DEVELOPMENT OF ALTERNATIVE FUELS FROM COAL-DERIVED SYNGAS

DOE/PC/90018--T6

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Quarterly Status Report No. 6

For The Period 1 January – 31 March 1992

19 May 1992

We have no objection from a patent standpoint to the publication or dissemination of this material.
3/12/93
Date
Office of Intellectual Property Counsel
DOE Field Office, Chicago

Contractor

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Allentown, PA 18195-1501

Prepared for the United States Department of Energy
Under Contract No. DE-AC22-91PC90018
Contract Period 1 October 1990 – 1 July 1994

NOTICE

~~This report contains information which is potentially patentable. U.S. patent applications covering these concepts will be filed with the U.S. Patent Office shortly. As per instructions from the Office of Patent Counsel, U.S. Department of Energy, Argonne, Illinois, the following notice is in effect:~~

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DISTRIBUTION LIST

Alternative Fuels I
Quarterly Technical Progress Report
(Final Version)

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AIR PRODUCTS

1 February 1993

Mr. Gary J. Stiegel
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Subject: Contract No. DE-AC22-91PC90018
"Development of Alternative Fuels from
Coal-Derived Syngas"
Quarterly Status Report No. 6

Dear Gary:

Pursuant to Item 4.F of the Reporting Requirements Checklist (Attachment B) of the subject Contract, enclosed please find two (2) copies of the quarterly status report for 1 January –31 March 1992. This report contains information that is potentially patentable, and is subject to the notice appearing on the title page. If you have any questions, please feel free to contact me.

Sincerely,

Dennis Brown/agb

Dennis M. Brown
Program Manager

cc: DOE (See Attached Distribution)

Air Products:
D. W. Tyndall

DISCLAIMER

DEVELOPMENT OF ALTERNATIVE FUELS FROM COAL-DERIVED SYNGAS

Quarterly Technical Progress Report
1 January – 31 March 1992

Contract Objectives

The overall objectives of this program are to investigate potential technologies for the conversion of coal-derived synthesis gas to oxygenated fuels, hydrocarbon fuels, fuel intermediates, and octane enhancers; and to demonstrate the most promising technologies at DOE's LaPorte, Texas, Slurry Phase Alternative Fuels Development Unit (AFDU). The program will initially involve a continuation of the work performed under the Liquid Phase Methanol Program but will later draw upon information and technologies generated in current and future DOE-funded contracts, as well as test commercially available catalysts.

Summary of Activity

- BASF continues to have difficulties in scaling-up the new isobutanol synthesis catalyst developed in Air Products' laboratories. Investigations are proceeding, but the proposed operation at LaPorte in April is now postponed. DOE has accepted a proposal to demonstrate Liquid Phase Shift (LPS) chemistry at LaPorte as an alternative to isobutanol. There are two principal reasons for carrying out this run. First, following the extensive modifications at the site, operation on a relatively "benign" system is needed before we start on Fischer-Tropsch technology in July. Second, use of shift catalyst in a slurry reactor will enable DOE's program on coal-based Fischer-Tropsch to encompass commercially available cobalt catalysts—up to now they have been limited to iron-based catalysts which have varying degrees of shift activity. In addition, DOE is supportive of continued fuel testing of LaPorte methanol—tests of M100 at Detroit Diesel have been going particularly well. LPS offers the opportunity to produce methanol as the catalyst, in the absence of steam, is active for methanol synthesis.

- Final preparations are underway for the LPS demonstration at LaPorte. The Design Verification Review (DVR) and Operational Readiness Inspection (ORI) were completed and the run plan issued. The NEXTGEN Data Acquisition System was commissioned, and the new analytical lab became operational with the link between lab HP computer and the VAX/NEXTGEN established. The process team is now on-site and catalyst slurry preparation is underway.

- A meeting was held in Pittsburgh during March for the prospective Fischer-Tropsch partners. Exxon, Statoil, and UOP attended with DOE and Air Products. Shell, whose agreement is pending, did not attend. The criteria of a successful run were established; stable reactor operation over a large number of days with at least 50% CO conversion; correlation between lab and

LaPorte reactor performance is important, as is some measure of column hydrodynamics. Efficient catalyst-wax separation was not viewed as critical and a decision was made to investigate a low alpha (C_8-C_{20}) catalyst option with the manufacturer. This is probably a wise move as recent filter tests showed some problems in efficient separation of catalyst particles from the F-T wax.

- The mystery deepens over BASF's inability to scale-up the cesium doped S3-86 catalyst for isobutanol synthesis. PSG personnel successfully prepared catalysts using the exact same precursors used by BASF. Subtle differences in preparation technique are suspected, and closer cooperation with BASF Ludwigshafen will be needed. Meanwhile, Haldor-Topsoe's MK101 methanol catalyst was tried as a substrate rather than S3-86. The resulting catalyst performed less well than the cesium promoted BASF S3-86.

- Alcohol injection experiments were conducted in the #1 300 ml autoclave to study the effect of lower alcohol recycle on the synthesis of isobutanol. A simulation of total recycle of methanol, ethanol, and propanol showed a 60% enhancement in isobutanol production rate.

- The reaction chemistry responsible for the conversion of DME to isobutanol over an oxide catalyst appears to be unique. Presently the gas phase oxidation of DME and isobutanol to CO and CO_2 are responsible for the low yields.

- A literature search has pointed out several catalyst candidates for the dehydration of isobutanol to isobutylene, although nothing seems to have been practiced commercially. Initial lab tests with a Catapal gamma (8)-alumina dispersed in Drakeol-10 mineral oil show high conversions (>90%) and high selectivities to isobutylene (>80 mol%). A group of metal phosphate catalysts identified in the literature have also been evaluated in Air Products' gas phase reactor and are demonstrating similar high conversions with almost 100% selectivity to butylenes.

Future Plans

- Initiate operations at the LaPorte AFDU to demonstrate Liquid Phase Shift (LPS). Commission and debug new control and data acquisition systems, and the new analytical laboratory. Produce 20,000 gallons of crude methanol for further fuel tests over the next two years. Demonstrate ability to tailor H_2/CO within the LPS reactor for use with oxygenates or F-T catalysts, for a variety of feed gases.

- Finalize membership of the Fischer-Tropsch consortium. Implement necessary steps when the AFDU is ready for operation in July: obtain catalyst from UCI, mineral oil for start-up, analytical services, mechanical modifications.

- Solve the scale-up issue of the cesium doped S3-86 and continue to optimize the cesium catalyst for maximum iC_4OH yield.

- Assess status of DME/O_2 coupling technology. Decide on respective level of effort for this and for promoting secondary alcohol formation in the methanol to isobutanol reaction sequence.

RESULTS AND DISCUSSION

Task 1: Engineering and Modifications

Control Room and Lab Room Relocation and Upgrade

This project was finished during the second quarter. The five major items completed were:

1. Relocate the control room to the new shelter and convert the existing control system to a Bailey distributed control system (DCS).
2. Physically relocate the GC lab, wet lab, and sample hot box to the new shelter.
3. Purchase, configure, and install three new GCs in the new lab.
4. Replace the old AIM data acquisition system with NEXTGEN.
5. Link the various computer systems through communication wiring.

1. Convert Control System to Bailey DCS

The signal terminations, tie-ins, and rewiring construction work was completed. Both above-ground and underground wiring between the field, the DCS building (formerly the GC Lab Building), the plant interface panel (located in the old control room), and the new control room are now in place. The Miscellaneous Cabinet (which contains hard-wired safety switches and the reactor's nuclear density gauge controls/readout) was also installed in the new control room. The DCS operator terminals were installed in the control room and commissioned. This commissioning work included a complete check-out of the new and existing controls and instruments.

2. Relocate Laboratory Facilities

The construction and furnishing of the wet lab was completed. Wet lab commissioning will be completed when required. The commissioning of the GC lab was also completed. The installation of the cabinets, hood, and the HVAC (heating, ventilation, and air conditioning) was finished in January. The air exhaust rates were balanced in February. In February, the drawings for the sample-line layout were received and construction began. This was followed by the construction and arrival of a new flow control box which was subsequently mounted and tied into the sample lines.

3. Purchase, Configure And Install New GCs

The GC laboratory setup was completed by connecting two of the new GCs, one of the older GCs, and one liquid GC to the newly installed flow control box. These analytical devices were then commissioned and calibrated. Each of the GCs are connected to, and driven by, an HP computer. The reconfiguration of this computer was also completed as part of the general laboratory commissioning work.

4. Upgrade the Data Acquisition System (DAS)

The data acquisition system (DAS) has been completely revamped. New hardware from Digital Equipment Corporation (DEC) was purchased and delivered to Air Products' Trexlertown campus. While on campus, the computer was outfitted with a new DAS software named NEXTGEN. The database definition was also completed and installed. Finally, communication software (which allowed the HP computer to send GC data to the DEC computer) was written and debugged. Once the initial DAS setup was completed, the HP and DEC computers and peripherals were shipped down to the AFDU where the final setup and staging was completed.

5. Link Computer Systems

With all the computer hardware in place, the final step was to complete the communication links. Ethernet cable was run from the GC lab to the control room for HP-to-DEC communications. The ethernet link was also extended from the DEC computer to selected offices for DEC-to-PC communications. The HP-to-DEC and DEC-to-PC communication protocol (using a Local Area Network, LAN) was then installed and tested. Finally, the Bailey DCS-to-DEC link (handled via modem communications) was connected.

6. Summary

The relocation and upgrade of the process control and data acquisition systems has been completed. The major, on-site equipment are itemized below:

TABLE 1.1.1
Major On-Site Equipment

Item	No.	Function
Bailey Multifunction Controller Cabinet	2	Interface between field instrumentation/controls and the control room displays.
Bailey Operator Terminal	2	Used by operators to view and control operation of the plant.
Bailey Printer	2	Generate hard copy of alarms and reports.
HP 5890 GC (Series II)	2	Analyze gas samples (6 samples per GC, continuous analysis)
Carle GC	2	Analyze reactor feed gas (only one is fully functional, the other is used as a spare)
HP Liquid GC	1	Analyze liquid products (batch). This is also fitted with an electron capture device (ECD) for gas-phase carbonyl analysis.
HP Computer/Terminal/Storage	1	Receives data from the various GCs, directs integration/normalization, transfers results to DEC computer.
HP Integrator	4	Connected to each GC. Controls valve switching/timing and prints "raw" hard copy.
HP Printer	1	Prints normalized hard copy reports for all the GCs.
DEC Computer/Terminal/Storage	1	Main data acquisition machine. Communicates with the Bailey, the HP, and PCs. Displays current plant and analytical data as well as historical data. Computer is also used to perform data analysis and produce reports.
DEC Printer	1	Hard copy device for DEC computer.

TABLE 1.1.1 (cont'd)
Major On-Site Equipment

Item	No.	Function
Bailey Workstation	1	An Intel brand PC which is connected to both the Bailey and DEC computers. When in Bailey-mode, this machine is used to configure controllers off-line. When in DEC-mode, this machine is used to download data from the DEC and, in the near future, will be able to "emulate" a DEC terminal. When in PC-mode, this machine is used to work-up plant data and to write daily reports.

In addition to the analytical equipment on site, an FID (flame ionization detector) was purchased and configured, but not installed.

Future work includes:

1. Reconfigure and stage the analytical equipment for the Fischer-Tropsch demonstration.
2. Complete the software installation to allow PCs to emulate DEC workstations. This will allow engineers and other staff to view the "live" plant data without physically being in the control room.
3. Write and stage computer software to allow the DEC computer to send data to the Bailey. This feature would make it possible for the Bailey to receive molecular weight data from the DEC and use that data to correct the displayed flow. (Currently, flow as displayed by the Bailey is only corrected for pressure and temperature while that on the DEC is corrected for molecular weight as well.)

All three of these items are scheduled to be completed prior to the Fischer-Tropsch demonstration.

Engineering, Design, and Modifications for the Spring Isobutanol Demonstration

By early January, the bulk of the detailed engineering and design work was completed. Most of our efforts were devoted to making the necessary site modifications and completing the final hazards review.

By the end of January, the installation of new equipment items was finished and fabrication of new field piping/insulation was 90% complete. Reactivation of existing equipment also commenced in January. The overhaul of the 01.10/01.20 compressor was undertaken. Motors for all pumps, fans, and agitators were set in place. Twenty of the safety relief valves were removed and sent out for inspection and any necessary repair. In February, pressure testing and x-ray testing (where required) were performed on the new equipment and piping.

In February, it was decided that the spring demonstration of isobutanol production would be postponed and replaced with the demonstration of liquid-phase-shift (LPS). Nevertheless, we did complete the final hazards review (Design Verification Review) for IBOH (see Appendix 1).

Engineering, Design, and Modifications for the Spring Liquid-Phase Shift Demonstration

As of February, the run plan called for the demonstration of the water-gas shift reaction in the liquid phase (LPS). The switch form IBOH to LPS was brought about by the supplier's inability to prepare the isobutanol catalyst which met our performance targets. The LPS demonstration requires much of the same equipment as would have been required to carry-out isobutanol. A commercial shift catalyst, which has been thoroughly tested in our labs previously, would be used.

All required engineering, design, and modification work was completed. Highlights are summarized below.

1. Technology

The shift reaction is described as follows:

$$H_2O + CO = H_2 + CO_2$$

Most state-of the art gasifiers produce a syngas with a H_2:CO ratio between 0.5:1 and 1:1. In contrast, the stoichiometry of oxygenate synthesis and Fischer-Tropsch synthesis requires H_2:CO ratios of 1:1 to 2:1. As a result, coal derived syngas cannot be completely converted to these fuels without the use of a shift step to upgrade the hydrogen content. Therefore, shift is viewed as an integral unit operation in the overall syngas-to-fuels process. Gas-phase shift has been commercially practiced for years; liquid-phase shift has been previously demonstrated in the labs but, to our knowledge, has yet to be demonstrated in a bubble column.

2. Demonstration Plan

At the AFDU, LPS will be carried-out by injecting 500 psi steam into the feed gas prior to introduction to the reactor. The steam will react with the CO to form H_2 and CO_2 ; the reaction will be carried-out at 250°C and 400 to 450 psig. The objective of this demonstration is to prove feasibility. Thus, the focus will be to study different feed gas types and produce products with a H_2:CO ratio between 1:1 and 2:1 (or more). Process variables such as pressure and temperature are not to be considered here but could easily be studied in the laboratory autoclave reactors.

The shift catalyst we intend to use is made by BASF (K3-110). This catalyst is one of the commercial "low temperature" shift catalysts and is composed of CuO, ZnO, and alumina. Since these components are the same as those found in many methanol catalysts it is also possible to use the catalyst to produce methanol. Methanol production at the AFDU as part of the Spring 1992 demonstration is advantageous for two reasons:

1. It provides a means to shakedown and calibrate the DCS and DAS systems under real operating conditions. The alternative is to shakedown without catalyst (fill the reactor and vessels with oil and circulate syngas).

2. It provides a means of replenishing our dwindling supply of liquid phase methanol product for engine tests. Recent tests by Detroit Diesel have been extremely successful and we are anticipating demand for "LaPorte Methanol" to exceed our existing stock. The alternative would be to restart the AFDU at some later date for the sole purpose of making methanol.

After consultation with PETC, a run plan was adopted which included the demonstration of both LPM and LPS technologies. The run plan is reproduced in Table 1.1.

TABLE 1.1
Run Plan for Spring 1992 LPS Demonstration

Run #	Operation	Duration
CATALYST ACTIVATION		
AF-A2	Activation of 550# of K3-110 catalyst	2.0 days
LPM DEMONSTRATION		
AF-R4	Methanol synthesis w/K3-110	6.5
	Drain reactor to 275# of catalyst (oxide basis)	0.5
LPS DEMONSTRATION		
AF-R5 .1	Texaco Gas, SV=10000, H_2:CO=1:1	2.0
.2	Texaco Gas, SV=10000, H_2:CO=2:1	1.0
.3	Texaco Gas, SV= 6000, H_2:CO=2:1	1.0
.4	Texaco Gas, SV= 6000, H_2:CO=1:1	1.0
	Change-out methanol in CO_2 removal section	0.5
AF-R5 .5	Shell Gas, SV=7000, H_2:CO=2:1	1.0
.6	Shell Gas, SV=7000, H_2:CO=1:1	1.0
.7	Shell Gas, SV=4000, H_2:CO=1:1	1.0
.8	Shell Gas, SV=4000, H_2:CO=2:1	1.0
	Prepare for once-through operation	0.5
AF-R5 .9	H_2 Lean Gas, SV=6000, H_2:CO=2:1	1.0
.10a	POX Gas, SV=6000, H_2:CO=20:1	1.0
.10b	POX Gas, SV=6000, H_2:CO=40:1	1.0
	TOTAL	22.0

SV is space velocity expressed as sL/kg-hr. Runs R5.6, R5.7, and R5.10b are optional and will be carried-out if the schedule can be maintained. The feed gas compositions to be used are presented in Table 1.2.

TABLE 1.2
Feed Gas Compositions for Spring 1992 LPS Demonstration

Component:	H_2	CO	CO_2	N_2
Shell Gas	31.0	65.0	3.0	1.0
Texaco Gas	35.0	51.0	13.0	1.0
H_2 Lean Gas	1.5	72.0	13.4	13.1
POX Gas	60.7	37.7	1.6	0.0

3. Process Development

From the viewpoint of the AFDU, operation of LPS is similar to IBOH with some exceptions. The operation is similar in the sense that some level of CO_2 removal is required to allow unreacted syngas to be recycled. However, some modifications to the plant are necessary: new tie-in of HP steam to the process feed, installation of a throttling valve downstream of the 01.10 feed compressor (to allow for low pressure operation of the reactor), new tie-ins to the flare, and repiping around the 10.85 pump.

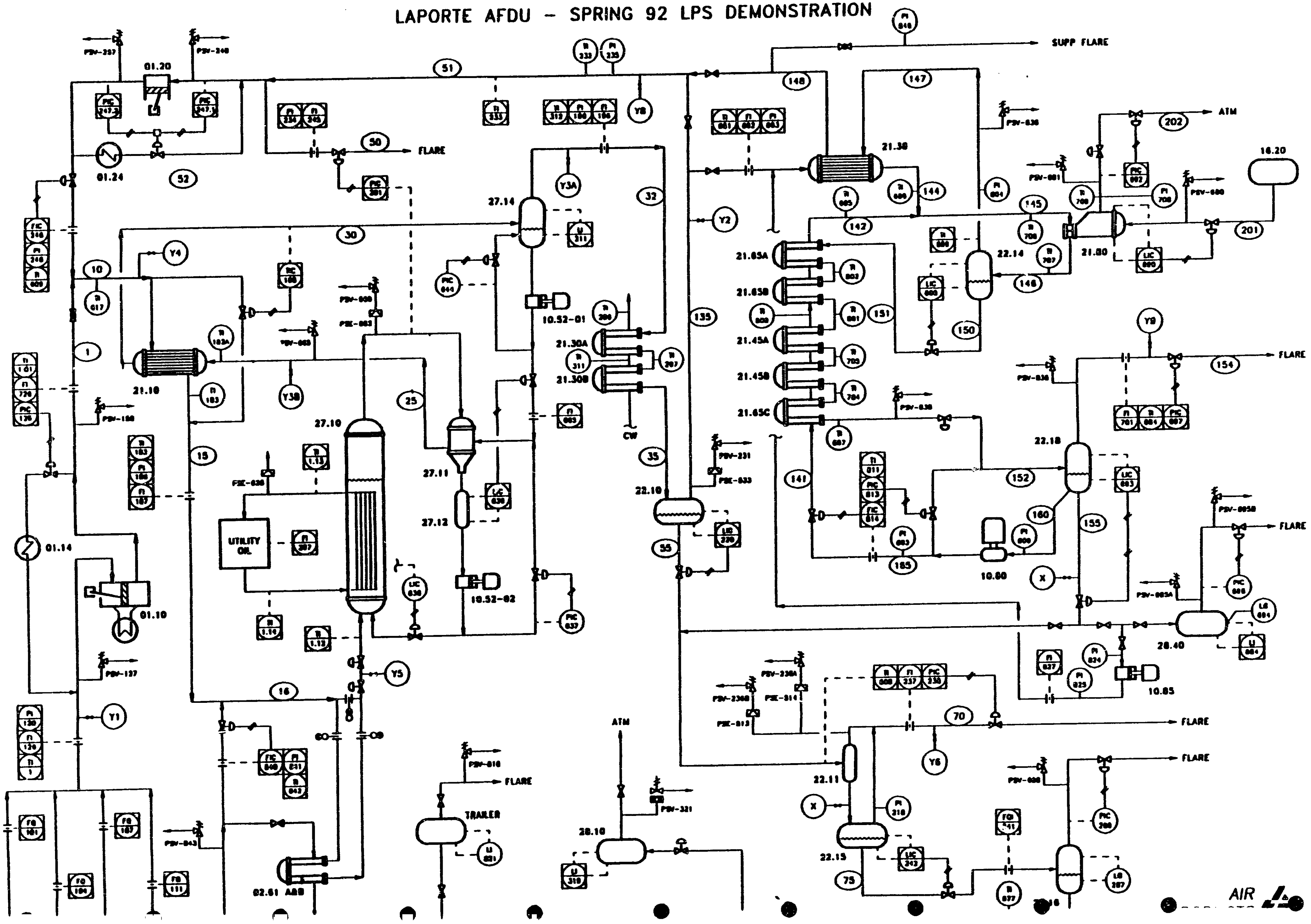
Process Description (see Figure 1.1—Flowsheet)
Hydrogen, carbon monoxide, and carbon dioxide are blended and compressed, then mixed with recycle gas to form the desired syngas composition and flow. This reactor feed is preheated (in the 21.10) then combined with high pressure steam. The mixed feed is directed to the 02.61 where it is further heated by condensing HP steam, and then finally introduced to the bottom of the 27.10 slurry reactor.

The syngas flows upward through the slurry (catalyst-mix plus mineral oil) where water and CO react to form H_2 and H_2O; some methanol may also be formed as a by-product. The heat of reaction is absorbed by the oil and then rejected to an internal heat exchanger. The gross reactor effluent is passed through the 27.11 cyclone to remove catalyst fines, then cooled in the 21.10 to condense traces of slurry oil. The resultant vapor is considered to be the net reactor effluent. This stream is subsequently chilled against cooling water (in the 21.30), and introduced to a 22.10 separator where virtually all the unreacted water (and any methanol) are recovered as liquid.

The vapor from the 22.10 is cooled in the 21.38 exchanger and combined with a circulating MeOH fluid. This combined stream is then chilled to 0°F in the 21.80 kettle evaporator. Simultaneously, CO_2 is absorbed into the liquid MeOH. This stream enters the 22.14 where approximately 50% of

FIGURE 1.1

LAPORTE AFDU – SPRING 92 LPS DEMONSTRATION



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the contained CO_2 is recovered in the liquid. The remaining CO_2 and syngas is rewarmed by cross exchange in 21.38. A portion of this vapor is sent to flare and the remainder recycled to the front-end.

The liquid from the 22.14 is let down in pressure, then warmed to ambient in the 21.45 and 21.65 hairpin exchangers. The MeOH-rich stream is then degassed in the 22.18. The off-gas, which contains the previously absorbed CO_2, is sent to flare. The liquid from the 22.18 is pumped in the 10.80 and then chilled in the 21.65 and 21.45 prior to being combined with the 22.10 vapor take-off.

A small amount of the methanol and water is carried over from the 22.10. To maintain a constant volume in the cold end, a bleed line is required. The bleed will empty into the 22.11. (Throughout the run, the cold end will operate in an unsteady state as the composition in the cold end changes. The change in composition will affect the level of CO_2 removal. Consequently, the liquid inventory is periodically dumped and then recharged.)

The vapor off the 22.10 is saturated with water. This water would normally condense and potentially freeze on the tubes of the 21.38. To keep this from happening, a small methanol flow will be drawn from the 22.18, pumped in the 10.85 and injected into the gas steam prior to its introduction to the 21.38.

4. Engineering and Design

First, preliminary heat and material balances were developed. A revised P&ID and associated FCNs (flowsheet change notices) were drafted, issued for review, and approved. These were used to design/size valves, instruments and lines. Specifications were released to Design Engineering, where the detailed specifications were drawn up and issued for purchase. The preliminary Hazards Review was conducted which identified action items for further review. Calculations in support of the Design Hazards Review were then completed and discussed with the review team. In March, the final review, Design Verification Review, was completed (see Appendix 2).

5. Site Modifications

Required piping modifications and instrument installations were completed in March. At the same time, shakedown activities continued: controller function check-out was conducted with nitrogen and oil. Finally, syngas was introduced to the plant during the last week of March. Regular operations will be ready to begin 1 April.

Engineering and Design for the Summer Fischer-Tropsch Demonstration

P&ID development work was completed for the Summer 1992 Fischer-Tropsch demonstration run. New control valves as well as new safety valves were specified and approved for purchase. The 21.85 double pipe heat exchanger was also ordered. Piping design work was completed and construction packages were released. Reactor heat load calculations were performed for various F-T process conditions. The calculations indicate significantly higher heat load for F-T at highest space velocity (6000 sl/hr-kg Fe) compared to LPM. Even though the space velocities are lower for F-T, CO conversions are much higher and heat of reaction is somewhat higher. The heat load on the reactor heat exchanger at 6000 GHSV, 600 psig and 0.95 alpha, was calculated to be about 1.1 MM Btu/hr compared to the maximum LaPorte capacity of about 0.9 MM Btu/hr. The fin fan on the utility oil is the limiting equipment. As a result of the heat transfer limitations in the reactor, the highest space velocity was decreased from 6000 to 5000 sl/hr-kg-Fe. Also, in order to obtain a minimum of 0.14 ft/sec inlet gas velocity, the lowest space velocity was increased from 2000 to 2500 sl/hr-kg. Heat and mass balances were developed for the new conditions.

A filter test was conducted at Mott Metallurgical to check the cross-flow filter design for catalyst-wax separation. Drakeol-10 oil was used as a slurry medium with UCI Fe catalyst for the test. The test was conducted at about 150°F to simulate viscosity of wax at 250°F. Initial results indicated excellent filter performance with 1 micron grade filter element at 20 wt% slurry concentration. After four hours of operation, the filtrate flow stabilized at 0.17 – 0.18 gpm/ft^2 for next 4 hours. This was about 35% above the design flux of 0.13 gpm/ft^2. Also, no backflush was necessary throughout the day. The slurry was maintained at 150°F overnight with the filter shut off. On the second day, the slurry was concentrated to 25 wt%. The filter now needed a backflush every 20 minutes to maintain the design flux. Overnight on the second day, the slurry got overheated to 250°F. On the third day, the filter plugged right away when a test with 20 wt% slurry was attempted. Even when the filter element was replaced with a new element, only 5 minute cycles were achieved. It appeared that the slurry properties had changed. Particle size measurements indicated reduction in particle size from a median (by particle number) of 12 microns to 6 microns in 16 hours of operation. Mott did not believe that particle size was the cause since they have had better performance with finer catalysts in the past. Also, the step changes in performance after overnight shutdowns at temperature indicated possible change in the chemical nature of the slurry. One possibility was that water came off the catalyst and leached potassium oxide from the catalyst forming potassium hydroxide. Hydroxides are known to inhibit filter performance because they make the particles slippery and allow finer particles to penetrate the filter, thus plugging up the filter. Several analytical tests were conducted to investigate the cause of filter plugging problems. Fresh, intermediate, and spent slurry samples were analyzed. Titrations of the oil samples indicated no alkalinity (hydroxides) or acidity in any of the samples. Atomic adsorption of the oil samples did not detect the presence of any metals (Fe, Cu, K or Si). The brown tint in the spent oil was attributable to very fine Fe particles. These particles would not settle or centrifuge and were only removed by filtration using a fine membrane. Infrared analysis of the oil samples did not show any evidence of breakdown or oxidation of the oil. XRD on the catalyst samples indicated that crystallite of Fe_2O_3 represented only 7.7 to 9.6% of the defraction pattern with no difference in crystallite size between samples. So, it appears that there was no change in the chemical nature of the slurry. Perhaps the physical grinding of the catalyst at high concentrations through the 1/4" test filter element was the cause of the plugging problems.

