 750 psig)
Limiting Line for
Two-Phase Holdup
20 wt%
25 wt%
30 wt%
35 wt%
40 wt%
25 wt%
28-32 wt%
34-37 wt%
Vapor Volume Fraction
Vapor Velocity (ft/sec)
0.0
0.2
0.4
0.6
0.8

5. CONCLUSIONS AND RECOMMENDATIONS

Overall, this demonstration went according to plan and met objectives.

- Under mixed DME/MeOH synthesis conditions, syngas conversions greater than 30% over all-MeOH were achieved (syngas conversions 1.3 times that obtained for all-MeOH).

- Water-gas shift activity appeared to be greater than expected (based on laboratory work).[9] This is commercially significant since downstream water handling may be downsized and/or simplified. In addition, the quality of the coproduced methanol product was better than anticipated.

- The newly-installed CO_2/DME removal unit was more effective than predicted and was easy to operate.

- Over 15,000 gallons of MeOH product were collected. Roughly 7,000 gallons of "typical AFDU methanol" were collected and directed to a tank-trailer and sent off-site for storage; the remainder, which contained greater proportions of both DME and H_2O, was collected in the underground tank.

- During AF-R3.2 roughly 700 gallons of crude DME product were collected and will be held for future testing (estimated to be 74 wt% DME with the balance primarily CO_2 and H_2O). The bulk of DME produced during operations was burned in the flare.

An unexpected event was that some slurry settled in the bottom head of the reactor during the final run series. This settling was clearly unanticipated since operation at low gas velocity had been successfully carried out under the previous operations using 100% methanol catalyst. At present, it is felt that the low velocity through the gas sparger was responsible for the catalyst settling. To review, the gas sparger is doughnut shaped with holes on the underside. The sparger is currently positioned approximately 8" off the bottom of the reactor. Vapor exits the sparger and is directed diagonally downward to sweep slurry from the bottom head. The depth of vapor penetration is a function of gas flowrate; previous experience with this sparger indicted good performance at superficial gas velocities as low as 0.1 ft/sec. It is suspected that the addition of alumina caused the slurriability properties of the catalyst-mix to change such that the low gas velocity was insufficient to fully sweep the catalyst from the bottom head. One must therefore conclude that the current sparger orientation and operation is not entirely satisfactory for all types of catalyst slurries.

The future direction of many technology demonstrations at the AFDU will be towards lower space velocity. Chain building chemistries such as mixed-alcohols and Fischer-Tropsch are favored by low space velocity (high residence time). Associated with the low space velocity comes low superficial velocity (and low sparger velocity). Hence, modifications to the sparger system and its operation appear warranted since slurriability issues cannot always be definitively addressed before the actual demonstration.

Based on the success of this demonstration, and assuming that it is commercially attractive to coproduce DME and MeOH, it is worthwhile to carry out additional demonstrations at the LaPorte AFDU, such as:

- Operation at very low space velocity (1000 to 2000 sL/kg-hr). This would study high CO conversion as well as high selectivity to DME.

- Operation at higher catalyst loadings (35wt% to 50wt%) and low levels of dehydration catalyst (less than 10%). This would help identify the operational limits of the dual-catalyst system

6. REFERENCES

1. Air Products and Chemicals, Inc., "Synthesis of Dimethyl Ether and Alternative Fuels in the Liquid Phase from Coal-Derived Syngas", Final Report under DOE Contract # DE-AC22-90PC89865, 1993.

2. Moore, R. B., Brown, W. R., Klosek, J. and Brown, D. M., "Coproduction of Power and Methanol via CGCC and Liquid Phase Methanol Process", World Methanol Conference, December 5-7, 1989.

3. Karpuk, M. E. and Cowley, S. W., "On Board Dimethyl Ether Generation to Assist Methanol Engine Cold Starting", SAE Technical Paper Series 881678, presented in Int. Fuels and Lubricants Meeting and Exposition, Portland, Oregon, October 10-13, 1988.

4. Chang, C. D., "Hydrocarbons from Methanol", Catal. Rev. Sci. Eng., 25(1), pp 1-118, 1983.

5. Shikada, T., Fujimoto, K. and Tominaga, H., "Vapor-Phase Carbonylation of Dimethyl Ether and Methyl Acetate with Supported Transition Metal Catalysts", ACS Symposium series 328, D. R. Fahey ed., 1987.

6. Bhatt, B.L., Underwood, R.P., Hsiung, T.H., Herron, D.M., "Synthesis of Dimethyl Ether and Alternative Fuels in the Liquid Phase from Coal-Derived Syngas", DOE Indirect Liquefaction Contractors' Review Meeting, Pittsburgh, November 1990.

7. Air Products and Chemicals, Inc., "Liquid Phase Methanol LaPorte Process Development Unit: Modification, Operation, and Support Studies—Task 2.2: Process Variable Scan Run E-8 and In-Situ Activation with Syngas Run E-9", Topical Report, 1991.

8. Air Products and Chemicals, Inc., "Liquid Phase Methanol LaPorte Process Development Unit: Modification, Operation, and Support Studies", Final Report, 1991.

9. Air Products and Chemicals, Inc., "Synthesis of Dimethyl Ether and Alternative Fuels in the Liquid Phase from Coal-Derived Syngas—Task 2.2: Definition of Preferred Catalyst System; Task 2.3: Process Variable Scans on the Preferred Catalyst System; Task 2.4: Life Test on the Preferred Catalyst System", Topical Report under DOE Contract # DE-AC22-90PC89865, 1992.

10. Air Products and Chemicals, Inc., "Liquid Phase Methanol LaPorte Process Development Unit: Modification, Operation, and Support Studies—Task 2.0: Run E-5, Gas Hold-up and Equipment Evaluation Studies", Topical Report, 1991.

APPENDIX A : DESIGN VERIFICATION REVIEW REPORT

This document is provided to illustrate the types of operational hazards addressed during the engineering phase.

DESIGN VERIFICATION REVIEW (DVR)

Alternative Fuels Development Unit (AFDU)

Spring 1991 DME Run

LaPorte, Texas

14 February 1990

Review Team

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Design Verification Review (DVR)
Alternative Fuels Development Unit (AFDU)
Spring 1991 DME Run
LaPorte, Texas

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Appendices

Tables

References

1. Preliminary Process Hazards Review Report - March 1991 Run (DME), 16 October 1990.

2. Alternative Fuels Development Unit (AFDU) Engineering Flow Sheet No. ATT-1016, Rev. 1.

3. Liquid Phase Methanol Engineering Flow sheet No. 87-7-1533, Rev. 13.

I. INTRODUCTION

A Design Verification Review (DVR) meeting was conducted on 14 February 1991 for the Spring '91 DME (dimethyl ether) run of the Alternative Fuels Development Unit (AFDU) located in LaPorte, Texas. The Spring '91 run requires modifications and additions to the Liquid Phase Methanol Process Development Unit which are funded under the Alternative Fuels I contract. The objective of this run is to demonstrate higher conversion levels of snygas by coproducing dimethyl ether and methanol. Verification of R&D lab and simulation results is also desired.

The purpose of the DVR was to ensure that all items relating to the Preliminary Hazards review (PrHR) have been satisfactorily resolved and to review any additional safety concerns. The PrHR meeting was conducted on 16 October 1990. Due to this project's relatively short schedule, it was decided to not conduct a Design Hazards review meeting. The Hazards review process will be concluded with an on-site Operational Readiness Inspection (ORI) prior to start-up.

The DVR confirmed that a satisfactory review of most of the PrHR items has been performed. Those items requiring further review will be confirmed during the ORI. Furthermore, additional hazard items were reviewed and are documented in part III B. The matrix attendance to the ORI was discussed and a meeting will be conducted in approximately two weeks prior to the ORI to outline the ORI requirements.

II. Scope Changes and Process Modifications

There have been no significant scope changes or process modifications since the PrHR was conducted.

III. Status of Hazard Items

A. The following table (labeled III A., Status of PrHR Items) documents the status of the conclusions and recommendations that were developed during the Preliminary Hazards Review (PrHR).

B. Table III B., Additional Hazard Items, documents the results and status of additional hazard items identified following the PrHR.

III A. STATUS OF PrHR ITEMS

Hazard	Preliminary Hazards Review (PRHR) Recommendation/Follow-up	Design Verification Review (DVR) Status
1. Runaway reaction in the 27.10 reactor vessel caused by a loss of oil flow or fin fan in the utility oil loop.	Although the catalyst composition will be different from previous runs, it was determined that the existing high temperature shutdowns should provide sufficient protection. The appropriate high temperature shutdown set points on the existing switches need to be determined by Process Engineering but will probably be the same as was used for previous runs.	High temperature SD set points will be the same as those used in previous runs. The existing high temperature shutdowns will be calibrated and proof tested prior to the ORI.
✓ 2. Personnel exposure to the new alumina catalyst that will be used in the 27.10 reactor.	The existing procedures for catalyst reduction, handling of catalyst, and sampling will apply and should be utilized.	No further review was required.
3. Equipment or piping system corrosion or damage caused by material incompatibilities due to the presence of DME and larger quantities of CO_2 and water in the system downstream of 27.10 reactor. DME is a solvent.	Review material composition requirements of existing equipment, piping, gaskets, o-rings, etc.	A comprehensive review of existing plant machinery, piping systems, and valves was performed with the scope limited to the equipment that will be used during the DME run. The review was focused on identifying equipment that contain Viton, Buna-N, or neoprene materials in contact with the DME process stream. The Air Products technical manual on DME

Hazard	Preliminary Hazards Review (PRHR) Recommendation/Follow-up	Design Verification Review (DVR) Status
3. Continued		identifies these materials as being unacceptable with DME aerosol filling equipment and highlights Teflon and EPR o-rings as exhibiting acceptable performance. A list of questionable valves was developed (Table 1) and reviewed during the DVR meeting. The DVR recommendation is to not replace the subject valves due to the anticipated short DME production operating period (5 days) and the relatively low concentration of DME in the associated process streams (~2-10%). It was agreed that these valves will be periodically monitored for signs of leaks during the run and afterwards, disassembled and inspected for signs of deterioration from DME incompatibilities. The review of existing machinery is in progress and will be completed prior to the ORI. It was agreed to replace all DME process-side Viton, Buna-N, or neoprene seals during the machinery refurbishment process as long as an acceptable alternative material is readily available. The results will be reviewed during the ORI.

Hazard	Preliminary Hazards Review (PRHR) Recommendation/Follow-up	Design Verification Review (DVR) Status
3. Continued		A review of existing valve packing material resulted in the acceptance of existing materials which is either John Crane I87-1 asbestos or Grafoil.
4. Rupture of 22.10 separator vessel caused by deterioration of vessel walls from corrosion that may have occurred during previous operating runs. The vessel is carbon steel construction.	Measure the wall thickness of vessel to determine if any corrosion has taken place. Project Engineering will initiate.	The vessel will be internally visually inspected and dye penetrate tested for indications of corrosion. Further testing (i.e., ultrasonic) will be performed if the visual inspection indicates significant corrosion.
5. Improper disposal of methanol from the storage tank after the run is complete. The methanol composition will contain larger quantities of CO_2 and water and may include DME.	This is an environmental issue. Address the potential options for disposal of the methanol and determine if any new risks exist. Project Engineering will initiate.	A customer has been identified for the sale of the methanol. A market search is being performed for the sale of the DME product.

Hazard	Preliminary Hazards Review (PRHR) Recommendation/Follow-up	Design Verification Review (DVR) Status
6. An operability concern was identified with the recycle compressor and the potential for exposing its suction side to low temperatures due to a failure of the new CO_2 exchanger's (21.80) temperature control system.	Although this concern was not identified as a hazard, these follow-up items were recommended: a) Determine the need and appropriate set point for a low temperature alarm on the compressor's suction line. b) Review the compressor material compatibilities at low operating temperatures.	A low temperature alarm TAL-233 on the inlet to the 22.12 has been included in the design and will be installed to protect the compressor from exposure to temperatures below -20°F.
7. Carry over of alumina catalyst into equipment (new and existing) downstream of 27.10 reactor could cause a reaction.	Review the reactivity grid. Process Engineering	Process Engineering completed a reactivity review associated with the carry over of alumina and methanol catalyst (See Table 2). The temperature rise in downstream equipment is not expected to exceed design limits. Because the alumina catalyst in the reactor will be at nearly saturated conditions (w/ H_2O and CO_2), the additional heat effect is negligible.

Hazard	Preliminary Hazards Review (PRHR) Recommendation/Follow-up	Design Verification Review (DVR) Status
8. Damage or rupture of the 22.14 separator vessel caused by the presence of cold gas into the vessel as a result of a failure of the pressure control system on the CO_2 exchanger (21.80). The vessel is 1-1/4 Cr - 1/2 Mo construction.	A review of the temperature/ pressure capabilities of the equipment downstream needs to be performed considering the short duration of the proposed run. A low temperature protection system may have to be installed in accordance with results from previous fault trees developed for similar systems. In addition to the 22.14 vessel, other equipment located downstream (21.38, 22.18, DME storage tank) could be exposed to the low temperatures.	A fitness for services analysis of the 22.38, 22.14, and 22.18 vessels was performed and a conclusion reached stating that these vessels are satisfactory for both the expected and worst upset conditions (Reference Appendix A, 4 Dec. '90 memo from J. C. Tafuri). It was decided, however, to provide in the design redundant low temperature shutdown interlocks. A supplemental shutdown circuit (SD-1A) was added.
9. Liquid carry-over from the 22.18 separator vessel vent to downstream equipment due to a failure of the vessel's LIC.	The thermal effects of introducing liquid to the knockout pot which is located downstream of the vapor outlet nozzle on the 22.18 should be reviewed.	The equipment and piping located downstream of the 22.18 vent are of carbon steel construction. The minimum low temperature exposure as a result of a failure of the LIC-693 circuit was determined to be -13°F. As a result, it was agreed no further action is required. Additionally, it was noted that the time required to overfill the 22.18 would be at least 2-3 hrs.

Hazard	Preliminary Hazards Review (PRHR) Recommendation/Follow-up	Design Verification Review (DVR) Status
10. Equipment or piping overpressurization due to the presence of a different fluid composition. (The addition of DME.)	Review the sizing of existing relief devices and establish criteria for relief devices on new equipment. Process Engineering/ Start-Up	A comparison of vapor mole weights for MeOH and DME runs was performed and is attached as Table 3. Additionally, the adequacy of all affected existing relief devices was reviewed and all were determined acceptable (excluding the following) for the DME run (Table 4). Safety device PSE-628 was identified as requiring further review. Following the DVR, Process has reviewed the tube rupture case associated with PSE-628 and concluded the device is adequately sized. (Reference Appendix C) However, the associated forces (in the event of a rupture) in the piping system attached to PSE-628 have been identified as being significantly increased (approximately 70% greater). A stress engineering review of this system will be performed and modifications implemented as required prior to the plant start-up. The ORI will verify that proper action has been taken.

Hazard	Preliminary Hazards Review (PRHR) Recommendation/Follow-up	Design Verification Review (DVR) Status
11. Methanol storage tank fire.	The existing fire protection system should be adequate. The incremental DME levels in the methanol poses no additional fire risks that cannot be handled by existing equipment.	No further review was required.
12. DME storage tank fire (external) caused from a leak, overfill, or open drain valve.	Review the plant design layout with regard to the location of DME storage tank and methanol storage tank. Review the need for additional fire protection systems.	It was decided that the existing fire protection system (fire monitors) will sufficiently cover the DME storage tank. The tank is designed and located in accordance with the requirements of NFPA-58. The NFPA-58 requirements for installation and operation will be verified during the ORI.

III B. ADDITIONAL HAZARD ITEMS IDENTIFIED FOLLOWING THE PrHR

Hazard	Recommendation/Follow-up	Status
13. 21.80 Vent Stacks		
a) Exposure of personnel to hazardous levels of CO_2	a) The CO_2 release rates from the 21.80 vent stack during the DME recovery and no DME recovery cases need to be calculated. Additionally, the CO_2 vent stack discharge nozzle diameter and height above the top platform need to be established.	a) The CO_2 release rates for both operating cases were established and a dispersion analysis was conducted. The resulting vent stack recommendation calls for a 1" diameter discharge nozzle located 10' above the highest working platform. (Reference 3 Jan. '91 memo from G. A. Peters) Additionally, it was recommended that a heat collar be installed on the vent tip to prevent ice buildup.
b) Exposure of personnel to hazardous levels of flame radiation from the venting fluid (21.80 tube-rupture case)	b) The extent of personnel exposure to excessive heat levels should be estimated. Based on this finding and the vent sizing/height conclusions from part 13a, a recommendation should be made.	b) The flame radiation exposure review resulted in the same vent stack height recommendation as in hazard 13a. Additionally, it was suggested that personnel access to the top platform during the runs should be limited. ORI to confirm.
14. Failure or rupture of the purge nitrogen system due to inadequate protection.	A detailed review of the existing and new purge nitrogen systems needs to be performed to verify conformance with current APCI standards.	Start-up Engineering performed a detailed review of the purge nitrogen system and the areas requiring modification are detailed on the Rev. 13 P&ID (F/S 87-7-1533). These modifications will be made prior to the DME run.

Hazard	Recommendation/Follow-up	Status
15. High pressure process gas leakage from the new piping system SS10X3 (i.e., leaking flange) due to high temperate exposure - above 350°F - during a plant upset.	Include in the design a high temperature shutdown interlock in the SD-2 circuit protecting the piping system installed for the DME run.	A shutdown interlock was added to the existing high temperature switch - TSH-309 - which is located downstream of the 21.30 exchangers. Although the maximum design temperature under SS10X3 is 350°F, it was decided to set this switch at 175°F, as this temperature should never be reached under normal conditions.
(The following items are not considered hazards but are documented for the purpose of maintaining a record of the entire meeting discussions.)		
16. 21.80 vent noise levels	It was recommended that the noise levels caused by the CO_2 vent system be estimated and corrective action be included in the design as necessary.	A preliminary noise level estimation performed by Design indicated a continuous sound pressure level in excess of 90 dBA. However, a second review was conducted and the estimated level reduced to 73 dBA. No sound attenuation measures are being taken.
17. Tie-in to 16.20 CO_2 tank and selection of associated safety relief valves.	Due to the lack of sufficient information available from the CO_2 tank supplier, the proper selection and set points of the required safety relief valves were deferred until the completion of the tank delivery and installation.	Operations will provide Process and Design Engineering with information required to properly check the size of safety relief valves for this system. The completion of this issue will be verified during the ORI.

IV. Follow-Up Work

The following items have been identified as requiring development and documentation:

Item	Responsibility
A. Process design limitations	Process Engr.
B. Process Run-Authorizations	Process Engr.
C. Operator Training Documentation	Operations
D. Start-up procedures	Process/Start-up/Operations
E. ORI check list	Project Engr.
F. ORI planning meeting	HR Team
G. ORI	HR Team

APPENDIX B: RUN CHRONOLOGY

The run chronology covering the period 23 April 1991 to 21 May 1991 is included in this section.

Time on stream (TOS) is assigned 0 hours at 08:00 on 1 May. This is when catalyst reduction had been completed and syngas was introduced to the reactor.

The activation run and material balance periods cover the following times:

Run #	Start of Period			End of Period		
	Date	Time	TOS	Date	Time	TOS
AF-A1	4/29	18:30		5/1	05:00	
AF-R1.2	5/3	03:00	43	5/5	13:00	101
AF-R1.1	5/5	21:00	108	5/6	17:00	129
AF-R1.3	5/6	21:00	133	5/7	06:00	142
AF-R2.1	5/9	00:00	184	5/9	17:00	201
AF-R2.2	5/10	09:00	217	5/11	12:00	244
AF-R2.3	5/11	16:00	248	5/12	16:00	272
AF-R2.4	5/12	20:00	276	5/13	04:00	284
AF-R3.1	5/14	00:00	304	5/14	16:00	320
AF-R3.2	5/15	06:00	334	5/16	08:00	360
AF-R3.3	5/16	12:00	364	5/17	09:00	385

References to flow rates, gas compositions, and space velocities reflect real-time values and have not been corrected. This has been done to retain a correspondence with the operations, start-up, and process log books and data sheets.

