# 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 $\gamma$-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:

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

In the second step MeOH is dehydrated to form DME:

$$2\,MeOH \Longleftrightarrow DME + H_2O \qquad\qquad \text{(step 2)}$$
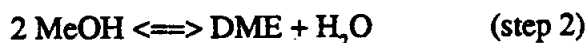
Both these steps are reversible and exothermic. At equilibrium, the MeOH production step is favored by higher pressure; the DME step is pressure neutral. Each of these steps is catalyzed by a different material: MeOH is produced using a mixed metal catalyst such as copper-zinc on alumina, while DME is produced using an acid dehydration catalyst such as alumina.

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

$$H_2O + CO \Longleftrightarrow CO_2 + H_2 \qquad\qquad \text{(step 3)}$$
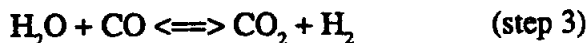
Shift is necessary to increase the hydrogen availability when processing CO-rich synthesis gases (typical of modern efficient coal gasification).

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

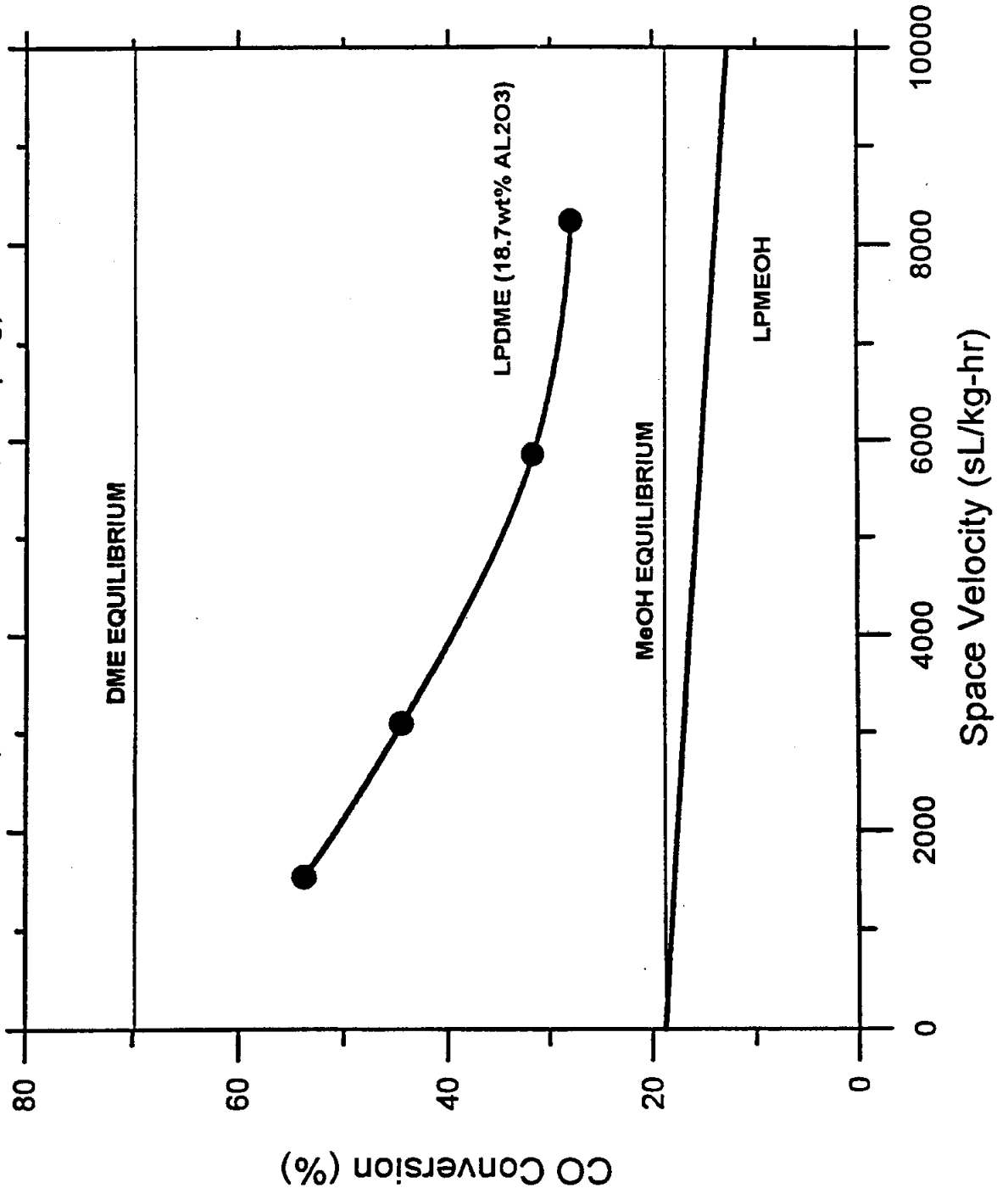COMPARISON OF LPDME AND LPMEOH
(Texaco Gas, 482 F, 750 psig)