As a result of filter plugging problems, the catalyst-wax separation design was changed. It was decided to attempt some settling prior to filtration. This would reduce concentration of the slurry going to the filter. The connections to the slurry holding vessel (27.13) were changed such that the connections to and from the reactor will be at the bottom while the connections to and from the filter will be near the liquid level (3 ft). The settling is expected to be substantial at the base condition; however, it will only be partial at the high production condition.

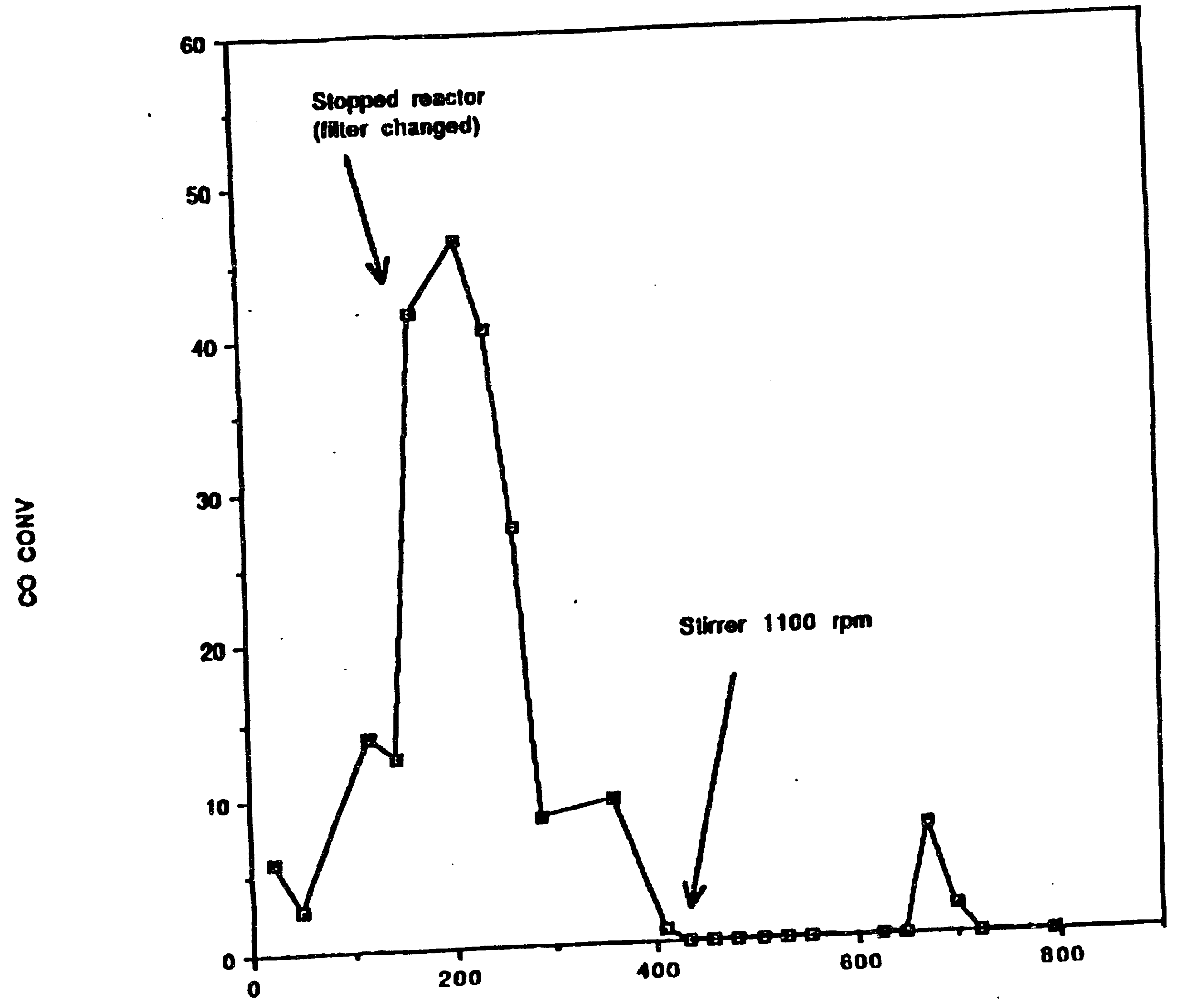
CAER, Kentucky completed activity tests with the UCI catalyst to compare Drakeol-10 with Ethylflow-164 as a starting slurry medium. Both the tests showed poor catalyst activities (see Figures 1.2 and 1.3). This is in contrast to acceptable and comparable activities observed at both UOP and Texas A&M. It appears that the catalyst samples at CAER went through a slow activation and were never fully activated. CAER also had filter plugging problems in both the tests. Even though attempts were made at CAER to duplicate UOP activation procedures, two differences emerged as a result of detailed discussions with both the parties. UOP switches from N_2 to syngas at 280°C while CAER heated up the slurry from 25°C to 280°C in 2.2 hours under syngas flow. Also, the CAER stirring rate appears to be low—750 rpm compared to 1100 – 1200 rpm typically used by UOP and Air Products in the autoclaves. CAER plans to conduct another test.

Following completion of a partnership agreement between Air Products and Exxon, we visited Exxon on 25 February to discuss plans for the F-T run. Exxon has abandoned catalyst systems with SiO_2. They have observed catalyst instability when the catalyst was supported on SiO_2. Also, they find these catalysts hard to activate reproducibly. Instead, they are prefer unsupported catalysts with Fe, Cu and K. Exxon is concentrating on low alpha operations (about 0.75), producing low molecular weight HC liquids. This reduces wax cracking and catalyst-wax separation requirements.

A meeting was held on 19 – 20 March in Pittsburgh with DOE and industrial partners to discuss catalyst selection, run plan and analytical assistance. Our partners to date include Exxon, UOP and Statoil; an agreement with Shell is pending. At the partners' meeting, it was decided to pursue a lower alpha catalyst, which would minimize heavy wax (C_{26}^+) production and increase lower molecular weight hydrocarbon liquid products (C_8 - C_{20}). It was generally felt that, in view of filtering difficulties experienced by Air Products at Mott and by Rentech in Colorado, it was worth minimizing the load on the catalyst-wax separation system and focusing on reactor performance, which is the main goal of this first run. After the meeting, follow-up discussions were held by Air Products and Exxon with UCI regarding the catalyst preparation. UCI has agreed to prepare two different low alpha catalysts on a small scale by end of April. One batch will made with about 1% K_2O and 1.6% SiO_2, starting with potassium silicate. This requires a minimum change from the current method of producing high alpha catalyst which also uses potassium silicate as starting material (5.9% K_2O and 9.7% SiO_2). The K_2O to SiO_2 ratio will remain the same. The second batch will involve adding extra SiO_2 from another source making up to 5% SiO_2. The second batch will be a back-up catalyst, in case the first batch has less than acceptable physical properties due to lower silica content. Both the samples will be tested by UCI for physical properties such as attrition resistance. UOP will then activity-test the catalyst selected from the two in early May. By mid-May, a decision will be made on whether to proceed with a high or a low alpha catalyst. UCI has blocked out pilot plant time to prepare 2000 lbs of the selected catalyst between mid-May and mid-June. Thus, the catalyst will be prepared in time for the July run as scheduled.

Data from "R2LBX009(L3950-U)" Ethyl C_{30}

(SLURRY OIL)



CAER ACTIVITY TEST OF UCI CATALYST

SYN HRS

FIGURE 1.2

Data from "R4 L~~B~~GX010(L3950-oil)" Drakeol-10

(SLURRY OIL)

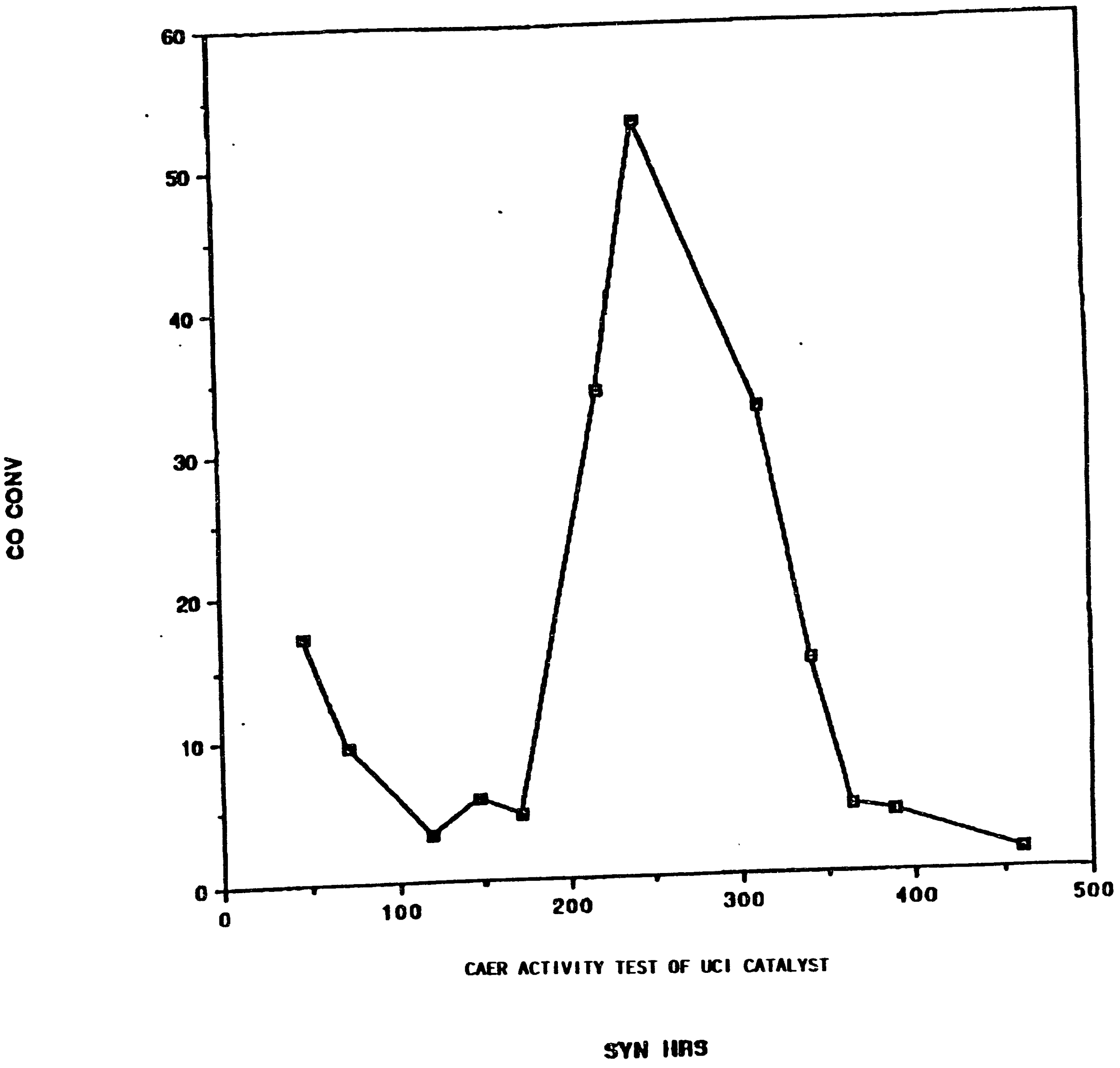


FIGURE 1.3

During the meeting, Exxon offered the use of their process wax as a starting slurry medium to eliminate the time needed to displace Drakeol-10 with product wax. Follow-up discussions were held between Air Products and Exxon regarding the supply of the starting wax. For Exxon to supply process wax, they would need to restrict access to their wax and would require those with access to sign a non-disclosure agreement. However, since starting wax will end up with the product wax, it will be very difficult to limit the access to the starting wax. Also, with the run coming up in about three months, there is not enough time to get legal agreements in place. Exxon offered Isopar, which is a C_{20}-C_{30} saturated isoparaffin liquid. However, in the absence of available wax, it was decided to use Drakeol-10, since it has been extensively and successfully used at LaPorte for LPM and LPDME. Drakeol-10 is a C_{16}-C_{38} saturated hydrocarbon liquid which includes straight chain and branched paraffins as well as naphthenic compounds. The catalyst performance would be independent of starting medium so long as it does not contain any contaminants. Drakeol-10 will be used by UOP in future tests after a catalyst decision has been made.

The run plan proposed at the meeting (see Table 1.1) was accepted by the partners. About 780 lbs of catalyst and 210 gallons of Drakeol-10 will be loaded in the reactor to make about 35 wt% slurry. The catalyst will be activated using 0.7 H_2/CO syngas at 2000 sl/hr-kg Fe, 150 psig, and 280°C for about 12 – 16 hours. About 1% N_2 will be added to the syngas as an internal standard. The inlet gas velocity of about 0.23 ft/sec will be sufficient for adequate mixing. Expanded slurry height of 20 ft, which is maximum, will be maintained throughout the run. The decline in CO_2 and rise in CH_4 content of the product gas will be monitored; when they level off the operating conditions will be changed to run conditions. The baseline run (Run No. 1) will be conducted with 0.7 H_2/CO syngas (1% N_2) at 2500 sl/hr-kg Fe, 200 psig, and 265°C. It is estimated that the reactor will contain about 490-500 lbs of catalyst during the run; the remaining catalyst will be in the slurry holding tank and the cross-flow filter system. The slurry concentration in the reactor will be about 26 wt%. The inlet gas velocity will be about 0.14 ft/sec, which is the minimum velocity required for adequate mixing. The run at these conditions will be continued for ten days to check for stabilization of the catalyst performance. These conditions will be repeated for four days at the end of the run to check for any catalyst deactivation. Two other conditions will be studied for three days each during the run. The space velocity will be doubled to 5000 sl/hr-kg Fe at 200 psig and 265°C to study the effect of space velocity (Run No. 2). The inlet gas velocity will be about 0.27 ft/sec. The reactor pressure will then be doubled to 400 psig at 5000 sl/hr-kg Fe and 265°C to study the effect of reactor pressure (Run No. 3). The inlet gas velocity will be back to about 0.14 ft/sec.

Discussions were held with DOE at the meeting for analytical assistance. It was decided that Air Products will ship HC liquid and solid wax samples to DOE's Pittsburgh Energy Technology Center (PETC) daily during the run for analysis. PETC is already set up for these analyses and has promised a 1 – 2 day turn-around time. Gas analysis will be conducted on-line at LaPorte using PETC's analytical methods. Two GCs will be set up to analyze up to C_8 in the gaseous product.

TABLE 1.1
Run Plan for F-T Synthesis

Syngas Comp. = 0.7% H_2/CO, 1% N_2
Expanded Slurry Ht = 20 ft (max)

Run No.	Space Vel. NL/KG-FE-HR	Rx Prs. psig	Rx Temp. °C	No. of Days On-Stream	Catalyst Conc, Wt%	Lin. Gas Vel. (in), ft/sec	Lin. Gas Vel. (out), ft/sec	Co Conv. %	6-F Alpha	Wax GPD	Liq HC GPD	Water GPD
Activation	2000	150	280	1	35	0.23						
1	2500	200	265	10+4	26	0.14	0.09	58	0.95	164	74	47
									0.90	118	117	47
									0.85	55	149	47
2	5000	200	265	3	26	0.27	0.19	47	0.95	255	120	77
									0.90	171	193	77
									0.85	65	243	77
3	5000	400	265	3	26	0.14	0.09	59	0.95	349	125	94
									0.90	241	219	94
									0.85	125	286	94

Task 3: Research Program

Task 3.1: New Fuels From Syngas

a. Isobutanol/Higher Alcohols:

Process Variable Scans on Cs-Cu/ZnO/Al_2O3 (BASF S3-86)

Model Predictions:

Process variable studies were done (last Quarterly Report) on Cs-promoted Cu/ZnO/Al_2O_3 (1.1 wt% Cs) to quantify the effect of various process variables on the performance of the catalyst. The influence of four variables was investigated: 1) temperature, 2) pressure, 3) gas-hourly-space-velocity (GHSV), and 4) the feed CO_2 concentration in a Shell gas matrix. A Box-Behnken statistical experimental design, with three levels of each of the above four variables, was used; a total of 30 experimental observations at 25 different conditions. The levels used for each variable were: temperature (285, 300, and 315°C), pressure (500, 750, and 1,000 psig), GHSV (2,000, 5,000, and 8,000 std. lit./kg-hr), and feed CO_2 concentration (0, 1.5, and 3.0 mol%). Response variables, such as rates and selectivities for the individual products, were regressed and fit to 2^{nd}-order equations. The experimental results and discussion of the goodness of fit were presented in the last quarterly report (October-December 1991). More detailed model results are presented here.

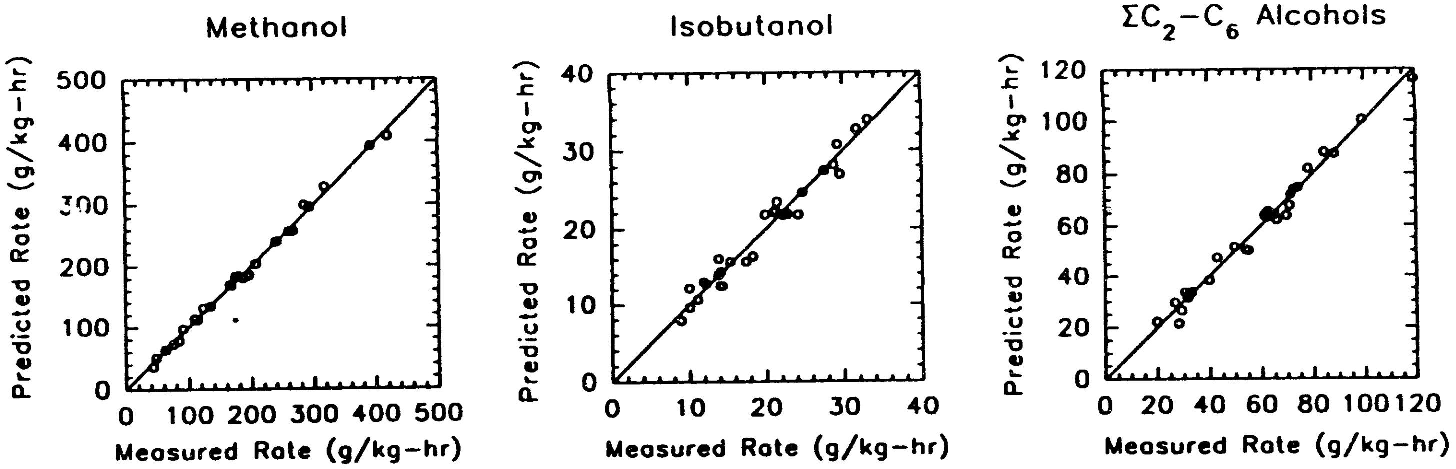
Regression parameters were determined for a total of 25 key response variables. These parameters were used in the 2^{nd}-order equation to predict the response variable as a function of the four independent variables. As an indication of the quality of fit, parity plots for the methanol rate, isobutanol rate, ΣC_2-C_6 alcohols rate are shown in Figure 3.1.1. Figure 3.1.1 shows, for each measured rate, a corresponding predicted rate as obtained by the 2^{nd}-order model. The 2^{nd}-order fit is quite good for these three products. The average absolute prediction error per observation is 3.4%, 6.3%, and 5.3 % for methanol, isobutanol, and ΣC_2-C_6 alcohols, respectively. The equation for methanol rate required 10 parameters, while the isobutanol and ΣC_2-C_6 alcohols rate equations required 11 and 12 parameters, respectively.

Previously obtained data, which were not part of the Box-Behnken experimental matrix, on the effect of GHSV at 300°C and 850 psig using Shell gas with 3% CO_2 is compared to model predictions in Figure 3.1.2. As shown, the model does an excellent job of predicting the individual product rates, as well as the ΣC_2-C_6 alcohols rate. Noteworthy is the fact that the 9,000 GHSV condition is slightly outside the range of GHSV used to generate the models, but the fit is still quite good. However, extreme caution should be taken in extrapolating the data to any combination of reaction conditions which is outside the range. The models developed are purely empirical and have no basis in physical or chemical phenomena.

Model predictions of the major product rates and selectivities as a function of temperature, pressure, GHSV, and feed CO_2 concentration were generated. These rate and selectivity correlations are presented as functions of GHSV at three levels of another variable (temperature, pressure, or feed CO_2 concentration) while holding the remaining two variables constant. These model predictions are shown in Figures 3.1.3-3.1.8.

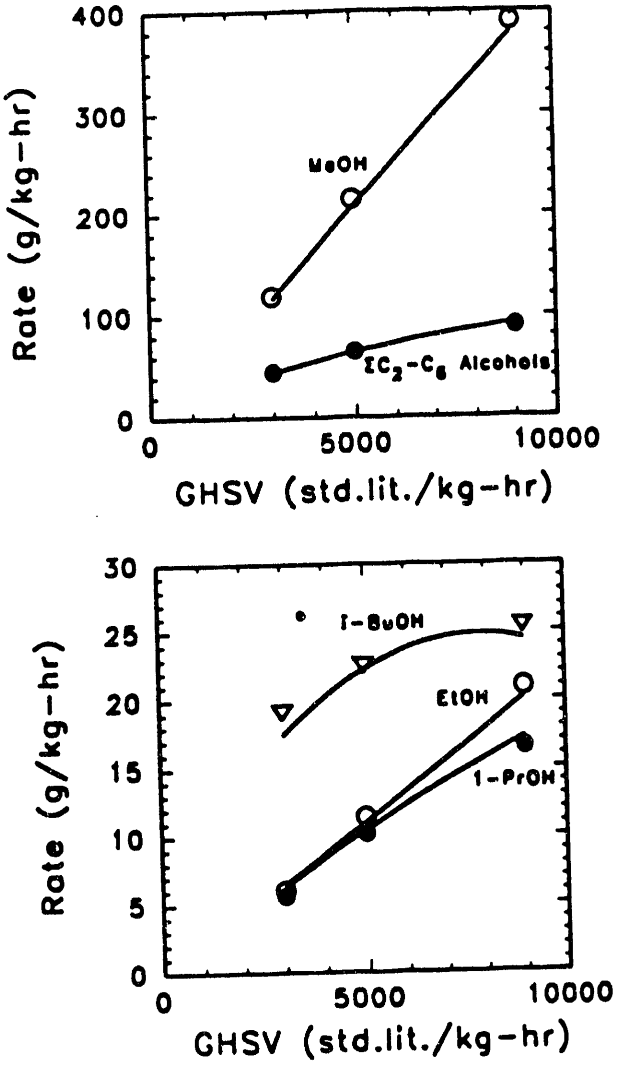
FIGURE 3.1.1

Parity Plots for Product Rates



pvspar.spg

FIGURE 3.1.2



Measured vs Predicted Rates

$Cs-Cu/ZnO/Al_2O_3$

Shell Gas, 300°C, 850 psig

Lines are model prediction

Symbols denote measured data

pvspre1.spg

The effect of temperature on product rate and selectivity for Shell gas with 3% CO_2 at 750 psig, is shown in Figures 3.1.3 and 3.1.4. The rates of synthesis of methanol, ethanol, and 1-propanol decrease monotonically with increasing temperature, while the isobutanol rate increases monotonically. The influence of temperature on the ΣC_2-C_6 alcohols rate is affected by the particular GHSV, as shown in Figure 3.1.3. Increasing temperature also increases the rate of synthesis of C_1-C_6 hydrocarbons. The effect of GHSV on isobutanol rate at the various temperatures is interesting. At 285°C, the isobutanol rate goes through a maximum with increasing GHSV, while, at 315°C, the rate increases continuously with GHSV. Another interesting observation is that the C_1-C_6 hydrocarbons rate decreases monotonically with GHSV at 285°C and 300°C, but is barely influenced by GHSV at 315°C. The selectivity results in Figure 3.1.4 clearly show that methanol selectivity decreases with increasing temperature, while the isobutanol, ΣC_1-C_6 hydrocarbons, and ΣC_2-C_6 alcohols rates all increase with temperature. Also shown is the fact that the selectivity to ΣC_1-C_6 hydrocarbons decreases dramatically with increasing GHSV, at each temperature.

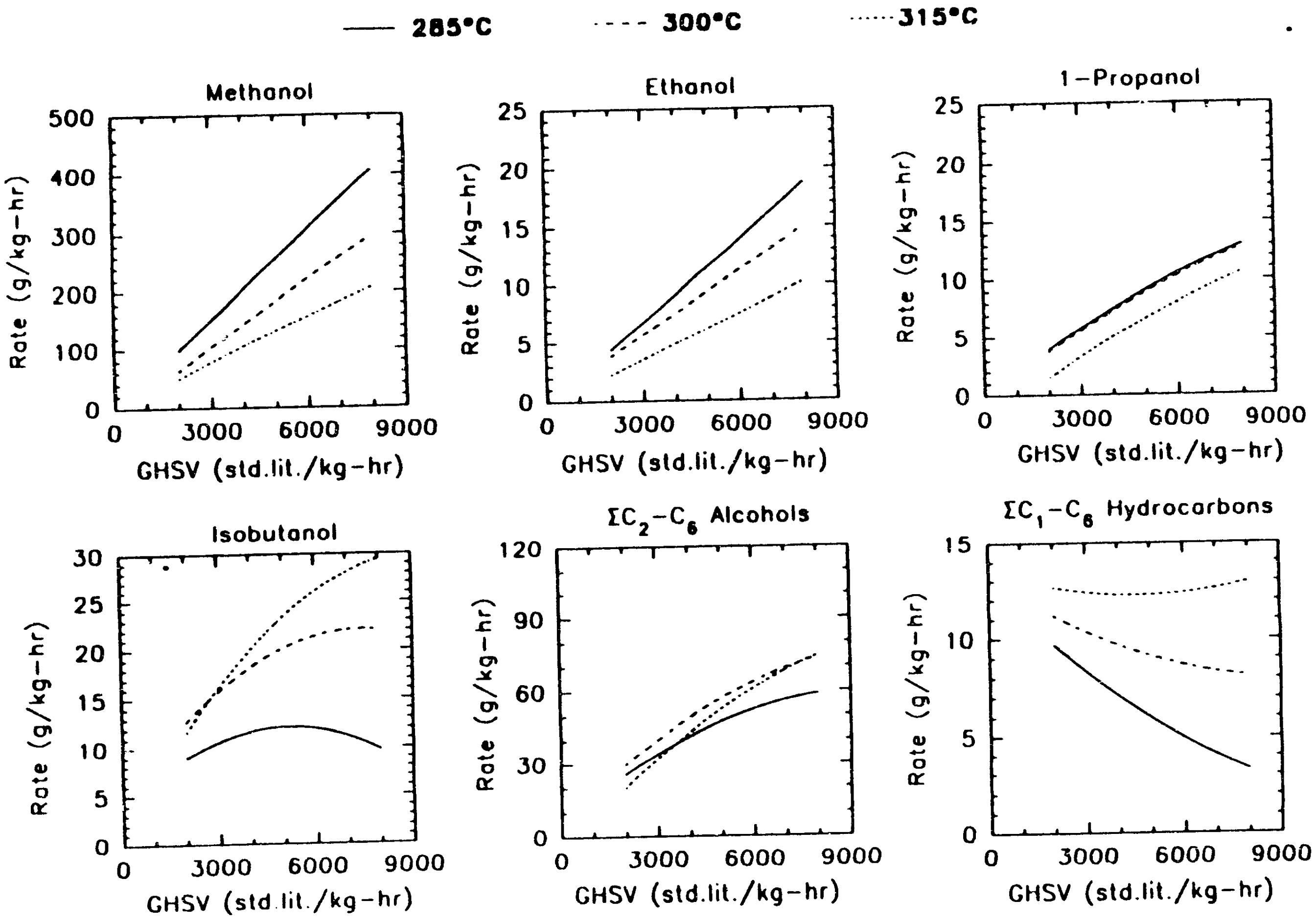
Figures 3.1.5 and 3.1.6 show the effect of pressure on product rate and selectivity for Shell gas with 3% CO_2 and a reaction temperature of 300°C. Figure 3.1.5 shows that a substantial increase in the rate of synthesis of all products with increasing pressure is quite evident. As shown in Figure 3.1.6, the selectivity to methanol and isobutanol is not a strong function of pressure. However, selectivities to ethanol and 1-propanol increase with increasing pressure, while selectivity to ΣC_1-C_6 hydrocarbons decreases with increasing pressure. Pressure has little effect on the selectivity to total higher alcohols (ΣC_2-C_6 alcohols).