DATE	TIME	TOS	DESCRIPTION
4/23/91			Blinds on feedgas swung into position
4/25			First NDG calibration with nitrogen.
4/26	16:00		Introduced syngas to begin carbonyl burnout. Operation is once-through. Samples taken to measure concentration of carbonyls, sulfides, and chlorides.
4/28	11:40		Began recycling syngas
	16:30		Syngas backed-out; begin bringing nitrogen into the plant.
4/29	08:00		Charged 129 gallons of oil to Prep Tank.
	11:00		Added 489 lbs of BASF S3-86 to preheated oil in Prep Tank.
	14:00		Transferred slurry from Prep Tank to Reactor.
	15:30		Flushed Prep Tank with 97 gallons of oil and transferred to Reactor.
	18:30		Reduction gas composition lined-up at 1.2% H2, 1.8% CO, 0.5% CO2 (remainder nitrogen). Reduction begins: Reactor at 220 F and 100 psig. Reduction gas flow is 15,000 SCFH.
	18:55		Cut flow momentarily to take an NDG scan. Level at 99" on the tape.
	19:35		Reduction gas composition 1.4% H2, 1.8% CO and flow is 15,000 SCFH. This is fairly typical reactor feed composition. Reactor temperature is 221.4 F.
	21:00		Reactor up to 230 F
4/30	11:00		Reactor temperature at 390.5 F. Temperature ramp averaged 11 F per hour over the last 14 hours. Beginning the temperature hold.
	22:55		Reactor temperature at 391.4 F. Have maintained 391 F for 12 hours with negligible uptake of syngas. End of reduction data collection period. Beginning the ramp to 464 F.
5/1	04:00		Temperature at 464 F. Temperature ramp averaged 15 F per hour. Begin 1 hour temperature hold.

DATE	TIME	TOS	DESCRIPTION
	05:00		Temperature hold period over. Begin reactor cooldown
	06:35		Reactor at 437 F, 100 psig.
	07:34		Started the feed/recycle compressor. Begin pressurizing plant. Nuke reading indicating 80" (gassed).
	07:45		Zero-flow NDG scan indicates liquid level at 69" on the tape. T=439 F, P=419 psig.
	07:50		Pressure up to 450 psig. Temperature profile in reactor ranges from 399-434F (average = 425F).
	08:00	0:00	Time zero mark. Beginning regular operations - syngas into plant
	08:03	0:03	Pressure = 690 psig. Temp profile is 407-450F (avg = 483.4F).
	08:07	0:07	PV-201 opened to 100%.
	08:18	0:18	Pressure = 760 psig. Temp profile is 409.8-468F (avg = 451F).
	08:42	0:42	Effluent sample from GC shows: H2=26.9 mole%, CO=54.8, N2=12.9, CH4=0.07, CO2=5.87, MeOH=0.37.
	08:43	0:43	NDG scan shows level at 84." FQ241 initial reading is 34819.2, FT126A=18258.1 SCFH, FT 187A=15961.8 SCFH.
	09:00	1:00	Transfer started from the 27.12 back to the reactor.
	09:07	1:07	Pump discharge pressure at the 27.12 increased to raise reactor level.
	09:20	1:20	Level detected in the 22.10. Reactor level is 90." Target is 140."
	09:30	1:30	Pressure = 752 psig. Temp profile is 393.3-463.1F (avg = 439F).
	10:02	2:02	Reactor Feed is 39% H2, 56% CO, 5% CO2. Reactor feed is FT187B=20125 SCFH. Tavg=448 F, P=751 psig

DATE	TIME	TOS	DESCRIPTION
	10:30	2:30	Oil drained from flare KO pot = 46 lbs. A small amount of clumpy catalyst was removed but oil was relatively clear.
	10:35	2:35	Reactor effluent is 23.5% H2, 61.3% CO, 7.8% CO2, 10.8% MeOH
	10:40	2:40	Pressure = 748 psig. Temp range is 409.2-468.8F (avg = 449.8F). Level is at 108". FT126A=17543, FT187A = 4066, FT187B=19400.
	10:53	2:53	Level is at 112."
	11:58	3:58	Level is at 131."
	12:10	4:10	Recycle flow started. Nuke indicating a level of 140."
	12:17	4:17	FT126A = 20139, FT187A=40421, FT187B=40129. Level = 168."
	12:40	4:40	Oil addition stopped.
	13:27	5:27	Nuke on automatic control, level at 180." Temp range is 444.1-478.9F (avg=478F).
	15:15	7:15	Started raising nuke level to 213."
	16:59	8:59	Started to transfer product from 22.15 to day tank. FQ241 not registering. 22.15 level is at bottom of 10th bolt, day tank starting point is 19.5."
	18:38	10:38	Slurry sample taken off reactor.
	22:30	14:30	The 8.5% MeOH standard was suspected of partial condensation in the cylinder. The 3.8% std will now be used for the GC calibration. John Wallace correction factors: GC1: 0.9562 for MeOH > 8% GC2: 0.9375 for MeOH > 8%
5/2	00:00	16:00	Increased recycle to reactor.
	00:15	16:15	Transfer from 22.16 to 28.10. 22.16 readings: start=43.5," end=19.5."

DATE	TIME	TOS	DESCRIPTION
	04:00	20:00	Plant and GCs have been running steady. Reactor flow =63,000 SCFH Inlet Comp = 38% H2, 48% CO, 13% CO2 Effluent = 24% H2, 48% CO, 16% CO2, 10% MeOH Reactor T = 480 F, P = 751 psig
	09:00	25:00	Oil addition stopped to let level drop.
	12:20	28:20	Oil sample taken off the 27.14, MeOH sample taken off the 22.11 (96.7 wt% MeOH).
	12:45	28:45	Flow to the reactor was increased to 85,000 SCFH to bring SV to 9000. Will maintain this condition to track activity reduction and eventually enter the AF-R1.2 data period. With the increase in flow, the bottom four TI's in the reactor tightened to within 2F. Previously, these TI's ranged up to 10F. Better mixing is noted. Reactor level is above nuke, recycle is reduced to bring level down.
	13:35	29:35	Reactor TI's started diverging again. Flow had been dropped to only 83,000 SCFH.
	14:20	30:20	Level is 211." Temp profile varies 4.5 F between TI262-2 and TI626-5.
	18:30	34:30	First transferred from day tank to tanker (approx. 315 gallons)
	23:20	38:40	The iron carbonyl level in reactor feed was measured with GCs to be 2-3 ppb .
	23:45	39:40	MeOH in reactor effluent is consistent and around 10.7 mole%.
5/3	03:00	43:00	Start of Data Collection Period for AF-R1.2
	03:10	43:10	Began transfer from day tank to trailer.
	05:40	45:40	End of transfer (770 gallons)
	10:30	50:30	Methanol composition in effluent continues to fluctuate. Blew out sample pots.
	12:00	52:00	Transferred from day tank to trailer. Unloaded about 1480 gals, current production is about 3000 gals. New tubing installed which made transfer go quickly.

DATE	TIME	TOS	DESCRIPTION
	12:00	52:00	Oil sample taken off the 27.14, MeOH sample taken off the 22.11 (96.8 wt% MeOH).
	14:00	54:00	Problem found with LIC 292 on 22.15. The level in the sight glass must be taken into account when day tank readings are taken. Began to fill the 21.80 evaporator with CO2.
	16:00	56:00	Mass balances between 0600-1600 5/3 indicate productivity to be: 33.2 gmole/kg-hr by GC and flows 28.3 gmole/kg-hr by day tank.
	23:40	63:40	DEC computer did not update from now until 5/4, 0300.
5/4	00:30	64:30	Mass balances between 5/3 1600-5/4 0030 show productivity to be : 32.6 gmole/kg-hr by GC and flows 27.6 gmole/kg-hr by day tank.
	11:25	75:25	Transferred from day tank to trailer (1710 gal).
	12:00	76:00	Oil sample taken off the 27.14, MeOH sample taken off the 22.11 (96.7 wt% MeOH).
	18:00	82:00	Needle gauge on CO2 supply was found to be off. CO2 is used with discretion.
5/5	10:35	98:35	Transferred from day tank to trailer (1700 gal).
	12:00	100:00	Oil sample taken off the 27.14, MeOH sample taken off the 22.11 (96.7 wt% MeOH).
	13:00	101:00	End of AF-R1.2 Data Period. Reactor flow reduced to 46,780 SCFH, SV is nominally 5000.
	20:00	108:00	Plant as lined-out sufficiently to begin AF-R1.1 Data Period.
5/6	00:00	112:00	Begin to purge-out the DME recovery section.
	11:00	123:00	Charged the prep tank with estimated 110 gallons of oil. Will begin heating to a target temperature of 180 F.
	11:15	123:15	Transferred from day tank to trailer(1340 gal). Oscillations in measured methanol composition of reactor effluent are fairly substantial - time average composition is stable.

DATE	TIME	TOS	DESCRIPTION
	12:00	124:00	Oil sample taken off the 27.14, MeOH sample taken off the 22.11 (96.1 wt% MeOH).
	18:00	130:00	Mark end of AF-R1.1 Data Period. Begin to increase rates to the original SV=9000 conditions (AF-R1.2). Will discontinue oil pump-back from 27.14 to force the slurry to thicken. Current level at 211" on the tape.
	21:30	133:30	Added 32 lbs of alumina to oil in the prep tank and continue heating. The objective is to heat mix in prep tank at 250 F for 12 hours to drive off water. Prep tank is under N2 Purge.
5/7	0:00	136:00	Prep tank contents at 256 F. Pressurized then depressurized three times to aid in getting the water into the N2 purge.
	01:10	137:10	Down to approx. 157" on tape slurry level. Effluent MeOH composition has returned to AF-R1.2 levels, as expected.
	02:45	138:45	Level control for reactor put back on automatic to hold slurry level at 149" on the tape.
	07:30	143:30	Level set point had been reduced further, level now at 140". Gas-to-reactor is temporarily cut-out and slurry allowed to degas and settle. After settling, level was 67" on the tape.
	09:15	145:15	Syngas backed-out and replace with nitrogen (+2% H2) - End of AF-R1 series. Will begin cooling the reactor in preparation for the slurry transfer operation.
	11:00	147:00	Drained MeOH out of 22.10 and 22.15 into the day tank.
	11:40	147:40	Dropped plant pressure to 150 psig.
	12:25	148:25	Reactor at 250 F, prep tank at 265 F. Drained 78 lbs of reactor slurry to drum S1.
	13:00	149:00	Transferred 1/3 of reactor contents to prep tank, withdrew a slurry sample from reactor, then transferred the rest of the reactor contents to prep tank . Begin 2 hour hold in prep tank under agitation to blend alumina with MeOH catalyst.
	14:50	150:50	Begin transfer of prep tank contents to reactor. To be followed by flush of prep tank with 35 gallons of oil.

DATE	TIME	TOS	DESCRIPTION
	15:30	151:30	Transfer prep tank rinse to reactor and bring-in N2 purge flow (+2% H2) to reactor and begin heat-up.
	17:00	153:00	Drained 27.12 and 27.14 to bottom of their respective sight glasses.
	20:50	156:50	Reactor at 430 F. The new slurry level is too high in the reactor (above the span of the NDG). Will have to carefully boil-off oil with nitrogen flow. Continue increasing reactor temperature towards 450 F.
5/8	05:15	165:15	Emptied day tank into trailer.
	08:20	168:20	Cut-out N2 flow to measure degassed level. Level is 137" degassed (70 psig, 450 F) - sufficient to proceed with regular operations.
	08:45	168:45	Begin to raise reactor pressure under nitrogen.
	09:45	169:45	Reactor at 756 psig, recycle flow started.
	10:28	170:28	Flow stabilized at 40,000 SCFH. Reactor at 737 psig, 421 F.
	11:00	171:00	Begin to bring-in syngas.
	12:41	172:41	Reactor at 744 psig, 443 F. Reactor flow is approx. 44,000 SCFH. Reactor effluent composition is 21%H2, 41% CO, 8% CO2, 25% N2, 4% MeOH and 2% DME. The reaction is hot! Will ramp the temperature up slowly.
	16:05	176:05	Reactor at 756 psig, 470 F. Reactor flow is approx. 48,200 SCFH. Reactor effluent composition is 22%H2, 49% CO, 16% CO2, 3% N2, 5% MeOH and 5% DME.
	17:30	177:30	Levels are building in 22.10 and 22.15
	20:20	180:20	22.10 and 22.15 operating on level control - liquid being transferred to day tank. Back-end is cooled, 22.18 is at 10 bolts - begin to transfer liquid from 22.14 to 22.18.
5/9	00:00	184:00	Begin data collection period for run AF-R2.1 (SV=5500). Reactor at 750 psig, 481 F. Reactor feed flow is 40,000 SCFH at 36%H2, 50.5% CO, 1% N2, 11% CO2, 1% DME. Effluent composition is 22% H2, 46% CO, 1% N2, 19% CO2, 5.8% DME, 6.3% MeOH.

DATE	TIME	TOS	DESCRIPTION
	06:30	190:30	Alumina catalyst appears to have initial hyperactivity. DME concentration in reactor effluent has dropped to 5.7%.
	08:30	192:30	22.11 liquid sample taken at 03:45 contained 9% DME and degassed considerable. Will attempt to reduce DME in liquid by increasing 22.10 temperature. To achieve this, cooling water flow to 21.30 is reduced.
	11:00	195:00	Cooling water temperature exit 21.30 is too hot (150 F) and has had no effect on 22.10 temperature (21.30 is oversized and pinched). Cooling water flow is returned to normal.
	12:15	196:15	DME in effluent continues to decline, now at 5.6%. MeOH in effluent remains fairly stable. Liquid has been accumulating in the 22.18 (level at 1 bolt).
	14:00	198:00	Begin to thicken slurry - stop returning oil flow from 27.14.
	15:00	199:00	Completed construction of a special sample bomb for 22.11 liquid. Sample will be taken at 22.11 pressure, weighed, blown- down to atmospheric pressure, then weighed again. The weight loss is the quantity of degassed vapor.
	17:00	201:00	End of AF-R2.1 data period. Final DME concentration in effluent is 5.4%. Will begin to increase rates and continue to boil-off oil. Target reactor feed gas flow is 74,500 SCFH.
5/10	03:30	211:30	Reactor feed flow up to 64,500 SCFH. Level continues to build slowly in 22.18 (now at 3 bolts).
	09:00	217:00	Up to desired rates. Begin data period for run AF-R2.2 (SV=9000). Reactor at 481 F, 750 psig. Reactor feed flow is 75,600 SCFH at 36% H2, 51% CO, ½% N2, 12% CO2, 1% DME. Reactor effluent is 24% H2, 48% CO, ½% N2, 17% CO2, 3.7% DME, 6.7% MeOH. Level in 22.18 is now at 5.5 bolts.
	12:00	220:00	Liquid sample from 22.11 shows 3.5% DME, 93.5% MeOH.
	21:20	229:20	Lost FT187A from 20:45 (loose wire - short), now back on line.

DATE	TIME	TOS	DESCRIPTION
5/11	0:00	232:00	Plant has been running steady. No change in MeOH or DME concentration in reactor effluent. 22.18 level up to 15 bolts.
	07:15	239:15	22.18 is at 21.5 bolts will dump liquid to 28.10 storage tank.
	08:30	240:30	Transfer complete, level is 2 bolts. Sample from 22.18 indicates 86% MeOH, 9% DME, 3% water.
	12:00	244:00	End of data period for run AF-R2.2. Begin to reduce rates to for next condition, target flow is 47,000 SCFH.
	16:00	248:00	Plant responded quickly to condition change. Begin data period for run AF-R2.3 (SV=5400). Reactor at 482 F, 750 psig. Reactor feed flow is 46,900 SCFH at 35% H2, 52% CO, ½% N2, 12% CO2, 1% DME. Reactor effluent is 21% H2, 48% CO, ½% N2, 19% CO2, 5.1% DME, 6.5% MeOH. Level in 22.18 is now at 6 bolts.
5/12	04:30	260:30	Plant operation very steady. 22.18 at 10 bolts.
	10:15	266:15	Alumina prep for next campaign underway. Approx. 62 gallons of oil added to prep tank, followed by 67.5 lb of alumina, followed by another 25 gallons of oil. Begin heating prep tank under nitrogen.
	14:15	270:15	Prep tank temperature is at 246 F.
	16:00	272:00	End of data period for AF-R2.3. Increase rates (target is 76,000 SCFH) and begin to thicken slurry (stop oil return from 27.14).
	20:00	276:00	Are at new conditions and stable. Begin supplemental data period (run AF-R2.4, SV=9000). Reactor at 481 F, 750 psig. Reactor feed flow is 76,400 SCFH at 36% H2, 51% CO, ½% N2, 11% CO2, 1% DME. Reactor effluent is 23% H2, 50% CO, ½% N2, 15% CO2, 3.6% DME, 6.9% MeOH.
	21:30	277:30	Prep tank at 293 F.
5/13	02:10	282:10	Transferred day tank to 28.10.
	04:00	284:00	Operation has been steady and quite similar to run AF-R2.2. Thickening of the slurry has been going slowly so will begin to increase rates further - end of data period for run AF-R2.4.

DATE	TIME	TOS	DESCRIPTION
	05:30	285:30	22.18 liquid transferred to 28.10. Prep tank holding at 290 F.
	06:30	286:30	Feed flow to reactor at 93,700 SCFH.
	08:40	288:40	Begin reactor cooldown. Target temperature 250 F
	09:15	289:15	Reactor at 430 F. Back-out syngas and bring in N2 (+2% H2).
	11:40	291:40	Reactor at 301 F and 504 psig. Temporarily cut-out N2 flow to measure degassed slurry level (54") - OK to proceed.
	12:05	292:05	Drained 150 lb of slurry into a drum and took a sample. Transferred the remainder to prep tank. Will agitate in prep tank with the fresh alumina until 14:00.
	14:15	294:15	Transferred prep tank contents to reactor.
	14:30	294:30	Rinsed prep tank with 24 gallons of oil and transferred to reactor. Reactor at 272 F, 42.5 psig - level is 116". Begin heating slurry in reactor under nitrogen.
	18:00	298:00	Reactor at 400 F, 750 psig. Bring in syngas and operate once-through to purge N2.
	19:00	299:00	Reactor at 430 F. Reactor flow is 36,000 SCFH (operating with partial recycle).
	20:30	300:30	Reactor at 460 F. Reactor flow is 48,000 SCFH. Reactor effluent composition is 24% H2, 48% CO, 8% N2, 12% CO2, 5% DME, 3% MeOH. Once again, the catalyst mix is extremely active.
	21:15	301:15	Reactor up to 480 F.
5/14	00:00	304:00	Plant is pretty well lined-out. Begin data period for run AF-R3.1 (SV=5400). Reactor at 481 F, 750 psig. Feed flow is 49,400 SCFH at 36% H2, 51% CO, 1.5 N2, 10.5% CO2, 1% DME. Reactor effluent composition is 23% H2, 46% CO, 1.5% N2, 19.5% CO2, 7.6% DME, 2.4% MeOH.
	04:40	308:40	Levels in 22.10 and 22.15 lined-up - beginning to transfer to day tank. Levels in 22.14 lined-up; level in 22.18 at 15 bolts.