# FIGURE 2.2-2

# EFFECT OF TEMPERATURE ON DME SYNTHESIS

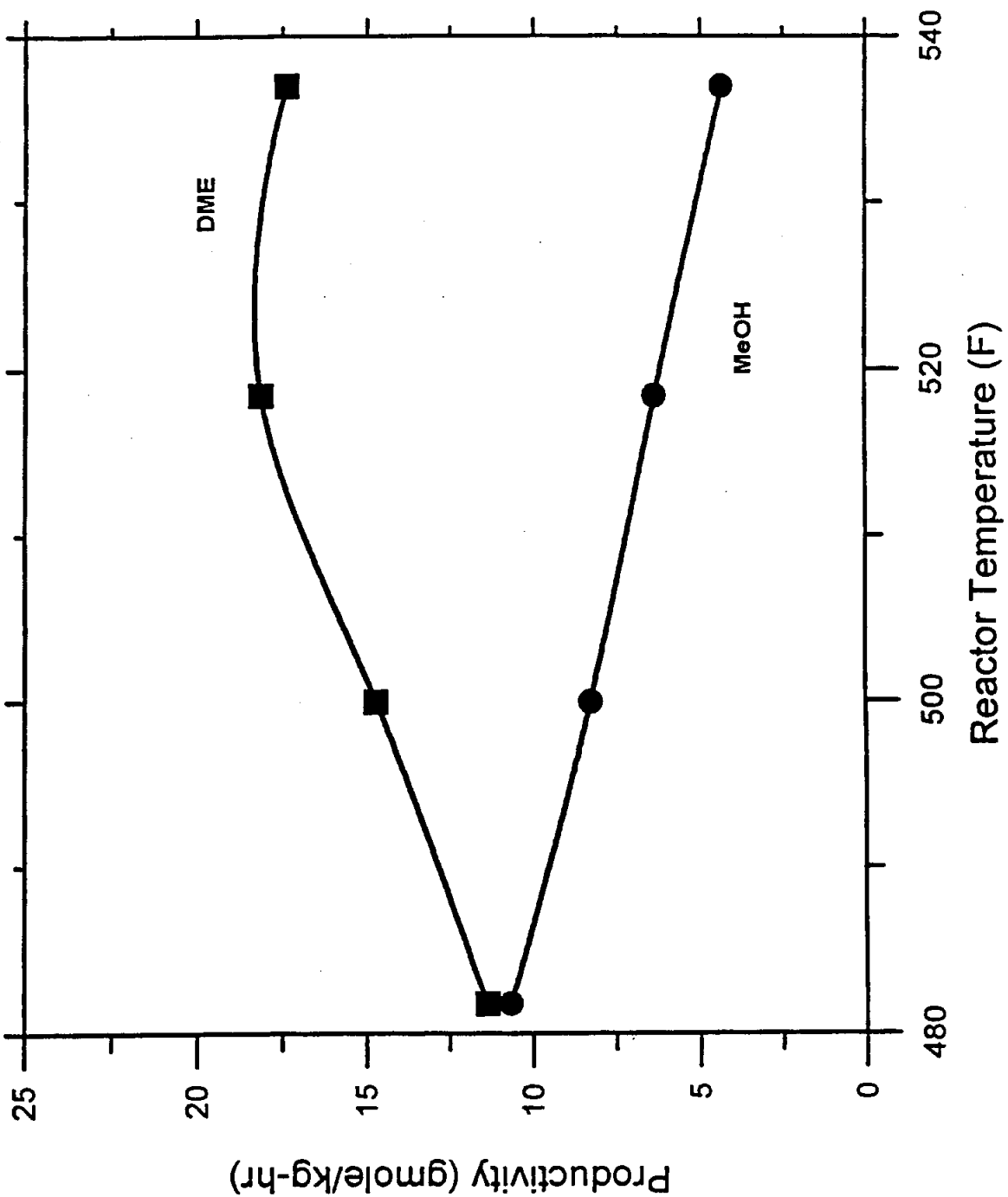(Texaco Gas, 750 psig, 8100 sL/kg-hr, 18.7% Al2O3)