The effect of feed CO_2 concentration on product rate and selectivity for Shell gas at 750 psig and 300°C, is shown in Figures 3.1.7 and 3.1.8, respectively. Methanol rate is not affected by varying CO_2 concentration, while the rate of synthesis of all other products increases with decreasing feed CO_2 concentration. Figure 3.1.8 shows that selectivities to higher alcohols increase with decreasing feed CO_2 level.

Another response variable correlated was the reactor exit H_2O concentration. This quantity is important because it determines how much H_2O may be present in the product alcohols, and also may influence catalyst life by determining the rate of hydrothermal sintering. The catalyst, in particular the copper phase, is expected to sinter faster in the presence of high partial pressure of H_2O. The reactor exit H_2O concentration was experimentally determined using the on-line Karl-Fischer titrator. Figure 3.1.9 shows the effect of pressure, temperature, and feed CO_2 concentration on the reactor exit H_2O concentration. The results indicate that exit H_2O concentration increases dramatically with decreasing GHSV. This correlation suggests that the use of low GHSV may be disadvantageous from the standpoint of product quality and catalyst life.

FIGURE 3.1.3

Model Prediction of Product Rates vs GHSV at Different Temperatures
750 psig, Shell Gas (3% CO_2)



pvspre4.spg

FIGURE 3.1.4

Model Prediction of Product Selectivities vs GHSV at Different Temperatures

750 psig, Shell Gas (3% CO_2)

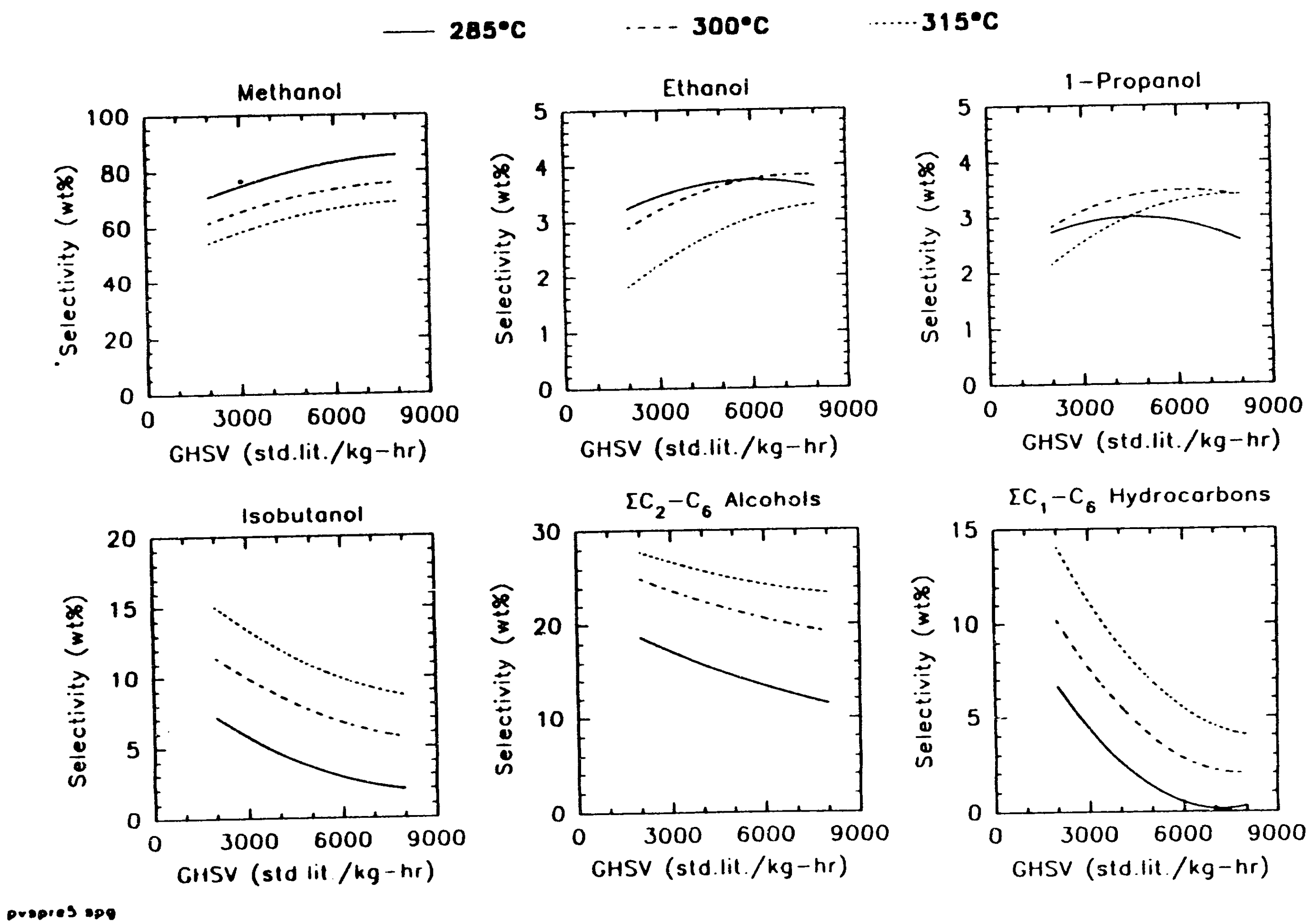
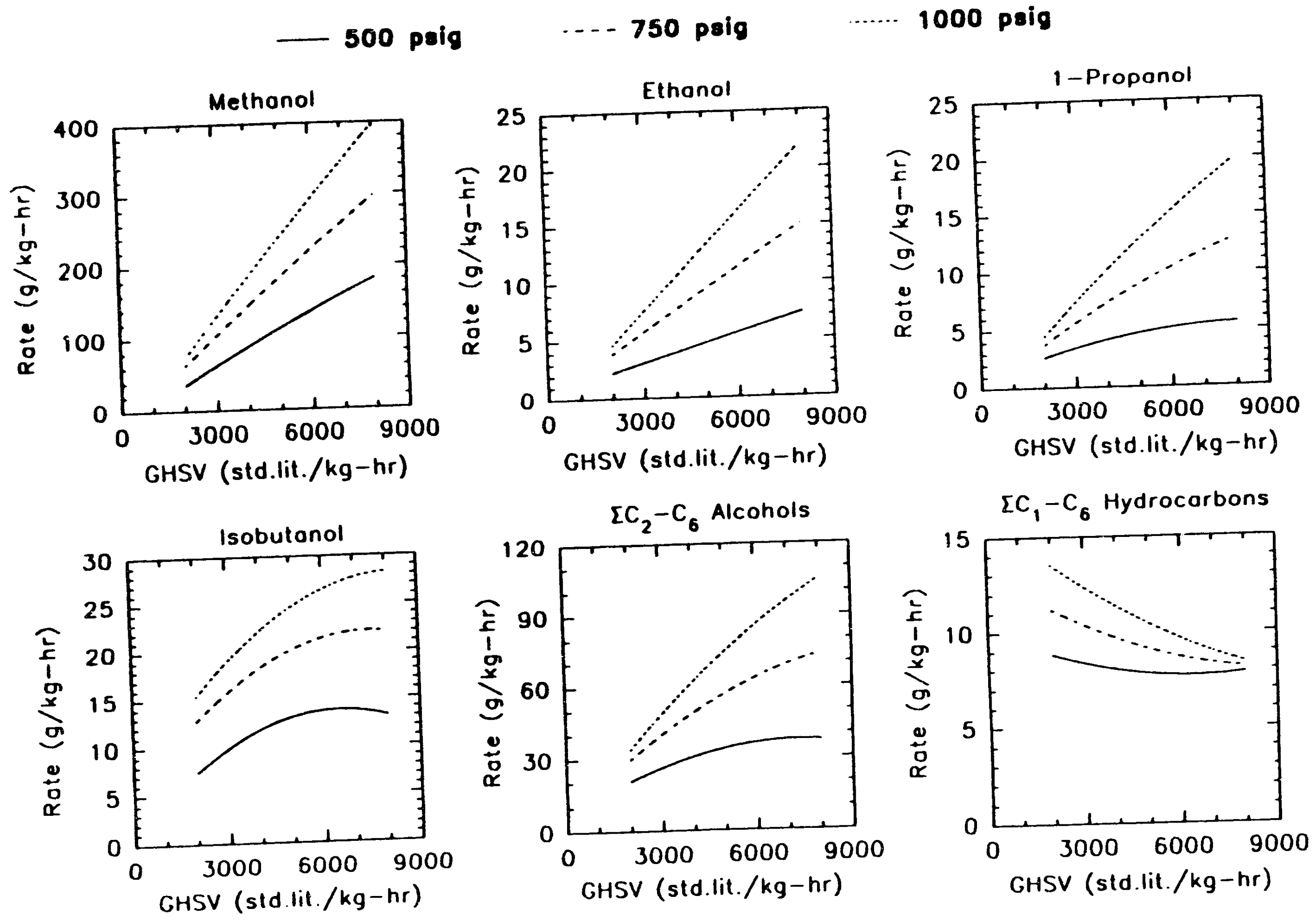


FIGURE 3.1.5

Model Prediction of Product Rates vs GHSV at Different Pressures

300°C, Shell Gas (3% CO_2)

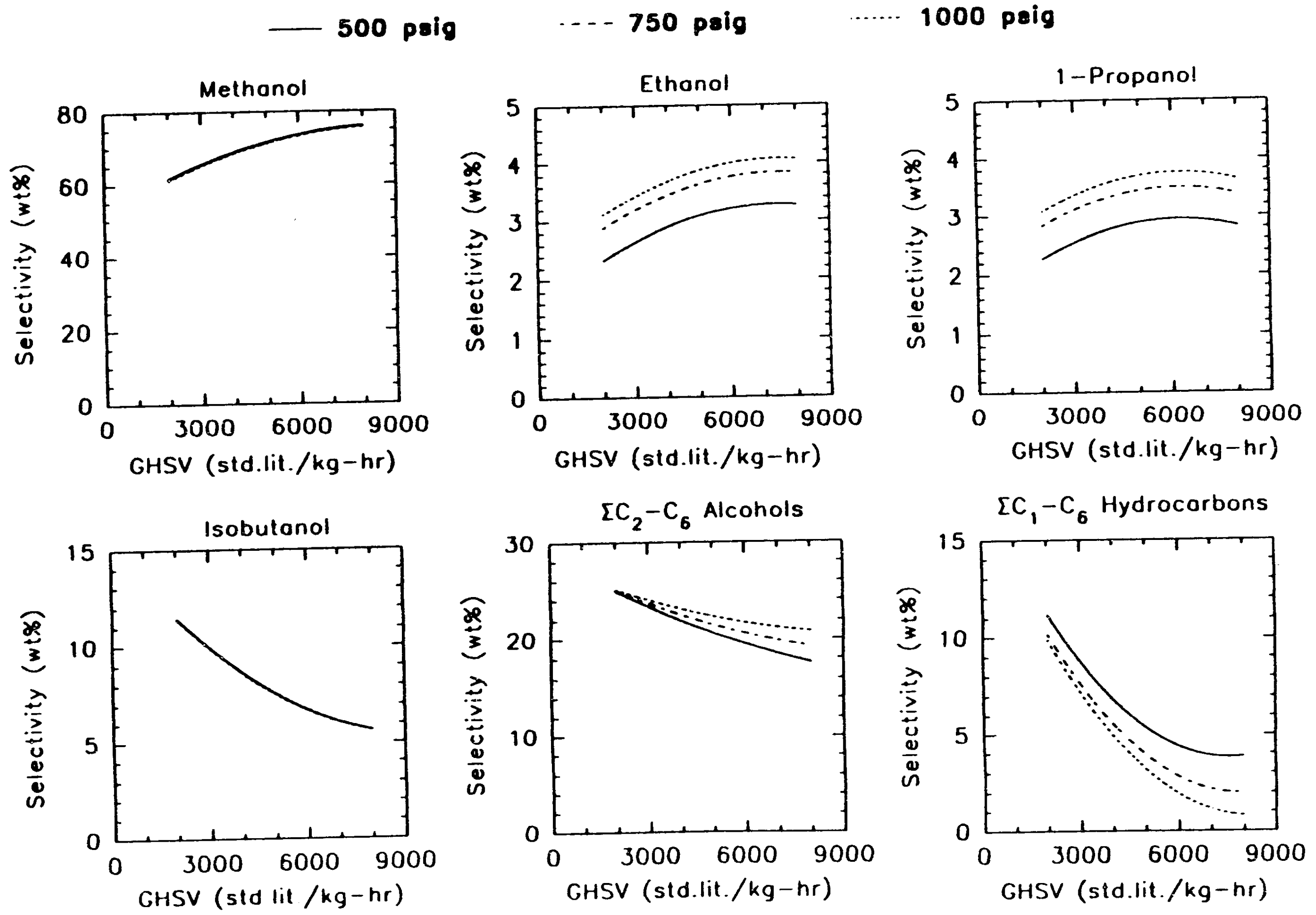


pvspre2.spg

FIGURE 3.1.6

Model Prediction of Product Selectivities vs GHSV at Different Pressures

300°C, Shell Gas (3% CO_2)



pvspre3 spg

FIGURE 3.1.7

Model Prediction of Product Rates vs GHSV at Different Feed CO_2 Concs.
300°C, 750 psig, Shell Gas

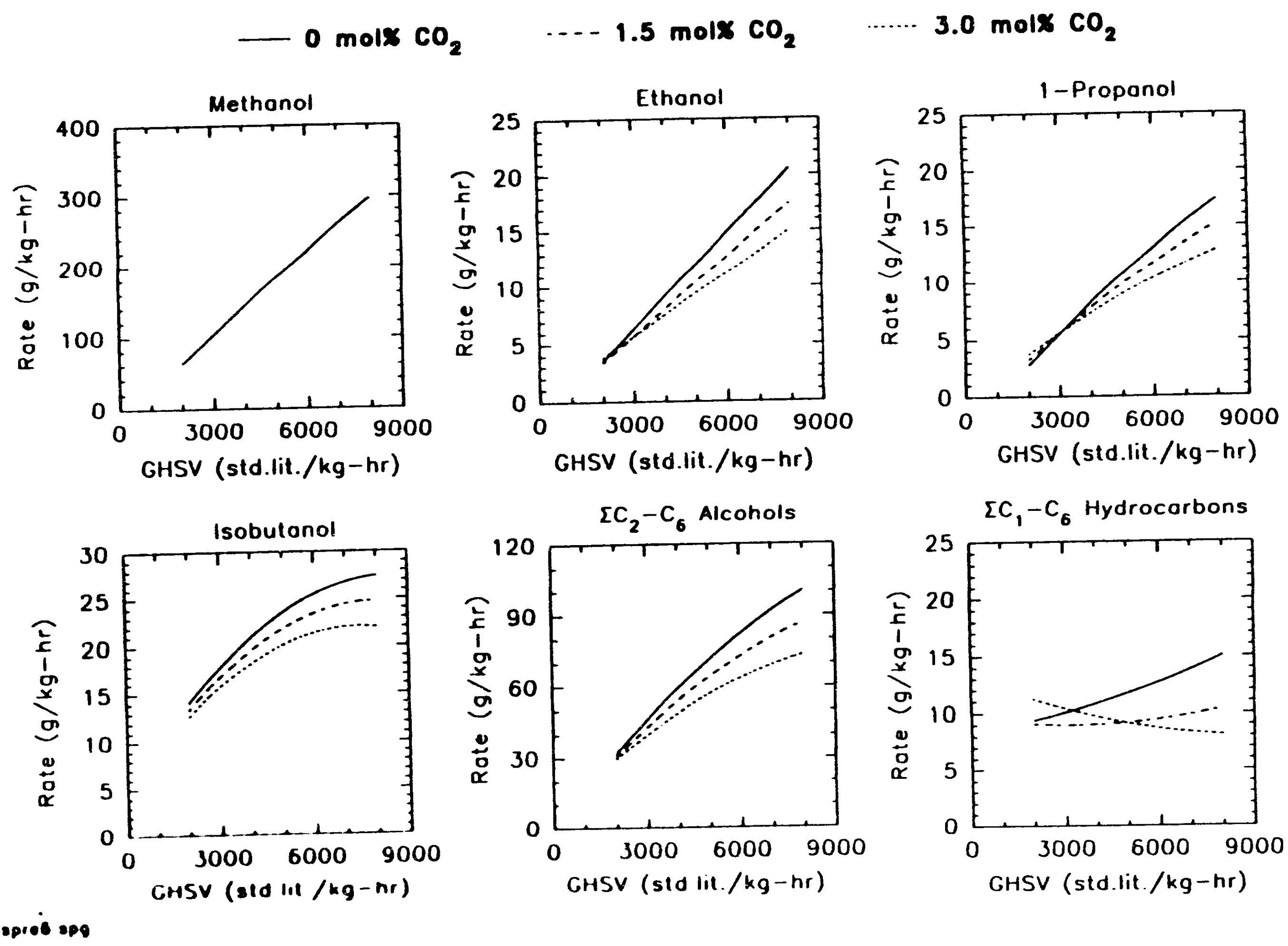
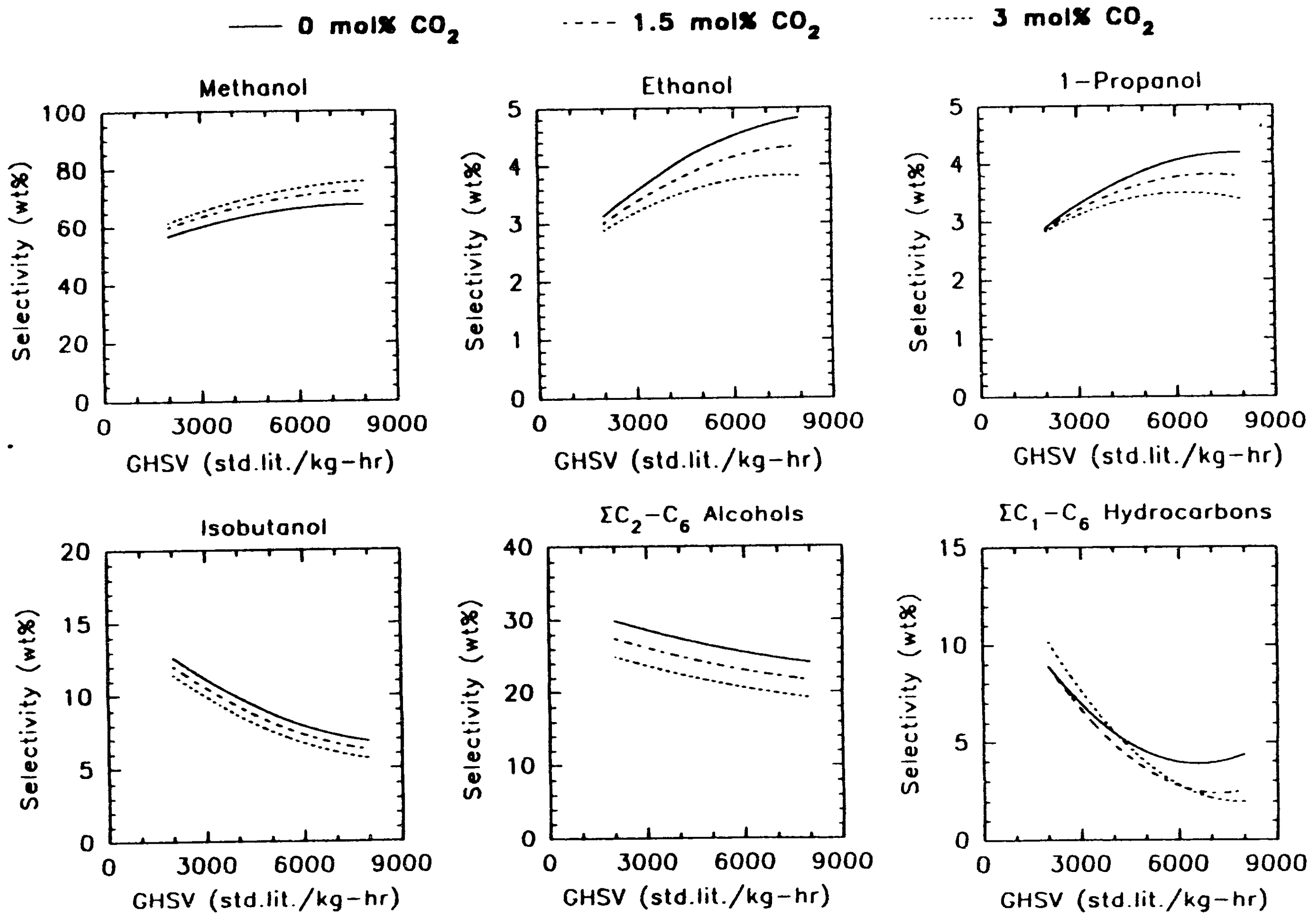


FIGURE 3.1.8

Model Prediction of Product Selectivities vs GHSV at Different Feed CO_2 Concs.

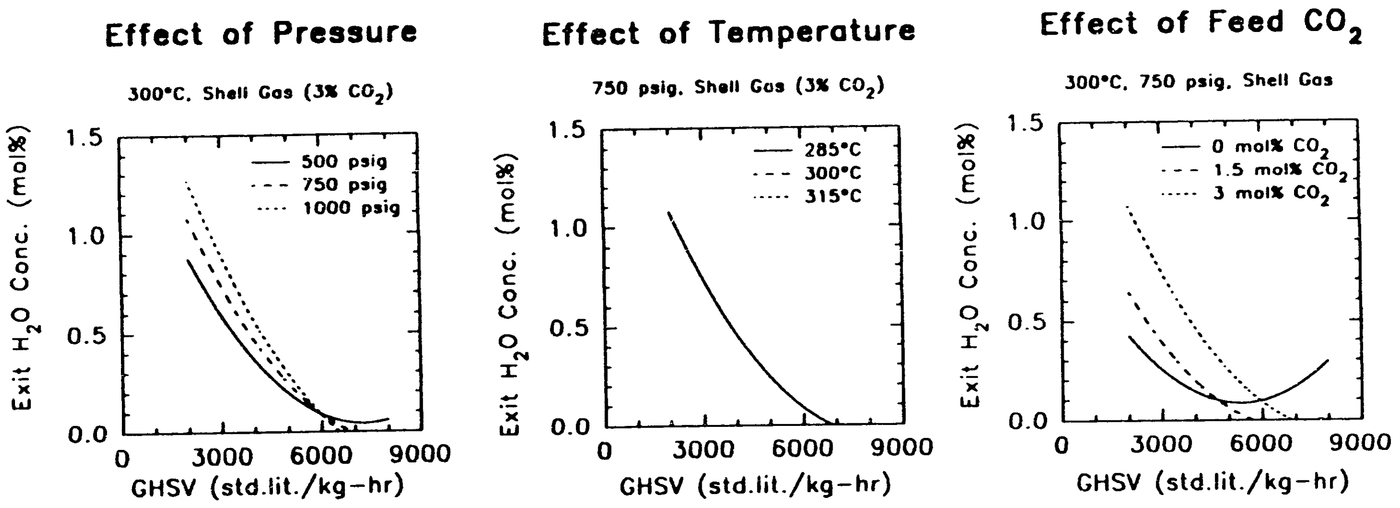
300°C, 750 psig, Shell Gas



pvspre7.spg

FIGURE 3.1.9

Model Prediction of Reactor Exit H_2O Concentration vs GHSV



pvspre8 spg

Optimization:

Within the ranges of process variables explored, certain of the important response variables were optimized. For these optimizations, temperature, pressure, GHSV, and feed CO_2 concentration were constrained to be within the ranges for the Box-Behnken experiments (285-315°C, 500-1000 psig, 2000-8000 std. lit./kg-hr, and 0-3 mol% CO_2). Conditions were determined where each variable (isobutanol rate, isobutanol selectivity, ΣC_2-C_6 alcohols rate, ΣC_2-C_6 alcohols selectivity, and ΣC_1-C_6 alcohols rate) was maximized. Table 3.1.1 shows the results for these determinations.

As shown in Table 3.1.1, isobutanol rate and ΣC_2-C_6 alcohols rate are maximized at the maximum temperature, pressure, and GHSV, and the minimum feed CO_2 content. Selectivity to isobutanol is maximized at maximum temperature and pressure, but minimum GHSV and CO_2 content. Low GHSV favors high selectivity to isobutanol, while high GHSV favors high productivity. Interestingly, the maximum selectivity to ΣC_2-C_6 alcohols occurs at an intermediate temperature and the lowest pressure, GHSV, and CO_2 content. Finally, the ΣC_1-C_6 alcohols rate (total alcohol productivity) is maximized at the lowest temperature (largely because that is where methanol rate is maximized) and feed CO_2 content and the highest GHSV and pressure.

TABLE 3.1.1
Optimum Conditions* for Selected Response Variables

Response Variable	Maximized Result	Optimum Conditions in Range: Temp. (°C)	Press. (psig)	GHSV (std. lit./kg-hr)	Feed CO_2 (mol%)
Isobutanol Rate (g/kg-hr)	45.1	315	1000	8000	0
Isobutanol Selectivity (wt%)	16.6	315	1000	2000	0
ΣC_2-C_6 Alcohols Rate (g/kg-hr)	136.5	315	1000	8000	0
ΣC_2-C_6 Alcohols Sensitivity (wt%)	33.21	310	500	2000	0
ΣC_1-C_6 Alcohols Rate (g/kg-hr)	628.0	285	1000	8000	0

*Allowed ranges of process variables correspond to their ranges in the Box-Behnken experimental design:
Temp. (285-315°C), Press. (500-1000 psig), GHSV (2000-8000 std. lit./kg-hr)
Feed CO_2 (0-3 mol%)

Optimization of the same response variables was done for Shell gas of 3 mol% CO_2 (i.e., Shell gas without CO_2 removal) to obtain more information on the relative importance of CO_2 removal. The results are shown in Table 3.1.2. In agreement with the results obtained when CO_2 content was allowed to vary (see Table 3.1.1), the isobutanol and ΣC_2-C_6 alcohols rates are maximized at the maximum temperature, pressure, and GHSV. Also, the isobutanol selectivity is maximized at the highest temperature and pressure but lowest GHSV, in agreement with the results in Table 3.1.1. Finally, also in agreement with Table 3.1.1, the ΣC_1-C_6 alcohols rate is maximized at the lowest temperature but highest pressure and GHSV. The results in Tables 3.1.1 and 3.1.2 suggest that, to maximize isobutanol rate and selectivity, high temperature and pressure is essential.

TABLE 3.1.2

Optimum Conditions* for Selected Response Variables for Shell Gas with 3 mol% CO_2

Response Variable	Maximized Result	Temp. (°C)	Press. (psig)	GHSV (std. lit./kg-hr)
Isobutanol Rate (g/kg-hr)	39.7	315	1000	8000
Isobutanol Selectivity (wt%)	15.8	315	1000	2000
ΣC_2-C_6 Alcohols Rate (g/kg-hr)	111.7	315	1000	8000
ΣC_2-C_6 Alcohols Sensitivity (wt%)	29.7	315	1000	2000
ΣC_1-C_6 Alcohols Rate (g/kg-hr)	605.7	285	1000	8000

*Allowed ranges of process variables correspond to their ranges in the Box-Behnken design: Temp. (285-315°C), Press. (500-1000 psig), GHSV (2000-8000 std. lit./kg-hr)

At the end of the process variable experiments, the reactor was run at aggressive conditions to obtain high rate and selectivity to isobutanol, using the results of the process variable scans as a guide. It should be noted that these results were obtained on a catalyst sample which had been in use during the process variable experiments for almost 200 hours on stream. The maximum temperature and pressure were set by practical considerations, i.e., the maximum achievable by the unit. The feed gas used was Shell gas with 3 mol% CO_2, that is, no CO_2 removal. The pressure was 1400 psig and the temperature was 315°C; space velocities of 2000 and 8000 std. lit/kg-hr were used. The results obtained are shown in Table 3.1.3. These experiments produced the highest rate of isobutanol synthesis (49.4 g/kg-hr at 8000 GHSV) ever recorded in our labs.