DATE	TIME	TOS	DESCRIPTION
	06:30	310:30	Reactor effluent composition is 23% H2, 46% CO, 1% N2, 20% CO2, 7.6% DME, 2.4% MeOH
	12:00	316:00	Operation still steady - effluent is 7.5% DME, 2.4% MeOH. Sample from 2218 shows 8% DME, 89% MeOH. Level in 22.18 still 15 bolts.
	12:45	316:45	Begin draining 22.18 to the 28.10.
	14:00	318:00	End of data period for run AF-R3.1. Begin to thicken slurry in preparation for higher rates.
	16:30	320:30	22.18 drained down to 1 bolt. Begin to increase flow rate to reactor.
	18:00	322:00	Reactor flow at 55,400 SCFH, will stay here for a while and continue thickening. Have increased pressure of 22.18 to 170 psig - will now begin draining 22.18 into 28.40.
5/15	00:30	328:30	Reactor flow up to 59,800 SCFH.
	05:30	333:30	Reactor flow at 74,000 SCFH.
	06:00	334:00	Plant is now lined-out. Begin data period for run AF-R3.2 (SV=9000). Reactor at 482 F, 750 psig. Feed flow is 74,900 SCFH at 36% H2, 50.5% CO, ½% N2, 12% CO2, 1.5% DME. Reactor effluent composition is 27% H2, 47% CO, ½% N2, 17% CO2, 5% DME, 2.9% MeOH. Blocked 22.18 discharge to allow level in 22.18 to rise as a means of estimating rates.
	08:35	336:35	Level in 22.18 is up to 16 bolts. Open valve to allow liquid to continue to drain into 28.40 (28.40 is currently 25% of max. level).
	18:30	346:30	Level in 28.40 at 46%. Operation is pretty steady with some small variations in H2 concentration in the loop.
5/16	01:45	353:45	Level in 28.40 is 70%. Block-in 22.18 discharge line and drop 22.18 pressure back to 23 psig. Plant operation largely unaffected.
	08:00	360:00	End of data period for run AF-R3.2. Begin reducing rates.
	09:30	361:30	Rates are at design flow of 46,400 SCFH.

DATE	TIME	TOS	DESCRIPTION
	12:00	364:00	Temperature oscillating somewhat which is showing up as +/- 0.2% in DME concentration in reactor effluent. Currently returning controllers. Average production is not affected so will mark this as beginning of run AF-R3.3 data period. Reactor at 480 F, 750 psig. Reactor feed flow is 46,800 SCFH at 36% H2, 51% CO, ½% N2, 11% CO2, 1% DME. Reactor effluent is 25% H2, 47% CO, ½% N2, 15% CO2, 6.9% DME, 2.9% MeOH.
	18:00	370:00	Reactor temperature back under tight control - DME composition in effluent has stabilized.
5/17	00:30	376:30	Plant running steady.
	09:00	385:00	End of data period for run AF-R3.3. Have been operating at reduced level. Begin to pump oil from 27.14 to reactor in order to increase level to 100%.
	10:00	386:00	Level up to 100% in reactor. Will take data for 6 hours to see if productivity/selectivity change.
	13:40	389:40	There is no significant change in productivity but may be a slight increase in DME selectivity.
	14:00	390:00	Regular operations end. Begin reactor/plant cooldown. Syngas out, N2 in
	17:30	393:30	Compressor shut down.
	17:50	393:50	Reactor at 200 F. Shutdown data computer. Begin draining liquid from reactor. Drain into drums D1-D5.
5/20			Plant has been down under nitrogen purge over the weekend
	07:00		NDG calibration performed under nitrogen at 198, 55, and 6.5 psig.
			Reactor top and bottom heads removed for vessel inspection. Top head is very clean, internal heat exchanger piping has 1/8" of crusted catalyst on horizontal runs, reactor walls show slight "film" but can clearly see metal surface. Bottom head and 4" liquid slurry line are a different story.

DATE	TIME	TOS	DESCRIPTION
			Bottom head is filled with slurry up to about 1" below the bottom of the sparger. Scooped-out 74 lbs of mixed oil and catalyst. Most of this material was black with intermixed brown and red. Some material was very dry and crumbled when held. The 4" line between reactor head and block valve was also filled - 14 lbs removed.
5/21			Bottom plate was removed from 27.14. Inside was clean with only 3/4" of slurry covering the 12" plate. The inlet head was removed from the 22.10 exchanger to inspect tubes. Very clean inside tubes with a little bit of catalyst on the tubesheet.

APPENDIX C : NUCLEAR DENSITY GAUGE CALIBRATION

The nuclear density gauge (NDG), which is used to measure the vapor void fraction in the slurry reactor, was calibrated on 25 and 29 April 1991 and recalibrated on 20 May 1991. The derivation of operative equations and the details of standard measurement positions have been previously documented and discussed in detail (*).

The equation used to determine the vapor holdup is defined below:

$$\ln\left(\frac{I_o}{I}\right) = GL((\alpha\rho\varepsilon)_v + (\alpha\rho\varepsilon)_L + (\alpha\rho\varepsilon)_s)$$

where

I_o	=	radiation intensity of source, corrected for absorptance of the empty vessel and insulation.
I	=	radiation intensity as measured at detector
G	=	geometric factor for the system
L	=	path length the beam travels inside the reactor
α	=	absorptance of phase i
ρ	=	density of phase i
ε	=	volume fraction of phase i

$_{v,L,s}$ denotes the vapor, liquid, and solid (catalyst) phases

Calibration of the NDG is performed with nitrogen at different densities (pressures). For the single-phase system, the general equation above reduces to:

$$\ln(I) = \ln(I_o) - GL \bullet (\alpha\rho)_v$$

When the natural log of the measured intensity (I) is plotted against the product $\alpha\rho$, then the slope yields the product GL and the intercept yields the natural log of the corrected source intensity, I_o.

Calibration is carried out at different positions along the height of the reactor. It is found that small variations in the corrected source intensity, I_o, exist at different positions. These variations are due to small differences in wall and insulation thickness as well as the state of the insulation. It is convenient to define a source intensity at the standard position. I_{os},

and relate all other intensities through correction factors, C_R. Thus, at any position, the intensity is given by,

$$I_o = I_{os} \cdot C_R$$

The NDG was initially calibrated on 25 April. The standard position source intensity, I_{os}, appeared low when compared to the previous calibration (June 12, 1988) while the geometric factor, GL, was virtually the same. The decline in I_{os} with time is to be expected since the radiation source intensity decays with time (half-life is 11074 days). However, the observed decline in I_{os} was slightly greater than one would expect from a simple exponential decay. It was concluded that the insulation was probably not completely dried out and, as a consequence of water absoption, the apparent source intensity was being understated.

On 29 April (after the reactor had been heated with syngas and oil for 3 days) a calibration scan was conducted at low pressure (11.5 psig) and is was observed that, indeed, I_{os} had increased to a level more in-line with expectations. Upon completion of operations a three pressure calibration was also conducted (on 20 May). Indeed the source intensity appeared as-expected based on source decay theory. The final calibration to be used for the subsequent analyses was based on the values of GL and C_R determined during from the data collected on 20 May. These calibration constants are presented in Table C1 and compared to the June 12, 1988 and 25 April calibrations.

TABLE C1
CALIBRATION CONSTANTS

Date	(m/d/y)	6/12/88	4/25/91	5/20/91
I_{os}	(cps)	456,900	412,600	431,415
GL	(cm)	47.23	47.41	47.41
Half Life	(days)	11074	11074	11074
C_R	Position (inch)			
	36	1.00	1.00	1.00
	54	1.01	1.01	1.01
	88	1.00	1.04	0.97
	108	0.99	1.05	0.99
	120	0.99	1.01	0.99
	156	1.01	1.03	1.01
	184	1.03	1.07	1.05
	213	1.07	1.09	1.08

The raw calibration data is presented in Table C2; a plot of the NDG calibration is presented in Figure C1. The top line in the figure represents the prior calibration from June 12, 1988; the dashed line represent the calibration from 29 April, 1991.

In order to properly use the holdup equation, the absorptance and densities of the syngas (vapor), slurry oil (liquid), and catalyst (solid) are required. The absorptance of the syngas is calculated from the mass average absorptance of each element (see *); the density is a function of composition, temperature and pressure. For the condensed phases, at reactor conditions (482°F), the absorptance (α) and densities are as follows:

	Absorptance (cm^2/g)	Density (g/cm^3)
Drakeol 10 Oil	0.08776	0.67
BASF S-386 (reduced)	0.07343	5.73
Alumina (dried)	0.07618	3.31
Elements:		
H	0.15370	
N	0.07750	
O	0.07750	

(*) References:

The detailed description and documentation of the nuclear density gauge equations as well as the June 12, 1988 calibration data can be found in - "Liquid Phase Methanol LaPorte Process Development Unit: Modification, Operation, and Support Studies", Topical Report: "Task 2.0: Run E-5, Gas Hold-up and Equipment Evaluation Studies, Appendix A.", 2 January, 1991, No. DE-AC22-87PC90005.

TABLE C2

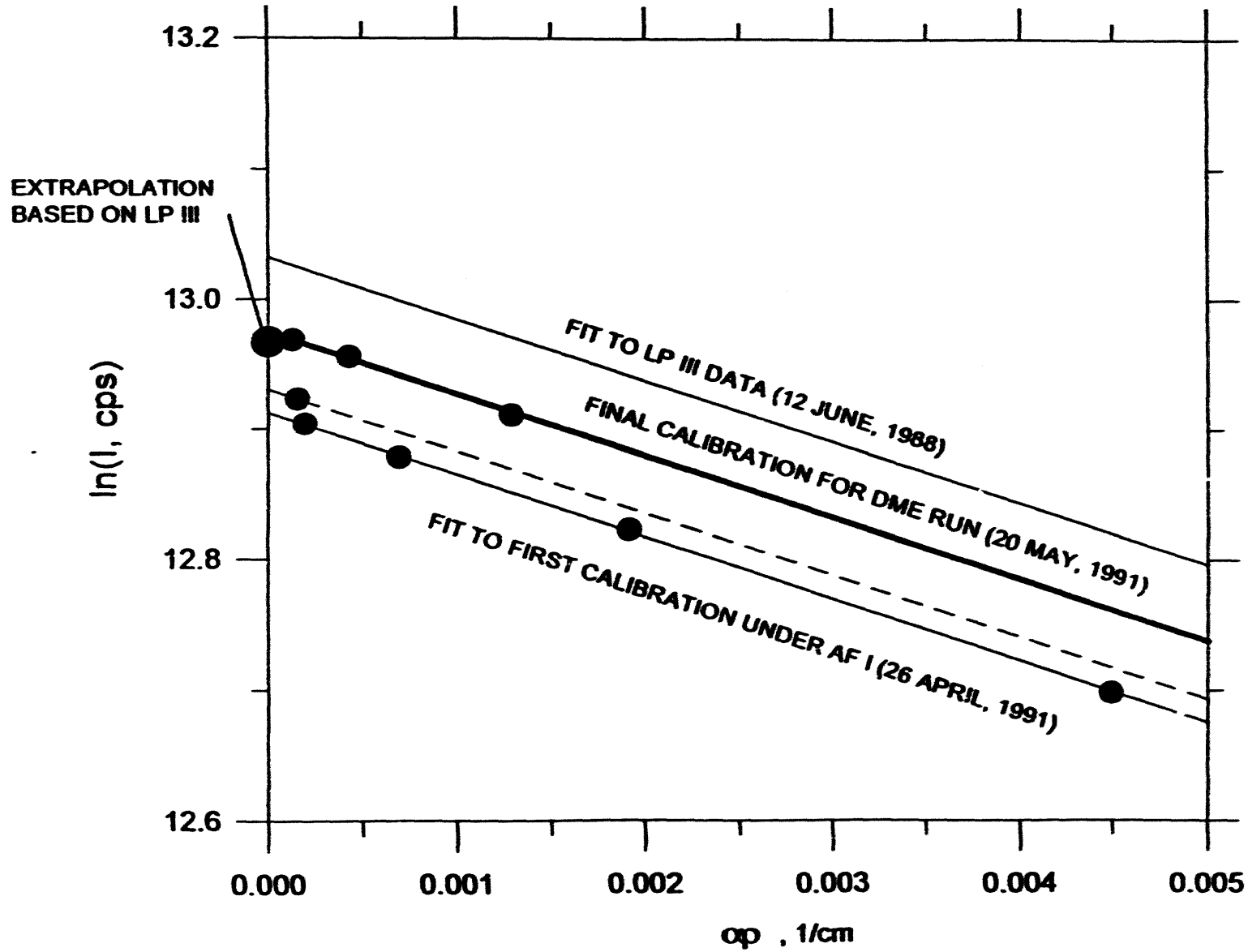
CALIBRATION DATA FOR THE NUCLEAR DENSITY GAUGE

Date		26-Apr-91		26-Apr-91		26-Apr-91		26-Apr-91			
Gas		N2		N2		N2		N2			
Temp	°F	88		90		90		95			
Pressure	psig	18		103		310		753			
Density	g/cm3	0.0025		0.0090		0.0247		0.0579			
Absorptivit	cm2/g	0.0775		0.0775		0.0775		0.0775			
RAW DATA											
Number	Position in on Tape	Intensity cps/1000	CR	Intensity cps/1000	CR	Intensity cps/1000	CR	Intensity cps/1000	CR		
1	213	437.8	1.09	427.2	1.09	402.7	1.09	358.0	1.09		
2	184	430.2	1.07	421.1	1.08	397.6	1.07	351.4	1.07		
3	156	414.4	1.03	404.2	1.03	381.7	1.03	337.9	1.03		
4	120	404.7	1.01	395.0	1.01	373.6	1.01	329.9	1.01		
5	108	419.3	1.04	409.1	1.04	386.9	1.04	342.0	1.05		
6	88	418.9	1.04	409.0	1.04	386.0	1.04	341.5	1.04		
7	54	406.9	1.01	396.4	1.01	374.4	1.01	331.0	1.01		
8	36	401.8	1.00	391.5	1.00	370.7	1.00	327.1	1.00		
AVG		416.8		406.7		384.2		339.9			

Date		29-Apr-91		20-May-91		26-Apr-91		26-Apr-91			
Gas		N2		N2		N2		N2			
Temp	°F	90		74		86		70			
Pressure	psig	11.5		196		56		6.5			
Density	g/cm3	0.0020		0.0167		0.0055		0.0017			
Absorptivit	cm2/g	0.0775		0.0775		0.0775		0.0775			
RAW DATA											
Number	Position in on Tape	Intensity cps/1000	CR	Intensity cps/1000	CR	Intensity cps/1000	CR	Intensity cps/1000	CR		
1	213	455.7	1.11	437.5	1.08	456.2	1.08	463.8	1.08		
2	184	435.8	1.06	425.5	1.05	441.0	1.04	448.9	1.05		
3	156	416.5	1.02	409.5	1.01	425.4	1.00	431.7	1.01		
4	120	406.4	0.99	403.2	1.00	419.4	0.99	425.5	0.99		
5	108	423.4	1.03	399.5	0.99	416.2	0.99	423.3	0.99		
6	88	425.8	1.04	400.6	0.99	410.6	0.97	415.1	0.97		
7	54	411.7	1.01	409.9	1.01	427.9	1.01	434.0	1.01		
8	36	409.6	1.00	404.8	1.00	423.5	1.00	429.0	1.00		
AVG		423.1		411.3		427.8		433.9			

FIGURE C1

CALIBRATION RESULTS FOR THE NUCLEAR DENSITY GAUGE



APPENDIX D: TRACE COMPONENT ANALYSIS OF SYNGAS

During the carbonyl burnout prior to Run No. AF-A1 (4/26/91-16:00 to 4/28/91-16:30), the syngas was analyzed for trace components such as iron carbonyl, nickel carbonyl, chloride and H_2S. The samples were taken at sample port #5 (hot reactor inlet) as well as sample port #3A (hot reactor outlet).

The carbonyl results are summarized in Table D1. Two methods were used to test for the presence of carbonyls: wet chemical analysis and gas chromatography using an electron capture detector (ECD). The GC analysis indicated 0-5 ppb iron carbonyl and 0-7 ppb nickel carbonyl. The wet chemical analysis showed about 6 ppb iron and 2 ppb nickel carbonyl. These levels are extremely low and very near the detection limits. The good agreement between these two methods lends credibility to the GC method.

The chloride and H_2S results are presented in Table D2. The H_2S content of the gas was < 2 ppb. Colorimetric tests for chloride indicated 1-2 ppb chloride. Wet chemical analysis was not sufficiently precise. Additional tests for chlorides by NUS Laboratory Services using NIOSH method P&CAM #115 (ion selective method for chlorine ion) indicated 3-8 ppm.

CONCLUSION: The trace component analysis indicates insignificant levels of catalyst poisons in the syngas.

TABLE D1
IRON AND NICKEL CARBONYL ANALYSIS OF SYNGAS

(Prior to Run No. AF-A1)

Results from GC Analysis

Date	Time	Gas Condition	Sample Port	Carbonyl Concentration (ppb) Iron	Nickel
4/26/91	1800-1845	Cold, Once-Thru	5	0-3	0-4
4/26/91	1800-1845	Cold, Once-Thru	3A	0-5	0
4/27/91	0900-1630	Hot, Once-Thru	5	0-2	0
4/27/91	0900-1630	Hot, Once-Thru	3A	0-3	0
4/28/91	1020-1040	Hot, Once-Thru	5	0-3	0-7
4/28/91	1020-1040	Hot, Once-Thru	3A	0-2	0-6
4/28/91	1600-1620	Hot, Recycle	5	0-2	0
4/28/91	1600-1620	Hot, Recycle	3A	0-1	0

Results from Wet Chemical Analysis

Date	Time	Gas Condition	Sample Port	Carbonyl Concentration (ppb) Iron	Nickel
4/26-27	2025-0825	Heating, Once-Thru	5	< 20	2
4/26-27	2025-0825	Heating, Once-Thru	3A	< 20	0.8
4/27/91	0950-1050	Hot, Once-Thru	5	< 5	< 5
4/27/91	0950-1050	Hot, Once-Thru	3A	6	< 5
4/27/91	1220-1830	Hot, Once-Thru	3A	6	< 2
4/27-28	2000-0850	Hot, Once-Thru	5	< 10	0.5
4/27-28	2000-0850	Hot, Once-Thru	3A	< 10	0.9
4/28/91	1020-1140	Hot, Once-Thru	3A	< 10	< 10

TABLE D2
CHLORIDE AND SULFIDE (H_2S) ANALYSIS OF SYNGAS

(Prior to Run No. AF-A1)

Results from Wet Chemical Analysis

Date	Time	Gas Condition	Sample Port	Chloride (ppb)	H_2S (ppb)
4/26/91	1825-2000	Cold, Once-Thru	5	< 1000	< 2
4/26/91	1825-2000	Cold, Once-Thru	3A	< 1000	< 2
4/26-27	2050-0825	Heating, Once-Thru	5	< 600	< 1
4/26-27	2050-0825	Heating, Once-Thru	3A	< 250	< 1
4/27/91	0930-1130	Hot, Once-Thru	5	< 1500	< 2
4/27/91	0930-1130	Hot, Once-Thru	3A	< 1500	< 2

Results from Chloride Colorimetric Test

Date	Time	Gas Condition	Sample Port	Chloride (ppb)
4/27/91	1920-2100	Hot, Once-Thru	5	< 10
4/27/91	1920-2100	Hot, Once-Thru	3A	< 10
4/28/91	1000-1515	Hot, Once-Thru	5	< 2
4/28/91	1000-1515	Hot, Once-Thru	3A	1-2

Results from Chloride Ion Selective Electrode Test

Date	Time	Gas Condition	Sample Port	Chloride (ppb)
4/27-28	2000-0850	Hot, Once-Thru	5	< 3
4/27-28	2000-0850	Hot, Once-Thru	3A	< 3
4/28/91	1000-1630	Hot, Once-Thru	5	< 6
4/28/91	1000-1630	Hot, Once-Thru	3A	< 6
4/28/91	1200-1630	Hot, Once-Thru	5	< 8

APPENDIX E: CATALYST ACTIVATION

The catalyst activation run, AF-A1, was conducted over the period 29 April 1991 to 1 May 1991.