FIGURE 2.2-3

**EFFECT OF PRESSURE ON DME SYNTHESIS**
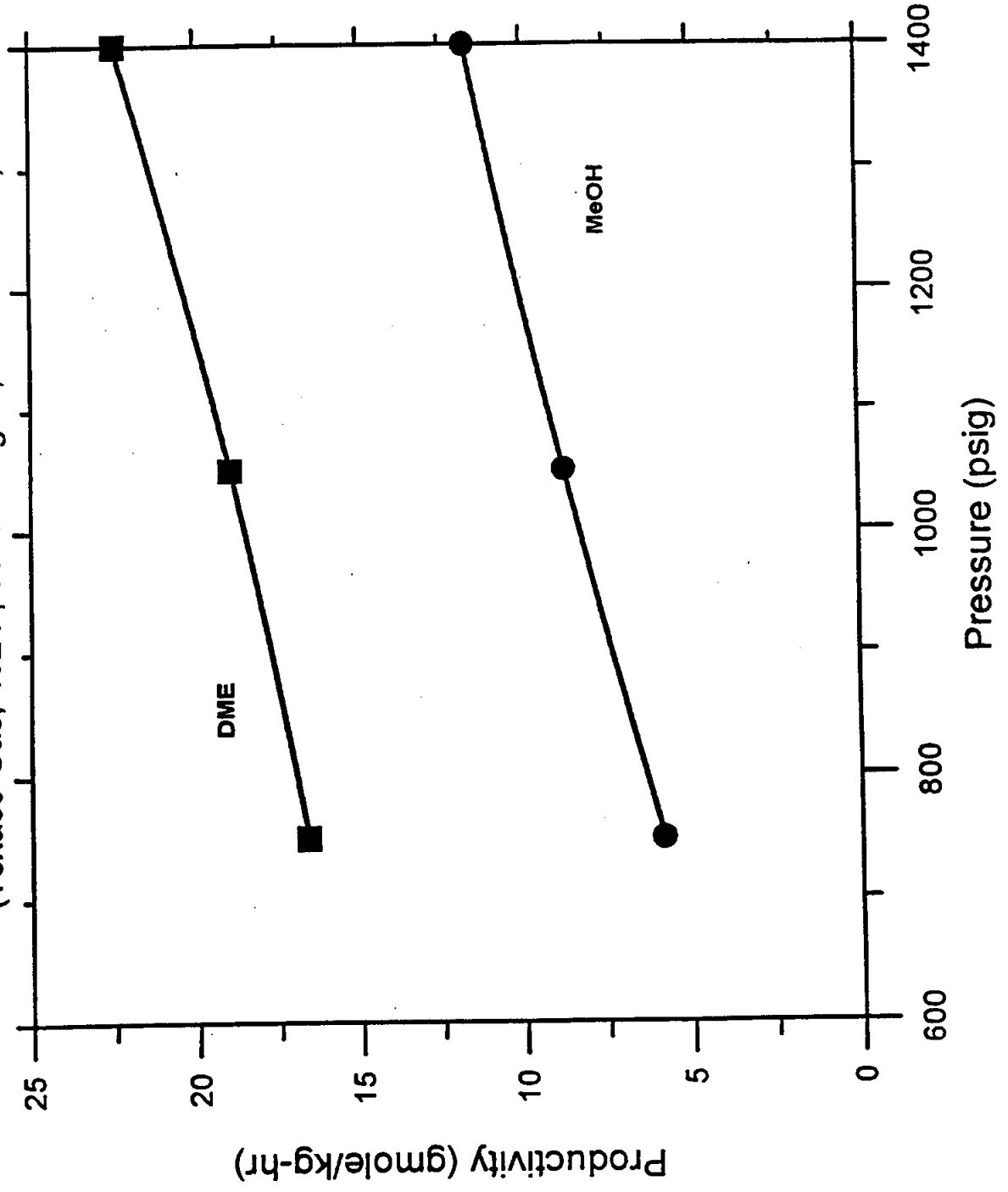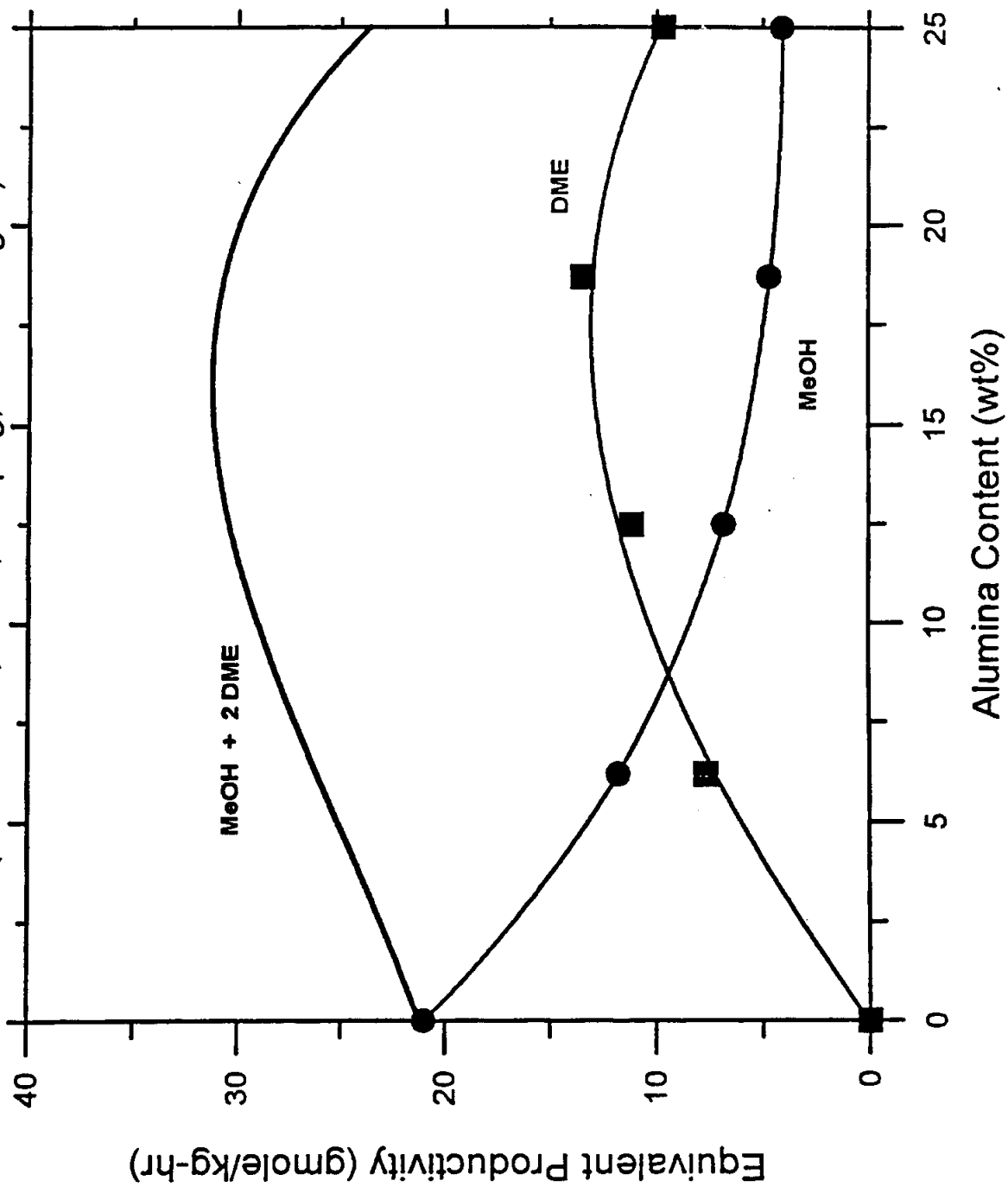(Texaco Gas, 482 F, 9500 sL/kg-hr, 18.7% Al2O3)