TABLE 3.1.3

Measured Performance of Catalyst at 315°C and 1400 psig

Feed: Shell gas with 3 mol% CO_2

	Rate (g/kg-hr)			Selectivity (wt%)		
GHSV	Methanol	Isobutanol	ΣC_2-C_6 alcohols	Methanol	Isobutanol	ΣC_2-C_6 alcohols
2000	77.5	19.5	37.7	58.1	14.6	28.3
8000	420	49.4	140	70.1	8.2	23.3

Scale-up of Cs-Cu/ZnO/Al_2O_3 for LaPorte Isobutanol Run:

Work continued on scaling up the preparation of Cs-promoted Cu/ZnO/Al_2O_3 for the LaPorte AFDU isobutanol run. In the last quarterly report (October-December 1991), results were presented for some advance samples of Cs-promoted Cu/ZnO/Al_2O_3 received from the catalyst vendor. These samples ranged in Cs loading from 1.1 to 1.4 wt%, loadings in the optimum range as determined in sample preparations done at Air Products. Recall that none of these samples had an acceptable performance level, in terms of productivity for higher alcohols or isobutanol, and there was no clear trend with cesium loading in the data. The vendor prepared these samples using a cesium precursor consisting of cesium hydroxide plus formic acid at pH=7.0, instead of "straight" cesium formate, which was the precursor used in preparations at Air Products and has a different pH. Since the pH of the impregnating solution used in the preparation of the catalyst may have a profound effect on the final catalyst performance, the low performance of these samples may be due to the pH or precursor used.

Additional samples, now prepared using cesium formate as the cesium precursor, were received from the vendor and tested in our microclaves. Results for testing of these samples are presented in Table 3.1.4. Additionally, shown in Table 3.1.5 are results for samples prepared at Air Products.

Before discussing the results presented in Tables 3.1.4 and 3.1.5, some explanation regarding the notation used in the tables is in order. Cesium precursor denotes the cesium compound used to promote the Cu/ZnO/Al_2O_3 substrate. "Formate (1)" denotes Alfa Products cesium formate, which was used in preparation of most of the samples at Air Products. "Formate (2)" is the cesium formate used by the vendor to prepare samples; this cesium formate was chemically the same as that used by Air Products, but from a different supplier. "Hydroxide" denotes cesium hydroxide, which was used to prepare some samples at Air Products. In addition, three different Cu/ZnO/Al_2O_3 substrates are indicated in Tables 3.1.4 and 3.1.5. All three are the same methanol synthesis catalyst, but different production lots. Two cesium deposition methods are also indicated in the tables: incipient wetness impregnation (abbr. "incip. wetness") and a spray deposition technique (abbr. "spray"). In the incipient wetness procedure, an aqueous solution of the cesium precursor was added dropwise to the Cu/ZnO/Al_2O_3 powder substrate with manual stirring until the point of incipient wetness (paste formation) was reached. The spray technique, which is more conducive to scale-up, was the only technique used by the vendor to prepare samples, and was also used at Air Products. This technique involves spraying the cesium precursor solution onto the Cu/ZnO/Al_2O_3 powder substrate which is being mechanically mixed by tumbling in a vessel. A quantity of more concentrated solution equal to approximately ½ of that required in the incipient wetness technique, is employed to ensure that the powder remains free flowing and non-clumping. Finally, two methods of drying were employed. The method designated "impregnator", where drying of the powder was done by heating the same tumbling vessel that was used for the spray deposition technique, was used only by the vendor. For the drying method labeled "oven", the wetted powder, after deposition of the cesium precursor solution, was transferred to dishes and dried in a standard laboratory convection oven. After either method of drying, all samples, whether prepared by the vendor or Air Products, were calcined in a laboratory convection furnace.

TABLE 3.1.4

Performance Results for Cs-Cu/ZnO/Al_2O_3 Samples Prepared by Vendor

Test Conditions: 300°C, 850 psig, 5000 GHSV, Shell Gas, 24 hr on stream

Performance Test Run No.	Cesium Precursor*	Cu/ZnO/Al_2O_3 Substrate **	Precursor Deposition Method	Drying Method	Cesium Loading (wt%)	Production Rate (g/kg-hr)		
						Methanol	Isobutanol	ΣC_2-C_6 Alcohols
12432-48	(none, as- rec'd)	(c)	------	------	0	229	15.7	55.7
12648-50	formate (2)	(c)	spray	impregnator	0.8	219	19.1	61.4
12648-14	formate (2)	(c)	spray	impregnator	1.3	206	15.8	51.2
12432-37	formate (2)	(c)	spray	impregnator	1.5	193	12.6	43.4
12432-50	formate (2)	(c)	spray	oven	1.1	213	7.2	29.5
12432-52	formate (2)	(c)	spray	oven	1.1	221	21.8	66.4

* formate (1) = cesium formate from Alfa Products; formate (2) = formate used by catalyst vendor to prepare samples.

** (a) = Lot# 8518672; (b) = Lot# 5535072; (c) = Lot#? (Cu/ZnO/Al_2O_3 used by vendor to prepare samples).

TABLE 3.1.5

Performance Results for Representative Cs-Cu/ZnO/Al_2O_3 Samples Prepared by Air Products

Test Conditions: 300°C, 850 psig, 5000 GHSV, Shell Gas, 24 hr on stream

Performance Test Run No.	Cesium Precursor*	Cu/ZnO/Al_2O_3 Substrate **	Precursor Deposition Method	Drying Method	Cesium Loading (wt%)	Production Rate (g/kg-hr)		
						Methanol	Isobutanol	ΣC_2-C_6 Alcohols
12071-98	(none, as-rec'd)	(a)	-------	--------	0	215	15.1	52.1
12432-04	formate (1)	(a)	incip. wetness	oven	0.69	207	21.2	66.6
12200-48	formate (1)	(a)	incip. wetness	oven	1.1	211	25.1	70.7
12071-95	formate (1)	(a)	incip. wetness	oven	1.36	199	26.0	70.8
12200-62	formate (1)	(a)	incip. wetness	oven	1.69	214	28.2	72.6
12648-30	formate (2)	(a)	incip. wetness	oven	1.1	209	26.8	74.2
12071-85	formate (1)	(a)	spray	oven	1.1	215	25.5	72.6
12648-19	hydroxide	(a)	incip. wetness	oven	1.25	212	25.0	71.2
12432-43	(none, as-rec'd)	(b)	-------	--------	0	228	12.7	49.2
12432-47	formate (1)	(b)	incip. wetness	oven	1.1	230	17.5	61.0
12648-27	hydroxide	(b)	incip. wetness	oven	1.1	215	17.9	58.6
12648-24	formate (1)	(b)	spray	oven	1.1	225	17.2	58.5
12432-45	hydroxide	(b)	spray	oven	1.1	235	18.5	63.2
12432-54	formate (1)	(c)	spray	oven	0.6	222	20.2	67.2
12648-38	formate (1)	(c)	spray	oven	0.9	209	24.6	72.6
12648-32	formate (1)	(c)	spray	oven	1.1	215	27.5	76.6
12648-41	formate (1)	(c)	spray	oven	1.1	209	26.2	72.5

* formate (1) = cesium formate from Alfa Products; formate (2) = same formate used by catalyst vendor to prepare samples.

** (a) = Lot# 8518672; (b) = Lot# 5535072; (c) = same Cu/ZnO/Al_2O_3 used by vendor to prepare samples.

The Cs-Cu/ZnO/Al_2O_3 samples prepared by the vendor range in Cs loading from 0.8 wt% to 1.5 wt% (see Table 3.1.4). These samples were prepared using the two different drying methods: in an impregnator and in an oven. The first issue worth noting about the performance results in Table 3.1.4 is the large degree of inconsistency in the results, particularly in the isobutanol and ΣC_2-C_6 alcohols rates. For example, the isobutanol rate ranges from 7.2 to 21.8 g/kg-hr for these Cs-Cu/ZnO/Al_2O_3 samples. A second issue is that the performance of all of these samples is significantly below that which was expected based on results of samples prepared at Air Products. Based on results obtained with Air Products-prepared samples, an isobutanol rate of at least 25 g/kg-hr and a ΣC_2-C_6 alcohols rate of at least 70 g/kg-hr at the indicated "standard" reaction conditions are considered to be the performance criteria.

Samples prepared at Air Products were produced using all three lots of Cu/ZnO/Al_2O_3 catalyst substrate and three different cesium precursors. A large portion of the samples shown in Table 3.1.5 were prepared in an attempt to identify why the vendor-prepared samples had low and inconsistent performance. The results in Table 3.1.5 are presented in three groups, each group corresponding to a different Cu/ZnO/Al_2O_3 substrate production lot. The early results obtained at Air Products, which prompted interest in this particular catalyst for isobutanol and mixed alcohols synthesis, were obtained on samples prepared using Cu/ZnO/Al_2O_3 substrate of lot# 8518672, designated (a) in Table 3.1.5. As can be seen, consistent results were obtained, which established the aforementioned performance criteria for this catalyst. In addition, it is noteworthy that a sample prepared using cesium hydroxide precursor (#12648-19) showed similar performance to those prepared using formate. Also, a sample prepared (#12648-30) using the same cesium formate that the vendor used showed high performance consistent with the other lab samples. This result strongly suggests that the cesium precursor (i.e., supplier) is not responsible for the low performance results obtained for the vendor-prepared samples.

Table 3.1.5 also shows results obtained for samples prepared at Air Products using Cu/ZnO/Al_2O_3 substrate from production lot# 5535072. These samples were prepared at 1.1 wt% Cs using the two different cesium deposition techniques with formate or hydroxide as the cesium precursor. As shown in Table 3.1.5, the performance results are consistent, but the level of performance is below that which was expected based on the samples prepared using Cu/ZnO/Al_2O_3 substrate designated (a). These results indicate that the particular lot of Cu/ZnO/Al_2O_3 substrate used has an impact on the final result. One possible reason is that the surface properties, perhaps the surface acidity, of the Cu/ZnO/Al_2O_3 substrate may differ from lot to lot, raising the possibility that the optimum cesium loading may be different depending on the particular lot. Surface acidity can vary with variation of the Al_2O_3 content of the substrate. Indeed, examination of the product distribution for the samples prepared using Cu/ZnO/Al_2O_3 substrate (b) indicates that the cesium loading is too low for these samples.

The results described above for samples prepared using Cu/ZnO/Al_2O_3 substrate (b) indicate that a possible reason why the vendor prepared samples had low performance was because of differences in the Cu/ZnO/Al_2O_3 substrate used. However, the results shown in Table 3.1.5 for samples prepared at Air Products using substrate (c), the same substrate used by the vendor, indicate that the

$Cu/ZnO/Al_2O_3$ substrate is not the culprit. The four samples prepared at Air Products using substrate (c) showed consistently high performance, very much in line with the results for samples prepared at Air Products using substrate (a). Note that the 0.6 wt% Cs sample exhibits slightly lower performance, but has a cesium loading outside the optimum range (considered to be 1-1.5 wt% Cs).

The collective results in Tables 3.1.4 and 3.1.5 do not give a clear indication as to why samples prepared by the vendor gave inconsistent and lower than acceptable performance. At this point it appears that the reason lies in some subtle difference in preparation technique, an issue that can most likely be resolved by direct interaction with the catalyst vendor's technical staff. This will take place early in the next quarter. Thus, scale-up of the preparation of this catalyst was not ready in time to proceed with the scheduled isobutanol AFDU run in April 1992. The isobutanol run will be rescheduled for a later date.

Lower Alcohols Recycle on Cs-Promoted $Cu/ZnO/Al_2O_3$ *Catalyst:*

Recycle of C_1-C_3 product alcohols during isobutanol synthesis on Cs-promoted $Cu/ZnO/Al_2O_3$ was experimentally investigated by injecting alcohols into the autoclave reactor syngas feed. The addition of methanol alone, a mixture of methanol, ethanol and 1-propanol, and a mixture of ethanol and 1-propanol was done and the product rates were compared to the case of syngas only feed. All experiments were done using Shell syngas at 300°C, 850 psig, and 5000 GHSV.

The 300 cc #1 autoclave reactor system was used for this investigation. Since this system is not equipped with downstream separation equipment or recycle equipment, recycle of alcohols was simulated by addition of alcohols to the feed syngas. Alcohol addition was done by feeding pure liquid alcohol, or a mixture of alcohols, by a high pressure syringe pump to a heated feed vaporizer. In the feed vaporizer the liquid alcohol stream was vaporized into the feed syngas stream. Some attempts were made to simulate total recycle of particular alcohol products. Determination of the pump rate and composition of the liquid stream is obviously an iterative process, since, for the total recycle situation, the rate of addition must equal the rate of production of that alcohol or alcohols at the reactor exit. The match is fairly close for some of the experiments reported here.

The catalyst used was 1.25 wt% Cs on $Cu/ZnO/Al_2O_3$ prepared by the incipient wetness technique. The sample was reduced in situ using dilute syngas in N_2. The reaction conditions used were: Shell syngas feed, 300°C, 850 psig, and a GHSV (based on syngas) of 5000 std. lit/kg-hr. The reactor was run at the above conditions throughout the experiments. Periodically, the product rates were determined for the case of no alcohol addition to gather information on catalyst stability and also to provide a basis for comparison for runs involving alcohol addition.

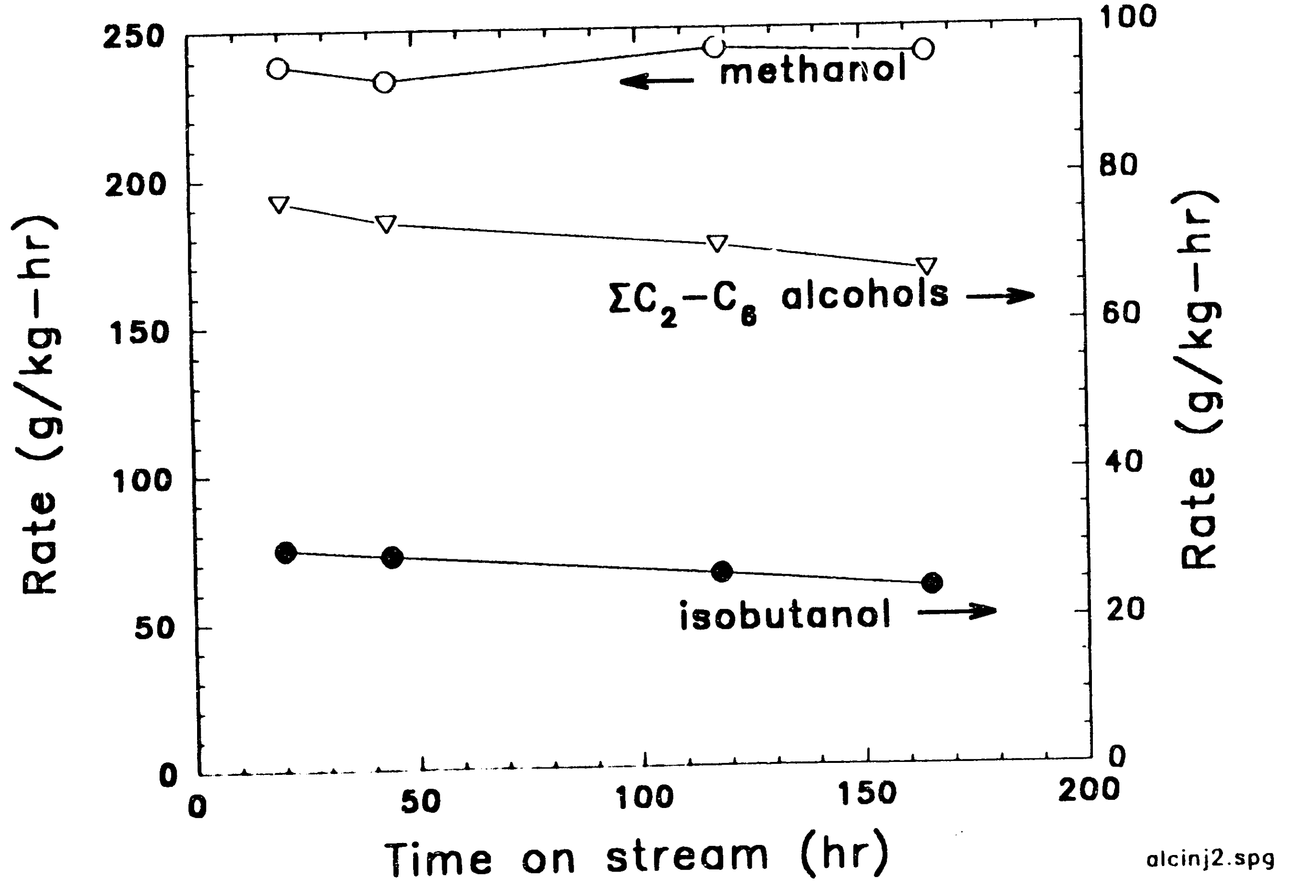
Figure 3.1.10 shows the major product rates as a function of on-stream time for the periodic runs for no alcohol addition. The catalyst deactivated at a slightly higher rate than that observed for samples run in the microclave reactors. A couple of possible reasons are that alcohol addition may increase the deactivation rate or that the new vaporizer used was not fully passivated for carbonyl production

FIGURE 3.1.10

Product Alcohols Rates vs Time on Stream

1.25 wt% Cs/S3-86 (Cat. #12432-35)

Shell Gas, 300°C, 850 psig, 5000 GHSV



during the runs. In a previous attempt at an experiment, the catalyst sample deactivated extremely rapidly upon heat-up of the feed vaporizer, indicating that it was not passivated. After this previous run, an attempt was made to passivate the vaporizer by heating in flowing syngas for several hours. Whether the vaporizer was sufficiently passivated is not known at this time. In any case, the deactivation rate was low enough to render the results useful.

The other point to make regarding Figure 3.1.10 is that the alcohols rates observed are higher than those observed in the microclave reactors. For example, after 20 hours on stream, the isobutanol rate observed in this study was 30 g/kg-hr, compared to 26 g/kg-hr measure in the microclave. This is probably a result of the mixing or gas-liquid contacting deficiency which is characteristic of the microclaves, a deficiency observed in the past.

Methanol addition to the feed was investigated. The results for this experiment, along with a run done without methanol addition (for comparison), are shown in Table 3.1.6. The rate of methanol addition for this experiment was less than that corresponding to total methanol recycle, actually corresponding to the production rate without methanol addition. As can be seen, the addition of methanol substantially increased the rate of production of ethanol and 1-propanol, while resulting in only a modest increase in isobutanol rate. The ethanol plus 1-propanol rate increased by 38% upon methanol addition, but the isobutanol rate increased by only 10%. The rate of production of all C_2-C_6 alcohols increased by 22% upon methanol addition.

TABLE 3.1.6
Addition of Methanol to Feed
Reaction Conditions: Shell gas, 300°C, 850 psig, 5000 GHSV

	Time on Stream (hr)	Rate (g/kg-hr)				
		MeOH	EtOH	1-PrOH	i-BuOH	ΣC_2-C_6 alcohols
No alcohol addition	44	233	12.6	14.2	28.9	74
Alcohol addition	47	324	17.7	19.2	31.7	90
(Alcohol addition rate)		233	0	0	--	0

If the synthesis of higher alcohols occurs by a sequential homologation mechanism, as the literature suggests, then the fact that methanol addition has the largest impact on the ethanol rate is quite reasonable. Perhaps greater incorporation of methanol into products higher than ethanol would occur at lower GHSV (higher reactor residence time).

Table 3.1.7 shows results for the addition of a mixture of methanol, ethanol, and 1-propanol; an attempt to simulate total recycle of these three products. A fairly good match between the methanol, ethanol, and 1-propanol production rates and the rates of addition of these products was obtained, indicating a situation quite close to total recycle of these products. Addition of the mixture of these alcohols results in a much larger increase in isobutanol rate than that for methanol addition alone. The isobutanol rate increases by 60% upon addition of this alcohol mixture to the feed. The C_{4+}

liquid product obtained in this simulated total recycle of C_1-C_3 alcohols would contain an estimated 56 wt% isobutanol, with the balance of the liquid products being esters and C_{5+} alcohols.

TABLE 3.1.7
Addition of Mixture of Methanol, Ethanol, and 1-Propanol to Feed

Reaction Conditions: Shell gas, 300°C, 850 psig, 5000 GHSV

	Time on Stream (hr)	Rate (g/kg-hr)				
		MeOH	EtOH	1-PrOH	i-BuOH	ΣC_2-C_6 alcohols
No alcohol addition	118	243	12.4	13.7	26.1	70
Alcohol addition	122	359	25.8	33.2	41.7	122
(Alcohol addition rate)		332	27.3	30.5	--	57.8

The addition of a mixture of ethanol and 1-propanol, to simulate recycle of these products without methanol, was also investigated. The results of this experiment are shown in Table 3.1.8. For this experiment also, the rates of addition of ethanol and 1-propanol are quite close to the rates of production, indicating that this condition closely simulates total recycle of these products. The isobutanol rate increased from 24.1, for syngas alone, to 34.1 upon addition of ethanol and 1-propanol, a 41% increase in rate. This is significantly lower than the 60% increase observed for the case of addition of methanol, ethanol, and 1-propanol (see Table 3.1.7). The reason why the isobutanol rate is higher for the case when methanol is also recycled is probably primarily that methanol recycle increases the ethanol and 1-propanol available for recycle. Recall that the results in Table 3.1.6, for the recycle of methanol alone, indicate that methanol addition substantially increases the ethanol and 1-propanol rates.

TABLE 3.1.8
Addition of Mixture of Ethanol and 1-Propanol to Feed

Reaction Conditions: Shell gas, 300°C, 850 psig, 5000 GHSV

	Time on Stream (hr)	Rate (g/kg-hr)				
		MeOH	EtOH	1-PrOH	i-BuOH	ΣC_2-C_6 alcohols
No alcohol addition	165	241	12.4	13.4	24.1	66
Alcohol addition	169	239	17.0	22.7	34.1	92
(Alcohol addition rate)		0	18.6	20.6	--	39.2

The results in the last column of Table 3.1.8 indicate that all of the added ethanol and 1-propanol was not incorporated into only C_2-C_6 alcohols. Specifically, the sum of the alcohol addition rate plus the rate of production of C_2-C_6 alcohols for syngas feed is larger than the production rate of C_2-C_6 alcohols during alcohol addition. A small portion of the added alcohols is incorporated into other products: alcohols greater than C_6 and hydrocarbons. The results in Table 3.1.8 indicate that recycle of ethanol and 1-propanol is a technically viable means of increasing isobutanol productivity.

Literature Search on the Dehydration of 2-Methyl-1-Alkanols:

We completed the literature search on the dehydration of 2-methyl-1-alkanols, in particular isobutanol, to their corresponding olefins. A report was issued on 24 March and it is attached as Appendix 3.

From the literature search, several catalysts were identified for lab screening evaluations. These catalysts include gamma aluminas, calcium phosphate (hydroxyapatite) and zirconium sulfate. Alumina is the most widely used dehydration catalyst that has been implemented into at least two pilot plant evaluations for the dehydration of isoamyl alcohol.

The bulk of the work in the literature has been carried out in packed-bed reactors under reaction conditions of 300-400°C and atmospheric pressure. A limited amount of literature describes a process for the dehydration of tert-butyl alcohol using a slurry reactor.

Liquid Phase Water-Gas Shift Lab Experiments:

In support of the AFDU demonstration of the liquid phase shift process, two experiments were performed in the lab using a 300 cc stirred autoclave. The first experiment (Run #11782-58) used ground-up (-200 mesh) BASF K3-110 low temperature shift catalyst and the second experiment used the "LaPorte catalyst". The second experiment (Run #11782-63) was actually a "quality control" test of the LaPorte catalyst batch, a powder K3-110 catalyst.

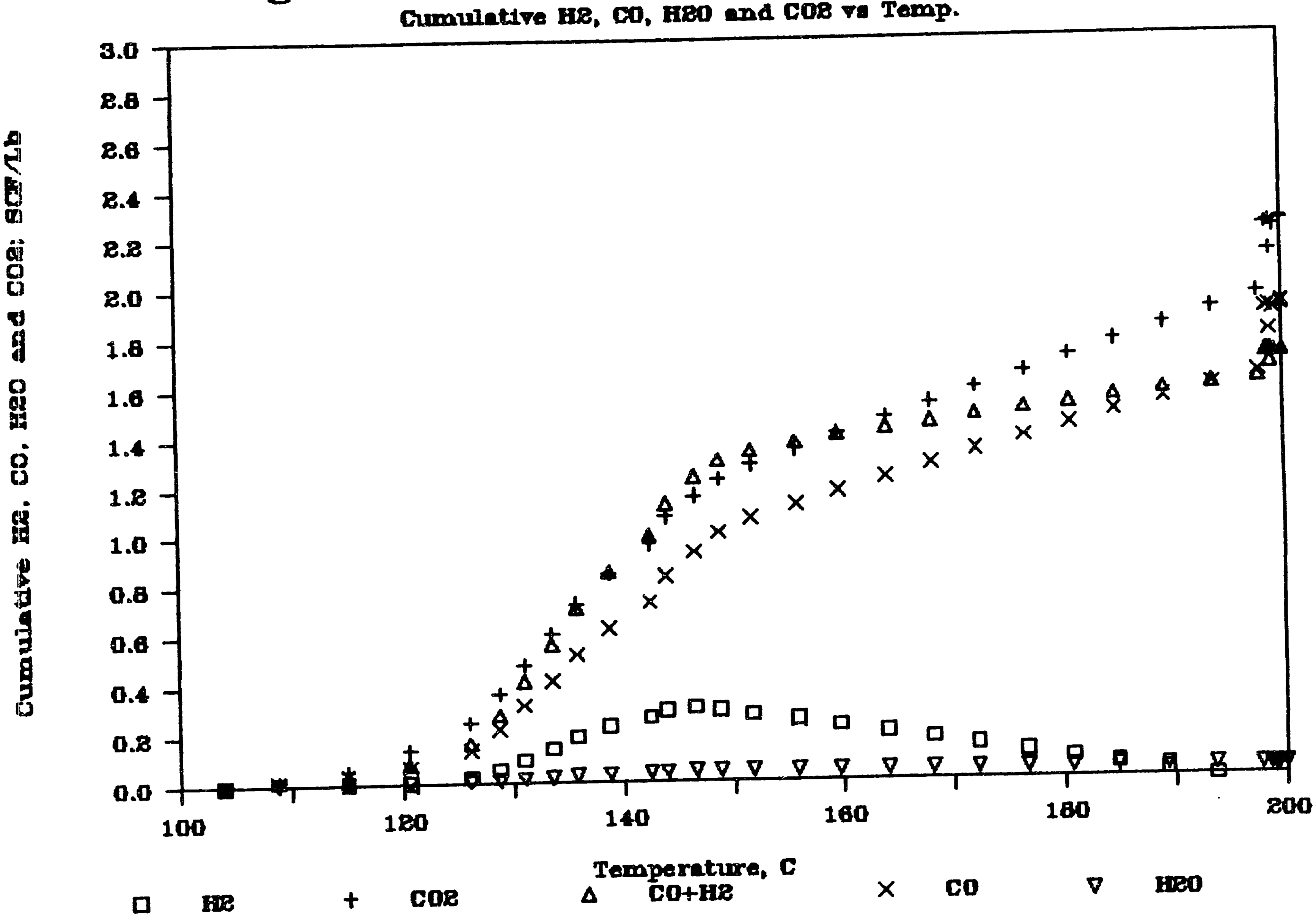
Dilute syngas was used to activate the catalyst in both experiments. The activation procedure was identical to that for a methanol catalyst as described in the finial report of a prior DOE contract, Contract # DE-AC22-87PC90005. Figure 3.1.11 shows typical cumulative changes of H_2, CO, H_2O, and CO_2 over the period of the catalyst activation. The total consumption of H_2 and CO was around 1.6 scf/lb-catalyst. It should be pointed out that the water numbers are not quantitative because the analytical equipment (GC) was not calibrated for accurate water analysis.