489 pounds of catalyst was slurried with mineral oil and transferred to the reactor on 29 April. At 18:30 the reduction gas composition was lined-up at a nominal composition of:

1.2% H_2, 1.8% CO, 0.5% CO_2, 96.5% N_2

The reduction gas flow was approximately 15,000 SCFH. The catalyst activation took place at 100 psig. The temperature in the reactor was ramped while under reduction gas in accordance with established procedures.

The initial temperature of the slurry was 220°F. By 11:00 on 30 April the temperature was at the first hold point of 391-392°F. At this point the uptake of H_2 and CO was complete. The slurry temperature was held at 392°F for 12 hours.

At 23:00 on 30 April the ramp to the second hold temperature (464°F) began. By 04:00 on 1 May the slurry temperature was at 464°F. The temperature was held for one hour then cooldown began.

The reduction data, which includes: gas composition in-to and out-of the reactor, slurry temperature, and reduction gas flow, is presented in Table E1.

The compositions were measured using both GCs (GC#1 and CG#2). A comparison of the agreement between the two GCs is shown in Figures E1 and E2 for inlet and outlet compositions, respectively.

The instantaneous total-gas uptake is computed as:

$$U_I = F_{GAS} (\Delta Y_{H2} + \Delta Y_{CO}) / M_{CAT}$$

where,

U_I	=	instantaneous uptake (SCF/lb-hr)
F_{GAS}	=	flow of gas to reactor (SCFH)
ΔY_{H2}	=	change in composition of H_2 (in-out, mole fraction)
ΔY_{CO}	=	change in composition of CO (in-out, mole fraction)
M_{CAT}	=	mass of catalyst, oxide basis (lb)

The total uptake is computed by integrating the instantaneous uptake over the period of the activation. The cumulative uptake is displayed in Figure E3 as a function of slurry temperature. Note that the final uptake was 2.27 SCF/lb oxide which is 80% of the theoretical maximum (if all the copper in the catalyst were reduced the uptake would be 2.82 SCF/lb).

TABLE E1

REDUCTION DATA: MEASURED COMPOSITIONS

GC #	Day	Time	H2 in mole%	CO in mole%	GC #	Day	Time	H2 out mole%	CO out mole%	Day	Time	Temp (F)	Flow (SCFH)
2	4/29/91	18:34	1.105	1.585	1	4/29/91	18:45	1.239	1.731	4/29/91	18:30	220.0	15,200
2	.	19:07	1.288	1.827	2	.	18:51	1.137	1.790	.	18:58	221.1	15,202
1	.	19:35	1.370	1.838	1	.	19:18	1.284	1.603	.	19:17	221.1	15,107
2	.	19:40	1.402	1.895	1	.	19:51	1.192	1.302	.	19:31	221.4	14,928
2	.	20:14	1.390	1.924	2	.	19:57	1.174	1.149	.	20:00	225.6	14,621
1	.	20:41	1.562	1.828	1	.	20:25	1.143	0.907	.	20:30	229.1	14,613
2	.	20:47	1.470	1.826	2	.	21:03	0.914	0.861	.	21:00	229.8	15,224
2	.	21:20	1.284	1.758	1	.	21:39	1.021	0.861	.	21:31	229.0	15,325
2	.	21:53	1.442	1.809	2	.	22:10	0.901	0.899	.	22:00	236.5	14,681
1	.	21:55	1.429	1.737	1	.	22:12	0.980	0.885	.	22:30	246.8	14,289
2	.	22:27	1.475	1.860	1	.	22:45	1.035	0.941	.	23:00	250.6	14,177
2	.	23:01	1.499	1.800	2	.	23:17	1.072	1.083	.	23:31	250.6	13,907
1	.	23:02	1.491	1.797	1	.	23:18	1.174	1.102	4/30/91	0:00	257.7	15,204
2	.	23:34	1.499	1.800	1	.	23:54	1.215	1.003	.	0:30	268.0	15,679
2	4/30/91	0:07	1.442	1.770	2	4/30/91	0:24	1.135	1.075	.	1:00	276.0	15,127
1	.	0:10	1.431	1.744	1	.	0:27	1.230	1.064	.	1:30	280.2	15,015
2	.	0:40	1.341	1.748	1	.	0:49	1.393	1.131	.	2:00	290.1	15,038
1	.	1:05	1.441	1.757	1	.	1:22	1.499	1.405	.	2:31	300.7	15,224
2	.	1:14	1.323	1.769	2	.	1:30	1.546	1.461	.	3:06	306.4	14,669
2	.	1:47	1.335	1.787	1	.	1:55	1.495	1.441	.	3:30	307.7	13,748
1	.	2:11	1.485	1.781	1	.	2:28	1.561	1.380	.	4:01	312.1	14,737
2	.	2:20	1.455	1.787	2	.	2:37	1.464	1.421	.	4:32	319.4	14,508
2	.	2:53	1.491	1.842	1	.	3:02	1.636	1.503	.	5:00	324.5	14,979
1	.	3:18	1.499	1.832	1	.	3:35	1.710	1.657	.	5:30	328.6	14,684
2	.	3:27	1.521	1.833	2	.	3:43	1.618	1.584	.	6:01	333.1	14,443
2	.	4:00	1.390	1.852	1	.	4:08	1.623	1.620	.	6:36	340.4	13,928

TABLE B1

REDUCTION DATA: MEASURED COMPOSITIONS (continued)

GC #	Day	Time	H2 in mole%	CO in mole%	GC #	Day	Time	H2 out mole%	CO out mole%	Day	Time	Temp (F)	Flow (SCFH)
2	4/30/91	4:33	1.526	1.839	2	4/30/91	4:50	1.630	1.656	4/30/91	7:30	346.7	14,912
2	.	5:05	1.497	1.780	1	.	5:15	1.549	1.568	.	7:59	346.7	15,015
1	.	5:31	1.512	1.765	1	.	5:48	1.551	1.562	.	8:29	349.6	14,746
2	.	5:39	1.335	1.704	2	.	5:56	1.607	1.586	.	9:00	356.9	14,610
2	.	6:13	1.568	1.743	1	.	6:21	1.579	1.596	.	9:28	362.9	14,590
1	.	6:38	1.549	1.796	1	.	6:54	1.507	1.544	.	10:02	372.7	14,539
2	.	6:46	1.327	1.675	2	.	7:03	1.391	1.581	.	10:30	380.3	13,843
2	.	7:21	1.573	1.761	1	.	7:31	1.470	1.663	.	11:00	390.5	14,192
1	.	7:48	1.445	1.839	1	.	8:04	1.470	1.763	.	11:30	389.5	14,255
2	.	7:54	1.591	1.833	2	.	8:10	1.618	1.751	.	12:00	390.8	15,211
2	.	8:27	1.473	1.907	1	.	8:37	1.519	1.854	.	12:29	390.5	14,992
1	.	8:54	1.526	1.985	1	.	9:10	1.556	1.908	.	13:00	391.1	14,621
2	.	9:00	1.640	1.978	2	.	9:17	1.636	1.894	.	13:59	391.4	14,127
2	.	9:33	1.633	1.965	1	.	9:44	1.566	1.935	.	14:30	391.7	14,268
1	.	10:01	1.503	1.988	1	.	10:17	1.581	1.971	.	14:59	391.4	14,160
2	.	10:06	1.642	1.981	2	.	10:23	1.731	1.955	.	15:30	391.7	14,938
2	.	10:40	1.536	2.105	1	.	10:50	1.636	2.039	.	16:00	391.4	16,314
1	.	11:07	1.546	2.099	1	.	11:24	1.604	2.038	.	16:33	391.7	14,802
2	.	11:13	1.509	2.067	2	.	11:30	1.727	2.019	.	17:00	391.4	13,662
2	.	11:46	1.601	1.943	1	.	11:57	1.514	1.890	.	17:30	391.4	14,566
1	.	12:13	1.460	1.955	1	.	12:30	1.499	1.892	.	18:00	391.4	14,881
2	.	12:20	1.439	1.928	2	.	12:36	1.649	1.870	.	18:35	391.7	13,317
2	.	12:53	1.620	1.947	1	.	13:03	1.499	1.904	.	19:06	390.2	13,879
1	.	13:20	1.516	1.972	1	.	13:37	1.524	1.957	.	20:05	391.5	14,222
2	.	13:26	1.638	1.956	2	.	13:43	1.660	1.927	.	20:33	391.4	14,398
2	.	13:59	1.474	1.957	1	.	14:10	1.552	1.778	.	21:19	391.4	13,919

TABLE E1

REDUCTION DATA: MEASURED COMPOSITIONS (continued)

GC #	Day	Time	H2 in mole%	CO in mole%	GC #	Day	Time	H2 out mole%	CO out mole%	Day	Time	Temp (F)	Flow (SCFH)
1	4/30/91	14:26	1.516	1.713	1	4/30/91	14:43	1.542	1.707	4/30/91	22:15	391.4	14,473
2	.	14:33	1.668	1.693	2	.	14:49	1.637	1.660	.	22:40	391.7	14,829
2	.	15:06	1.715	1.650	1	.	15:16	1.633	1.836	.	22:55	391.4	14,214
1	.	15:33	1.541	1.664	1	.	15:49	1.642	1.830				
2	.	15:39	1.555	1.790	2	.	15:56	1.780	1.759				
2	.	16:12	1.763	1.780	1	.	16:23	1.677	1.856				
1	.	16:39	1.498	1.943	1	.	16:56	1.488	2.027				
2	.	16:46	1.575	1.880	2	.	17:02	1.609	1.987				
2	.	17:50	1.418	1.970	2	.	17:34	1.458	1.898				
1	.	17:59	1.363	1.939	1	.	17:42	1.374	1.899				
2	.	18:24	1.510	2.005	1	.	18:15	1.358	1.904				
2	.	18:57	1.538	2.126	2	.	18:40	1.600	2.142				
1	.	19:05	1.470	2.052	1	.	18:48	1.549	2.216				
2	.	19:30	1.360	2.072	1	.	19:22	1.411	1.966				
2	.	20:07	1.527	2.132	2	.	19:47	1.392	2.099				
1	.	20:15	1.405	2.085	1	.	19:58	1.444	2.111				
2	.	20:57	1.255	1.788	1	.	20:31	1.414	2.061				
1	.	21:21	1.417	2.180	1	.	21:05	1.329	2.045				
2	.	21:30	1.468	2.182	2	.	21:13	1.382	2.003				
2	.	22:03	1.379	2.052	1	.	21:40	1.394	2.130				
1	.	22:30	1.310	2.181	1	.	22:14	1.378	2.151				
2	.	22:36	1.407	2.140	2	.	22:20	1.433	2.117				

FIGURE E1

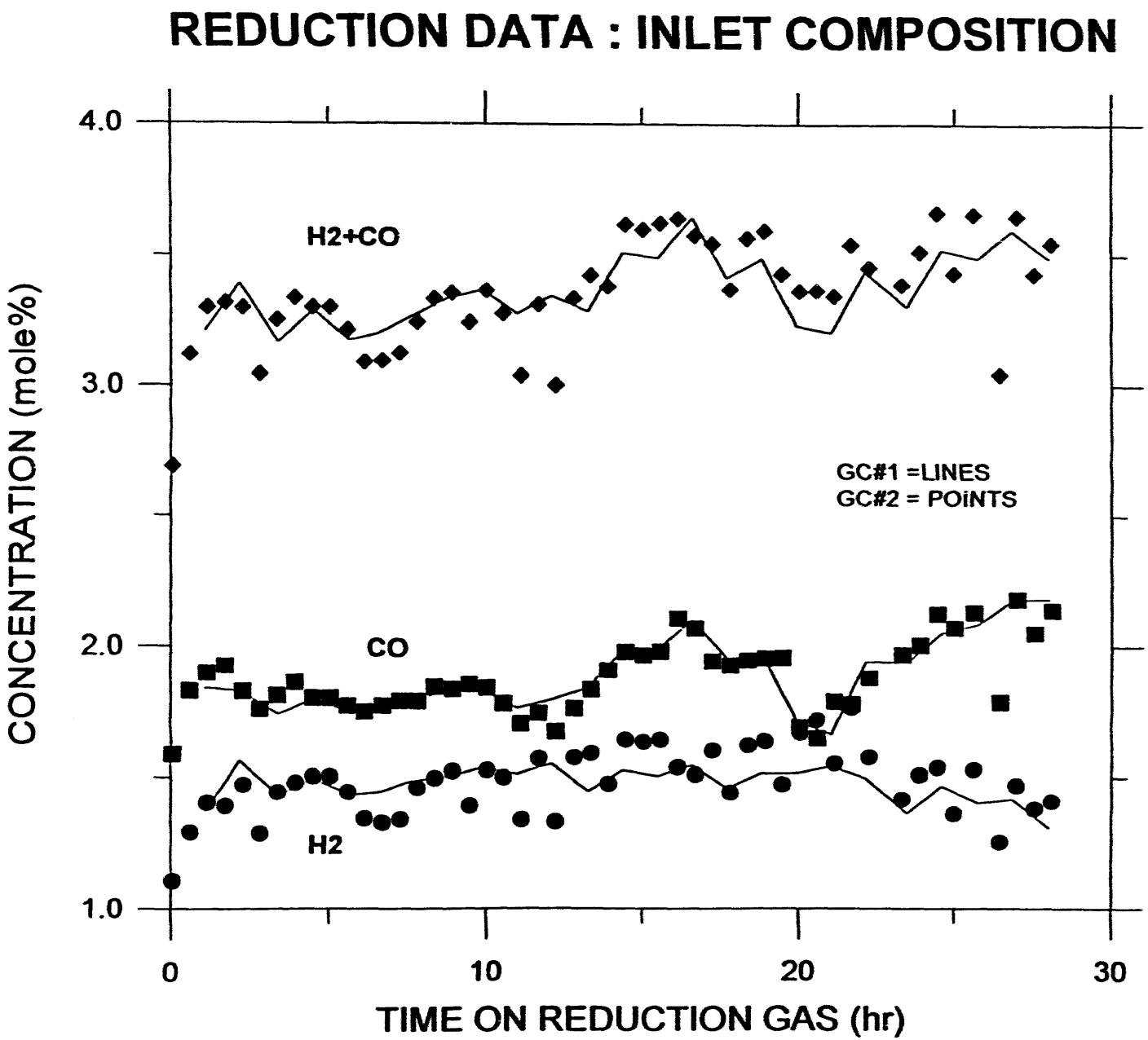

REDUCTION DATA : INLET COMPOSITION
4.0
3.0
2.0
1.0
CONCENTRATION (mole%)
H2+CO
CO
H2
GC#1 =LINES
GC#2 = POINTS
0
10
20
30
TIME ON REDUCTION GAS (hr)

FIGURE E2

REDUCTION DATA: OUTLET COMPOSITION

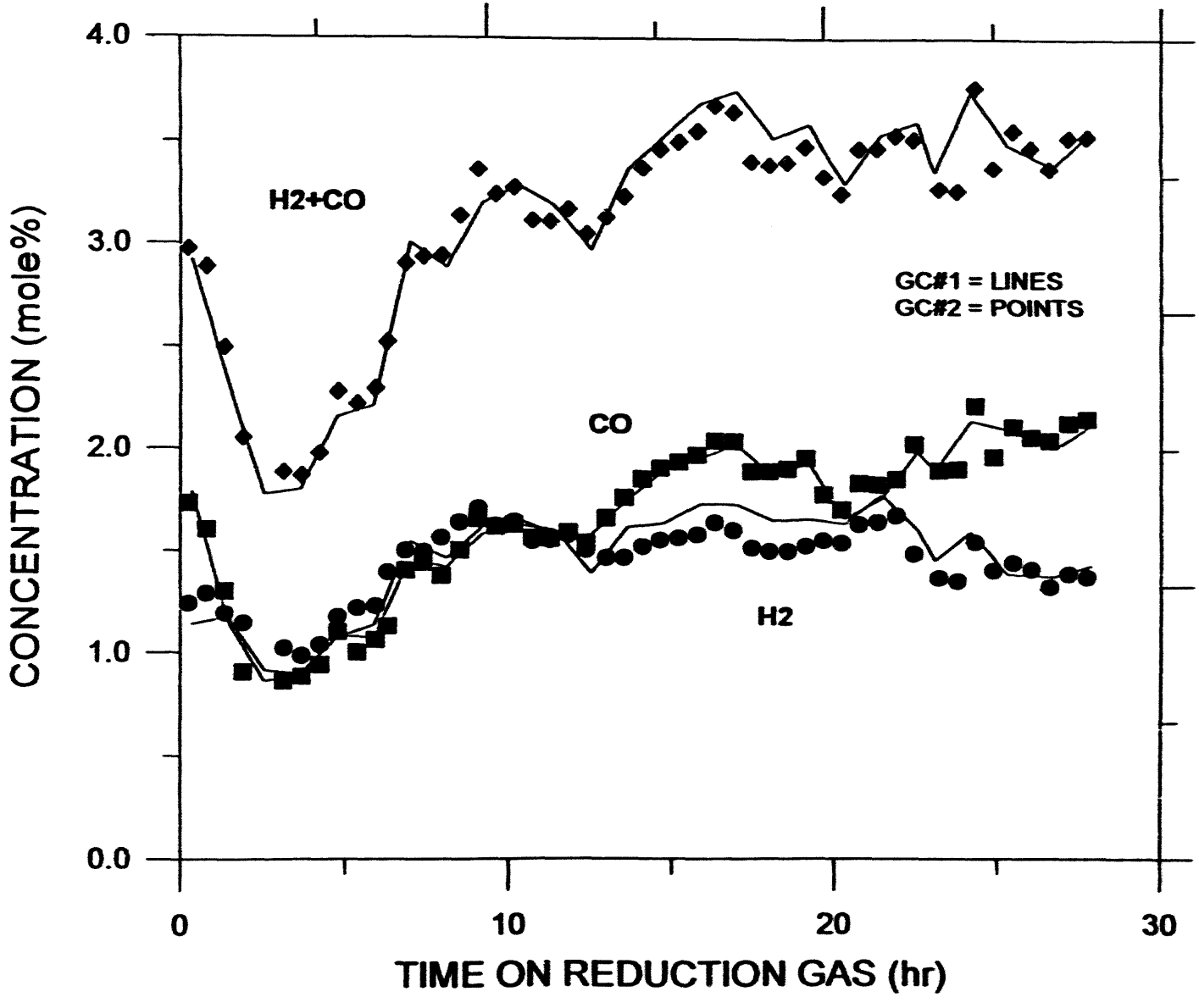
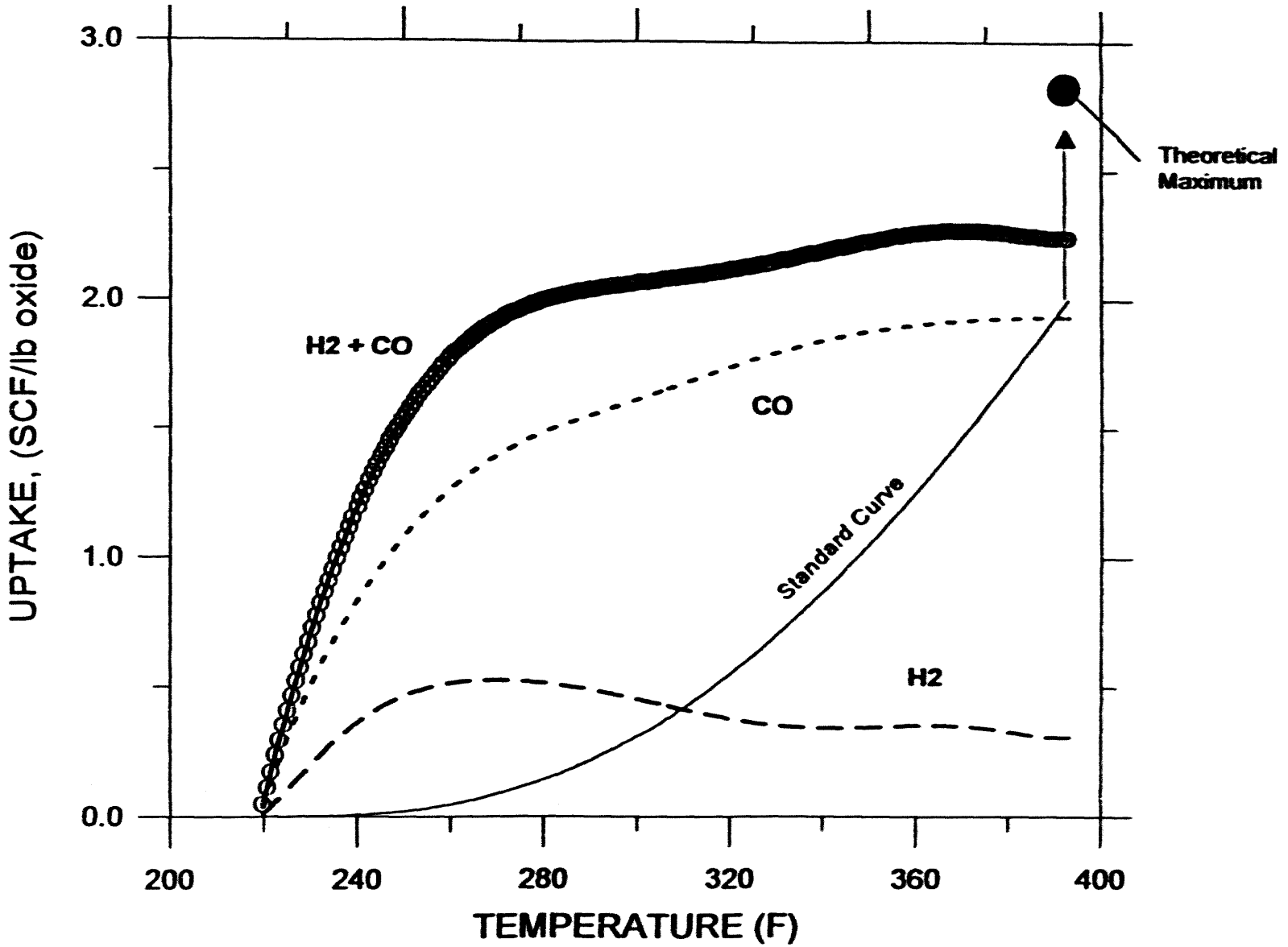


FIGURE E3

ACTIVATION A2: Reduction Gas Uptake vs. Temperature



APPENDIX F :
ANALYTICAL DATA / LIQUID PRODUCTION / CATALYST RECONCILIATION

Most of the run data was recorded by the data acquisition computer and can be retrieved from tape in the future, if necessary. Some of the data, however, is not. This section documents such data as well as "corrected" data.