# 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.

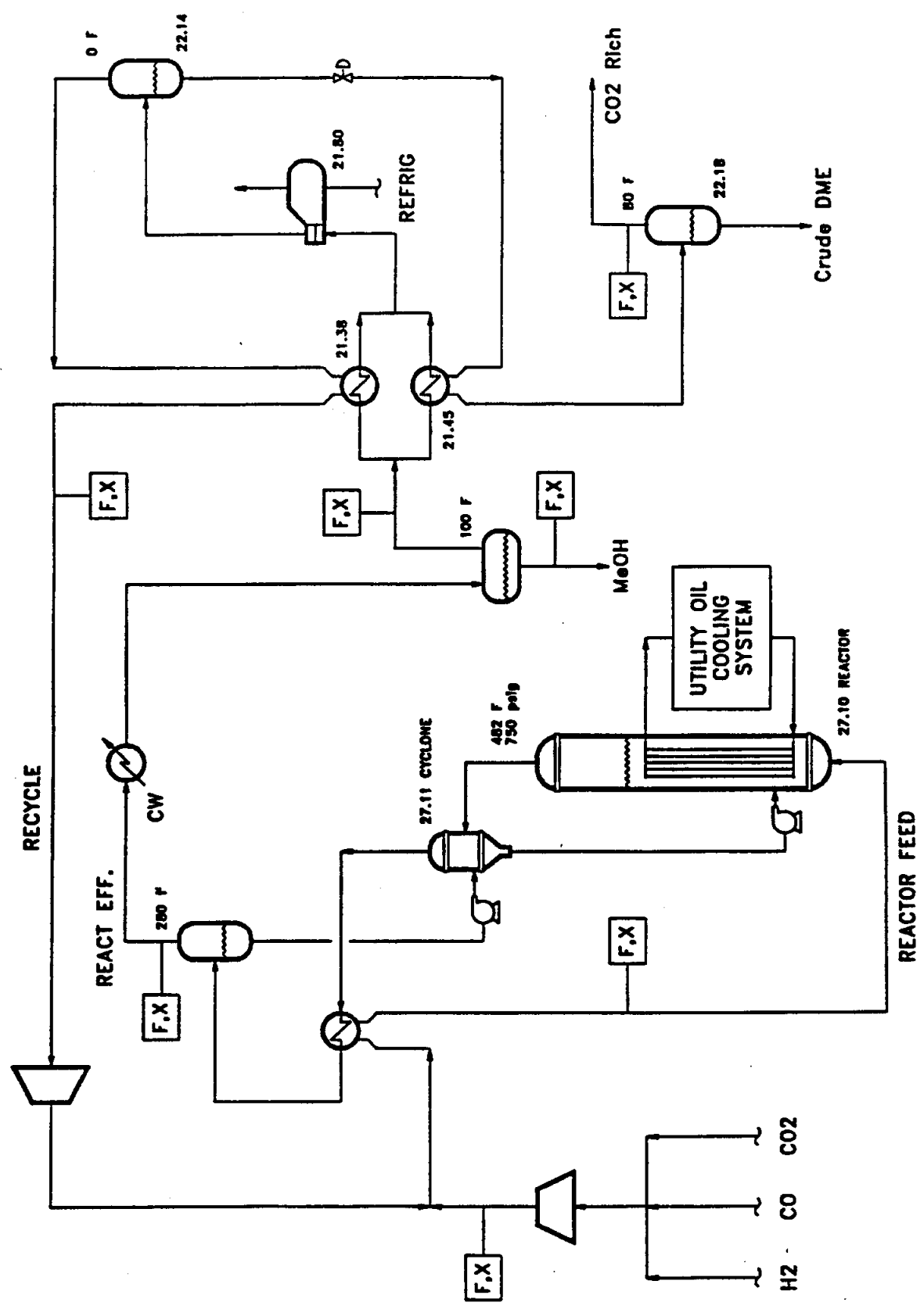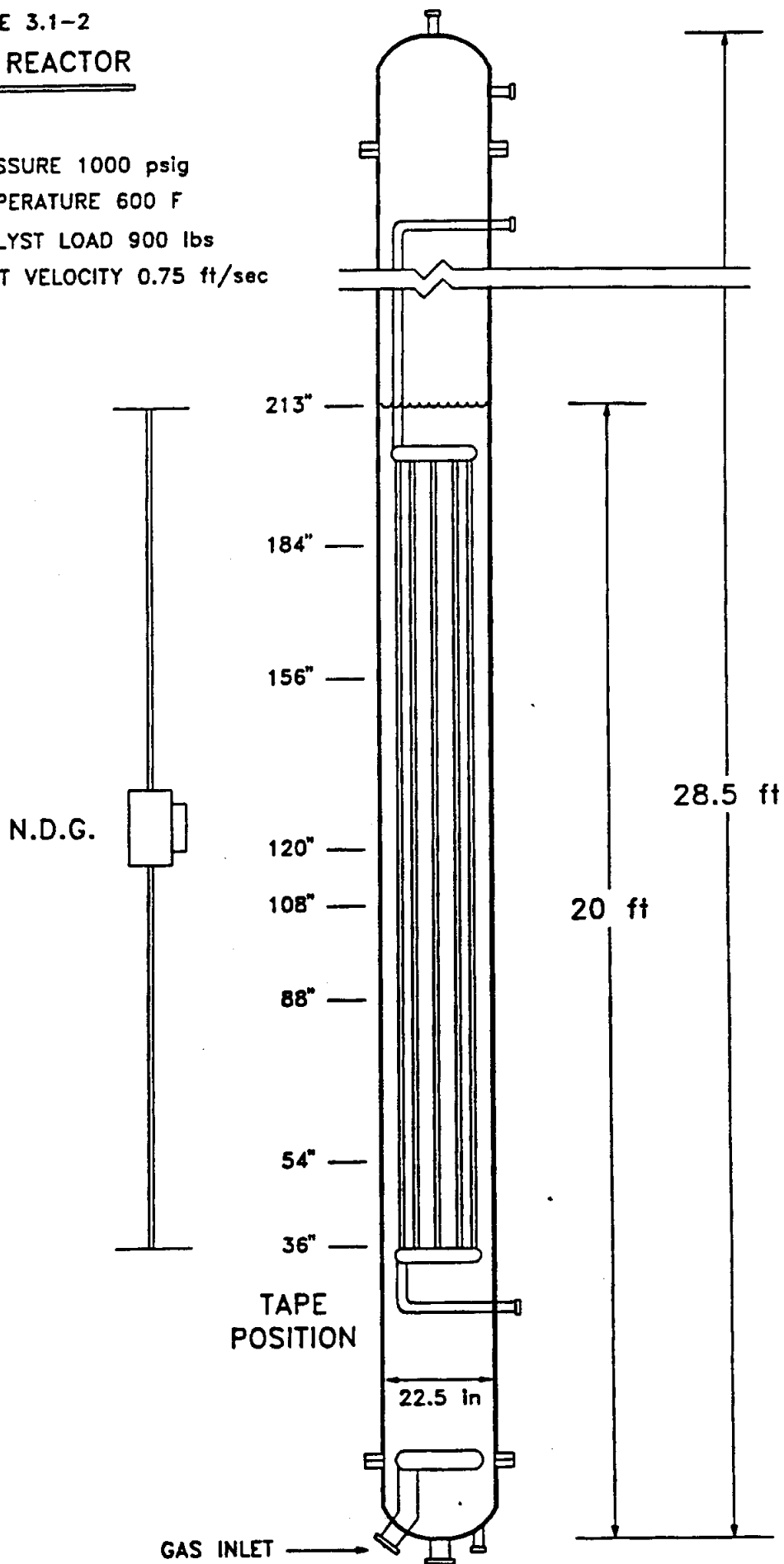FIGURE 3.1–1: SCHEMATIC OF AFDU – CONFIGURED FOR DME/MeOH

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

213"

184"

156"

N.D.G.