The activity of these catalysts are comparable. Both catalysts were first tested for their methanol activity using Texaco gas. The powder catalyst (Run #11782-63) seemed to have slightly higher activity and produce more by-products. After the initial methanol synthesis, steam was introduced to continue the water-gas shift reaction.

Several water-gas shift conditions were tested on the ground-up catalyst in Run #11782-58. Run #11782-58B through #11782-58I include results using both Texaco gas and Shell gas as the feed. Detailed results and material balances are shown in Appendix 4.

Only one water-gas shift experiment was conducted on the powder K3-110 catalyst. Run 11782-63C summarizes the result using Texaco gas as the feed. The test suggested that the powder K3-110 has similar activity to its ground-up counterpart, and the data obtained from both catalysts can be used to predict the performance for the AFDU.

Figure 3.1.11: Run # 11782-58RED



Task 3.2 New Fuels From Dimethyl Ether (DME)

Overall 2QFY'92 Objectives

The following set of objectives appeared in Quarterly Technical Progress Report No. 5.

- Continue modifying the mass balance (C and H_2) for the DME to isobutanol scheme.
- Define a series of catalyst compositions of one of the screened catalysts for a reactor parameter determination in the BTRS.
- Develop an octane number database for establishing a structure vs. octane number correlation.

Laboratory Reactor Procurement

- An existing Varian 6000 GC was modified to act as a pulse/adsorption reactor to study the reaction of dimethyl ether, oxygen, and methanol with basic catalysts.
- A Management of Change was issued to change the original PHR for the dual atmospheric screening reactors to include the dehydration of isobutanol to butenes.

Chemistry and Catalyst Development

During this quarter, research activity has been split between 1) the conversion of dimethyl ether and oxygen to isobutanol, and 2) dehydration of isobutanol to isobutylene.

Catalyst Screening for Isobutanol

A series of lanthanide group oxides were screened for the conversion of DME and methanol to isobutanol. Pr_6O_{11}, Nd_2O_3, and Eu_2O_3 were active, while Sm_2O_3 was not. The chemistry is outlined in eqn. 1 or 1'.

$$CH_3OCH_3 + 2CH_3OH \rightarrow (CH_3)_2CHCH_2OH + 2H_2O \qquad (1) \text{ or}$$

$$2CH_3OCH_3 \rightarrow (CH_3)_2CHCH_2OH + H_2O \qquad (1')$$

Atmospheric pressure gas phase reaction experiments were conducted at 300° to 450°C with 2 or 20 grams of catalyst. The dimethyl ether to oxygen ratio was varied between 5:1 and 50:1. Total flow rate was varied between 5 and 100 sccm. Contact times were on the order of 1 – 30 seconds. Pr_6O_{11} powder was pressed and sieved to 1 mm sized particles.

Reaction studies at 300 psig were performed at 300° to 450°C with 10 grams of catalyst. The oxygen was supplied from a 10% oxygen/nitrogen cylinder. Contact times were on the order of 1 – 20 seconds.

TABLE 3.2.1
Conversion of Dimethyl Ether and Oxygen over Basic Catalysts

Catalyst	Press atm	Contact Time	DME Conv.	Weight % Selectivity					
				i-BuOH	DMET	CH_3OH	CO	CO_2	CH_4
2 g Pr_6O_{11}	1	1	8	0.3	0.0	30	22	28	1
20 g Pr_6O_{11}	1	26	8	0.2	0.0	30	23	25	1
	1	5	8	0.4	0.1	34	21	25	2
10 g Pr_6O_{11}	20	13	14	0.6	2.6	24	26	23	16
10 g 5% Li/MgO	20	26	11	2.6	2.3	24	24	28	14
	20	4	11	0.4	3.4	38	18	25	9
10 g 3% Sn/MgO	20	26	12	0.6	2.5	14	23	36	18

Temperature 400°C
Feed Composition: 1 atm: 8% O_2, 92% DME
20 atm: 5% O_2, 50% DME, 45% N_2

Under these conditions both DME and O_2 were required for the formation of isobutanol. Addition of methanol slightly increased the formation of isobutanol. The coupling product of two DME molecules, 1,2-dimethoxyethane, is dependent upon concentration. This product has been observed at pressures as low as 1.5 atmospheres.

Experiments with an empty reactor tube indicated that 100% of the CO_2 and 50% of the CO formation was due to thermal oxidation of the DME, either in the gas phase or on the hot walls of the reactor. Passing a solution of 1% isobutanol/methanol through an empty reactor resulted in combustion on 75% of the isobutanol. The apparent independence of catalyst loading and flow rate on the isobutanol yield indicate that oxidation of DME on the walls or in the gas phase of the reactor is responsible for most of the conversion in the screening studies. Attempts to minimize these effects through reactor configuration have been unsuccessful to date.

Concentration of the reactor effluent revealed traces of acetaldehyde, ethanol, 1-propanol and 1,2-dimethoxyethane. The existence of trace amounts of acetaldehyde, ethanol, and propanol suggest that these are intermediates in the formation of isobutanol. A sequential reaction scheme utilizing aldol condensation/dehydration reactions as demonstrated in the literature could be formulated (Appl. Cat, 77 (1991), 123, and Wang and Lee, J. Chem. Soc., Chem. Comm, (1991), 1760).

$$\mathrm{CH_3CH_2OH} \xrightarrow{-\mathrm{H_2}} \mathrm{CH_3CHO} \xrightarrow{\mathrm{HCHO}} \mathrm{CH_2{=}CHCHO} \xrightarrow{\mathrm{H_2}} \mathrm{CH_3CH_2CHO} \xrightarrow{\mathrm{HCHO}}$$

$$\mathrm{CH_2{=}C(CH_3)CHO} \xrightarrow{\mathrm{H_2}} \mathrm{(CH_3)_2CHCHO} \xrightarrow{\mathrm{H_2}} \mathrm{(CH_3)_2CHCH_2OH}$$

Ethanol was added to the feed so that the concentration was about 1%. Ninety percent of the ethanol was converted at 7 second contact time; the amount of isobutanol in the product increased from 0.3% to 0.5% and the propanol content was measurable. At 2 second contact time 50% of the ethanol was converted and the isobutanol content was still 0.5%, but the amount of propanol increased to 0.5%. Most of the ethanol was converted to propanol and isobutanol, supporting the reaction scheme above. Increasing the concentration of ethanol in the feed to 5% resulted in the formation of many products which were assumed to be the result of cross-condensation reactions occurring over the basic catalyst support.

Addition of acetaldehyde to the feed produced an identical response as ethanol addition. The acetaldehyde in the exit stream (estimated at 0.2% of the product) was the same whether the amount in the feed was 0%, 1% or 5%. Ethanol, propanol and isobutanol yields increased with the addition of acetaldehyde to the feed. Trace amounts of isobutyraldehyde and propionaldehyde were also observed.

Addition of methanol to the feed also effected an increase in the amount of isobutanol formed. The isobutanol yield is a maximum when the methanol in the hydrocarbon feed is between 10 and 40%. The addition of methanol provided a source for the formaldehyde.

TABLE 3.2.2
Effect of Methanol Cofeed on the Conversion of Dimethyl Ether and Oxygen

MeOH: DME	DME Conv.	MeOH Conv.	Weight % Selectivity				
			i-BuOH	CH_3OH	CO	CO_2	CH_4
0:1	7.7	—	0.28	30	23	28	1.0
1:8	7.9	0.0	0.45	22	27	29	0.9
1:5	7.5	0.0	0.54	14	29	30	0.8
2:3	6.4	5.4	0.45	—	33	28	0.8
1:1	7.9	7.5	0.38	—	25	32	0.9

Temperature:	400°C, 1 atmosphere
Feed Composition:	8% O_2, 92% DME, 18 sccm
2 g Pr_6O_{11}:	Contact time ~1 second

The overall conversion of DME was directly related to the amount of O_2 in the feed. The yield of isobutanol was a maximum when the feed contained between 8 and 12% O_2. Dimethoxyethane formation decreased to zero when the O_2 content was above 12%. The formation of methanol decreased with increase in O_2 content, while the H_2O formation increased.

TABLE 3.2.3
Effect of Oxygen Concentration on the Conversion of Dimethyl Ether over Basic Catalysts

Oxygen mol %	DME Conv.	Weight % Selectivity				
		i-BuOH	CH_3OH	CO	CO_2	CH_4
2	2.5	0.24	34	24	28	3.0
4	4.3	0.29	33	23	29	1.9
8	7.7	0.28	30	23	28	1.0
16	14.5	0.14	24	26	25	0.4

Temperature: 400°C, 1 atmosphere
Feed Composition: O_2 varied, DME balance, 18 sccm
2 g Pr_6O_{11}: Contact time ~1 second

a. Aldol Condensation/Dehydration Reactions to Isobutanol

The cesium-promoted catalyst to be used in the LaPorte pilot plant for the higher alcohols campaign was used in the gas-phase atmospheric pressure reactor to screen aldol condensation/dehydration conditions and products. Two grams of the catalyst were reduced in a 2% H_2/He stream using standard conditions. Reactions were carried out with a 5 wt% ethanol in methanol feed diluted to 10 and 50% in N_2. Total flow rates were either 20 or 100 ccm.

Because of the low pressure, methanol conversion was complete at 300°C. At 250°C the methanol conversion ranged between 60 and 90% depending upon the flow rate. The total ethanol conversion was 100% at 300°C and 90% at 250°C; however, the conversion to products positively identified as the result of the above reaction scheme was much less: 15% at 300°C and 40% at 250°C.

The major hydrocarbon product at all conditions was isobutyl alcohol; however, significant amounts of isobutyraldehyde, propanol, and methyl acetate were also detected. Other unidentified products were also detected. The unidentified products had GC retention times around the isobutyl alcohol peak and were assumed to be the result of aldol condensation of the C_2 and C_3 aldehydes. Although analyses of the above results are complicated due to the activity of the catalyst, these experiments provide a basis for comparison with other potential catalysts.

Praseodymium oxide, which was shown to be active for the conversion of DME to isobutyl alcohol, was tested under similar conditions of ethanol in methanol. The conversion of ethanol to isobutyl alcohol and related alcohols and aldehydes was approximately 1% in the absence of O_2. When 5% O_2 was added to the reactor feed, the conversion of ethanol was 40%, with about 30% selectivity to oxidative addition products. In the absence of O_2 co-feed, reoxidized catalyst produced a similar amount of oxidative addition products showing that adsorbed or lattice O_2 may participate in the reaction.

b. Eu_2O_3 Catalyst

With Eu_2O_3 at 400°C, 8.2% of DME reacted with 1.1% DME going to isobutanol, 62% to CO, 35% to CO_2 and balance methane. Carbon accountability was 90%. Hydrogen accountability was 74%.

Catalyst Screening for Dehydration of Isobutanol

Some of the preliminary findings on dehydration are summarized in Table 3.2.4. Gas phase conditions (flow and cat. amt.) have been adjusted to give ~1 second contact time in order to compare with the slurry phase reactor at Iron Run. Al_2O_3 and $Ca_3(PO_4)_2$ are reasonable catalysts. To date, the GC capillary column does not separate isobutylene from 1-butene. The molar mass balances from experiment to experiment are very good with respect to C, H, and O. At this time it appears that controlling Bronsted acidity will minimize skeletal rearrangement to linear olefins. The data in the table reflects screening and does not address lifetime performance.

TABLE 3.2.4
Gas Phase Isobutanol Dehydration

								Molar Mass Balance	
						% Selectivity		ΣC_4 i-BuOH at 0% Conv.	ΣC_4= H_2O
ntry	Cat.	Temp. (°C)	Contact Time (sec)	% Conv. i-BuOH	i-C_4=+ 1-C_4=	t-2-C_4=	c-2-C_4=		
1	Al_2O_3	250	13.7	99.2	97.5	0.5	2.0	0.94	1.0
2	Al_2O_3	300	13.1	100	95.5	1.9	2.5	0.81	0.88
3	$CaHPO_4$	300	13.1	100	80.7	9.1	10.2	0.95	0.97
4	$CaHPO_4$	290	13.3	96.5	85.1	5.7	9.2	0.97	0.99
5	$CaHPO_4$	250	13.7	19.3	86.5	4.8	8.7	0.90	0.80
6	ZrO_2	300	13.1	100	73.3	16.3	10.4	0.93	0.85
7	WO_3	250	13.7	100	66.2	20.2	12.9	0.83	0.86
	5 ml cat.; 10.4 cc/min N_2 @ 298K; 1.54 cc/min. i-BuOH @ 298K								
8	$CaHPO_4$	325	6.2	100	81.5	8.7	9.8	0.94	0.93
9	$CaHPO_4$	300	6.5	78.9	85.7	5.7	8.6	0.91	1.0
	5 ml cat.; 20.8 cc/min N_2 @ 298K; 3.26 cc/min i-BuOH @ 298K								
10	$CaHPO_4$	325	1.2	79.5	85.9	5.1	9.0	0.98	0.94
11	$CaHPO_4$	300	1.3	31.3	86.7	3.3	10.0	0.97	1.0
12	$Ca(H_2PO_4)_2$	325	1.2	92.1	80.4	9.4	10.2	1.0	0.99
13	$Ca(H_2PO_4)_2$	250	1.4	9.4	86.1	5.0	8.9	0.90	0.71
14	$Ca_3(PO_4)_2$	325	1.2	90.9	86.5	5.2	8.3	0.83	0.90
15	$Ca_3(PO_4)_2$	300	1.3	37.3	87.5	3.8	8.7	0.78	0.94
16	$Ca_2P_2O_4$	325	1.2	20.6	86.7	4.4	8.9	1.0	1.0
17	$Ca_2P_2O_4$	250	1.4	0	--	--	--	1.0	--
18	$Zn_2P_2O_7$	325	1.2	100	73.2	14.9	11.9	0.98	0.98
19	$Zn_2P_2O_7$	300	1.3	98.7	75.4	12.9	11.7	1.0	1.0
20	$Mg_2P_2O_7$	300	1.3	10.7	--	--	--	0.89	--
21	$Mg_2P_2O_7$	250	1.4	7.8	--	--	--	0.95	--
22	K_2HPO_4	300	1.3	20.3	--	--	--	0.84	--
23	K_2HPO_4	250	1.4	0	--	--	--	0.94	--
	1 ml cat., 20.8 cc/min N_2 @ 298K; 3.26 cc/min i-BuOH @ 298K								

3QFY92 Objectives

Future plans for Task 3.2 will focus on the following areas:

- Continue to examine the lanthanide series of oxides Pr_6O_{11} and Eu_2O_3, in order to increase yield to isobutanol.
- Examine different reactor configuration to decrease the gas phase oxidation of DME and isobutanol to CO, CO_2.
- Determine the effect of calcination on Bronsted acidity of the phosphate catalyst for dehydration.
- Screen sulfate catalysts for isobutanol dehydration.

Task 3.3: Catalyst Poisons Studies

No activity in this period.

Task 4: Program Support

No activity to report. A comprehensive study of DME, isobutanol and MTBE economics is currently underway. A report in the June quarterly is expected.

Task 5: Program Management

Task 5.1 Planning and Reports

Monthly reports for January and February 1992 were prepared and issued to DOE. A draft Quarterly Report for October – December 1991 was also submitted. The Milestone Schedule Status Report and Milestone Log have been updated and are attached. In addition, monthly Cost Summaries continue to be issued to DOE.

During March, a meeting was held in Pittsburgh with DOE and a number of private organizations to organize the run plan for a July Fischer-Tropsch demonstration at LaPorte. The private partners include Exxon, UOP, Statoil, and Shell Oil. Criteria of run success, catalyst requirements, and analytical needs were addressed, as was the challenge of catalyst-wax separation. A run plan was approved, subject to Shell's input as they could not attend this particular meeting. Details of the meeting and the decisions made can be found in a report by Dr. B. L. Bhatt (see Appendix 5).

Task 5.2 Management Activities

DOE PETC has accepted a proposal to demonstrate Liquid Phase Shift (LPS) chemistry at LaPorte as an alternative to isobutanol. There are two principal reasons for carrying out this run. First, following the extensive modifications at the site, operation on a relatively "benign" system is needed before we start on Fischer-Tropsch technology in July. Second, use of shift catalyst in a slurry reactor will enable DOE's program on coal-based Fischer-Tropsch to encompass commercially available cobalt catalysts—up to now they have been limited to iron-based catalysts which have varying degrees of shift activity. DOE is also supportive of continued fuel testing of LaPorte methanol—tests of M100 at Detroit Diesel have been going particularly well—and are favorably disposed to a run where methanol can be made to supplement the dwindling pool. LPS offers the opportunity to produce methanol as the catalyst, in the absence of steam, is active for methanol synthesis.

The proposed contract between M. W. Kellogg and Air Products to assist in the design of a PETC generic unit is still under negotiation. Nevertheless, technical assistance was provided at meetings in Pittsburgh and Houston. DOE has decided to go with 6" diameter reactors for more authentic hydrodynamic studies providing the funding for gas supplies is available. A fallback to 2" (or 4") reactors is also recommended which will, at a minimum, provide information on catalyst activity.

Methanol from LaPorte was used in a 100 hour engine test at Detroit Diesel Corporation (DDC). The goal was to assess what compositional changes, if any, would need to be made in the crude methanol product anticipated in the CCT III CoolWater project, for it to be used in M100 applications. A particular concern was the water content (~0.5 wt% on average in CoolWater product) as the preferred specification (based on chemical grade methanol) in 0.3 wt% maximum. The LaPorte material passed the test, in DDC's new 6V-92TA 276 hp methanol engine, with flying colors. An understanding of why, and the potential for running with even higher water levels, is being developed with DDC.

OPEN ITEMS:

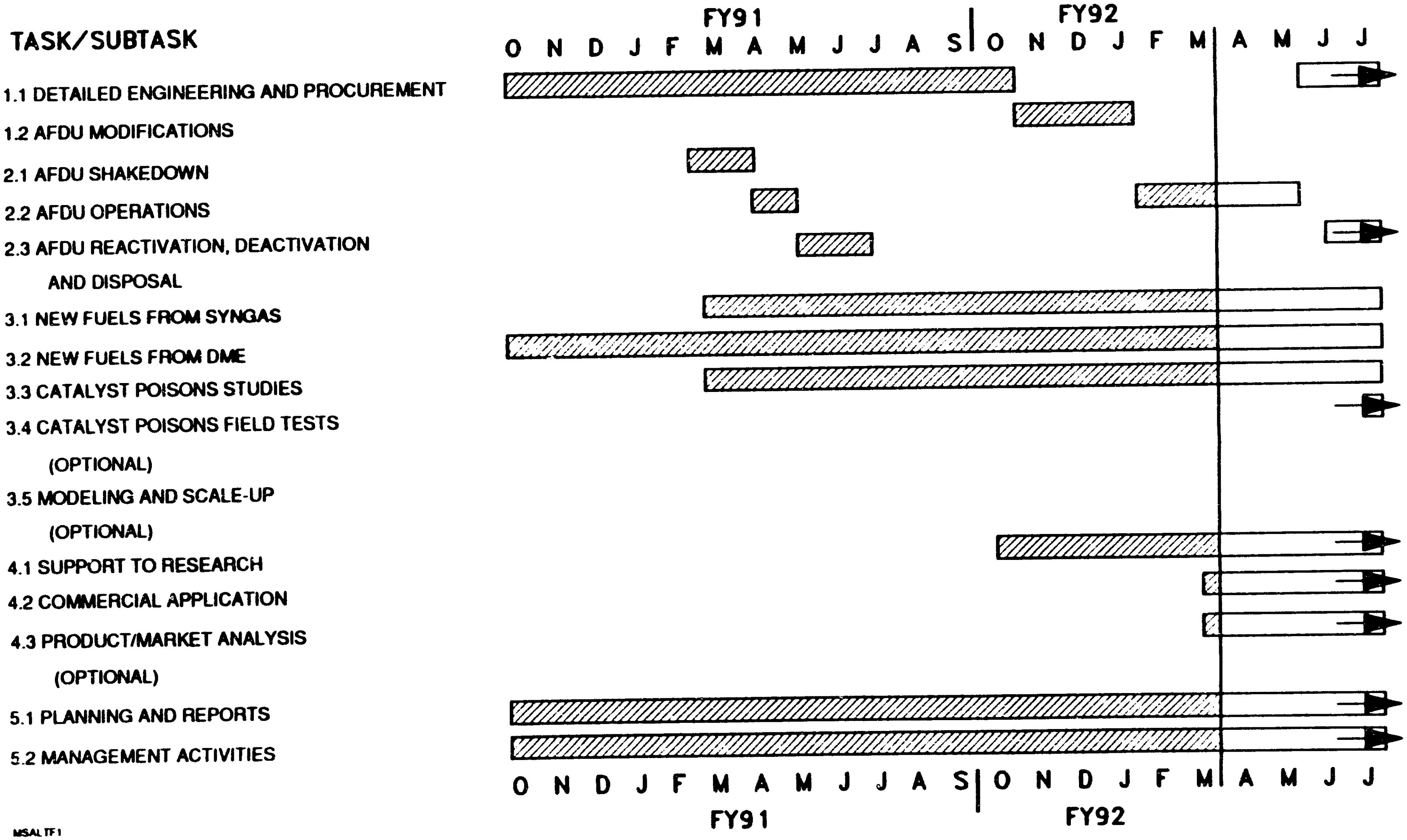
None

ATTACHMENTS:

Milestone Schedule Status Report
Milestone Log

Appendix 1: Design Hazards Review Report; March 1992 IBOH Run
Appendix 2: Design Hazards Review Report; April 1992 Liquid Phase Shift (LPS) Run
Appendix 3: Literature Search on Dehydration of Isobutanol to Isobutylene
Appendix 4: Material Balance Sheets for A. Run #11782-58 (Ground-up K3-110) and B. Run #11782-63 (Powder K3-110, LaPorte Batch)
Appendix 5: Meeting Notes from Partners' Meeting in Pittsburgh, March 19 - 20, 1992.

Milestone Schedule Status Report
(In lieu of DOE Form F1332.3)
Development of Alternative Fuels from Coal-Derived Syngas
DE-AC22-91PC90018
Reporting Period: January – March 1992



MSAL TF1
AGB (5/20/92)

MILESTONE LOG

Report Date: 31 January 1992

Contract No. DE-AC22-91PC90018

Ident. No.	Description	Planned Completion Date	Actual Completion Date	Comments
1.1	Detailed Engineering and Procurement	Apr 92		
1.2	AFDU Modification	Oct 92		
2.1	AFDU Shakedown	Apr 91		Completed for DME Operation
2.2	AFDU Operations	Jul 93		
2.3	AFDU Reactivation, Deactivation, and Disposal	Sep 93		Started 5/91
3.1	New Fuels from Syngas	Oct 92		Started 3/91
3.2	New Fuels from DME	May 93		On Schedule
3.3	Catalyst Poisons Studies	Oct 92		Started 4/91
3.4	Catalyst Poisons Field Tests (Optional)	Jan 93		
3.5	Modeling and Scale-up (Optional)	Jul 93		
4.1	Support to Research	Oct 93		
4.2	Commercial Application (Optional)	Oct 93		
4.3	Product/Market Analysis (Optional)	Oct 93		
5.1	Planning and Reports	Oct 93		
5.2	Management Activities	Oct 93		

APPENDIX 1

DESIGN HAZARDS REVIEW REPORT
MARCH 1992 IBOH RUN

Memorandum

To: Distribution
Dept./Loc.: –
From: M.R. Jocsak
Dept./Ext.: Project Eng./3649
Date: 27 February 1992
Subject: Design Verification Review Report
March 1992 IBOH Run - AFDU, LaPorte, TX (ATT1016)

Distribution:

W.C. Allen (MC#83)
A.G. Barbieri
D.M. Brown
T.E. Conway
D.A. Kosciusko
S. DeWire (LaPorte AFDU)
E.C. Heydorn (LaPorte AFDU)
T. Hsiung/R.P. Underwood
G.A. Peters
D.M. Herron
E. Schaub/B. Bhatt/D. Studer
R.L. Williams

Attached is a copy of the Design Verification Review report for the isobutanol demonstration at the Alternative Fuels Development Unit (AFDU) in LaPorte, TX.

The schedule for performing the isobutanol run has been delayed due to problems in manufacturing the required catalyst. It is uncertain as to when the run will be performed, but most likely it will be within the next two years. This document serves to finalize the hazard review process for the isobutanol demonstration.

Efforts are currently underway in preparation for an alternative run this Spring at the AFDU: water gas shift (WGS) demonstration. A separate Hazards Review will be performed and documented for the WGS run, but since this run will utilize all of the recently installed equipment, many of the same hazards addressed for the isobutanol run will apply to the WGS run.

Please contact me if you have any questions or comments.

Michael R. Jocsak

MRJ/026

RECEIVED
MAR 02 1992
PROCESS ENGINEERING

DESIGN VERIFICATION REVIEW (DVR)

Alternative Fuels Development Unit (AFDU)

March 1992 Iso-Butanol Run

LaPorte, Texas

21 February 1992

Review Team

T. E. Conway	Start-Up Engineering
D. M. Herron	Process Engineering
M. R. Jocsak	Project Engineering
G. A. Peters	PSG Engineering Safety
E. S. Schaub	Process Engineering

Design Verification Review (DVR)
Alternative Fuels Development Unit (AFDU)
March 1992 Iso-Butanol Run
LaPorte, Texas
21 February 1992

Table of Contents

Page No.

I. Introduction 1

II. Project Status 1

III. Status of Hazard Items 1

Appendices

A. Process Flow Diagram

B. Justification for Changing the High Temperature Shutdown SD-2 Setpoints

C. MSDS - Isobutanol Catalyst

D. LaPorte AFDU Operations in the Spring of 92 - Materials Review

E. CO_2 Vent Stack Review for the Spring '92 Demo at the AFDU

F. CO_2 Vent Stack for Spring '92 Run

References

1. Preliminary Process Hazards Review Report - 12 September 1991

2. Design Hazard Review (DHR) Report - 4 November 1991

3. Engineering Flowsheet (P&ID) for the Spring '92 ISOBUTANOL DEMONSTRATION - ATT1016B, revision 2, January 3, 1992

4. Engineering Flowsheet (P&ID) 87-7-1533, Liquid Phase Methanol, revision 15, 19 September, 1991.

5. FCN (to F/S 87-7-1533) #'s: 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 14, 15, 18, 19, 20, & 30.

I. INTRODUCTION

A Design Verification Review (DVR) meeting was conducted on 21 February 1992 for the isobutanol demonstration at the LaPorte, TX Alternative Fuels Development Unit (AFDU). The run objectives are to investigate mixed alcohol synthesis in a bubble column reactor and to study the influence of light alcohol recycle on isobutanol selectivity.

The purpose of the DVR was to review the status of each hazard item addressed during the Design Hazards Review (DHR) and to ensure these items have been satisfactorily considered during the design phase.

II. PROJECT STATUS

The schedule for performing the isobutanol demonstration has been delayed due to problems associated with manufacturing a suitable catalyst. In an effort to shake down the newly installed DCS system and GC laboratory equipment, an alternate operating campaign is being planned for the spring of 1992. This run will demonstrate a water-gas shift (WGS) reaction in our liquid phase reactor train and will utilize the recently installed methanol circulation equipment.

It is likely that the isobutanol demonstration will be performed during FY'93, assuming a suitable catalyst is available.

A separate Hazards Review will be performed and documented for the WGS demonstration.

III. STATUS OF HAZARD ITEMS

The following lists the status of each hazard item as discussed during the DVR meeting.