Liquid Samples

Liquid samples were taken from the bottom of the 22.11 flash pot. During methanol-only operation, this sample is representative of the methanol collected in the day tank. Table F1 present the analysis of individual samples taken roughly 12 hours apart during the AF-R1 series.

Table F2 contains the analysis of 22.11 liquid samples taken during the AF-R2 and AF-R3 series. Note that an additional component, called Volatiles, has been added. When significant quantities of DME are produced and a sample is taken from the 22.11, gasses are evolved. A method of determining the quantity of gases evolved was developed (based on weight differences) and applied to correct the GC analysis of the remaining liquid. Based on thermodynamic equilibrium calculations it is estimated that the volatiles contain 60% DME, 20% CO_2, 20% MeOH (by mole).

Table F3 contains some miscellaneous liquid samples taken during the course of operations.

Vapor Samples

During the DME runs, the vapors from the 22.11 flash pot and 22.18 DME degasser were taken at discreet times and not continuously, Table F4 contains the composition data for the 22.11; Table F5 contains the composition data for the 22.18.

The reactor effluent composition is key to developing accurate mass balances. Unfortunately, the Karle GCs are nonlinear in the response to methanol. This means that response factors determined for one methanol composition is not the same for either higher or lower concentration. The solution to this shortcoming in the GCs is to develop response factors charts to correct the analyses reported by the GCs.

Procedurally, a 3.82 mole% MeOH standard is used to calibrate the GCs and correction factors are applied when the measured composition is deviates from 3.82 mole %. The GC correction curves were developed based on available 1.22 mole% and 3.82 mole% standards and previously determined curves. A comparison of the previous correction curves and the "new" correction curves is presented in Figure F1.

The correction curves presented in Figure F1 were applied to the GC-reported data to correct the MeOH composition. The actual MeOH and DME concentrations in the reactor effluent are presented in Figures F2, F4, and F5 for runs AF-R1, R2, and R3, respectively.

Liquid Production

The liquid production is measured by tracking level rise in the 22.16 day tank with time. A plot of accumulated production with time is presented in Figure F5. The production rate is calculated from the slope of the production curve (as is reported on the figure).

Catalyst Reconciliation

Establishing the quantity of catalyst and catalyst proportion within the reactor was complicated by the fact that catalyst was withdrawn and added on two occasions and by the occurrence of catalyst settling. Fortunately, the catalyst "material balance" could be closed with reasonable certainty.

The quantities of catalyst added to the system are easily determined since catalyst was added by measured weight. The methanol catalyst was added once (489 lb). Alumina was added on two occasions (32 lb and 67.5 lb). When the methanol catalyst is activated there is a 25% weight loss; when the alumina is dried there is a 4% weight loss. From this the net weight of catalyst added can be calculated. These weights, summarized in Table F6.1, must be accounted for later.

When catalyst was removed from the plant it was drained into 55 gallon drums along with an unknown quantity of oil. The weight and volume of each mix was measured and from this the density of the slurry in each drum could be determined.

There were 12 different lots of catalyst and oil withdrawn from the plant. The weights and density of each lot is summarized in Table F6.2. To summarize, two drums were drained from the reactor during the run (marked S1 and S2), 5 drums were drained from the reactor at the end-of-run (denoted D1-D5), 3 drums of "rinse oil" were drained from plant (marked as R1-R3, these contained very little catalyst), and 2 lots of concentrated slurry were physically removed from the bottom of the reactor following shut-down and rinsing.

The density of the reduced or dried catalyst was known and the density of the oil-alone was measured. These densities are:

Component	Density lb/ft^3
BASF S3-86	357.6
Catapal γ-Alumina	206.5
Oil	53.3

If the proportion of alumina is known then the quantities of oil, methanol catalyst and alumina can be determined for each drum. To determine the alumina proportion the following sequence of events were assumed to occur:

Step	Action
1	489 lb Methanol catalyst was charged to the reactor and fully reduced
2	The 14 lb "lodged in piping" lot settled in the 4" piping in the reactor bottom during activation.
3	Drum S1 was withdrawn from the reactor at the end of AF-R1.
4	32 lb of alumina was dried then added to the remaining methanol catalyst
5	Drum S2 was withdrawn from the reactor at the end of AF-R2
6	67.5 lb of alumina was dried then added to the remaining alumina/methanol catalyst mix
7	The 74 lb "settled in reactor head" lot settled out in the bottom head right before AF-R3 began
8	Following run AF-R3, the slurry in the reactor was drained into drums D1-D5
9	Rinse oil was added to the reactor and drained into drums R1-R3

Given this sequence of events it was possible to calculate the proportion of alumina in the reactor at any point during the run. With this information the quantities of S3-86, alumina and oil were determined for each lot as summarized in Table F6.2. The weight of alumina and S3-86 was then summed for all the lots as indicated by "TOTAL" (in Table F6.2). These totals must agree with the "TOTAL" from Table F6.1. As can be seen, agreement is within 1% which is excellent.

As a check on the consistency of this method, elemental analysis of selected lots was performed as summarized in Table F7. As shown the agreement is reasonable.

To summarize, the quantity and proportion of catalyst in the reactor for each of the runs is presented below:

RUN	Mass of Catalyst (lb, As-Charged Basis)			Weight %
	BASF S3-86	Alumina	Total	Alumina
AF-A2	489.0	0.0	489.9	0.0
AF-R1	479.4	0.0	479.4	0.0
AF-R2	452.6	32.0	484.6	6.6
AF-R3	362.6	86.7	449.3	19.3

TABLE F1

LIQUID SAMPLES FROM 22.11 - RUN AF-R1

Date	5/2/91	5/3/91	5/3/91	5/3/91	5/4/91	5/4/91	5/5/91	5/6/91	5/6/91	5/6/91	Average
Time	12:20	0:55	14:45	23:55	12:00	23:58	12:00	0:10	12:30	23:50	wt%
Methanol	96.706	96.669	96.79	96.697	96.748	96.785	96.713	95.776	96.06	96.819	96.800
Ethanol	0.603	0.576	0.611	0.645	0.63	0.602	0.61	0.892	0.832	0.593	0.645
n-Propanol	0.213	0.211	0.217	0.233	0.229	0.217	0.221	0.334	0.294	0.209	0.232
IsoPropanol	0.01	0.012	0.013	0.013	0.013	0.013	0.013	0.017	0.008	0.012	0.012
n-Butanol	0.097	0.098	0.105	0.108	0.108	0.107	0.108	0.108	0.139	0.101	0.107
sec Butanol	0.036	0.028	0.034	0.04	0.034	0.036	0.033	0.043	0.042	0.034	0.036
IsoButanol	0.032	0.028	0.029	0.025	0.034	0.03	0.032	0.053	0.049	0.031	0.033
n-Pentanol	0.056	0.053	0.055	0.063	0.074	0.059	0.056	0.086	0.08	0.058	0.063
IsoPentanol	0.045	0.043	0.04	0.047	0.038	0.046	0.046	0.063	0.028	0.034	0.043
2,3-Pentanol	0.029	0.025		0.027	0.024	0.03	0.026	0.038	0.035	0.028	0.026
Methyl Formate	1.161	1.052	1.051	1.014	0.998	1.043	1.03	1.299	1.279	1.042	1.084
Methyl Acetate	0.156	0.132	0.141	0.151	0.145	0.137	0.135	0.279	0.248	0.136	0.159
Dimethyl Ether	0.034	0.031	0.029	0.027	0.028	0.027	0.026	0.036	0.036	0.027	0.030
Water	0.496	0.499	0.507	0.524	0.506	0.529	0.524	0.425	0.421	0.535	0.504
Mineral Oil	0.281	0.386	0.215	0.168	0.231	0.19	0.227	0.173	0.165	0.182	0.226
SUM	99.958	99.843	99.837	99.803	99.84	99.851	99.8	99.629	99.723	99.841	100

TABLE F2

LIQUID SAMPLES FROM 22.11 - RUN AF-R2 & AF-R3

Date	5/9/91	5/9/91	5/10/91	5/10/91	5/11/91	5/11/91	5/12/91	5/12/91	5/14/91	5/15/91	5/15/91	5/16/91	5/16/91	5/17/91
Time	3:45	14:20	0:10	12:00	1:00	13:00	0:15	12:05	12:05	0:30	12:56	0:15	18:00	6:20
Methanol	77.795	79.015	78.5124	84.0897	83.723	84.05	79.548	77.36	73.138	65.76	75.914	75.316	74.822	71.243
Ethanol	0.347	0.388	0.342	0.2826	0.298	0.307	0.385	0.394	0.062	0.049	0.048	0.049	0.058	0.056
n-Propanol	0.123	0.14	0.1224	0.1017	0.122	0.109	0.136	0.146	0.035	0.028	0.026	0.027	0.028	0.028
IsoPropanol	0.009	0.009	0.0081	0.0081	0.008	0.008	0.011	0.009	0	0	0	0	0.003	0
n-Butanol	0.052	0.057	0.0531	0.0549	0.046	0.049	0.061	0.061	0.045	0.01	0.012	0.008	0.009	0.01
sec Butanol	0.024	0.027	0.0252	0.0306	0.028	0.023	0.032	0.029	0.006	0.007	0.007	0.007	0.007	0.008
IsoButanol	0.025	0.034	0.0243	0.0324	0.019	0.017	0.025	0.028	0.008	0.008	0.006	0.006	0.008	0.008
n-Pentanol	0.022	0.025	0.0207	0.0189	0.021	0.02	0.02	0.026	0.005	0	0	0	0.006	0
IsoPentanol	0	0	0.0216	0	0	0	0	0	0	0	0	0	0	0
2,3-Pentanol	0.021	0.021	0.0207	0.0216	0.016	0.018	0.024	0.023	0	0	0	0	0	0
Methyl Formate	0.456	0.5	0.495	0.4329	0.449	0.447	0.506	0.503	0.639	0	0.57	0	0.348	0
Methyl Acetate	0.061	0.068	0.0549	0.0396	0.041	0.043	0.072	0.071	0	0	0	0	0	0
Dimethyl Ether	8.597	5.93	8.0505	3.1968	4.118	3.601	6.144	4.544	4.758	7.689	5.042	8.135	3.05	8.685
Water	1.074	1.053	1.0152	1.0386	1.186	1.039	0.908	0.887	4.087	4.228	3.871	3.989	4.061	3.719
Mineral Oil	0.781	0.661	0.7956	0.3375	0.463	0.36	0.362	0.4	0.948	0.622	0.522	0.762	0.841	1.08
Volatiles	10	11.5	10	10	9.1	9.6	11.25	14.92	16.13	21.51	13.93	11.639	16.67	15.04
SUM	99.388	99.428	99.5617	99.6859	99.638	99.691	99.484	99.401	99.861	99.911	99.948	99.938	99.911	99.877

• The volatile content was not measured for these samples. Volatile content shown is estimated.

TABLE F3

VARIOUS LIQUID SAMPLES FROM OTHER VESSELS

	22.18			22.16			28.10
Date	5/11/91	5/12/91	5/14/91	5/11/91	5/16/91	5/17/91	5/20/91
Time	8:00	5:00	12:00	13:00	0:30	7:45	-
Methanol	86.37	86.972	89.008	90.47	85.367	86.449	91.313
Ethanol	0.225	0.242	0.206	0.382	0.061	0.049	0.425
n-Propanol	0.043	0.054	0.05	0.136	0.034	0.031	0.165
isoPropanol	0.006	0.007	0.006	0.01	0	0	0.009
n-Butanol	0.012	0.011	0.009	0.059	0.012	0.011	0.071
sec Butanol	0.009	0.008	0.01	0.031	0.007	0.008	0.028
isoButanol	0.008	0	0.008	0.026	0.008	0.009	0.028
n-Pentanol	0	0	0	0	0	0	0.033
isoPentanol	0	0	0	0.026	0	0	0
2,3-Pentanol	0	0	0	0.023	0	0	0.022
Methyl Formate	1.153	0.931	0.581	0.52	0.787	0.557	0.608
Methyl Acetate	0.088	0.099	0.067	0.065			0.092
Dimethyl Ether	8.702	8.472	8.162	6.046	8.491	8.485	5.432
Water	2.893	2.633	1.515	1.117	4.372	4.318	1.463
Mineral Oil				0.61	0.762		
Volatiles							
SUM	99.509	99.429	99.622	99.521	99.901	99.917	99.689

TABLE F4

VAPOR SAMPLES FROM 22.11 - RUN AF-R2 & AF-R3

Date	5/10/91	5/10/91	5/11/91	5/11/91	5/11/91	5/11/91	5/12/91	5/12/91	5/14/91	5/14/91	5/14/91	5/17/91	5/17/91
Time	19:22	20:28	3:16	4:26	19:00	20:07	5:51	6:57	5:35	6:42	7:48	4:26	5:32
Hydrogen	3.285	3.166	3.206	3.22	2.381	2.409	2.456	2.502	2.012	1.884	1.864	2.048	2.059
Nitrogen	0.154	0.154	0.132	0.131	0.095	0.097	0.101	0.102	0.383	0.506	0.161	0.067	0.064
Methane	0.078	0.079	0.095	0.095	0.071	0.069	0.084	0.095	0	0.048	0.051	0	0
Carbon Monoxide	14.199	14.218	14.164	14.25	11.622	11.655	11.762	11.813	7.996	7.881	7.515	8.166	8.136
Carbon Dioxide	47.938	47.784	47.98	48	46.724	46.311	48.012	48.181	39.04	38.035	37.139	40.621	40.395
Water	0.084	0.094	0.075	0.083	0.088	0.076	0.071	0.06	0.156	0.185	0.204	0.238	0.187
Methanol	4.776	4.659	4.77	4.717	4.051	3.911	3.816	3.669	3.14	3.306	3.147	3.014	3.051
Dimethyl Ether	27.173	27.082	27.608	27.514	31.936	31.303	31.977	31.653	47.734	47.235	48.65	45.362	45.36
SUM	97.687	97.236	98.03	98.01	96.968	95.831	98.279	98.075	100.461	99.08	98.731	99.516	99.252

TABLE F5

VAPOR SAMPLES FROM 22.18 - RUN AF-R2 & AF-R3

Date	5/10/91	5/10/91	5/11/91	5/11/91	5/11/91	5/12/91	5/12/91	5/14/91	5/14/91	5/16/91	5/16/91	5/16/91
Time	17:09	18:16	5:33	6:39	21:14	8:04	9:10	8:55	10:00	6:58	8:04	5:51
Hydrogen	0.759	0.783	0.755	0.744	0.7	0.582	0.725	0.777	0.619	0.819	0.774	0.711
Nitrogen	0.052	0.052	0	0.041	0.041	0.042	0.043	0.069	0.067	0	0	0
Methane	0	0	0	0	0	0	0	0	0	0	0	0
Carbon Monoxide	4.695	4.74	4.864	4.543	4.754	4.886	4.866	4.738	4.65	4.048	3.81	3.38
Carbon Dioxide	40.91	40.88	40.913	41.029	41.609	43.303	43.245	43.422	43.159	35.836	33.973	31.869
Water	0.099	0.082	0.088	0.106	0.094	0.072	0.088	0.189	0.266	0.201	0.162	0.185
Methanol	5.713	5.251	6.625	6.626	6.726	7.17	7.542	5.089	5.067	7.793	7.638	6.502
Dimethyl Ether	46.433	45.877	45.025	45.973	42.073	42.5	42.57	45.608	45.65	55.306	52.998	57.617
SUM	98.661	97.665	98.27	99.062	95.997	98.555	99.079	99.892	99.478	104.003	99.355	100.264

Date	5/16/91	5/16/91	5/17/91	5/17/91
Time	19:12	21:33	6:39	7:45
Hydrogen	0.844	0.857	0.818	0.929
Nitrogen	0	0	0	0
Methane	0	0	0	0
Carbon Monoxide	4.746	4.73	4.674	4.631
Carbon Dioxide	42.239	42.704	42.218	42.036
Water	0.161	0.173	0.2	0.221
Methanol	4.637	4.758	5.436	5.553
Dimethyl Ether	46.265	46.357	46.088	45.846
SUM	98.892	99.579	99.434	99.216

TABLE F6
CATALYST INVENTORY RECONCILIATION

6.1 Catalyst Added

Date		Weight As Charged (lb) S3-86	Al2O3	Total		After Activation/Drying (lb) S3-86	Al2O3	Total
4/29/91	Initial Charge	489	0	489		367	0	367
5/6/91	1st Alumina Addition		32	32			31	31
5/12/91	2nd Alumina Addition		67.5	68			65	65
					TOTAL	366.8	95.7	462.4

6.2 Catalyst Recovered (Catalyst Data on Post Activation/Drying Basis)

Date		Total Wt Oil+Cat. (lb)	Density (lb/ft3)	Weight Fraction Catalyst	Wt % Al2O3	Catalyst Mass (lb) S3-86	Al2O3	Total
5/7/91	S1 - 1st Drain	78	68.56	0.2615	0	20.4	0	20.4
5/13/91	S2 - 2nd Drain	150	70.32	0.2874	8.31	39.5	3.6	43.1
5/17/91	D1 - Post Run Drain	348	63.72	0.1982	23.47	52.8	16.2	69.0
	D2 - Post Run Drain	388	63.15	0.1890	23.47	56.1	17.2	73.3
	D3 - Post Run Drain	378	63.43	0.1936	23.47	56.0	17.2	73.2
	D4 - Post Run Drain	402	62.74	0.1824	23.47	56.1	17.2	73.3
	D5 - Post Run Drain	323	62.61	0.1802	23.47	44.5	13.7	58.2
5/20/91	R1 - Post Run Rinse	386	54.17	0.0196	23.47	5.8	1.8	7.6
	R2 - Post Run Rinse	380	53.98	0.0152	23.47	4.4	1.4	5.8
	R3 - Post Run Rinse	286	53.48	0.0042	23.47	0.9	0.3	1.2
5/21/91	Lodged in Piping	14	-	-	0	7.4	0	7.4
	Settled in Reactor Head	74	92.82	0.5158	23.47	26.0	8.0	34.0
					TOTAL	369.9	96.4	466.4

TABLE F7
ELEMENTAL ANALYSIS OF CATALYST SAMPLES

Elemental Analysis

		Cu (wt%)	Zn (wt%)	Al (wt%)	Wt% Al2O3 * meas	assumed	Cu/Zn (lb/lb) * meas	vendor
5/13/91	S2 - 2nd Drain	67.81	23.75	8.44	5.9	6.6	2.86	2.6
5/17/91	D1 - Post Run Drain	59.54	20.61	19.85	20.6	19.3	2.89	2.6
	D3 - Post Run Drain	53.18	19.05	27.77	30.3	19.3	2.79	2.6
5/21/91	Settled in Reactor Head	54.25	18.55	27.20	29.5	19.3	2.92	2.6
	Settled in Reactor Head	56.06	19.71	24.23	25.9	19.3	2.84	2.6
	Settled in Reactor Head	55.99	19.56	24.45	26.2	19.3	2.86	2.6

* The "measured" Al2O3 content of the catalyst mix (oxide/wet basis) was calculated from the elemental analysis as was the "measured" Cu/Zn ratio. The "assumed" Al2O3 content was based on material charged and/or settled.