120"

108"

88"

54"

36"

TAPE
POSITION

22.5 in

28.5 ft

20 ft

GAS INLET

13

## 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
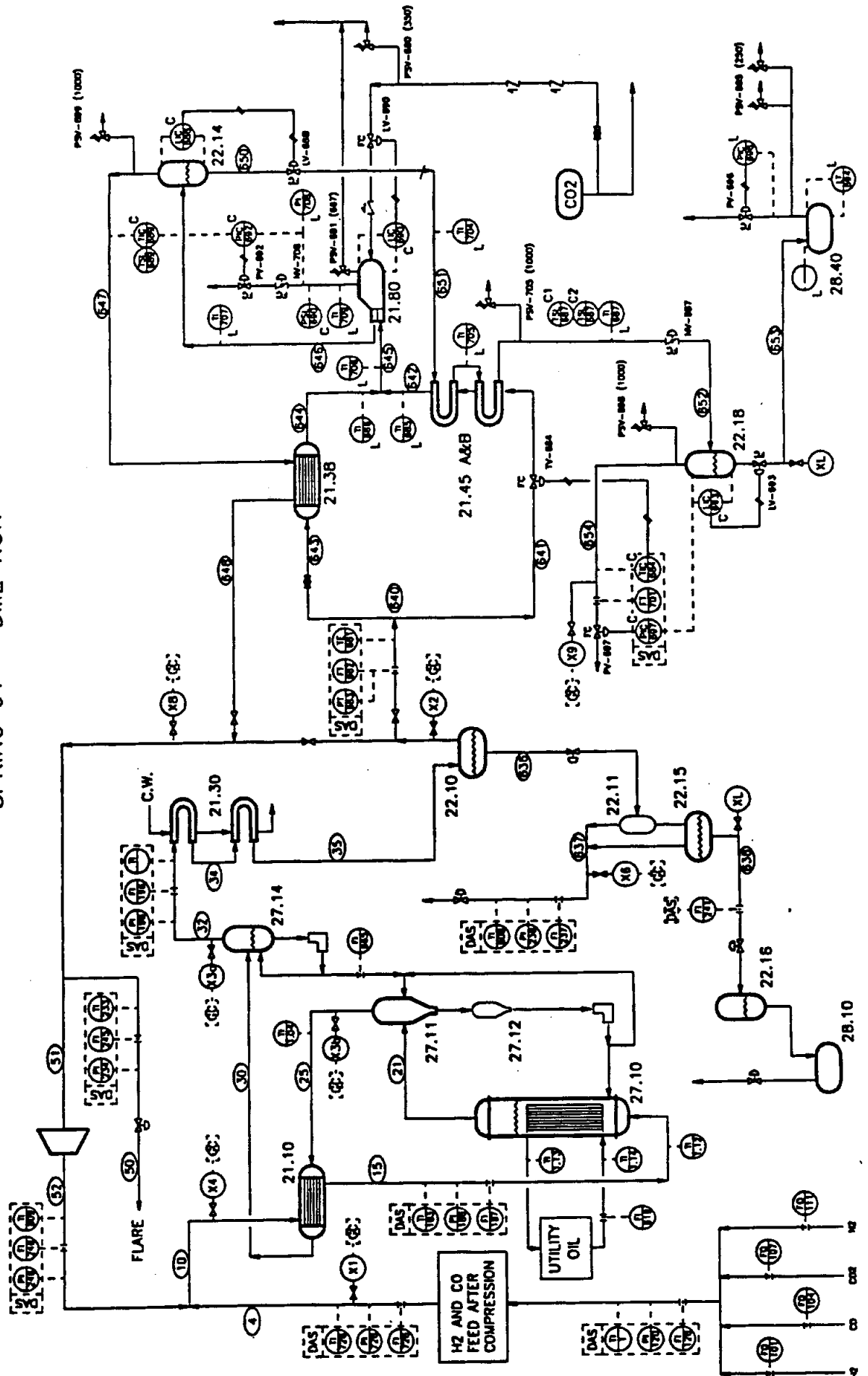
# 4. DEMONSTRATION AT THE AFDU

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 $\gamma$-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