MARCH 1992 ISOBUTANOL DEMONSTRATION
Alternative Fuels Program
LaPorte, TX AFDU

Hazard	12 September 1991 Preliminary Hazards Review (PrHr) Recommendation/Follow-Up	4 November 1991 Design Hazards Review (DHR) Status	21 February 1992 Design Verification Review (DVR) Status
1. Rupture or damage of alcohol injection tank trailer caused by backflow of reactor feedgas into the alcohol injection system.	Design the injection system with adequate backflow protection (i.e., checkvalves, and/or safety valves) to prevent tank trailer overpressurization. (Action: Process)	The design of the injection system includes two check valves (V-2246 and V-2247) on the discharge of the 10.85 injection pump. In addition, the 10.85 (a diaphragm pump) is equipped with a ball-type check valve on its suction and discharge. Two safety valves (PSV-816A&B) will be installed on the trailer loading/unloading vapor recovery lines to provide overpressurization protection for the trailers. The design assumes the trailers will be pressure rated for at least 25 psig. The team agreed that this design will provide adequate protection for the trailers from overpressurization.	The trailer design pressure was confirmed to be 25 psig, minimum. A total of four check valves are included in the system design. One PSV 816 will be installed and the trailer will be equipped with one PSV set at 20 psig.
2. Uncontrollable fire in the trailer loading/unloading areas due to a spill or leak and insufficient fire protection.	The baseline plan calls for two alcohol tank trailers on-site throughout the run (one for alcohol injection and one for alcohol product collection). The adequacy of the existing fire monitors to protect two trailers needs to be reviewed. In addition, the availability of a single tank truck with two (50% size) tanks will be pursued. (Action: Project/Operations)	The current design is based on utilizing a single trailer equipped with two (50% size) compartments. One tank will be used for product collection and the other for supplying alcohol required for injection. This design results in zero net increase in on-site trailer inventory levels from previous operating campaigns, thus it was agreed that in the event of a fire, the existing fire monitor will provide adequate fire protection in the trailer loading/unloading area.	No change in status.

MARCH 1992 ISOBUTANOL DEMONSTRATION
Alternative Fuels Program
LaPorte, TX AFDU

Hazard	12 September 1991 Preliminary Hazards Review (PrHr) Recommendation/Follow-Up	4 November 1991 Design Hazards Review (DHR) Status	21 February 1992 Design Verification Review (DVR) Status
3. Fire caused by undetected leakage of methanol from the 10.80 methanol recycle pump.	Incorporate a seal leakage detection/interlock system with the design of the 10.80 pump. (Action: Design)	The 10.80 circulation pump is a high speed centrifugal pump and will be equipped with a thermo-syphon low-pressure barrier fluid system. Jim Koniski (Machinery Applications presented and reviewed the mechanics of the pump and associated seal system with the Hazard Review Team. Refer to the 10.80 pump bid evaluation for a technical description of this pump (Appendix B). The barrier fluid pot will be equipped with a low level and high pressure SDIA interlock to shutdown the pump in the event of an excessive seal leakage.	No change in status.
4. 01.20 recycle compressor wreck due to liquid entrainment caused by a failure of LV-688 resulting in an overfill of the 22.14 separator vessel.	Include in the design of the 10.80 controls a high liquid level alarm interlock on the 22.14 (LAHH-688) to close the 10.80 flow control valve. This will prevent further flow to the 22.14. (Action: Design)	A high level SDIA interlock (LSHH-688) has been included in the design of the 22.14. In addition, a low temperature alarm (TAL-233) will be installed to provide early warning of low temperature gas entering the 01.20 recycle compressor in the event of an upset condition. (Refer to hazard #11).	Operations to include a procedure with operator training that confirms action will be taken to shut down in the event a TAL-233 is received.
5. Process upset caused by improper blind and block valve positions.	Update the existing block valve and blind checklist. (Action: Operations)	Completion will be verified during the Design Verification Review.	To be verified by ORI team.

Hazard	12 September 1991 Preliminary Hazards Review (PrHr) Recommendation/Follow-Up	4 November 1991 Design Hazards Review (DHR) Status	21 February 1992 Design Verification Review (DVR) Status
6. Runaway reaction in the 27.10 reactor vessel caused by a loss of oil flow or fin fan in the utility oil loop.	The reactor will be operated at a higher temperature than previous runs (482°F for DME versus 572°F for IBOH). New high temperature set points will be specified by Process. Safety will review the facility's hazards files to locate documentation on the determination for current set points and will review this with Process. (Action: Process/Safety)	No progress was reported on this issue during the DHR meeting. However, following the meeting, G. A. Peters issued a memo to the HR team (7 November 1991, Appendix C) which outlines the criteria used previously to determine high temperature alarm/shutdowns for the AFDU. In response to this memo, process engineering will prepare and document a justification for exceeding the current alarm setpoints. (Action: Process)	Process Engineering has documented a justification for the proposed alarm set points. (Appendix B, 18 February 1992 memo.) In addition, it was agreed that for future operating campaigns, the plant can be run up to its design limits (1000 psig, 600°F). It was noted that during the LPIII methanol campaign, the plant was safely run at 546°F with no significant evidence of carbonyls or methane present. Also noted was that in the event of a loss of reactor cooling, it is possible to exceed the design temperature limits. However, because the reactor is equipped with three independent on-line hard-wired high temperature shutdowns, this hazard was determined to be adequately protected. In addition, it was assumed that operations will ensure these shutdowns are adequately calibrated and tested prior to each operating campaign that is preceded by an extended plant outage.
7. Personnel exposure to the new catalyst that will be used in the 27.10 reactor (Cesium promoted methanol catalyst - BASF S3-86).	The recommendation is to review the handling procedures established by PSG R&D and apply them as appropriate at AFDU. (Action: Process/Operations)	Completion will be verified during the DVR meeting. In addition, Project Engineering will obtain and distribute an MSDS sheet for the catalyst.	R. P. Underwood (PSG R&D) advises that the handling procedure is the same as for S3-86. A MSDS sheet is included in Appendix C.

MARCH 1992 ISOBUTANOL DEMONSTRATION
Alternative Fuels Program
LaPorte, TX AFDU

Hazard	12 September 1991 Preliminary Hazards Review (PrHr) Recommendation/Follow-Up	4 November 1991 Design Hazards Review (DHR) Status	21 February 1992 Design Verification Review (DVR) Status
8. Equipment or piping system corrosion or damage caused by material incompatibilities due to the presence of higher alcohols in addition to methanol in the system downstream of 27.10 reactor.	The primary products of the reaction are C1-C6 alcohols, CO_2,and water; the byproducts are C1-C4 hydrocarbons, ethers (small), methyl acetate, and methyl formate. The recommendation was to review the material compatibilities of existing equipment, piping gaskets, O-rings, etc. with the new process fluid. (Action: Design Engineering) In addition, Operations will perform a visual inspection of the two 01.20 snubber drain valves (V-476 and V-591) as documented in the DME run DVR report.	Rich Underwood (PSG R&D) has provided some insight regarding the material capabilities of the mixed alcohols process stream. Refer to Appendix D. Based on the above information, a detailed material compatibility review will not be performed by design engineering. In general, the high alcohols share the same material capability characteristics as methanol. The recommendation is to monitor the plant for signs of leakage during this 20-day operating campaign. (Action: Operations). In addition, based on the information contained in Appendix D (DME compatibility with viton is reported to be better than methanol), it was decided that a visual inspection of the 01.20 snubber drain valves is not required.	No change in status.
9. 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. (Action: Operations) It was noted that during the DME run, the vessel's process discharge flange began leaking process fluid. The leak was repaired by applying a sealing compound to the flange surface. A materials compatibility review of the sealing compound will be performed. (Action: Operations)	The material used to repair leaks around the 22.10 flange was Loctite Master Gasket. Refer to Appendix E.	Operations to measure wall thickness prior to plant operation. In addition, action will be taken to investigate the compatibles of Loctitle Master Gasket. Completion to be verified during ORI (Project).

MARCH 1992 ISOBUTANOL DEMONSTRATION
Alternative Fuels Program
LaPorte, TX AFDU

Hazard	12 September 1991 Preliminary Hazards Review (PrHr) Recommendation/Follow-Up	4 November 1991 Design Hazards Review (DHR) Status	21 February 1992 Design Verification Review (DVR) Status
10. 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 not a hazard.	No change in status. In addition, DME will not be present in significant quantities.	No change in status.
11. 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.	Maintain the existing low temperature alarm (TAL-233).	Included in design.	Refer to item #4.
12. Carry over of catalyst into equipment (new and existing) downstream of 27.10 reactor could cause a reaction.	A review of the reactivity grid will be performed. (Action: Process)	Process will complete prior to DVR meeting.	Process Engineering has concluded that this issue is not a hazard. The analysis performed assumed that 20% of the catalyst volume is carried over at a constant rate. In addition, it was assumed that the carry-over catalyst is equally as active as in the reactor. (PSG R&D advises this assumption is very conservative.) The calculated result of this carryover is a 60°F temperature rise. This would be negated by ambient heat leak which can be as much as 80°F.
13. 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.	This hazard also applies to the 22.18 and 21.38 vessels. The recommendation is to maintain the existing SD-1A protection interlock circuit. In addition, the "fitness for services" analysis documented by J. C. Tafuri (4 Dec. '90 Memo) will be revisited. (Action: Process)	No change in status.	Process Engineering has advised J. F. Tafuri of the run plans (Appendix D, 18 February 1992 memo) and the 22.14, 22.18, and 21.38 vessel materials have been determined acceptable for the Spring '92 run.

MARCH 1992 ISOBUTANOL DEMONSTRATION
Alternative Fuels Program
LaPorte, TX AFDU

Hazard	12 September 1991 Preliminary Hazards Review (PrHr) Recommendation/Follow-Up	4 November 1991 Design Hazards Review (DHR) Status	21 February 1992 Design Verification Review (DVR) Status
14. 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 located downstream of the vapor outlet nozzle on the 22.18 should be reviewed. (Action: Process)	A hazard associated with the thermal effects does not exist. The minimum (upset) low temperature exposure in the event of a liquid carry-over is 40°F.	No change in status.
15. Equipment or piping overpressurization due to the presence of a different process fluid composition and an inadequacy of existing relief devices.	Review the sizing of existing relief devices and establish criteria for relief devices on new equipment. (Action: Process Engineering/Start-Up)	The review is in progress. Two areas have been identified as potentially being inadequate: recycle compressor and internal heat exchanger rupture case.	The review of existing and new relief valves is complete with the exception of the following two issues: 1. The relief valves provided with the liquid CO_2 storage tank need to be reviewed. 2. PSV-236A/B are inadequate in the event LV-693 fails open. New trim will be installed on LV-693 prior to the run in order to reduce the maximum flow so that PSV-236A/B will be sufficient.
16. Methanol storage tank (28.10) fire.	The current plan is to pipe product directly into tank trailers and not utilize the underground methanol storage tank. The existing monitor will provide adequate fire protection for one trailer.	No change in status.	The current plan now includes using the U/G methanol tank, but it was agreed that the existing fire monitor will provide adequate protection.
17. DME (28.40 - Alternative Fuel) storage tank fire (external) caused from a leak, overfill, or open drain valve.	The 28.40 tank will be utilized to collect purge (primarily methanol) from the CO_2 removal circuit. The existing fire protection system (fire monitor) will provide adequate protection for the 28.40 storage tank.	No change in status.	The 28.40 will be used to store make-up MeOH. There is no change in the hazard status.

MARCH 1992 ISOBUTANOL DEMONSTRATION
Alternative Fuels Program
LaPorte, TX AFDU

Hazard	12 September 1991 Preliminary Hazards Review (PrHr) Recommendation/Follow-Up	4 November 1991 Design Hazards Review (DHR) Status	21 February 1992 Design Verification Review (DVR) Status
18. 21.80 Vent Stacks a) Exposure of personnel to hazardous levels of CO_2 during normal or upset operating conditions.	a) The existing design of the CO_2 stack should be adequate. A dispersion model will be performed at the worst case CO_2 flow rates to verify the adequacy of the vent design. (Action: Process/Safety)	a) No change in status.	Process Engineering has documented the CO2 release flows and the 21.80 tube-rupture syngas release flows. (Appendix E, 11 February 1992 memo.) In response, Safety Engineering has reviewed these scenarios and has determined that the existing vent stack is adequate (Appendix F, 17 February 1992 memo.)
b) Exposure of personnel to hazardous levels of flame radiation from the venting fluid (21.80 tube-rupture case)	b) The recommendation is to restrict personnel access from the top platform during the run.	b) No change in status.	No change in status.
19. Failure or rupture of the purge nitrogen system due to inadequate protection.	This hazard was resolved prior to the DME run. The conformance to APCI standards of purge nitrogen system will be maintained.	No change in status.	The low pressure alarm setpoint of the protected nitrogen header needs to be verified as being consistent with APCI standards during the ORI.
20. 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.	The TSH-309 shutdown interlock will be maintained (21.30 discharge).	No change in status.	No change in status.
21. Failure of the SDIA protection circuit due to an unauthorized activation of the bypass switch.	This hazard was not addressed during the PrHR.	A software protection system will be built into the DCS configurations so that access to the SDIA bypass switch is controlled. A possible solution is to install a password. (Action: Process Controls Engineering)	Process Controls Engineering will document the protection systems that will be followed prior to the ORI.

MARCH 1992 ISOBUTANOL DEMONSTRATION
Alternative Fuels Program
LaPorte, TX AFDU

Hazard	12 September 1991 Preliminary Hazards Review (PrHR) Recommendation/Follow-Up	4 November 1991 Design Hazards Review (DHR) Status	21 February 1992 Design Verification Review (DVR) Status
22. Exposure of personnel to hot liquids or fire near the 15.90 flare area due to liquid flooding caused by undetected product trailer overfill.	This hazard was not addressed during the PrHR.	The loading flare (15.90E) will not be equipped with a liquid knock-out pot. The product loading operations will be administratively controlled by AFDU Operations Management. A level gauge (site gauge) will be included in the design of the product collection system (as well as the alcohol injection system). The HR team concludes that this level of control is sufficient due to: (a) the small total number of trailers to be filled during the run (4-8 fillings), (b) the relative volume of the "day" tank vs. the volume of the trailer product compartment, and (c) the filling will be performed in a batch mode through the "day" tank.	No change in status.

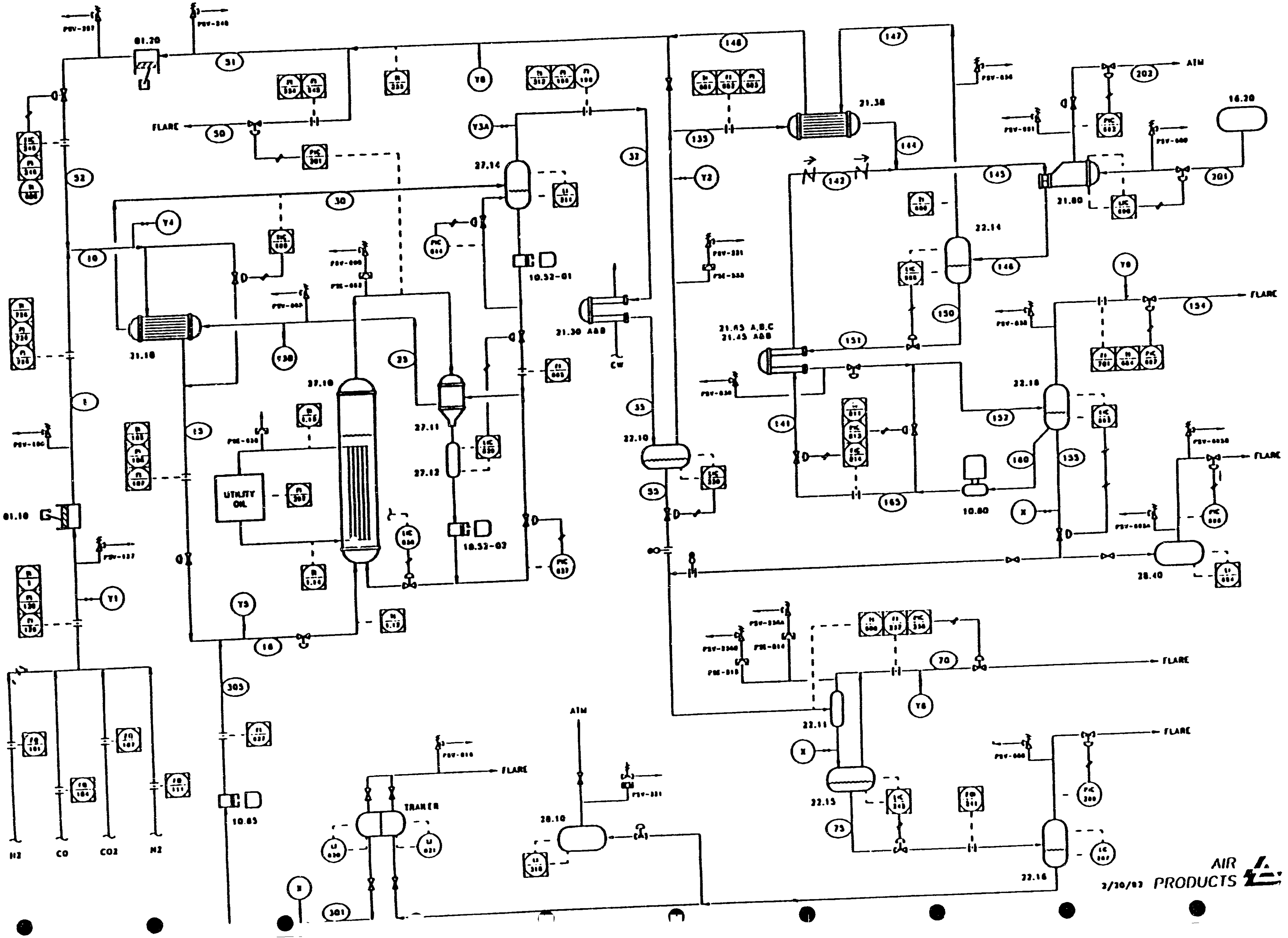
MARCH 1992 ISOBUTANOL DEMONSTRATION
Alternative Fuels Program
LaPorte, TX AFDU

(The following items are not considered hazards but are documented for the purpose of maintaining a record of the entire meeting discussions.)

Hazard	12 September 1991 Preliminary Hazards Review (PrHr) Recommendation/Follow-Up	4 November 1991 Design Hazards Review (DHR) Status	21 February 1992 Design Verification Review (DVR) Status
23. 21.80 vent noise levels	No design action was recommended. If high noise levels are encountered, the flow of CO_2 will be reduced to reduce the noise levels.	No change in status.	No change in status.
24. Tie-in to 16.20 CO_2 tank and selection of associated safety relief valves.	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.	No change in status.	Refer to item #15.

Appendix A

LAPORTE AFDU – SPRING 92 IBOH DEMONSTRATION



Appendix B

Memorandum AIR PRODUCTS

To:	Distribution	Dept./Loc.:	
From:	D. M. Herron	Dept./Ext.:	PSG-Process
Date:	18 February 1992		
Subject:	Justification for Changing the High Temperature Shutdown (SD02) Set-Points - Spring '92 IBOH Demo at the AFDU		

Distribution:

T. E. Conway
E. C. Heydorn
M. R. Jocsak
G. A. Peters

ISSUE:

Process and R&D would like to operate the reactor at 572 F and increase the high temperature shutdown set-points for the following devices:

TISH-182	21.10 Tubeside Inlet	590 F
TSHH-190	27.10 Reactor	590 F

POTENTIAL HAZARD WHICH IS BEING PROTECTED AGAINST:

1. Unexpected, violently exothermic side reactions being triggered at elevated temperature (primarily the methanation reaction).
2. Loss of coolant resulting in exceeding the design temperature of materials.

HISTORY:

G. A. Peters has determined that the installation of the existing high temperature shutdowns resulted from a hazards review following an exotherm in late 1983 (1). As explained by D. J. Silkworth (2)...

"A significant inventory of an old nickel catalyst was subsequently found to have remained in the product cooler, which had been a component of used equipment from a methanation pilot plant. Nickel catalyst particles had been able to recirculate through the original feed gas preheat system, and undoubtedly had provided a superior catalytic surface for the promotion of the methanation reaction during the December 1983 trials."

Following the '83 exotherm, the plant was thoroughly cleaned and according to Peters (1), the high temperature shutdowns were installed. The plant was subsequently operated over a two year period without incident. The normal reactor temperature was 482 F and the maximum was 507 F.

According to Heydorn, the normal high temperature shutdowns set-points used during the LP III contract and during the '91 DME Demo, were:

TISH-182	21.10 Tubeside Inlet	550 F
TISH-183	21.10 Shellside Outlet	550 F
TSHH-190	27.10 Reactor	515 F
TSHH-312	27.14 Separator	550 F
TSHH-550	02.62 Red. Gas Heater Outlet	550 F

Extended operations under the LP III contract were completed without any exothermic incident. The normal operating temperature of the reactor was 482 F. On at least one occasion, the reactor was operated at 545 F.

During the start-up for the DME Demonstration in 1991, testing for poisons was performed which revealed extremely low levels of iron and nickel carbonyls. This result indicates that the internals of the plant remain clean and devoid of loose nickel catalyst. Furthermore, continuous GC analysis of the gas streams during normal operations rarely picked-up methane.

EVALUATION:

It is my opinion that the lack of subsequent exotherms, low nickel carbonyl concentrations during carbonyl burn-out operations, and low to nil methane concentrations during normal operations support the supposition that the loose nickel catalyst has been successfully purged from the plant.

In addition, the risk of reintroducing nickel to the plant is minimal for the following reasons:

1. New stainless steel materials used in syngas service are passivated in nitric acid.

2. No electric heating elements are in direct contact with the syngas (excepting the reduction heaters which have been used previously, which process 96% N2 4% syngas, and which retain the existing high temperature shutdown temperature).

Finally, nickel carbonyls tend to decompose on, and poison the catalyst within the reactor. The presence of small amounts of nickel in the reactor, though not desirable, does not seem to be a major safety issue since the heat of methanation is absorbed by the slurry oil along with the heat release associated with the major reaction.

RECOMMENDATIONS:

1. We should continue to use the high temperature shutdowns for the purpose of guarding against plant upsets such as loss of utility oil coolant flow. If this is the case, the set-points should be based on intended operating temperature.

2. Implied in 1) is that high temperature shutdowns are being retained to protect equipment and materials from being subjected to temperatures exceeding their design values, which is currently 600 F at 1000 psig for some pieces in and around the reactor.

3. Concern for the presence of loose nickel in the existing plant should not be the basis for establishing shut-down set points. Rather, it should be demonstrated that the addition of new materials and equipment does not inadvertently introduce catalytic materials.

4. An exception to 3) is the high temperature shutdown on the electric reduction gas heaters. The current set point for TISH-550 (based on LP III) should be retained unless the exchanger is subjected to a controlled temperature-ramping demonstration. It may be useful to perform this work following the upcoming run.

5. Whenever we bring a piece of equipment to a new elevated temperature, the temperature should be ramped in a cautious and controlled manner.

6. Specific to the upcoming run, the set-points for TISH 182, and TSHH 190 should be increased to accommodate the new normal operating temperature of the reactor. The alarm and shut-down temperatures should be as near 572 F as possible and defined by operations to allow for small transients.

D. M. Herron

1) G.A. Peters to AFDU Hazards Review Team Members, "Criteria for High Temperature Alarms/Shutdowns on the LaPorte Alternative Fuels Development Unit", 7 November 1991.

2) D.J. Silkworth to D.W. Studer, "LPMEOH - Part III, 87-7-1565, Hazards Review", 28 March 1988.

APPENDIX C

MATERIAL SAFETY DATA SHEET

BASF Corporation Chemicals Division
100 Cherry Hill Road, Parsippany, New Jersey 07054, (201) 316-3000

BASF

PRODUCT NUMBER: 826931 BASF Catalyst S3-86 Modified W/CS

SECTION I

*Registered Trademark

TRADE NAME: BASF Catalyst S3-86	
CHEMICAL NAME: Copper Oxide Catalyst	
SYNONYMS: Low Pressure Methanol Synthesis Catalyst	FORMULA: N/A
CHEMICAL FAMILY: Heterogeneous Catalysts	MOL. WGT.: N/A

SECTION II - INGREDIENTS

COMPONENT	CAS NO.	%	PEL/TLV - SOURCE
BASF Catalyst S3-86		100	Not established
Contains:			
Copper Oxide	1317-38-0	61.8	1 mg/m3 as Cu ACGIH, OSHA (Trans/Final)
Zinc Oxide	1314-13-2	21.8	5 mg/m3; 10 mg/m3 STEL ACGIH 5 mg/m3 OSHA (Trans/Final)
Alumina	1344-28-1	4.8	10 mg/m3 ACGIH 5 mg/m3 OSHA (Trans/Final)
Water	7732-18-5		
Graphite	7782-42-5		2.5 mg/m3 ACGIH OSHA Final 20 mppcf OSHA (Trans)
Cesium Oxide	20281-00-9	1-1.5	.2 mg/m3 TWA as Cesium
All components are in TSCA inventory.			
SARA Title III Sect. 313: Listed.			

SECTION III - PHYSICAL DATA

BOILING/MELTING POINT @760 mm Hg: N/A	pH: ~8.5 (100 g/l water)
VAPOR PRESSURE mm Hg @20 C: N/A	
SPECIFIC GRAVITY OR BULK DENSITY: 1300 kg/m3	
SOLUBILITY IN WATER: 0.1 g/l @ 20 C	Color: Dk. Brown

APPEARANCE Powder ODOR: None INTENSITY: N/A

SECTION IV - FIRE AND EXPLOSION HAZARD DATA

FLASH POINT (TEST METHOD): N/A	AUTOIGNITION TEMP: N/A

FLAMMABILITY LIMITS IN AIR (% BY VOL) LOWER: N/A UPPER: N/A

EXTINGUISHING MEDIUM	Use water fog, alcohol foam or dry chemical extinguishing media.
SPECIAL FIREFIGHTING PROCEDURES	Firefighters should be equipped with self-contained breathing apparatus and turnout gear.
UNUSUAL FIRE AND EXPLOSION HAZARDS	None.

EMERGENCY TELEPHONE NUMBER

CHEMTREC 800-424-9300 201-316-3000

THIS NUMBER IS AVAILABLE DAYS, NIGHTS, WEEKENDS AND HOLIDAYS

DP102 12 87

SECTION V - HEALTH DATA

TOXICOLOGICAL TEST DATA:	RESULT:
BASF Catalyst S3-86	
Rat, Oral LD50	4650 mg/kg
Rabbit, Skin Irritation	Non-irritating
Rabbit, Eye Irritation	Moderately irritating

EFFECTS OF OVEREXPOSURE:

Contact with the powder or its dusts may result in moderate irritation of the eyes and mechanical irritation of the skin. Inhalation of dusts causes respiratory irritation. Chronic overexposure to copper compounds can lead to anemia, and damage to the liver, kidneys, lungs, and spleen. Gamm-alumina, a form of aluminum oxide, was fibrogenic when injected into the lungs of animals; however, aluminum oxide has not been implicated as a cause of lung disease in humans. Inhalation of zinc fumes may cause "metal fume fever". Symptoms of metal fume fever include metallic taste, dryness, and irritation of the throat, difficult breathing, weakness, fatigue, and fever. Thirteen of nineteen workers in a zinc powder factory were reported to exhibit inflammation of the upper respiratory tract after 2-3 years of employment. Ingestion of zinc oxide powder may cause gastric disturbances.

Existing medical conditions aggravated by exposure to this material:
No information found for this mixture.

FIRST AID PROCEDURES:

Eyes-Immediately wash eyes with running water for 15 minutes. If irritation develops, consult a physician.

Skin-Wash affected areas with soap and water. Remove and launder contaminated clothing before reuse. If irritation develops, consult a physician.

Ingestion-If swallowed, dilute with water and immediately induce vomiting. Never give fluids or induce vomiting if the victim is unconscious or having convulsions. Get immediate medical attention.

Inhalation-Move to fresh air. Aid in breathing, if necessary, and get immediate medical attention.

SECTION VI - REACTIVITY DATA

STABILITY: Stable.
CONDITIONS TO AVOID: N/A

CHEMICAL INCOMPATIBILITY: N/A

HAZARDOUS DECOMPOSITION PRODUCTS: N/A

HAZARDOUS POLYMERIZATION: Does not occur
CONDITIONS TO AVOID: N/A

CORROSIVE TO METAL: No

OXIDIZER: No

SECTION VII - SPECIAL PROTECTION

RESPIRATORY PROTECTION:
If dusts are generated, wear a NIOSH/MSHA approved dust mask.

EYE PROTECTION: Chemical goggles or side-shield safety glasses.

PROTECTIVE CLOTHING: Gloves and protective clothing as necessary to prevent skin contact.