FIGURE F1

GC FACTORS FOR CORRECTING COMPOSITION

(Comparison of old and new factors)

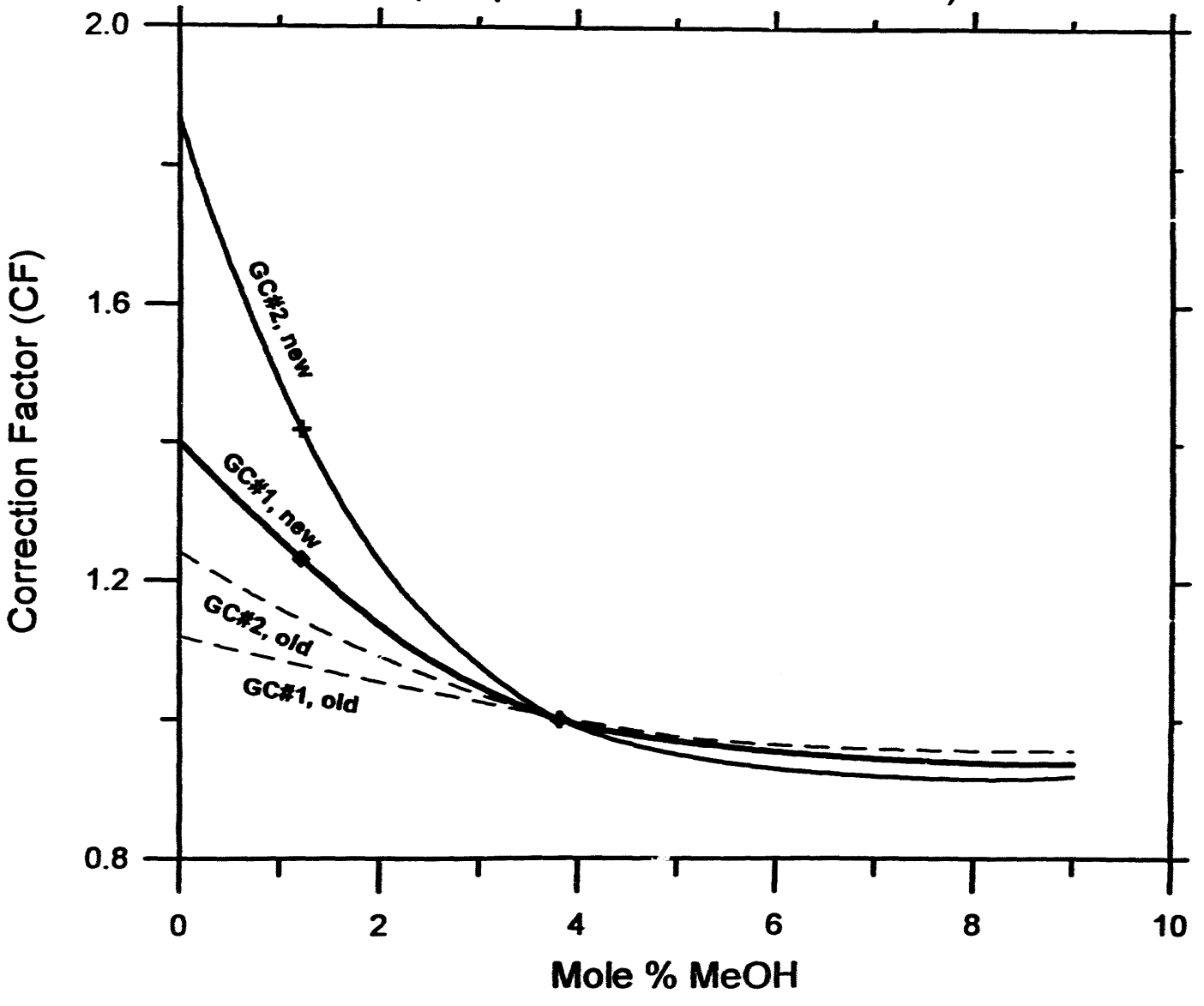


FIGURE F2

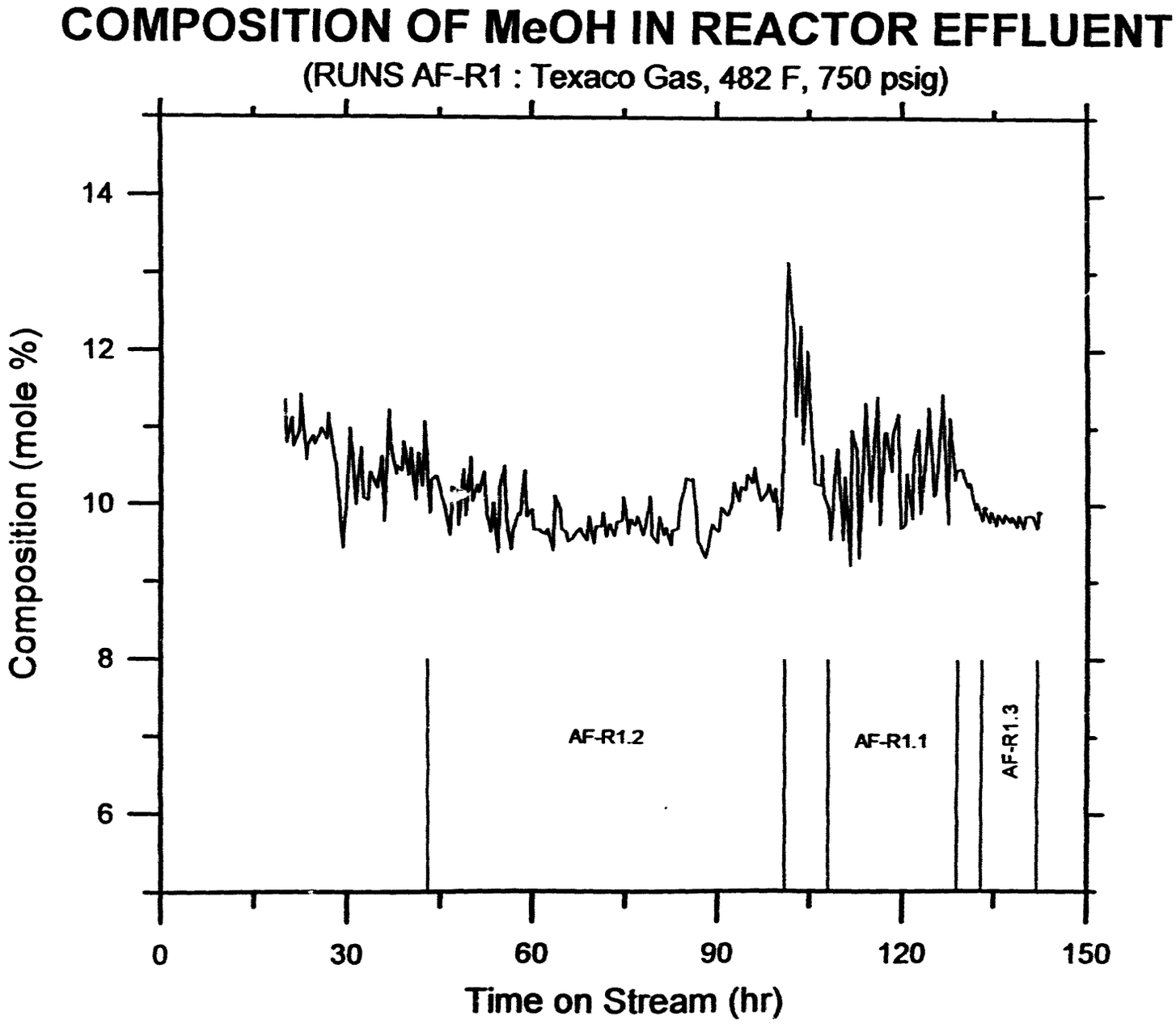

COMPOSITION OF MeOH IN REACTOR EFFLUENT
(RUNS AF-R1 : Texaco Gas, 482 F, 750 psig)
Composition (mole %)
14
12
10
8
6
AF-R1.2
AF-R1.1
AF-R1.3
0
30
60
90
120
150
Time on Stream (hr)

FIGURE F3

COMPOSITION OF DME AND MeOH IN REACTOR EFFLUENT

(RUNS AF-R2 : Texaco Gas, 482 F, 750 psig)

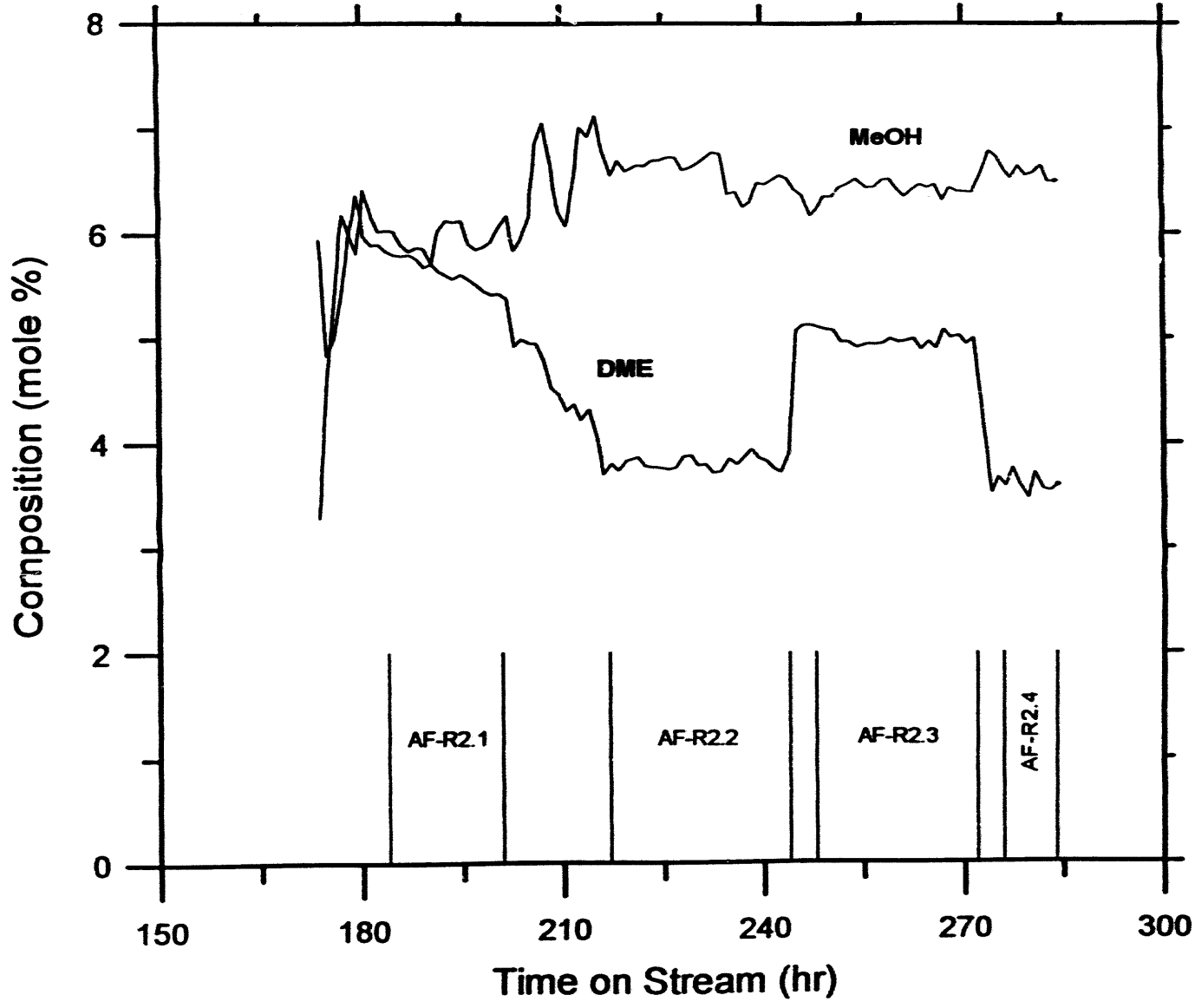


FIGURE F4

COMPOSITION OF DME AND MeOH IN REACTOR EFFLUENT

(RUNS AF-R3 : Texaco Gas, 482 F, 750 psig)

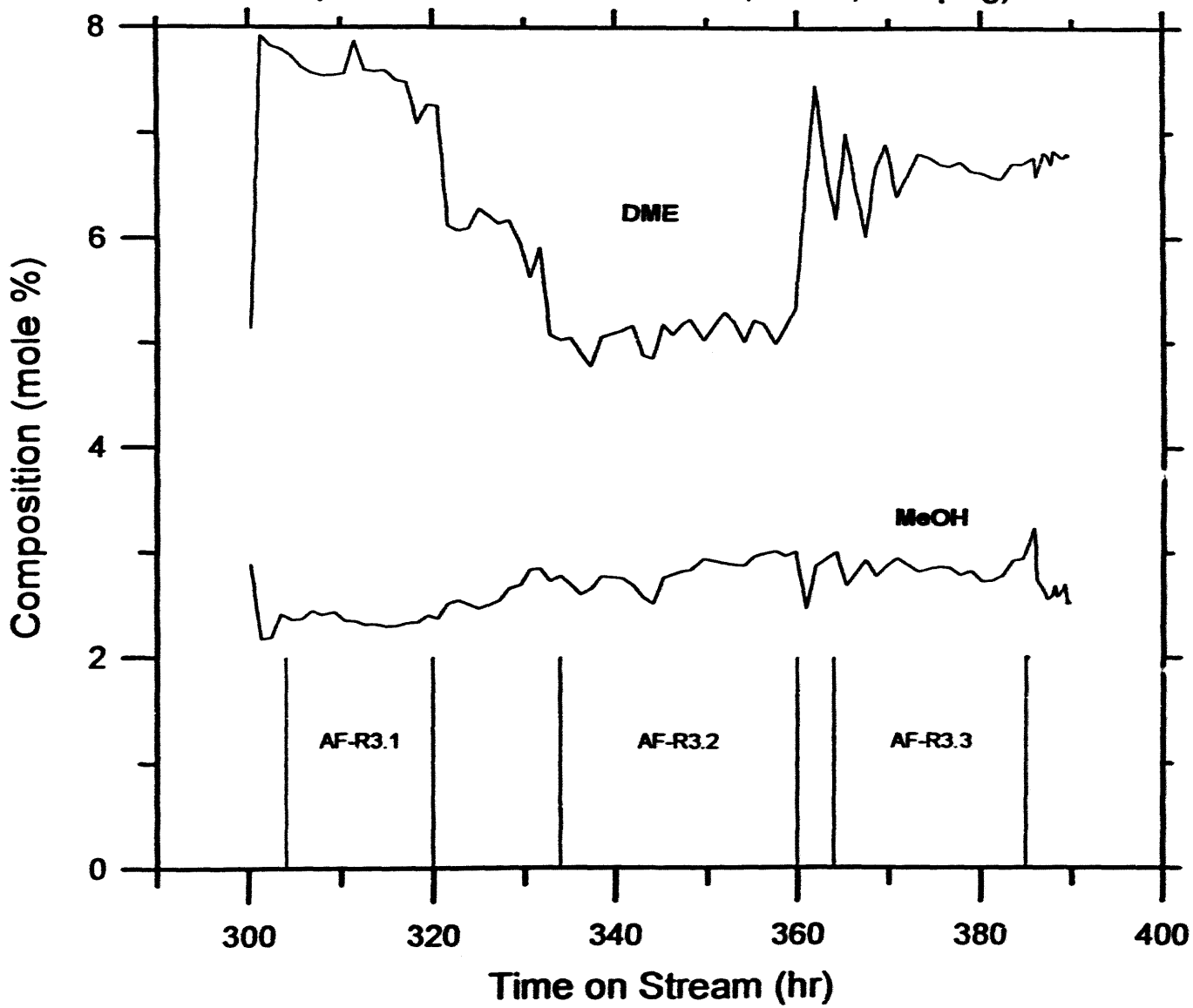
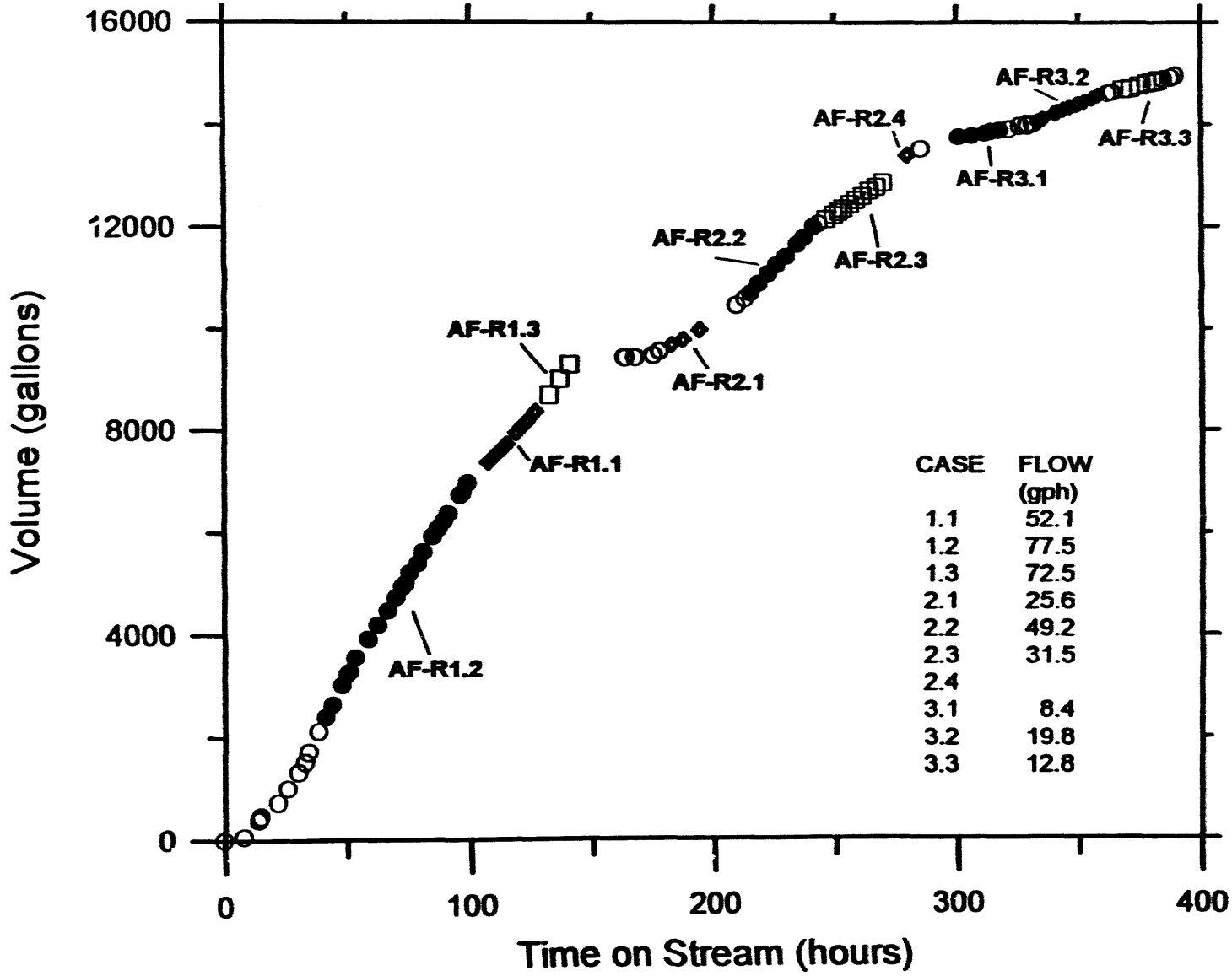


FIGURE F5

LIQUID PRODUCTION AS MEASURED IN DAY TANK

(All Runs)



APPENDIX G : MATERIAL BALANCE DATA SHEETS

Detailed material balance sheets are contained here. Table G1 provides definitions and clarifications. Tables G2-G11 contain the data for each of the runs.