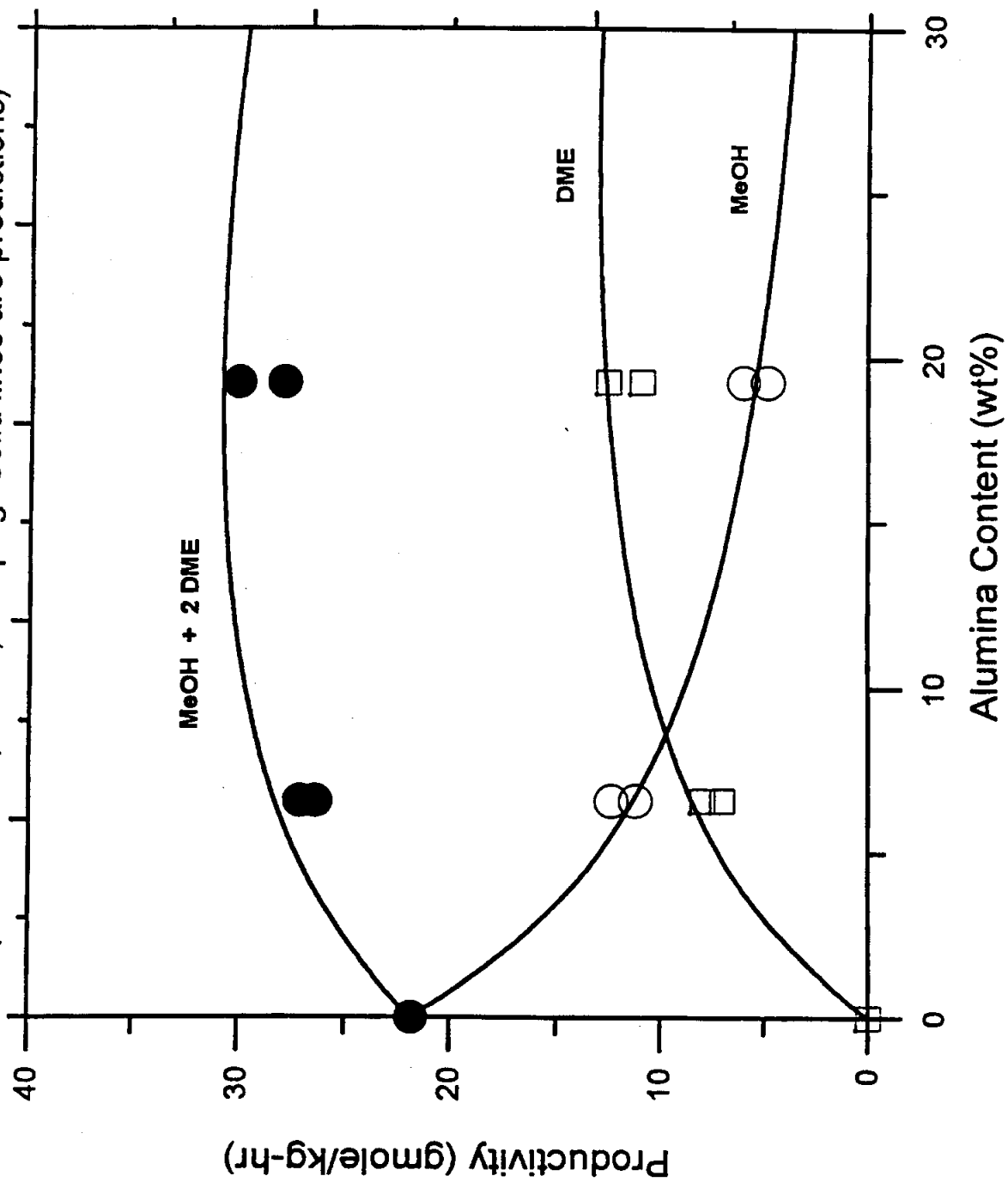(Texaco Gas, 482 F, 750 psig. Solid lines are predictions)