VENTILATION: Local exhaust required to control to P.E.L.

OTHER: Clean clothing should be worn daily.
Shower after handling.

PRODUCT NUMBER: 828931 BASF Catalyst S3-86 Modified W/CS

SECTION VIII - ENVIRONMENTAL DATA

ENVIRONMENTAL TOXICITY DATA:

None available.

SPILL AND LEAK PROCEDURES:

Spills should be contained and placed in suitable containers for disposal.
This material is not regulated under RCRA or CERCLA ("Superfund").

HAZARDOUS SUBSTANCE SUPERFUND: No RQ (lbs):

WASTE DISPOSAL METHOD:

Landfill in a licensed facility.
Do not discharge into waterways or sewer systems without proper authority.

HAZARDOUS WASTE 40CFR261: No HAZARDOUS WASTE NUMBER:

CONTAINER DISPOSAL:

Dispose of in licensed facility.
Recommend crushing or other means to prevent unauthorized reuse.

SECTION IX - SHIPPING DATA

D.O.T. PROPER SHIPPING NAME (49CFR172.101-102)

None

HAZARDOUS SUBSTANCE (49CFR CERCLA LIST)

No

REPORTABLE QUANTITY (RQ) N/A

D.O.T. HAZARD CLASSIFICATION (CFR172.101-102)

PRIMARY

None

SECONDARY

None

D.O.T. LABELS REQUIRED (49CFR172.101-102)

None

D.O.T. PLACARDS REQUIRED (CFR172.504)

None

POISON CONSTITUENT (49CFR172.203(K))

None

BILL OF LADING DESCRIPTION

Chemicals, NOIBN (Not Regulated By D.O.T.)

CC NO. 354

UN/NA CODE N/A

DATE PREPARED: 3 / 31 / 87

UPDATED: 7 / 6 / 89

SECTION X - PRODUCT LABEL

BASF Catalyst S3-86 Modified W/CS

WARNING:
CONTAINS COPPER OXIDE (CAS No.: 1317-38-0); ALUMINA (CAS No.: 1344-28-1); ZINC OXIDE (CAS No.: 1314-13-2).
CONTACT WITH EYES OR SKIN MAY RESULT IN IRRITATION.
INGESTION MAY RESULT IN GASTRIC DISTURBANCES.
INHALATION OF DUSTS MAY IRRITATE THE RESPIRATORY TRACT.
GAMMA ALUMINA, A FORM OF ALUMINUM OXIDE, WAS FIBROGENIC WHEN INJECTED INOT THE LUNGS OF ANIMALS.
CHRONIC OVEREXPOSURE TO COPPER COMPOUNDS CAN LEAD TO ANEMIA AND DAMAGE TO THE LIVER, KIDNEYS, LUNGS AND SPLEEN.
INHALATION OF ZINC OXIDE FUMES MAY CAUSE METAL FUME FEVER, SYMPTOMS OF WHICH INCLUDE METALLIC TASTE, DRYNESS AND IRRITATION OF THE THROAT, DIFFICULTY IN BREATHING, WEAKNESS, FATIGUE AND FEVER.

Avoid contact with eyes, skin or clothing. Avoid breathing dusts. Use with local exhaust. Wear a NIOSH/MSHA-approved dust respirator, chemical goggles, gloves, coveralls, apron, boots and other protective clothing as necessary to prevent contact. Shower after handling. Clean clothing should be worn daily.

FIRST AID:
Eyes-Immediately wash eyes with running water for 15 minutes. If irritation develops, consult a physician.
Skin-Wash affected areas with soap and water. Remove and launder contaminated clothing before reuse. If irritation develops, consult a physician.
Ingestion-If swallowed, dilute with water and immediately induce vomiting. Never give fluids or induce vomiting if the victim is unconscious or having convulsions. Get immediate medical attention.
Inhalation-Move to fresh air. Aid in breathing, if necessary, and get immediate medical attention.

IN CASE OF FIRE: Use water fog, alcohol foam or dry chemical extinguishing media. Firefighters should be equipped with self-contained breathing apparatus and turnout gear.

EMPTY CONTAINERS: All labeled precautions must be observed when handling, storing and transporting empty containers due to product residues. Do not reuse this container unless it is professionally cleaned and reconditioned.

DISPOSAL: Spilled material, unused contents and empty containers must be disposed of in accordance with local, state and federal regulations. Refer to our Material Safety Data Sheet for specific disposal instructions.

IN CASE OF CHEMICAL EMERGENCY: Call CHEMTREC day or night for assistance and information concerning spilled material, fire, exposure and other chemical accidents. 800-424-9300

ATTENTION: This product is sold solely for use by industrial institutions.

Refer to our Technical Bulletin and Material Safety Data Sheet regarding safety, usage, applications, hazards, procedures and disposal of this product. Consult your supervisor for additional information.

CAS Nos.: Graphite: 7782-42-5
Made in West Germany
Intermediates and Fine Chemicals
0489

Appendix D

AIR PRODUCTS

Memorandum

To:	J. C. Tafuri	Dept./Loc.:	PSG Engineering Technology
From:	D. M. Herron DMH	Dept./Ext.:	PSG Process Engineering (4765)
Date:	18 February 1992		
Subject:	LaPorte AFDU Operation in the Spring of 92 - Materials Review		

c: T. E. Conway
E. C. Heydorn
M. R. Jocsak
G. A. Peters

Last year I had asked you to review two phase separators and one heat exchanger for fitness of service. We had intended to use the 22.14, 22.18 and 21.38 in service where the normal and/or upset temperatures were below that which was originally intended. To review:

Item	Normal Temperature	Upset Temperature
22.14	0°F	-70°F
22.18	80°F	-20°F
21.38	0°F	-70°F

You had previously determined that these items were fit for use under these conditions for two, nominal two week runs. Low temperature shut-downs were incorporated in the design and operation of the plant.

The first use of these items in "low" temperature service was completed in May 1991. The temperature control of the 22.14 was very stable and neither the 22.14 nor the 21.38 were subjected to temperatures below 0°F. On one occasion the 22.18 was manually depressurized to near-atmospheric pressure; details of the event are not documented but it is possible that the temperature in the heal of the 22.18 may have reached -20°F (at atmospheric pressure) for a short period of time.

As part of the Hazards Review for an upcoming run (scheduled to begin early April this year) I have been asked to let you know that we intend to use these items again in similar service. Normal conditions are the same while the potential upset conditions result in less cool temperatures than previous. In addition, the probability for a repeat of the 22.18 depressurization event is much lower since this vessel will always be operated at near-atmospheric pressure. Following this run, these pieces of equipment will be permanently reconfigured and place back into high temperature service (for another run scheduled in July of this year).

I will stop up to discuss the use of these items in the upcoming run. A written response is not required unless you wish us not to proceed as indicated.

Appendix E.

Memorandum

AIR PRODUCTS

To: G. A. Peters Dept./Loc.: PSG-Engr Safety

From: D. M. Herron Dept./Ext.: PSG-Process

Date: 11 February 1992

Subject: CO2 Vent Stack Review for the Spring '92 Demo at the AFDU

---

cc:

T.E. Conway
E.C. Heydorn
M.R. Jocsak

For the purpose of completing the hazards review, we need to review the CO2 vent stack. To summarize, two cases need consideration:

1. Release of CO2 during normal operations, and
2. Release of syngas during the 21.80 tube-rupture event.

<u>Case 1:</u>
Currently, the design max CO2 vent flow is 833 lb/hr; the design minimum is 685 lb/hr. Both these flows fall between the minimum and maximum flows which we examined last time (299 to 1128 lb/hr).

<u>Case 2:</u>
I've looked at 8 different subcases for the tube rupture event. The results are tabulated in Tables 1,2 & 3.

Table 1 shows the assumptions made to arrive at each of the subcases. The maximum vent flow occurs when syngas blows into the 21.80 shell and vaporizes CO2 . The two cases you may want to focus on are 1 and 3.

Table 2 shows the flows and composition for the release through the 3" vent; Table 3 shows the flows and composition for the release through the 1" vent (assuming the PV on the 21.80 is fully open).

Please take a look these flows and make an operating recommendation.

DMH

D. M. Herron

P.S.

Tables 4 & 5 Show the release rates and plant pressures during the events (Case 1-8) as a fuction of time

TABLE 1: KEY TO THE DIFFERENT CASES

CASE	1	2	3	4	5	6	7	8
Syngas through Tube?	Y	Y	Y	Y	Y	Y	Y	Y
Methanol through Tube ?					Y	Y	Y	Y
Syngas mixes with CO2 Liquid?			Y	Y			Y	Y
Methanol mixes with CO2 & Syngas?							Y	Y
PV-692 (evaporator vent) wide Open?	Y		Y		Y		Y	

TABLE 2: RELEASE TO THE 3" VENT

CASE		1	2	3	4	5	6	7	8
Flow	lb/hr	8132	8460	10780	10960	8070	8420	10491	10700
	lb mole/hr	370	385	369	375	367	383	373	381
Temperature	F	170	170	-20	-20	170	170	-15	-15
Pressure	psia	17.5	18	17	17	17	18	17.5	17.5
Mole Wt	-	22	22	29.2	29.2	22	22	28.1	28.1
Density	lb/ft3	0.057	0.059	0.105	0.105	0.055	0.059	0.103	0.103
Cp	BTU/lb-F	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35
Composition	mole %								
H2		26	26	18	18	26	26	22	22
CO		67	67	44	44	67	67	41	41
CO2		7	7	38	38	7	7	37	37
HHV	BTU/lb mole (77F)	113529	113529	75694	75694	113529	113529	76961	76961
Pipe ID	in	3	3	3	3	3	3	3	3
Tip Velocity	ft/sec	808	817	580	590	825	813	576	588

TABLE 3: RELEASE TO THE 1" VENT

CASE		1	2	3	4	5		7	8
Flow	lb/hr	10078		13370		10005		13006	
	lb mole/hr	458		458		455		463	
Temperature	F	170		-20		170		-15	
Pressure	psia	170		170		170		170	
Mole Wt	-	22		29.2		22		28.1	
Density	lb/ft3	0.553		1.052		0.553		1.001	
Cp	BTU/lb-F	0.35		0.35		0.35		0.35	
Composition	mole %								
H2		26		18		26		22	
CO		67		44		67		41	
CO2		7		38		7		37	
HHV	BTU/lb mole (77F)	113529		75694		113529		76961	
Pipe ID	in	1		1		1		1	
Tip Velocity	ft/sec	927		647		921		662	

TABLE 4: RELEASE PREDICTIONS WITHOUT METHANOL FLOW

KEY

time	Time into the event (sec)
mass	Vapor inventory in the plant (lb)
pres	Plant pressure (psia)
flow	Vapor flow into the 21.80 (lb/hr)
vent	Vapor flow to the vents (lb/hr)
liq add	Net volume of liquid added to the 21.80 (ft3)
tot liq	Cumulative liquid volume in 21.80 (ft3)

CASE 1

time	mass	pres	flow	vent	liq add	tot liq
0	905.3	1015	18210	18210	0.00	18.53
53	702.8	788	14150	14150	0.00	18.53
76	631.5	708	12560	12560	0.00	18.53
87	606.5	680	7760	7760	0.00	18.53
191	454.9	510	5720	5720	0.00	18.53
318	330.9	371	3830	3830	0.00	18.53

CASE 2

time	mass	pres	flow	vent	liq add	tot liq
0	905.3	1015	8460	8460	0.00	18.53
79	767.9	861	7160	7160	0.00	18.53
201	601.2	674	5600	5600	0.00	18.53
212	594.9	667	836	836	0.00	18.53
384	594.9	667	836	836	0.00	18.53

CASE 3

time	mass	pres	flow	vent	liq add	tot liq
0	869.8	975	11670	24150	0.00	18.53
63	718.9	806	9210	20260	-3.19	18.53
122	607.4	681	7770	17100	-5.75	15.34
128	599.4	672	4825	10620	-5.94	12.78
308	449.5	504	3555	7820	-9.82	12.59
522	328.2	368	2710	5310	-12.94	8.71

CASE 4

time	mass	pres	flow	vent	liq add	tot liq
0	869.8	975	5290	10960	0.00	18.53
148	726.0	814	4210	9270	-3.40	18.53
321	597.6	670	3480	7650	-6.80	15.13
329	594.9	667	836	1700	-6.89	11.73
384	594.9	667	836	1700	-7.09	11.64

TABLE 5: RELEASE PREDICTIONS WITH METHANOL FLOW

KEY

time	Time into the event (sec)
mass	Vapor inventory in the plant (lb)
pres	Plant pressure (psia)
flow	Vapor flow into the 21.80 (lb/hr)
vent	Vapor flow to the vents (lb/hr)
liq add	Net volume of liquid added to the 21.80 (ft3)
tot liq	Cumulative liquid volume in 21.80 (ft3)

CASE 5

time	mass	pres	flow	vent	liq add	tot liq
0	905.3	1015	18075	18075	0.00	18.53
52	709.1	795	14175	14175	1.73	20.26
77	630.6	707	12570	12570	2.58	21.11
86	611.0	685	7760	7760	2.86	21.39
190	457.6	513	5720	5720	6.36	24.89
317	333.6	374	3830	3830	10.61	29.14

CASE 6

time	mass	pres	flow	vent	liq add	tot liq
0	905.3	1015	8420	8420	0.00	18.53
79	769.7	863	7180	7180	2.63	21.16
198	604.7	678	5600	5600	6.63	25.16
214	595.8	668	836	836	7.14	25.67
475	595.8	668	836	836	15.88	34.41

CASE 7

time	mass	pres	flow	vent	liq add	tot liq
0	869.8	975	11350	23495	0.00	18.53
60	725.1	813	9660	20000	-1.35	17.18
117	611.9	686	8155	16880	-2.20	16.33
122	604.7	678	4940	10620	-2.23	16.30
300	452.2	507	3640	7820	-1.40	17.13
522	330.0	370	2480	5340	0.97	19.50

CASE 8

time	mass	pres	flow	vent	liq add	tot liq
0	869.8	975	5170	10700	0.00	18.53
155	718.9	806	4370	9040	0.61	19.14
306	600.3	673	3650	7550	1.72	20.25
318	595.8	668	836	1700	1.92	20.45
475	595.8	668	336	1700	5.37	23.90

Appendix F

AIR
PRODUCTS

EMORANDUM

o: D. M. Herron

Dept: PSG Process

rom: G. A. Peters

Dept/Ext: PSG Engineering Safety/8127

ate: 17 February 1992

ubject: CO_2 Vent Stack for Spring '92 Run - LaPorte AFDU

c: T. E. Conway
E. C. Heydorn
M. R. Jocsak

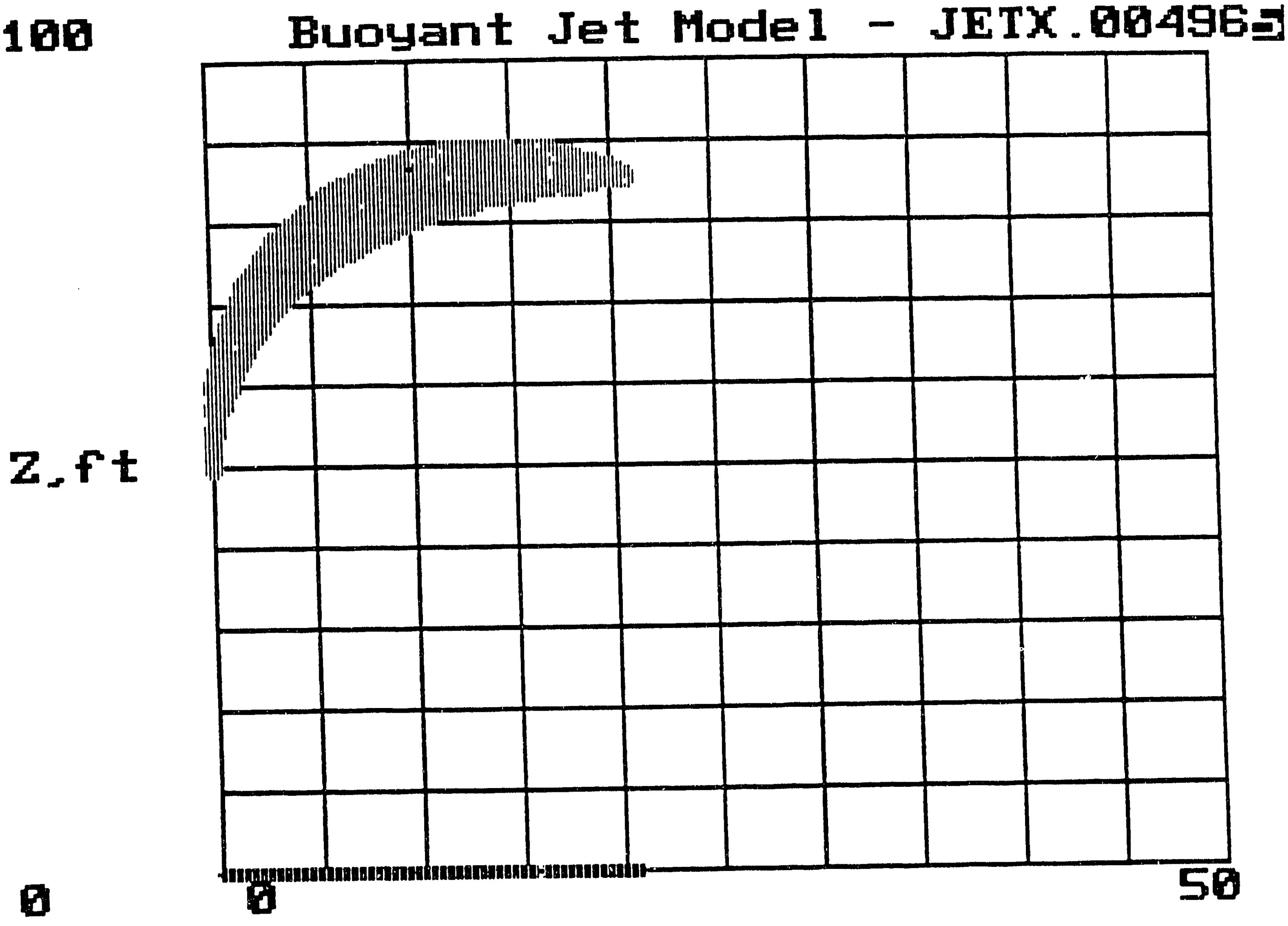
I have reviewed the CO_2 vent stack at the LaPorte AFDU for the release cases sent to me in your memo dated 11 February 1992 per your request. Using the release information provided, I have determined that the existing stack will not require any modifications for the Spring 1992 runs. The calculations have been performed for a stack that is 10 feet above the top operator platform.

Attached is some documentation supporting my conclusion. Attachment 1 includes the dispersion runs performed on the CO_2 releases from the 1" stack. The diagrams indicate that the CO_2 should not slump onto operating platforms at the release rates you provided. Attachment 2 is a graph of the radiation that can result from ignition of the releases as defined in cases 1 and 3 of your memo. The acceptable radiation level is 3000 BTU/hr-ft^2. Radiation levels slightly in excess of this level may be present at the upper most platform if the release occurs, the material ignites, the wind is blowing toward the platform, and an operator is present. As I recall, we made a commitment to limit operator access to the top platform during operation of the AFDU. This restriction should be enforced during the Spring 1992 runs.

I will be glad to provide any additional information on this issue.

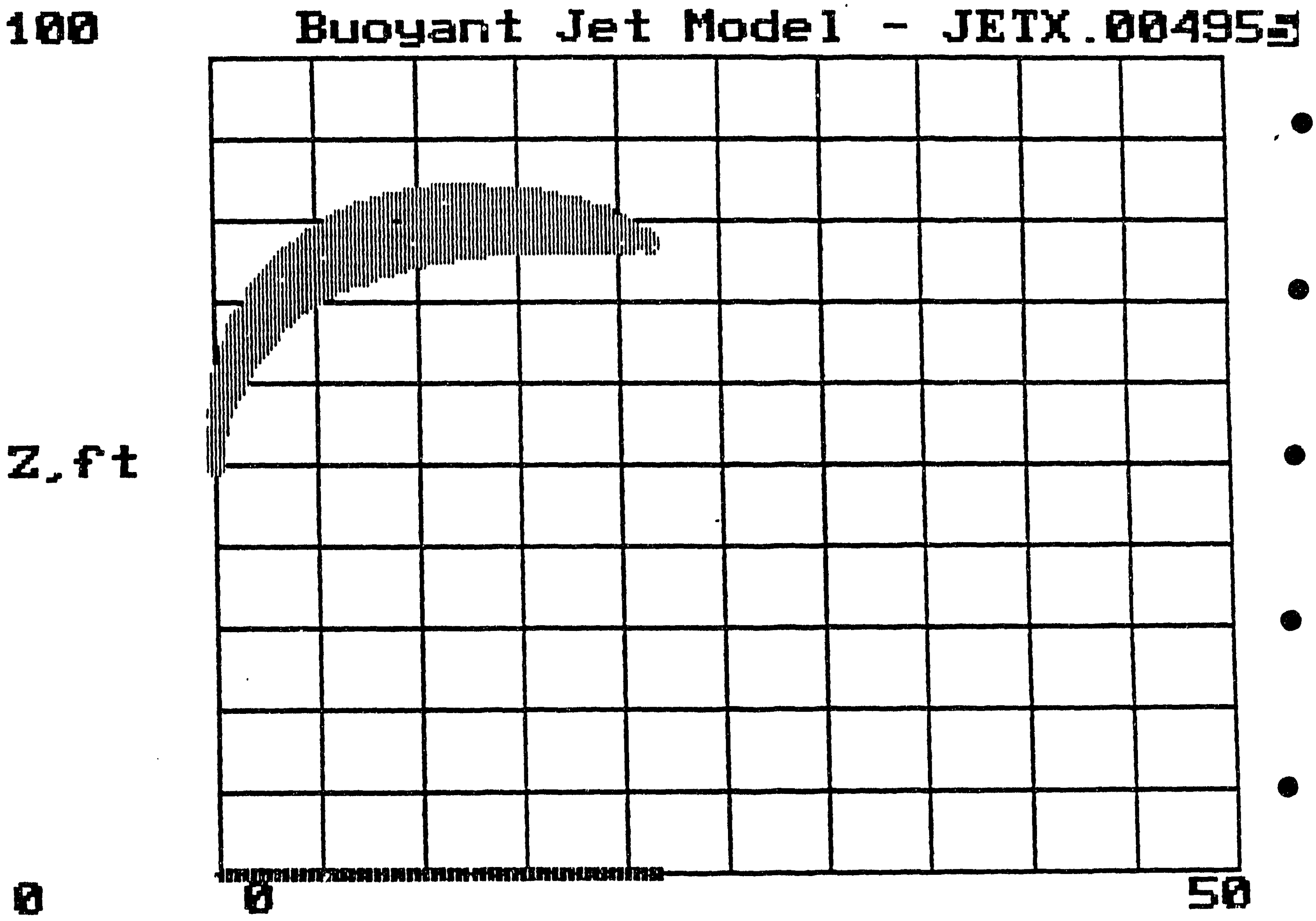
G. A. Peters

```
                  Buoyant Jet Model - JETX
                  LAPORTE AFDU CO2 VENT (1in)
          MAX. CO2 RELEASE CASE FOR SPRING '92 RUN (833 lb/hr)
 MDOT,lb/s        D,in           MW              LEL             UEL
 0.23000E+00      1.00000E+00    44.00000E+00    5.00000E-03     0.12500E+00
 UW,ft/s          TO,deg F       GAMMA(0)        RHOO,lb/ft3     STABILITY
 1.00000E+00      -6.50000E+01   89.99900E+00    0.15261E+00     6.00000E+00
 DS               1/Fr No.       Ta,deg F        UO,ft/s         ALPHA 3
 0.50000E+00      3.51087E-05    70.00000E+00    27.63295E+01    1.00000E+00
 MOLE FRACT       TUEL,sec       Z,ft            X,ft            MEX,lbs
 0.12404E+00      2.09859E-02    51.72908E+00    1.45380E-02     0.00000E+00
 MOLE FRAC        TLEL,sec       Z,ft            X,ft            MEX,lbs
 4.96478E-03      9.66173E+00    85.72976E+00    20.95962E+00    2.21737E+00
 GAMMA,deg        S,ft           U,ft/s          B,ft            Ho, ft
-1.78162E+01      48.06250E+00   1.11327E+00     13.29287E+00    50.00000E+00
 Isopleth Area, ft2 =      0.00000E+00           at Z =      0.00000E+00
          The Program Date is: 24 April, 1991 - Version 6.7
```

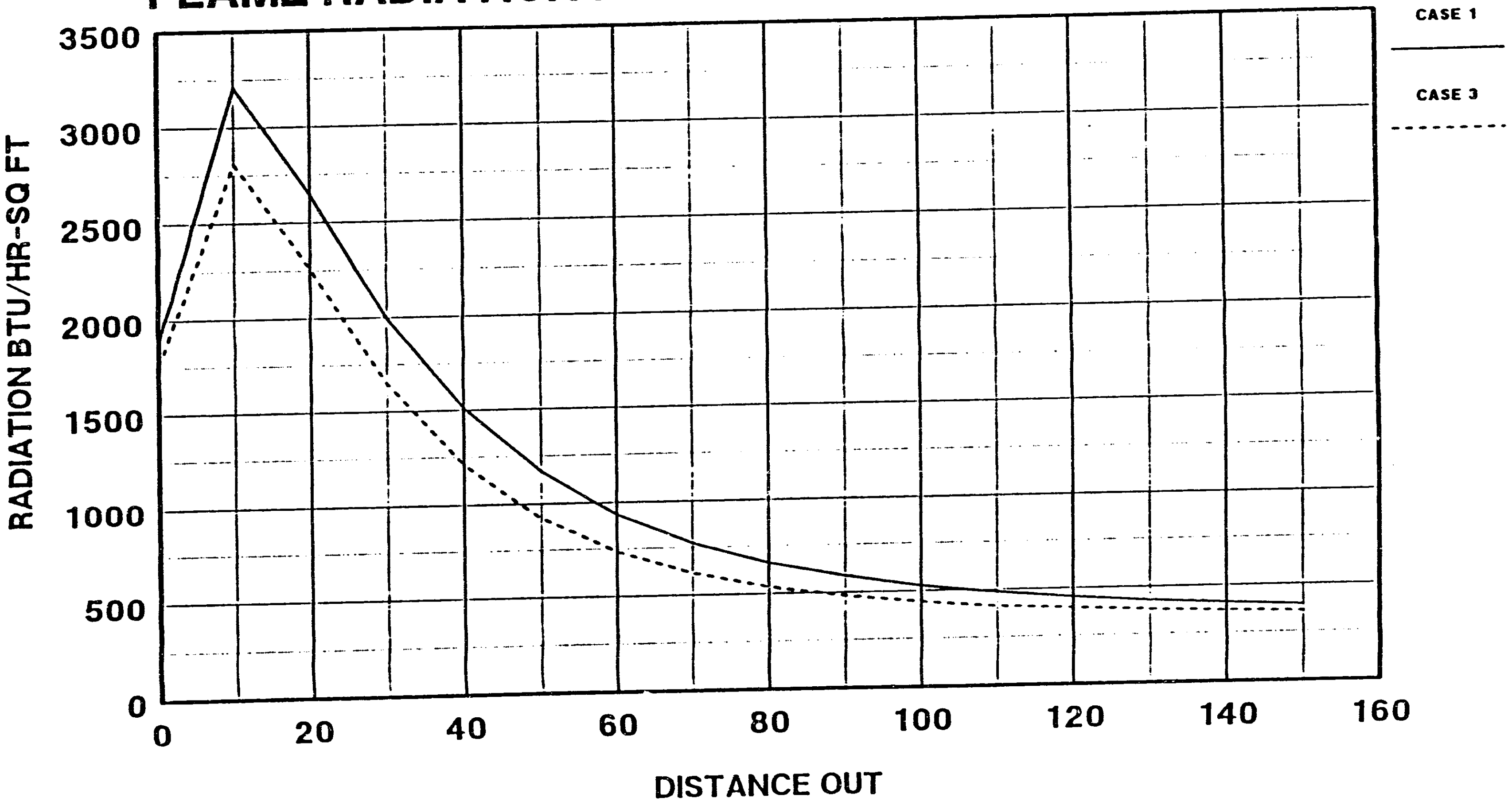


Buoyant Jet Model - JETX

```
            LAPORTE AFDU CO2 VENT (1in)
     MIN. CO2 RELEASE FOR SPRING '92 RUN (685 lb/hr)
MDOT,lb/s       D,in          MW             LEL            UEL
0.19000E+00     1.00000E+00   44.00000E+00   5.00000E-03    0.12500E+00
UW,ft/s         TO,deg F      GAMMA(0)       RHOO,lb/ft3    STABILITY
1.00000E+00     -6.50000E+01  89.99900E+00   0.15261E+00    6.00000E+00
DS              1/Fr No.      Ta,deg F       UO,ft/s        ALPHA 3
0.50000E+00     5.14474E-05   70.00000E+00   22.82722E+01   1.00000E+00
MOLE FRACT      TUEL,sec      Z,ft           X,ft           MEX,lbs
0.12403E+00     2.54115E-02   51.72905E+00   1.76278E-02    0.00000E+00
MOLE FRAC       TLEL,sec      Z,ft           X,ft           MEX,lbs
4.95460E-03     10.93143E+00  77.40084E+00   21.69444E+00   2.07214E+00
GAMMA,deg       S,ft          U,ft/s         B,ft           Ho, ft
-3.08401E+01    44.54167E+00  1.22100E+00    11.68291E+00   50.00000E+00
Isopleth Area, ft2 =     0.00000E+00        at Z =      0.00000E+00
      The Program Date is: 24 April, 1991 - Version 6.7
```



LAPORTE AFDU CO2 VENT TUBE RUPTURE CASE
VENT HEIGHT 10 FEET ABOVE TOP PLATFORM
FLAME RADIATION FOR CASES 1 & 3 SPRING '92 RUN



RADIATION FROM SUN OF 300 BTU/HR-SQ FT INCLUDED
WIND SPEED 27 MPH

17 February 1992

APPENDIX 2

DESIGN HAZARDS REVIEW REPORT
APRIL 1992 LIQUID PHASE SHIFT (LPS) RUN

Memorandum

AIR PRODUCTS

To: Distribution
Dept./Loc.: –
From: M.R. Jocsak MRJ
Dept./Ext.: Project Eng./3649
Date: 13 March 1992
Subject: Design Verification Review Report
April 1992 Liquid Phase Shift (LPS) Run

Distribution:

W.C. Allen (MC#83)
A.G. Barbieri
D.M. Brown
T.E. Conway
E.C. Heydorn (LaPorte AFDU)
T. Hsiung/R.P. Underwood
G.A. Peters
D.M. Herron – Proc Eng.
E. Schaub/B. Bhatt/D. Studer
R.L. Williams

Attached is a copy of the Design Verification Review report for the Liquid Phase Shift (LPS) demonstration at the Alternative Fuels Development Unit (AFDU) in LaPorte, TX.