TABLE G1 : DEFINITIONS

VARIABLE	DEFINITION
Temperature (°F)	Reactor Temperature
Pressure (psig)	Reactor Pressure
Reactor Level (inches on Tape)	Slurry level in reactor as measured on the tape (213" is 100% of max level)
Space Velocity (sL/hr-kg oxide)	Space velocity of reactor feed gas, catalyst weight is on as-charged basis
Catalyst Proportion (% Al2O3)	The weight % alumina in the alumina/83-86 mix
Catalyst Weight (lb)	Total amount of catalyst in reactor, as-charged basis
Slurry Concentration (wt %)	the weight % of catalyst in the catalyst/oil mix, as-charged basis
Inlet Superficial Vel. (ft/sec)	Gas velocity of reactor feed, based on cross-sectional area of reactor
Outlet Superficial Vel. (ft/sec)	Gas velocity of reactor effluent, based on cross-sectional area of reactor
Gas Holdup (vol %)	The volume % vapor in the slurry
CO Conversion (%)	The amount of CO in the reactor feed which is consumed in reaction (%)
Syngas Conversion (%)	The amount of CO+H2 in the reactor feed which is consumed in reaction
Eq. Productivity (gmoles/hr-kg)	Productivity of MeOH plus twice the productivity of DME
MeOH Make (Ton/day)	Amount of MeOH produced in the reactor
DME Make (Ton/day)	Amount of DME produced in the reactor
Stream Designation	
Fresh Feed	Flow of material into the plant
Recycle	The flow which combines with Fresh Feed to form the Reactor Feed
Reactor Feed	Recycle flow plus Fresh Feed flow, flow to reactor
Reactor Out	Vapor flow from the 27.14, reactor effluent less oil
22.10 Sep Vap	Vapor from 22.10 separator, sent to DME/CO2 section
22.11 Liq	Liquid flow from 22.11 flash pot, sent to day tank, exits plant
22.11 Vap	Flash gas generated when 22.10 liquid is sent to 22.11, exits plant
Plant Purge	Plant purge, same composition as Recycle, exits plant
DME Product	Liquid from the 22.14 separator, generally vaporized as rejected as gas
Flow (lb mole/hr)	Flow of designated stream in molar units
MW	Molecular weight of designated stream
Flow (lb/hr)	Flow of designated stream in mass units

TABLE G2
MATERIAL BALANCE FOR RUN AF-R1.1

Balance Period:		**Space Velocity (sL/hr-kg oxide)**	5711	**Gas Holdup (vol %)**	33.2
Start Date	5/5 20:00	**Catalyst Proportion (% Al2O3)**	0	**CO Conversion (%)**	18.1
End date	5/6 17:00	**Catalyst Weight (lb)**	479.4	**Syngas Conversion (%)**	31.4
TOS (hr)	108 to 129	**Slurry Concentration (wt %)**	30.7	**Eq. Productivity (gmoles/hr-kg)**	21.8
Temperature (°F)	480.1	**Inlet Superficial Vel. (ft/sec)**	0.24	**MeOH Make (Ton/day)**	4.0
Pressure (psig)	750	**Outlet Superficial Vel. (ft/sec)**	0.20	**DME Make (Ton/day)**	0.0
Reactor Level (inches on Tape)	154				

	Fresh Feed	Recycle	Reactor Feed	Reactor Out	22.18 Sep Vap	22.11 Liq	22.11 Vap	Plant Purge	DME Product
Hydrogen	53.21	24.19	35.50	21.53	24.19	0.00	3.64	24.19	0.00
Carbon Monoxide	40.80	57.23	50.80	50.77	57.23	0.00	23.27	57.23	0.00
Carbon Dioxide	5.80	17.74	13.13	16.34	17.74	0.00	68.32	17.74	0.00
Nitrogen	0.16	0.54	0.39	0.48	0.54	0.00	0.27	0.54	100.00
Methane	0.03	0.26	0.18	0.20	0.26	0.00	0.26	0.26	0.00
Water	0.00	0.00	0.01	0.08	0.00	0.76	0.00	0.00	0.00
Methanol	0.00	0.04	0.00	10.42	0.04	97.36	4.18	0.04	0.00
Other Oxygenates	0.00	0.00	0.00	0.19	0.00	1.85	0.00	0.00	0.00
Dimethyl Ether	0.00	0.00	0.00	0.00	0.00	0.03	0.05	0.00	0.00
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Flow (lb mole/hr)	45.20	76.15	122.26	100.14	89.65	10.60	0.01	13.50	0.00
MW	15.10	24.53	20.86	25.47	24.53	32.41	38.14	24.53	28.01
Flow (lb/hr)	682.66	1868.06	2550.72	2550.72	2199.22	343.70	0.34	331.14	0.00

Elemental Balances (Atoms In = Atoms Out)

Overall Balance:
Feed = Purge + MeOH Liq + Flash + DME Liq

	In	Out	(In-Out)*100 / In
Hydrogen	48.16	49.30	-2.4
Carbon	21.07	20.96	0.5
Oxygen	23.68	23.23	1.9
Nitrogen	0.14	0.15	-2.0
Total	93.06	93.64	-0.6

Reactor Balance
Reactor In = Reactor Out

	In	Out	(In-Out)*100 / In
Hydrogen	87.68	86.90	0.9
Carbon	78.38	78.28	0.1
Oxygen	94.23	94.35	-0.1
Nitrogen	0.94	0.95	-1.2
Total	261.23	260.49	0.3

Mole Balance (moles = moles)

Production Balance
Rxn Out-Rxn In = Products + Purges - Feed

	Made	Out-In	(M-O)*100 / Made
DME	0.00	0.00	9.6
MeOH	10.43	10.34	0.9
H2O	0.07	0.08	-10.3
CO2	0.30	-0.22	174.5
Total	10.81	10.20	5.7

TABLE G3
MATERIAL BALANCE FOR RUN AF-R1.2

Balance Period:		**Space Velocity (sL/hr-kg oxide)**	8866	**Gas Holdup (vol %)**	47.7
Start Date	5/3 3:00	**Catalyst Proportion (% Al2O3)**	0	**CO Conversion (%)**	16.8
End date	5/5 13:00	**Catalyst Weight (lb)**	479.4	**Syngas Conversion (%)**	29.9
TOS (hr)	43 to 101	**Slurry Concentration (wt %)**	30.3	**Eq. Productivity (gmoles/hr-kg)**	32.0
Temperature (°F)	480.3	**Inlet Superficial Vel. (ft/sec)**	0.37	**MeOH Make (Ton/day)**	5.9
Pressure (psig)	750	**Outlet Superficial Vel. (ft/sec)**	0.31	**DME Make (Ton/day)**	0.0
Reactor Level (Inches on Tape)	210				

	Fresh Feed	Recycle	Reactor Feed	Reactor Out	22.10 Sep Vap	22.11 Liq	22.11 Vap	Plant Purge	DME Product
Hydrogen	55.41	25.04	35.35	22.65	25.04	0.00	3.64	25.04	0.00
Carbon Monoxide	39.48	56.64	50.83	50.71	56.64	0.00	23.27	56.64	0.00
Carbon Dioxide	4.91	17.02	12.93	15.67	17.02	0.00	68.33	17.02	0.00
Nitrogen	0.17	0.68	0.50	0.60	0.68	0.00	0.26	0.68	100.00
Methane	0.02	0.30	0.21	0.25	0.30	0.00	0.26	0.30	0.00
Water	0.01	0.01	0.03	0.10	0.01	0.93	0.00	0.01	0.00
Methanol	0.00	0.31	0.16	9.89	0.31	97.64	4.18	0.31	0.00
Other Oxygenates	0.00	0.00	0.00	0.14	0.00	1.41	0.00	0.00	0.00
Dimethyl Ether	0.00	0.00	0.00	0.00	0.00	0.02	0.05	0.00	0.00
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Flow (lb mole/hr)	61.63	127.02	189.80	158.26	142.51	15.84	0.11	15.49	0.00
MW	14.39	24.20	20.87	25.03	24.20	32.28	38.14	24.20	28.01
Flow (lb/hr)	886.98	3074.27	3961.24	3961.24	3449.06	511.26	4.20	374.80	0.00

Elemental Balances (Atoms In = Atoms Out)

Overall Balance:
Feed = Purge + MeOH Liq + Flash + DME Liq

	In	Out	(In-Out)*100 / In
Hydrogen	68.36	71.64	-4.8
Carbon	27.37	27.61	-0.9
Oxygen	30.39	30.22	0.6
Nitrogen	0.21	0.21	-0.4
Total	126.33	129.68	-2.7

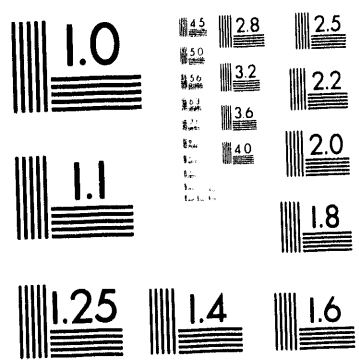
Reactor Balance
Reactor In = Reactor Out

	In	Out	(In-Out)*100 / In
Hydrogen	137.07	137.44	-0.3
Carbon	121.72	121.61	0.1
Oxygen	145.91	145.98	0.0
Nitrogen	1.88	1.89	-0.4
Total	406.59	406.92	-0.1

Mole Balance (moles = moles)

Production Balance
Rxn Out-Rxn In = Products + Purges - Feed

	Made	Out-In	(M-O)*100 / Made
DME	0.00	0.00	1.2
MeOH	15.35	15.62	-1.8
H2O	0.12	0.15	-28.2
CO2	0.26	-0.39	250.2
Total	15.73	15.38	2.2


1.0
1.1
1.25
1.4
1.6
2.8
3.2
3.6
4.0
2.5
2.2
2.0
1.8

2 of 2

TABLE G4
MATERIAL BALANCE FOR RUN AF-R1.3

Balance Period:		**Space Velocity (sL/hr-kg oxide)**	9137	**Gas Holdup (vol %)**	46.9 to 44.7
Start Date	5/6 21:00	**Catalyst Proportion (% Al2O3)**	0	**CO Conversion (%)**	16.4
End date	5/7 6:00	**Catalyst Weight (lb)**	479.4	**Syngas Conversion (%)**	28.2
TOS (hr)	133 to 142	**Slurry Concentration (wt %)**	34.2 to 37.0	**Eq. Productivity (gmoles/hr-kg)**	33.0
Temperature (°F)	481.0	**Inlet Superficial Vel. (ft/sec)**	0.38	**MeOH Make (Ton/day)**	6.1
Pressure (psig)	751	**Outlet Superficial Vel. (ft/sec)**	0.32	**DME Make (Ton/day)**	0.0
Reactor Level (inches on Tape)	170 to 140				

	Fresh Feed	Recycle	Reactor Feed	Reactor Out	22.10 Sep Vap	22.11 Liq	22.11 Vap	Plant Purge	DME Product
Hydrogen	56.67	24.89	34.65	22.40	24.89	0.00	3.65	24.89	0.00
Carbon Monoxide	38.53	56.52	51.02	50.71	56.52	0.00	23.34	56.52	0.00
Carbon Dioxide	4.53	17.17	13.33	15.88	17.17	0.00	68.52	17.17	0.00
Nitrogen	0.18	0.81	0.61	0.72	0.81	0.00	0.27	0.81	100.00
Methane	0.08	0.29	0.22	0.26	0.29	0.00	0.26	0.29	0.00
Water	0.00	0.00	0.02	0.10	0.00	0.90	0.00	0.00	0.00
Methanol	0.00	0.32	0.16	9.81	0.32	97.69	3.97	0.32	0.00
Other Oxygenates	0.00	0.00	0.00	0.12	0.00	1.39	0.00	0.00	0.00
Dimethyl Ether	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Flow (lb mole/hr)	58.90	136.25	195.61	164.45	149.12	14.88	0.02	12.87	0.00
MW	14.00	24.27	21.12	25.12	24.27	32.27	38.15	24.27	28.01
Flow (lb/hr)	824.40	3306.13	4130.54	4130.54	3618.49	480.25	0.84	312.37	0.00

Elemental Balances (Atoms In = Atoms Out)

Overall Balance:
Feed = Purge + MeOH Liq + Flash + DME Liq

	In	Out	(In-Out)*100 / In
Hydrogen	66.95	66.35	0.9
Carbon	25.41	24.62	3.1
Oxygen	28.04	26.75	4.6
Nitrogen	0.21	0.21	2.2
Total	120.61	117.93	2.2

Reactor Balance
Reactor In = Reactor Out

	In	Out	(In-Out)*100 / In
Hydrogen	138.58	141.41	-2.0
Carbon	126.61	126.54	0.1
Oxygen	152.29	152.20	0.1
Nitrogen	2.38	2.36	0.6
Total	419.87	422.51	-0.6

Mole Balance (moles = moles)

Production Balance
Rxn Out-Rxn In = Products + Purges - Feed

	Made	Out-In	(M-O)*100 / Made
DME	0.00	0.00	-6.3
MeOH	15.82	14.60	7.7
H2O	0.12	0.13	-8.0
CO2	0.04	-0.46	1416.6
Total	15.98	14.28	10.7

TABLE G5
MATERIAL BALANCE FOR RUN AF-R2.1

Balance Period:		**Space Velocity (sL/hr-kg oxide)**	5409	**Gas Holdup (vol %)**	n/a
Start Date	5/9 0:00	**Catalyst Proportion (% Al2O3)**	6.6	**CO Conversion (%)**	28.6
End date	5/9 17:00	**Catalyst Weight (lb)**	484.6	**Syngas Conversion (%)**	39.0
TOS (hr)	184 to 201	**Slurry Concentration (wt %)**	n/a	**Eq. Productivity (gmoles/hr-kg)**	27.1
Temperature (°F)	480.7	**Inlet Superficial Vel. (ft/sec)**	0.23	**MeOH Make (Ton/day)**	2.1
Pressure (psig)	751	**Outlet Superficial Vel. (ft/sec)**	0.18	**DME Make (Ton/day)**	2.1
Reactor Level (inches on Tape)	210				

	Fresh Feed	Recycle	Reactor Feed	Reactor Out	22.10 Sep Vap	22.11 Liq	22.11 Vap	Plant Purge	DME Product
Hydrogen	48.43	24.08	35.38	20.92	22.56	0.00	1.66	24.08	0.44
Carbon Monoxide	47.83	54.57	51.35	47.30	51.21	0.00	11.56	54.57	4.55
Carbon Dioxide	3.53	18.28	11.51	19.05	20.05	1.71	48.42	18.28	41.71
Nitrogen	0.19	0.94	0.58	0.79	0.87	0.00	0.10	0.94	0.04
Methane	0.01	0.16	0.10	0.13	0.15	0.00	0.08	0.16	0.00
Water	0.01	0.00	0.00	0.14	0.02	2.00	0.08	0.00	0.22
Methanol	0.00	0.00	0.00	5.96	0.26	84.72	3.98	0.00	9.36
Other Oxygenates	0.00	0.00	0.00	0.07	0.00	1.13	0.00	0.00	0.02
Dimethyl Ether	0.00	1.98	1.07	5.64	4.87	10.45	34.12	1.98	43.65
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Flow (lb mole/hr)	53.68	63.21	117.06	90.79	84.21	5.62	0.02	14.14	6.86
MW	15.99	25.01	20.84	26.87	26.22	33.71	41.61	25.01	42.79
Flow (lb/hr)	858.14	1581.07	2439.21	2439.21	2208.25	189.33	0.92	353.68	293.67

Elemental Balances (Atoms In = Atoms Out)

Overall Balance:
Feed = Purge + MeOH Liq + Flash + DME Liq

	In	Out	(In-Out)*100 / In
Hydrogen	52.02	52.41	-0.8
Carbon	27.58	26.90	2.4
Oxygen	29.47	28.63	2.9
Nitrogen	0.20	0.27	-33.3
Total	109.27	108.22	1.0

Reactor Balance
Reactor In = Reactor Out

	In	Out	(In-Out)*100 / In
Hydrogen	90.85	91.46	-0.7
Carbon	76.21	76.16	0.1
Oxygen	88.32	88.29	0.0
Nitrogen	1.37	1.43	-4.5
Total	256.74	257.34	-0.2

Mole Balance (moles = moles)

Production Balance
Rxn Out-Rxn In = Products + Purges - Feed

	Made	Out-In	(M-O)*100 / Made
DME	3.86	3.87	0.0
MeOH	5.41	5.42	-0.1
H2O	0.12	0.13	-6.0
CO2	3.82	3.65	4.6
Total	13.22	13.06	1.2

TABLE G6
MATERIAL BALANCE FOR RUN AF-R2.2

Balance Period:		**Space Velocity (sL/hr-kg oxide)**	8817	**Gas Holdup (vol %)**	46.4
Start Date	5/10 9:00	**Catalyst Proportion (% Al2O3)**	6.6	**CO Conversion (%)**	21.7
End date	5/11 12:00	**Catalyst Weight (lb)**	484.6	**Syngas Conversion (%)**	31.7
TOS (hr)	217 TO 244	**Slurry Concentration (wt %)**	30	**Eq. Productivity (gmoles/hr-kg)**	36.1
Temperature (°F)	481.0	**Inlet Superficial Vel. (ft/sec)**	0.37	**MeOH Make (Ton/day)**	4.0
Pressure (psig)	750	**Outlet Superficial Vel. (ft/sec)**	0.30	**DME Make (Ton/day)**	2.0
Reactor Level (Inches on Tape)	210				