25

# FIGURE 4.4-2

## PRODUCTIVITIES IN BUBBLE COLUMN AT SV=9100 sL/kg-hr
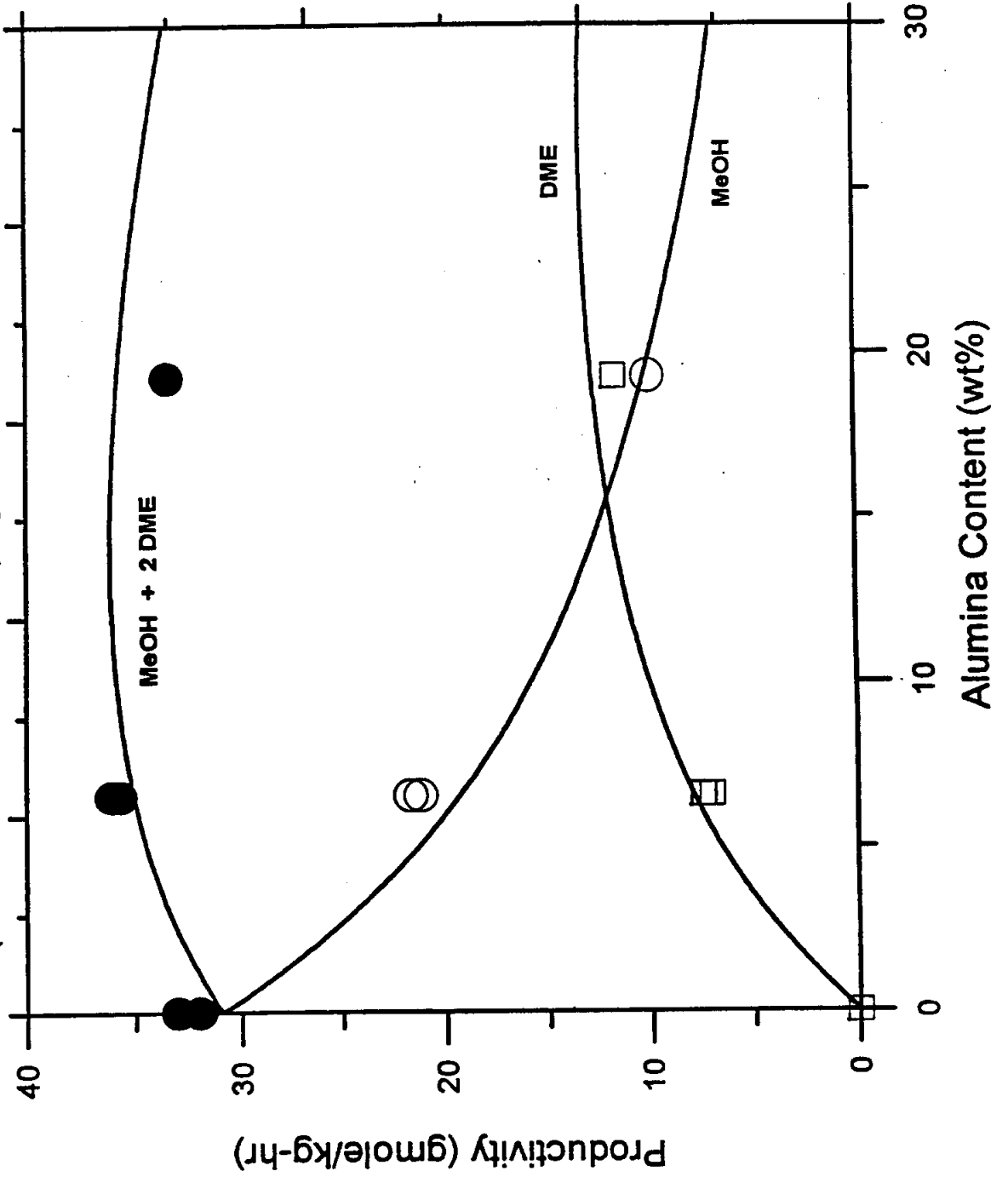
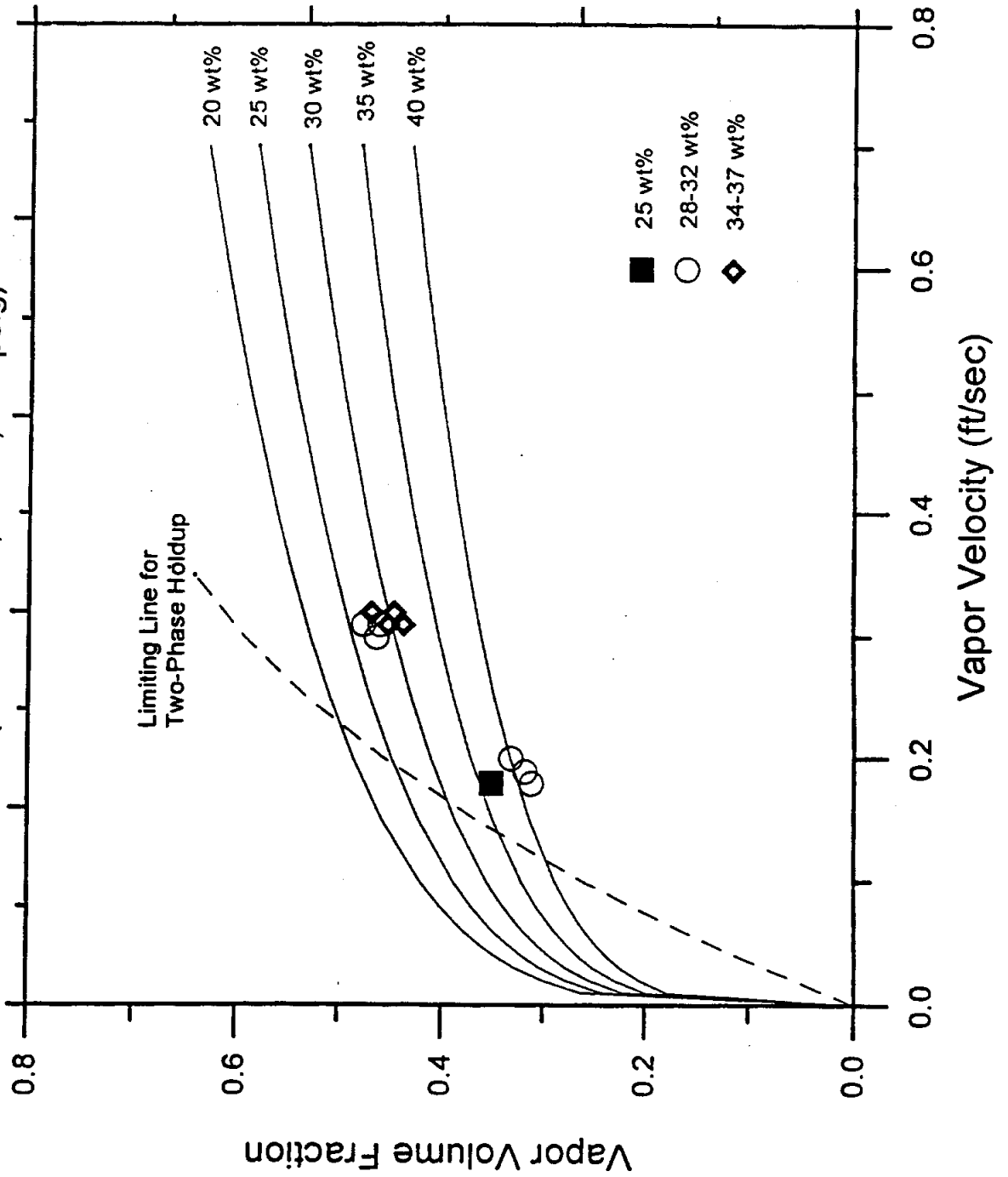(Texaco Gas, 482 F, 750 psig. Solid lines are predictions)

# 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)

# 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

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