	Fresh Feed	Recycle	Reactor Feed	Reactor Out	22.10 Sep Vap	22.11 Liq	22.11 Vap	Plant Purge	DME Product
Hydrogen	52.00	25.88	35.52	23.40	25.21	0.00	2.20	25.88	0.46
Carbon Monoxide	45.06	54.78	51.18	49.03	53.04	0.00	14.04	54.78	4.11
Carbon Dioxide	2.68	16.52	11.42	16.19	17.18	1.49	49.11	16.52	37.05
Nitrogen	0.20	0.70	0.51	0.62	0.66	0.00	0.15	0.70	0.03
Methane	0.00	0.19	0.13	0.16	0.17	0.00	0.09	0.19	0.00
Water	0.07	0.00	0.00	0.14	0.03	2.01	0.09	0.00	0.56
Methanol	0.00	0.00	0.00	6.59	0.35	88.61	4.88	0.00	13.53
Other Oxygenates	0.00	0.00	0.00	0.06	0.00	0.82	0.00	0.00	0.08
Dimethyl Ether	0.00	1.93	1.23	3.81	3.35	7.08	29.45	1.93	44.17
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Flow (lb mole/hr)	68.77	121.45	190.82	156.00	144.70	10.83	0.01	17.61	5.64
MW	14.92	24.25	20.81	25.46	24.80	33.14	40.77	24.25	42.28
Flow (lb/hr)	1025.80	2945.30	3971.10	3971.10	3589.00	358.99	0.36	427.06	238.34

Elemental Balances (Atoms In = Atoms Out)

Overall Balance:
Feed = Purge + MeOH Liq + Flash + DME Liq

	In	Out	(In-Out)*100 / In
Hydrogen	71.61	73.38	-2.5
Carbon	32.82	32.86	-0.1
Oxygen	34.71	34.56	0.5
Nitrogen	0.27	0.25	8.9
Total	139.42	141.05	-1.2

Reactor Balance
Reactor In = Reactor Out

	In	Out	(In-Out)*100 / In
Hydrogen	150.70	151.77	-0.7
Carbon	124.41	124.39	0.0
Oxygen	143.61	143.59	0.0
Nitrogen	1.94	1.93	0.7
Total	420.66	421.68	-0.2

Mole Balance (moles = moles)

Production Balance
Rxn Out-Rxn In = Products + Purges - Feed

	Made	Out-In	(M-O)*100 / Made
DME	3.59	3.60	-0.1
MeOH	10.29	10.37	-0.8
H2O	0.22	0.25	-14.6
CO2	3.46	3.32	4.0
Total	17.56	17.54	0.1

TABLE G7
MATERIAL BALANCE FOR RUN AF-R2.3

Balance Period:		**Space Velocity (sL/hr-kg oxide)**	5503	**Gas Holdup (vol %)**	31.1
Start Date	5/11 16:00	**Catalyst Proportion (% Al2O3)**	6.6	**CO Conversion (%)**	26.8
End date	5/12 16:00	**Catalyst Weight (lb)**	484.6	**Syngas Conversion (%)**	37.6
TOS (hr)	248 TO 272	**Slurry Concentration (wt %)**	30	**Eq. Productivity (gmoles/hr-kg)**	26.4
Temperature (°F)	480.7	**Inlet Superficial Vel. (ft/sec)**	0.23	**MeOH Make (Ton/day)**	2.3
Pressure (psig)	751	**Outlet Superficial Vel. (ft/sec)**	0.18	**DME Make (Ton/day)**	1.9
Reactor Level (Inches on Tape)	153				

	Fresh Feed	Recycle	Reactor Feed	Reactor Out	22.10 Sep Vap	22.11 Liq	22.11 Vap	Plant Purge	DME Product
Hydrogen	48.83	23.59	35.03	20.79	22.36	0.00	1.66	23.59	0.43
Carbon Monoxide	47.10	55.35	51.63	48.22	52.28	0.00	11.56	55.35	4.52
Carbon Dioxide	3.80	18.32	11.75	18.71	19.73	1.88	48.42	18.32	41.37
Nitrogen	0.20	0.61	0.41	0.52	0.58	0.00	0.10	0.61	0.04
Methane	0.01	0.18	0.11	0.15	0.17	0.00	0.08	0.18	0.00
Water	0.06	0.00	0.00	0.13	0.05	1.77	0.08	0.00	0.25
Methanol	0.00	0.00	0.00	6.42	0.45	86.34	3.98	0.00	10.02
Other Oxygenates	0.00	0.00	0.00	0.07	0.00	0.92	0.00	0.00	0.03
Dimethyl Ether	0.00	1.94	1.06	4.99	4.38	9.10	34.12	1.94	43.35
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Flow (lb mole/hr)	53.79	65.24	119.09	93.34	86.70	7.04	0.11	15.81	5.65
MW	15.92	25.14	20.96	26.75	26.14	33.53	41.61	25.14	42.71
Flow (lb/hr)	856.38	1640.01	2496.39	2496.39	2265.98	236.06	4.58	397.42	241.26

Elemental Balances (Atoms In = Atoms Out)

Overall Balance:
Feed = Purge + MeOH Liq + Flash + DME Liq

	In	Out	(In-Out)*100 / In
Hydrogen	52.61	55.49	-5.5
Carbon	27.39	28.14	-2.8
Oxygen	29.46	30.18	-2.4
Nitrogen	0.21	0.20	7.5
Total	109.67	114.01	-4.0

Reactor Balance
Reactor In = Reactor Out

	In	Out	(In-Out)*100 / In
Hydrogen	91.59	91.90	-0.3
Carbon	78.14	78.07	0.1
Oxygen	90.74	90.80	-0.1
Nitrogen	0.97	0.97	0.4
Total	261.44	261.74	-0.1

Mole Balance (moles = moles)

Production Balance
Rxn Out-Rxn In = Products + Purges - Feed

	Made	Out-In	(M-O)*100 / Made
DME	3.39	3.41	-0.4
MeOH	5.99	6.74	-12.5
H2O	0.12	0.14	-21.5
CO2	3.47	3.32	4.3
Total	12.97	13.61	-4.9

TABLE G8
MATERIAL BALANCE FOR RUN AF-R2.4

Balance Period:		**Space Velocity (sL/hr-kg oxide)**	8986	**Gas Holdup (vol %)**	45.3 to 43.8
Start Date	5/12 20:00	**Catalyst Proportion (% Al2O3)**	6.6	**CO Conversion (%)**	20.9
End date	5/13 4:00	**Catalyst Weight (lb)**	484.6	**Syngas Conversion (%)**	30.8
TOS (hr)	276 to 284	**Slurry Concentration (wt %)**	32.4 to 34.3	**Eq. Productivity (gmoles/hr-kg)**	35.7
Temperature (°F)	480.5	**Inlet Superficial Vel. (ft/sec)**	0.38	**MeOH Make (Ton/day)**	4.0
Pressure (psig)	750	**Outlet Superficial Vel. (ft/sec)**	0.31	**DME Make (Ton/day)**	1.9
Reactor Level (inches on Tape)	182 to 162				

	Fresh Feed	Recycle	Reactor Feed	Reactor Out	22.10 Sep Vap	22.11 Liq	22.11 Vap	Plant Purge	DME Product
Hydrogen	51.63	26.17	35.66	23.78	25.50	0.00	2.20	26.17	0.45
Carbon Monoxide	45.36	55.34	51.64	49.78	53.79	0.00	14.04	55.34	4.07
Carbon Dioxide	2.73	15.77	10.92	15.46	16.28	1.49	49.11	15.77	36.67
Nitrogen	0.19	0.59	0.43	0.52	0.58	0.00	0.15	0.59	0.03
Methane	0.01	0.19	0.14	0.17	0.18	0.00	0.09	0.19	0.00
Water	0.07	0.00	0.00	0.04	0.04	2.01	0.09	0.00	0.61
Methanol	0.00	0.00	0.00	6.58	0.42	88.61	4.88	0.00	14.30
Other Oxygenates	0.00	0.00	0.00	0.06	0.00	0.82	0.00	0.00	0.09
Dimethyl Ether	0.00	1.94	1.22	3.61	3.21	7.08	29.45	1.94	43.77
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Flow (lb mole/hr)	70.51	123.24	194.47	189.61	148.69	11.01	0.04	20.40	5.05
MW	15.02	24.06	20.69	25.21	24.56	33.14	40.77	24.06	42.18
Flow (lb/hr)	1059.03	2964.97	4023.99	4023.99	3651.26	364.83	1.80	490.69	213.16

Elemental Balances (Atoms In = Atoms Out)

Overall Balance:
Feed = Purge + MeOH Liq + Flash + DME Liq

	In	Out	(In-Out)*100 / In
Hydrogen	72.93	74.24	-1.8
Carbon	33.92	34.30	-1.1
Oxygen	35.89	36.28	-1.1
Nitrogen	0.27	0.24	8.5
Total	143.01	145.07	-1.4

Reactor Balance
Reactor In = Reactor Out

	In	Out	(In-Out)*100 / In
Hydrogen	153.94	154.25	-0.2
Carbon	126.65	126.65	0.0
Oxygen	145.26	145.27	0.0
Nitrogen	1.68	1.66	0.9
Total	427.53	427.84	-0.1

Mole Balance (moles = moles)

Production Balance
Rxn Out-Rxn In = Products + Purges - Feed

	Made	Out-In	(M-O)*100 / Made
DME	3.39	3.39	0.1
MeOH	10.51	10.52	-0.1
H2O	0.06	0.25	-295.8
CO2	3.44	3.31	3.8
Total	17.40	17.47	-0.4

TABLE G9
MATERIAL BALANCE FOR RUN AF-R3.1

Balance Period:		**Space Velocity (sL/hr-kg oxide)**	5934	**Gas Holdup (vol %)**	35.1
Start Date	5/14 0:00	**Catalyst Proportion (% Al2O3)**	19.3	**CO Conversion (%)**	31.0
End date	5/14 16:00	**Catalyst Weight (lb)**	449.3	**Syngas Conversion (%)**	38.6
TOS (hr)	304 to 320	**Slurry Concentration (wt %)**	24.8	**Eq. Productivity (gmoles/hr-kg)**	30.0
Temperature (°F)	481.6	**Inlet Superficial Vel. (ft/sec)**	0.23	**MeOH Make (Ton/day)**	0.8
Pressure (psig)	750	**Outlet Superficial Vel. (ft/sec)**	0.18	**DME Make (Ton/day)**	3.1
Reactor Level (inches on Tape)	210				

	Fresh Feed	Recycle	Reactor Feed	Reactor Out	22.10 Sep Vap	22.11 Liq	22.11 Vap	Plant Purge	DME Product
Hydrogen	45.66	26.56	35.60	23.08	23.99	0.00	1.27	26.56	0.46
Carbon Monoxide	50.16	52.48	51.39	45.58	46.95	0.00	7.45	52.48	4.45
Carbon Dioxide	3.88	17.49	11.08	19.99	20.21	2.50	37.70	17.49	42.59
Nitrogen	0.21	1.18	0.70	0.99	1.08	0.00	0.35	1.18	0.07
Methane	0.01	0.15	0.10	0.12	0.12	0.00	0.03	0.15	0.00
Water	0.09	0.00	0.01	0.30	0.09	7.51	0.18	0.00	0.23
Methanol	0.00	0.00	0.00	2.35	0.35	78.10	3.19	0.00	5.03
Other Oxygenates	0.00	0.00	0.00	0.06	0.00	1.00	0.00	0.00	0.00
Dimethyl Ether	0.00	2.14	1.12	7.54	7.21	10.89	49.83	2.14	47.18
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Flow (lb mole/hr)	56.48	62.66	119.07	92.62	90.81	2.00	0.09	17.41	10.75
MW	16.75	24.27	20.72	26.64	26.30	33.07	42.79	24.27	43.38
Flow (lb/hr)	946.20	1520.87	2467.07	2467.07	2388.19	66.08	3.77	422.50	466.14

Elemental Balances (Atoms In = Atoms Out)

Overall Balance:
Feed = Purge + MeOH Liq + Flash + DME Liq

	In	Out	(In-Out)*100 / In
Hydrogen	51.69	52.55	-1.7
Carbon	30.52	30.91	-1.3
Oxygen	32.76	33.04	-0.9
Nitrogen	0.24	0.43	-80.5
Total	115.21	116.93	-1.5

Reactor Balance
Reactor In = Reactor Out

	In	Out	(In-Out)*100 / In
Hydrogen	93.28	94.68	-1.5
Carbon	77.17	77.12	0.1
Oxygen	88.92	88.76	0.2
Nitrogen	1.67	1.83	-9.1
Total	261.04	262.38	-0.5

Mole Balance (moles = moles)

Production Balance
Rxn Out-Rxn In = Products + Purges - Feed

	Made	Out-In	(M-O)*100 / Made
DME	5.65	5.67	-0.4
MeOH	2.18	2.17	0.3
H2O	0.27	0.18	33.2
CO2	5.32	5.48	-3.1
Total	13.41	13.50	-0.7

TABLE G10
MATERIAL BALANCE FOR RUN AF-R3.2

Balance Period:		**Space Velocity (sL/hr-kg oxide)**	9445	**Gas Holdup (vol %)**	46.0
Start Date	5/15 6:00	**Catalyst Proportion (% Al2O3)**	19.3	**CO Conversion (%)**	20.6
End date	5/16 8:00	**Catalyst Weight (lb)**	449.3	**Syngas Conversion (%)**	26.8
TOS (hr)	334 TO 360	**Slurry Concentration (wt %)**	28.3	**Eq. Productivity (gmoles/hr-kg)**	33.4
Temperature (°F)	482.1	**Inlet Superficial Vel. (ft/sec)**	0.37	**MeOH Make (Ton/day)**	1.7
Pressure (psig)	752	**Outlet Superficial Vel. (ft/sec)**	0.31	**DME Make (Ton/day)**	2.9
Reactor Level (inches on Tape)	213				

	Fresh Feed	Recycle	Reactor Feed	Reactor Out	22.10 Sep Vap	22.11 Liq	22.11 Vap	Plant Purge	DME Product
Hydrogen	47.52	29.56	35.91	27.30	28.16	0.00	1.27	29.56	0.49
Carbon Monoxide	48.91	51.61	50.68	47.56	49.09	0.00	7.45	51.61	3.49
Carbon Dioxide	3.24	15.76	11.35	16.34	16.86	1.97	37.70	15.76	32.69
Nitrogen	0.22	0.55	0.42	0.50	0.51	0.00	0.35	0.55	0.00
Methane	0.02	0.13	0.09	0.11	0.11	0.00	0.03	0.13	0.00
Water	0.09	0.00	0.00	0.29	0.08	7.20	0.18	0.00	0.18
Methanol	0.00	0.00	0.00	2.81	0.34	79.87	3.19	0.00	7.09
Other Oxygenates	0.00	0.00	0.00	0.01	0.00	0.34	0.00	0.00	0.00
Dimethyl Ether	0.00	2.39	1.54	5.09	4.86	10.62	49.83	2.39	56.06
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Flow (lb mole/hr)	65.73	123.45	189.52	160.46	155.82	4.56	0.07	24.93	7.43
MW	16.17	23.26	20.76	24.52	24.26	32.84	42.79	23.26	43.47
Flow (lb/hr)	1062.55	2871.76	3934.31	3934.31	3779.48	149.85	2.83	579.92	323.13

Elemental Balances (Atoms In = Atoms Out)

Overall Balance:
Feed = Purge + MeOH Liq + Flash + DME Liq

	In	Out	(In-Out)*100 / In
Hydrogen	62.64	64.09	-2.3
Carbon	34.29	34.41	-0.3
Oxygen	36.47	35.90	1.6
Nitrogen	0.29	0.27	4.7
Total	133.68	134.67	-0.7

Reactor Balance
Reactor In = Reactor Out

	In	Out	(In-Out)*100 / In
Hydrogen	154.33	156.32	-1.3
Carbon	123.58	123.57	0.0
Oxygen	142.00	141.91	0.1
Nitrogen	1.61	1.60	0.7
Total	421.51	423.40	-0.4

Mole Balance (moles = moles)

Production Balance
Rxn Out-Rxn In = Products + Purges - Feed

	Made	Out-In	(M-O)*100 / Made
DME	5.25	5.25	-0.2
MeOH	4.50	4.22	6.2
H2O	0.46	0.35	25.2
CO2	4.71	4.32	8.3
Total	14.92	14.14	5.2

TABLE G11
MATERIAL BALANCE FOR RUN AF-R3.3

Balance Period:		**Space Velocity (sL/hr-kg oxide)**	5951	**Gas Holdup (vol %)**	31.8
Start Date	5/16 12:00	**Catalyst Proportion (% Al2O3)**	19.3	**CO Conversion (%)**	28.2
End date	5/17 9:00	**Catalyst Weight (lb)**	449.3	**Syngas Conversion (%)**	35.7
TOS (hr)	364 TO 385	**Slurry Concentration (wt %)**	29.5	**Eq. Productivity (gmoles/hr-kg)**	27.9
Temperature (°F)	481.8	**Inlet Superficial Vel. (ft/sec)**	0.23	**MeOH Make (Ton/day)**	1.0
Pressure (psig)	752	**Outlet Superficial Vel. (ft/sec)**	0.19	**DME Make (Ton/day)**	2.7
Reactor Level (inches on Tape)	156				

	Fresh Feed	Recycle	Reactor Feed	Reactor Out	22.10 Sep Vap	22.11 Liq	22.11 Vap	Plant Purge	DME Product
Hydrogen	45.81	27.33	35.76	24.12	24.87	0.00	1.36	27.33	0.57
Carbon Monoxide	49.66	52.37	51.19	46.23	47.94	0.00	7.80	52.37	4.47
Carbon Dioxide	4.27	17.52	11.45	19.31	19.79	2.38	40.21	17.52	41.79
Nitrogen	0.19	0.53	0.36	0.45	0.48	0.00	0.07	0.53	0.00
Methane	0.01	0.14	0.09	0.12	0.12	0.00	0.00	0.14	0.00
Water	0.07	0.00	0.01	0.29	0.11	10.42	0.21	0.00	0.19
Methanol	0.00	0.00	0.00	2.84	0.37	75.38	3.03	0.00	5.07
Other Oxygenates	0.00	0.00	0.00	0.02	0.00	0.64	0.00	0.00	0.00
Dimethyl Ether	0.00	2.11	1.14	6.61	6.32	11.18	47.32	2.11	47.91
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Flow (lb mole/hr)	55.02	64.53	119.41	94.91	91.95	3.07	0.07	18.77	8.66
MW	16.78	24.07	20.74	26.09	25.84	32.59	42.71	24.07	43.36
Flow (lb/hr)	923.25	1553.38	2476.63	2476.63	2376.22	100.00	2.82	451.84	375.31

Elemental Balances (Atoms In = Atoms Out)

Overall Balance:
Feed = Purge + MeOH Liq + Flash + DME Liq

	In	Out	(In-Out)*100 / In
Hydrogen	50.51	51.77	-2.5
Carbon	29.68	29.89	-0.7
Oxygen	32.06	32.27	-0.7
Nitrogen	0.21	0.20	4.7
Total	112.45	114.13	-1.5

Reactor Balance
Reactor In = Reactor Out

	In	Out	(In-Out)*100 / In
Hydrogen	94.03	95.32	-1.4
Carbon	77.62	77.60	0.0
Oxygen	89.83	89.80	0.0
Nitrogen	0.87	0.86	0.9
Total	262.36	263.58	-0.5

Mole Balance (moles = moles)

Production Balance
Rxn Out-Rxn In = Products + Purges - Feed

	Made	Out-In	(M-O)*100 / Made
DME	4.91	4.89	0.3
MeOH	2.70	2.80	-3.9
H2O	0.27	0.34	-28.0
CO2	4.65	4.63	0.4
Total	12.53	12.67	-1.1

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