Most of the hazard items have been satisfactorily addressed and included in the plant design and/or operating procedures. The status of all action items will be reviewed during the ORI-Safety Audit.

Please contact me if you have any questions or comments.

MRJ/029

RECEIVED
MAR 18 1992
PROCESS ENGINEERING

DESIGN VERIFICATION REVIEW (DVR)

Alternative Fuels Development Unit (AFDU)

April 1992 Liquid-Phase Shift (LPS) Run

LaPorte, Texas

11 March 1992

Review Team

T. E. Conway	Start-Up Engineering
D. M. Herron	Process Engineering
E. C. Heydorn	Operations
M. R. Jocsak	Project Engineering
G. A. Peters	PSG Safety Engineering

Design Verification Review (DVR)
Alternative Fuels Development Unit (AFDU)
April 1992 Liquid Phase Shift (LPS)
LaPorte, Texas
11 March 1992

Table of Contents

Page No.

I. Introduction 1

II. Status of Hazard Items 1

Appendices

A. E.S. Schaub, 13 March 1992 memo, Review of tube rupture anlysis.

B. G.A. Peters, 10 March 1992 memo, CO_2 Vent Stack safety review.

References

1. Design Hazards Review Report (DHR) - 3 March 1992 (LPS)
2. Engineering Flowsheet (P&ID) for the Spring '92 Liquid Phase Shift DEMONSTRATION - ATT1016C, revision 1, March 10, 1992
3. Engineering Flowsheet (P&ID) 87-7-1533, Liquid Phase Methanol, revision 15, 19 September, 1991.
4. FCN (to F/S 87-7-1533) #'s: 31, 32, & 33.

I. INTRODUCTION

A Design Verification Review (DVR) meeting was conducted on 11 March 1992 for the April 1992 Liquid Phase Shift (LPS) run.

The meeting was conducted by first reviewing the Rev. 1 P&ID and preliminary FCN's and then addressing hazard items. All of the hazard items identified for the iso-butanol demonstration were addressed and a determination was made as to their relevance to the LPS run. In addition, several new hazard items were discussed.

III. STATUS OF HAZARD ITEMS

The following lists the status of each hazard item as discussed during the DHR meeting.

LIQUID PHASE SHIFT (LPS) DEMONSTRATION
APRIL 1992
Alternative Fuels Program
LaPorte, TX AFDU

Hazard	4 November 1991 IBOH DHR and 21 February 1992 IBOH DVR Status	3 MARCH 1992 LPS Design Hazards Review (DHR)	11 MARCH 1992 LPS Design Verification Review
1. Rupture or damage of methanol injection source caused by backflow of reactor effluent into the methanol injection system (10.85).	The design of the injection system includes two check valves on the discharge of the 10.85 injection pump. In addition, the 10.85 (a diaphragm pump) is equipped with two ball-type check valves. Safety valve(s) were installed to prevent overpressure of trailers. The team agreed that this design will provide adequate protection for the trailers from overpressurization.	Injection point has been relocated to line 2"-FG-900 (upstream of the 21.38). The source of the methanol has been relocated to the discharge of LV-693 (on 1"-L1-911). The 22.11, 22.18, and 28.40 are all adequately protected from overpressure with safety valves. The rundown line (1"-L1-911) has be changed to CS14 with the exception of the flange and valve at the 28.40 (CS7.2). To protect these items, this valve should be locked open during operations - even though plant pressure should not exceed 600 psig during normal operations..	Ensure subject valve is included in valve/blind check sheet.
2. Uncontrollable fire in the trailer loading/unloading areas due to a spill or leak and insufficient fire protection.	The current design is based on utilizing a single trailer. This design results in zero net increase in on-site trailer inventory levels from previous operating campaigns, thus it was agreed that in the event of a fire, the existing fire monitor will provide adequate fire protection in the trailer loading/unloading area.	No change.	No change.

LIQUID PHASE SHIFT (LPS) DEMONSTRATION
APRIL 1992
Alternative Fuels Program
LaPorte, TX AFDU

Hazard	4 November 1991 IBOH DHR and 21 February 1992 IBOH DVR Status	3 MARCH 1992 LPS Design Hazards Review (DHR)	11 MARCH 1992 LPS Design Verification Review
3. Fire caused by undetected leakage of methanol from the 10.80 methanol recycle pump.	The 10.80 circulation pump is a high speed centrifugal pump and will be equipped with a thermo-siphon low-pressure barrier fluid system. Jim Koniski (Machinery Applications presented and reviewed the mechanics of the pump and associated seal system with the Hazard Review Team. Refer to the 10.80 pump bid evaluation for a technical description of this pump. The barrier fluid pot will be equipped with a low level and high pressure SD-1A interlock to shutdown the pump in the event of an excessive seal leakage.	No change.	Confirm that all shutdowns identified during this hazards review process have been installed and commissioned during the ORI.
4. 01.20 recycle compressor wreck due to liquid entrainment caused by a failure of LV-688 resulting in an overfill of the 22.14 separator vessel.	A high level SD-1A interlock (LSHH-688) has been included in the design of the 22.14 to close the 10.80 flow control valve. This will prevent further flow to the 22.14. In addition, a low temperature alarm (TAL-233) will be installed to provide early warning of low temperature gas entering the 01.20 recycle compressor in the event of an upset condition.	LSHH-688 will be retained. TAL-233 is redundant and will not be installed. In the event LV-688 fails closed the inventory in the 22.18 will drain and begin to dump it's liquid into the 22.14. If 22.18 drains completely (into 22.14) the aerated liquid will still be contained, and entrainment will be low (Ks=0.023 ft/sec). However, prior to the 22.18 draining, a low level SD-1A interlock (LSLL-693) will shut the plant down (providing redundancy). Finally, a demister is supplied at the suction of the 01.20.	Refer to item #3 status.
5. Process upset caused by improper blind and block valve positions.	Update the existing block valve and blind checklist prior to ORI. (Action: Operations)	No change.	No change.

Hazard	4 November 1991 IBOH DHR and 21 February 1992 IBOH DVR Status	3 MARCH 1992 LPS Design Hazards Review (DHR)	11 MARCH 1992 LPS Design Verification Review
6A. Runaway reaction in the 27.10 reactor vessel caused by a loss of oil flow or fin fan in the utility oil loop.	In the event of a loss of reactor cooling, it is possible to exceed the design temperature limits. However, because the reactor is equipped with three independent on-line hard-wired high temperature shutdowns, this hazard was determined to be adequately protected. In addition, it was assumed that operations will ensure these shutdowns are adequately calibrated and tested prior to each operating campaign that is preceded by an extended plant outage. Process Engineering has documented a justification for the proposed alarm set points. It was agreed that for future operating campaigns, the plant can be run up to its design limits (1000 psig, 600°F). It was noted that during the *LP III* methanol campaign, the plant was safely run at 546°F with no *significant* evidence of carbonyls or methane present.	The water gas shift reaction is exothermic and equilibrium limited. The per-pass extent of reaction is constrained by the limiting reactant, either water or CO. Process has calculated that the time required for the reactor to reach 600 F (from the normal operating temperature of 482 F) is between 13 and 24 minutes should loss of coolant occur. The shift catalyst used has properties similar to that of BASF-S-386: the components are the same and the catalyst deactivates (sinters) at elevated temperature. The tendency for methanation activity is equally low with this catalyst. *A possible side reaction with this catalyst is* methanol synthesis (also an exothermic, equilibrium limited reaction). Rising temperatures retard the methanol step more-so than the shift step. No change in status	No change in status.

LIQUID PHASE SHIFT (LPS) DEMONSTRATION
APRIL 1992
Alternative Fuels Program
LaPorte, TX AFDU

Hazard	4 November 1991 IBOH DHR and 21 February 1992 IBOH DVR Status	3 MARCH 1992 LPS Design Hazards Review (DHR)	11 MARCH 1992 LPS Design Verification Review
B. Runaway reaction in the 27.10 reactor vessel caused by failure of the steam flow control valve (FV-840).	Not applicable.	Process has calculated that the time required for the reactor to reach 600 F (from the normal operating temperature of 482 F) is between 9 and 28 minutes should excess steam be inadvertently added without any response from the utility oil cooling loop. CO becomes the limiting reactant in this case. No change in status	No change in status.
7. Personnel exposure to the new catalyst that will be used in the 27.10 reactor (BASF K3-110).	Not applicable.	The materials which make-up this catalyst are CuO (40%), ZnO (40%), and Al2O3 (20%) - the same materials used to make S-386. T. H. Hsiung (PSG R&D) advises that the handling procedure is the same as for S3-86. A MSDS sheet is included in Appendix B.	No change in status.

LIQUID PHASE SHIFT (LPS) DEMONSTRATION
APRIL 1992
Alternative Fuels Program
LaPorte, TX AFDU

Hazard	4 November 1991 IBOH DHR and 21 February 1992 IBOH DVR Status	3 MARCH 1992 LPS Design Hazards Review (DHR)	11 MARCH 1992 LPS Design Verification Review
8. Equipment or piping system corrosion or damage caused by the presence of water and CO_2 in addition to methanol in the system downstream of 27.10 reactor.	Not particularly applicable	CO2 in water is potentially corrosive to carbon steel. Corporate engineering has estimated a corrosion rate of 200 mils/year at a CO2 partial pressure over water of 200 psi. All the vessels in question are built with corrosion allowance (1/8" for 22.10, 22.11 and 22.15, for example). The recommendation is to monitor the plant for signs of leakage during this 10-day operating campaign and to inspect affected carbon vessels for signs of corrosion prior to subsequent operations. (Action: Operations).	No change in status. (Document that inspections have been taken at ORI.)
9. 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.	Operations to measure wall thickness prior to plant operation. It was noted that during the DME run, the vessel's process discharge flange began leaking process fluid. The leak was repaired by applying a sealing compound to the flange surface. Action will be taken to investigate the compatibles of Loctite Master Gasket. Completion to be verified during ORI (Project/Operations)	The recommendation is that the vessel be inspected for signs of pitting as an indication of corrosion. Based upon the results of this inspection further action may be required (such as measuring wall thickness). (Operations) Action will be taken to investigate the compatibles of Loctite Master Gasket. Completion to be verified during ORI (Project/Operations)	No change in status.

LIQUID PHASE SHIFT (LPS) DEMONSTRATION
APRIL 1992
Alternative Fuels Program
LaPorte, TX AFDU

Hazard	4 November 1991 IBOH DHR and 21 February 1992 IBOH DVR Status	3 MARCH 1992 LPS Design Hazards Review (DHR)	11 MARCH 1992 LPS Design Verification Review
0. 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 CO2 exchanger's (21.80) temperature control system.	Maintain the existing low temperature alarm (TAL-233).	In addition to the pressure control of the 21.80 refrigerant, a low temperature shut down is incorporated on the 22.14 (TSLL-689) to maintain temperatures no lower than 0 F. Item 10 is a carry-over from the '91 DME Run. In that run the bypass around the 21.38 exchanger (TV-684) created the potential for low temperature at the 01.20 suction. Since that run, the bypass around the 21.38 has been removed and so has the potential for the cold gas from the 22.14 to exit the cold-end without being reheated. The avoidance of cold temperatures at the 01.20 is achieved by retaining the cold-temperature switch (TSLL-689) and the low CO2 pressure switch (PSL-690) - both invoke SD-1A. TAL-233 will not be required for this hazard.	No change in status.

LIQUID PHASE SHIFT (LPS) DEMONSTRATION
APRIL 1992
Alternative Fuels Program
LaPorte, TX AFDU

Hazard	4 November 1991 IBOH DHR and 21 February 1992 IBOH DVR Status	LPS Design Hazards Review (DHR)	11 MARCH 1992 LPS Design Verification Review
11. Deposition and freezing of water on the tubes of the 21.38 exchanger may result in exchanger blockage or loss of performance. Loss of performance may result in exposing the suction side of the 01.20 to low temperatures.	Not applicable.	Complete exchanger blockage would effectively block-in the front-end. Numerous safety valves are provided for this event. The first to trip would be PSV-150 at the feed compressor discharge. Partial blockage of the exchanger, or plating-out of ice on the tubes, would result in loss of heat transfer performance and a gradual cooling at the 01.20 suction if no corrective action is taken. As a result, the 10.85 pump will be used to inject methanol into the gas stream prior to it's introduction to the 21.38. The injection flow to water flow ratio will be a minimum of 15 to 1 (lb/lb) at 0.2 gpm and can be increased to 150 to 1. Due to the low water content in the gas and large surface area in the 21.38, performance degradation due to ice deposition on the tube walls will be a slow process (0.15 inches/day). TAL-233 will be installed for this operation.	No change in status.

LIQUID PHASE SHIFT (LPS) DEMONSTRATION
APRIL 1992
Alternative Fuels Program
LaPorte, TX AFDU

Hazard	4 November 1991 IBOH DHR and 21 February 1992 IBOH DVR Status	3 MARCH 1992 LPS Design Hazards Review (DHR)	11 MARCH 1992 LPS Design Verification Review
12. Carry over of catalyst into equipment (new and existing) downstream of 27.10 reactor could cause a reaction.	Process Engineering has concluded that this issue is not a significant hazard. The analysis performed assumed that 20% of the catalyst volume is carried over. In addition, it was assumed that the carry-over catalyst is equally as active as in the reactor. (PSG R&D advises this assumption is very conservative.) The calculated result of this carryover is a 60°F temperature rise. This would be negated by ambient heat leak which can be as much as 80°F.	Process Engineering has concluded that this issue is not a significant hazard. The analysis performed assumed that 20% of the catalyst volume is carried over. In addition, it was assumed that the carry-over catalyst is equally as active as in the reactor. (PSG R&D advises this assumption is very conservative.) The calculated result of this carryover is a 10 to 74°F temperature rise. This would be negated by ambient heat leak which can be as much as 80°F.	No change in status.
13. 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 CO2 exchanger (21.80). The vessel is 1-1/4 Cr - 1/2 Mo construction.	This hazard also applies to the 22.18 and 21.38 vessels. The recommendation is to maintain the existing SD-1A protection interlock circuit. In addition, the "fitness for services" analysis documented by J. C. Tafuri was revisited. Process Engineering has advised J. F. Tafuri of the run plans and the 22.14, 22.18, and 21.38 vessel materials have been determined acceptable for the Spring '92 run.	Severity of service remains unchanged.	No change in status.
14. Liquid carry-over from the 22.18 separator vessel vent to downstream equipment due to a failure of the vessel's LIC.	A hazard associated with the thermal effects does not exist. The minimum (upset) low temperature exposure in the event of a liquid carry-over is 40°F.	No change	No change in status.

LIQUID PHASE SHIFT (LPS) DEMONSTRATION
APRIL 1992
Alternative Fuels Program
LaPorte, TX AFDU

Hazard	4 November 1991 IBOH DHR and 21 February 1992 IBOH DVR Status	3 MARCH 1992 LPS Design Hazards Review (DHR)	11 MARCH 1992 LPS Design Verification Review
15. Equipment or piping overpressurization due to the presence of a different process fluid composition and an inadequacy of existing relief devices.	The review of existing and new relief valves was complete with the exception of the following two issues: 1. The relief valves provided with the liquid CO2 storage tank need to be reviewed. 2. PSV-236A/B are inadequate in the event LV-693 fails open. New trim will be installed on LV-693 prior to the run in order to reduce the maximum flow so that PSV-236A/B will be sufficient.	The review of existing and new relief valves is complete with the exception of the following issue: 1. The relief valves provided with the liquid CO2 storage tank need to be reviewed. 2. The tube rupture cases for cooling water exchangers must be reviewed. 3. PSV-236A/B need to be reviewed.	1. CO2 tank review is outstanding (to be confirmed during ORI). 2. All tube rupture cases have been reviewed and determined to be acceptable. Refer to Appendix A, E.S. Schaub memo). 3. PSV-236A/B are adequate for this run.
16. Methanol storage tank (28.10) fire.	The current plan now includes using the U/G methanol tank, but it was agreed that the existing fire monitor will provide adequate protection.	No change.	No change.
17. 28.40 (Alternative Fuel) storage tank fire (external) caused from a leak, overfill, or open drain valve.	The 28.40 will be used to store make-up MeOH. There is no change in the hazard status.	No change.	No change.
18. 21.80 Vent Stacks a) Exposure of personnel to hazardous levels of CO2 during normal or upset operating conditions.	Process Engineering has documented the CO2 release flows and the 21.80 tube-rupture syngas release flows. In response, Safety Engineering has reviewed these scenarios and has determined that the existing vent stack is adequate	Process has transmitted flows to Safety for review. Refer to Appendix C.	Both CO2 (a) and flame radiation (b) cases have been reviewed by Safety and determined acceptable. Refer to Appendix B.

LIQUID PHASE SHIFT (LPS) DEMONSTRATION
APRIL 1992
Alternative Fuels Program
LaPorte, TX AFDU

Hazard	4 November 1991 IBOH DHR and 21 February 1992 IBOH DVR Status	3 MARCH 1992 LPS Design Hazards Review (DHR)	11 MARCH 1992 LPS Design Verification Review
b) Exposure of personnel to hazardous levels of flame radiation from the venting fluid (21.80 tube-rupture case)	The recommendation is to restrict personnel access from the top platform during the run.	Process has transmitted flows to Safety for review. Refer to Appendix C.	
9. Failure or rupture of the purge nitrogen system due to inadequate protection.	The low pressure alarm setpoint of the protected nitrogen header needs to be verified as being consistent with APCI standards during the ORI.	No change	No change
20. 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.	The TSH-309 shutdown interlock will be maintained (21.30 discharge).	No change	No change
21. Failure of the SD-1A protection circuit due to an unauthorized activation of the bypass switch.	A software protection system will be built into the DCS configurations so that access to the SD-1A bypass switch is controlled. A possible solution is to install a password. Process Controls Engineering will document the protection systems that will be followed prior to the ORI.	Access to the SD-1A bypass switch is suitably limited. In addition, the DCS memory is non-volitale, so the switch will return to its current setting after return from a power loss. Refer to memo from D.A. Kosciusko in Appendix D.	All hardwire bypass switches will be included on the jumper log maintained by Operations.

LIQUID PHASE SHIFT (LPS) DEMONSTRATION
APRIL 1992
Alternative Fuels Program
LaPorte, TX AFDU

Hazard	4 November 1991 IBOH DHR and 21 February 1992 IBOH DVR Status	3 MARCH 1992 LPS Design Hazards Review (DHR)	11 MARCH 1992 LPS Design Verification Review
22. Exposure of personnel to hot liquids or fire near the 15.90 flare area due to liquid flooding caused by undetected product trailer overfill.	The loading flare (15.90E) will not be equipped with a liquid knock-out pot. The product loading operations will be administratively controlled by AFDU Operations Management. A level gauge (site gauge) will be included in the design of the product collection system (as well as the alcohol injection system). The HR team concludes that this level of control is sufficient due to: (a) the small total number of trailers to be filled during the run (4-8 fillings), (b) the relative volume of the "day" tank vs. the volume of the trailer product compartment, and (c) the filling will be performed in a batch mode through the "day" tank.	No change	No change
23. Flow of syngas into and overpressure of the new HP steam header due to tube rupture in 02.61 and/or backflow into the steam injection line.	Not applicable	A safety valve, PSV-843, has been provided for protection. In both events, flow is minimized due to the installation of check valve(s).	Process Engineering will review the 02.61 tube rupture case during the reduction process. ORI will confirm the action.

LIQUID PHASE SHIFT (LPS) DEMONSTRATION
APRIL 1992
Alternative Fuels Program
LaPorte, TX AFDU

Hazard	4 November 1991 IBOH DHR and 21 February 1992 IBOH DVR Status	3 MARCH 1992 LPS Design Hazards Review (DHR)	11 MARCH 1992 LPS Design Verification Review
4. Uncontrolled flow of HP steam into the process during a flow control valve failure or shutdown.	Not applicable	The uncontrolled flow of high pressure steam (640 psig max) does not present a significant safety hazard (see item 6B) although free water in the reactor is detrimental to the catalyst. FV-840 will be driven closed under SD-1 and SD-2.	No change in status.
5. Overpressure of the supplemental flare line due to excessive flow and/or plugging of the flare tip..	Not applicable	a) In the event the throttling valve V-2287 is wide open at 1000 psig operating pressure, the pressure in the line could reach 130 psig. All material in this line is good for CS2.7. b) The flare will be flow-checked with nitrogen during shakedown to confirm no plugging exists.	No change in status.
26. Overpressure of associated lines and equipment during the event described in 25.	Not applicable	Both the nitrogen sweep and the trailer loading area are protected with safety valve(s). To minimize the release rate, multiple check valves have also been installed.	No change in status.

LIQUID PHASE SHIFT (LPS) DEMONSTRATION
APRIL 1992
Alternative Fuels Program
LaPorte, TX AFDU

(The following item is not considered a hazard but is documented for the purpose of maintaining a record of the entire meeting discussions.)

Hazard	4 November 1991 IBOH DHR and 21 February 1992 IBOH DVR Status	3 MARCH 1992 LPS Design Hazards Review (DHR)	11 MARCH 1992 LPS Design Verification Review
27. 21.80 vent noise levels	No design action was recommended. If high noise levels are encountered, the flow of CO2 will be reduced to reduce the noise levels.	No change	No change

APPENDIX 3

LITERATURE SEARCH ON DEHYDRATION OF ISOBUTANOL TO ISOBUTYLENE

Memorandum

To:	T.H. Hsiung	Dept./Loc.:	PG&E Research/Iron Run
From:	B. E. Latshaw	Dept./Ext.:	PG&E Research/3995
Date:	24 March 1992		

Subject: Literature Report and Related Information - Dehydration of Isobutanol to Isobutylene

---

cc: D. M. Brown
T. W. Copeman
D. M. Herron
R. P. Underwood
F. J. Waller

SUMMARY:

A thorough literature search was performed to obtain information on the dehydration of isobutanol to isobutylene. Because of the limited information available on this particular reaction, the search strategy was broadened to the dehydration of alcohols to alkenes with special interest in obtaining information on the catalyst, reactor type, and reaction conditions used in the work. Work on the dehydration of ethanol was not included because of the lack of correlation between the mechanisms followed for the dehydration of ethanol and isobutanol, i.e. isomerization is an important factor for isobutanol.

A number of catalysts have been used in the literature to study the dehydration of alcohols to alkenes. These catalysts can be divided into four groups: aluminas and modified aluminas, zeolites, metal phosphates and sulfates, and oxides. Alumina has been the most widely used dehydration catalyst and has been implemented into at least two pilot plant operations for the dehydration of isoamyl alcohol. From this information, it appears that the catalysts best suited for the dehydration of isobutanol would be a treated alumina or possibly just a less pure gamma-alumina, a phosphate or sulfate modified zirconia, or a calcium phosphate. These catalysts were specified because of their inactivity for producing the butanol isomers during the course of the reaction. The reaction conditions obtained from the literature indicate temperatures ranging from about 300 to 400 C and pressures around atmospheric. The thermodynamic calculations for the dehydration of isobutanol show that the reaction is endothermic and therefore, requires the higher temperatures in order to obtain a reasonable conversion. According to the literature, the majority of the work has been performed in packed bed reactors; however, a limited amount of literature has been found which describes a process for the dehydration of tertiary-butyl alcohol utilizing a slurry phase reactor. Attempts are being made to obtain more information on this matter. It was difficult to make any reasonable conclusions in regard to the catalyst life expectancy. It appears that the occurrence of side reactions which lead to carbon formation on the catalyst surface should be inhibited by the absence of strong acid sites.

INTRODUCTION:

The dehydration of isobutyl alcohol to isobutene is an important reaction because of the use of isobutene as a feed stock for the production of methyl tertiary butyl ether (MTBE). Since it has been shown that isobutyl alcohol can be successfully produced from coal derived syngas, the next step to the production of MTBE is to develop the dehydration process of isobutanol. A literature review of the dehydration of isobutyl alcohol has been conducted; however, there does not appear to be a large amount of information on this specific reaction. In regard to this fact, an expanded view of the literature was undertaken to obtain any available information on the dehydration of alcohols with a similar carbon structure, i.e. 2-methyl-1-alkanols. The desired product of the dehydration reaction is isobutene (2-methyl-1-olefin), but it is quite possible to obtain all of the butene isomers. Thus, a catalyst and reaction conditions need to be determined which will give isobutene as the primary product and inhibit to a large extent any isomerization from occurring.

DEHYDRATION REACTION:

Since the dehydration mechanism is undoubtedly a function of both the structure of the catalyst as well as the structure of the alcohol, a single reaction mechanism cannot be established. According to the literature though, alumina appears to have been the most widely used dehydration catalyst and therefore, the most widely studied. In order to obtain some insight into the reaction mechanism, information will be presented on the dehydration of alcohols over alumina with specific reference to isobutanol when applicable.

In general, dehydration of alcohols occurs over an acid catalyst. On alumina, two different acid sites are present, namely Lewis and Bronsted. The Bronsted acid sites result from the surface hydroxyl groups and are considered on average to be weakly acidic.[1] The Lewis acid sites result from the incomplete coordination of surface aluminum atoms by surrounding oxygen atoms.[2] These incompletely coordinated aluminum atoms arise due to removal of the surface hydroxyl groups through condensation with adjacent hydroxyl groups and evolution of water. This removal of surface water also creates Lewis base sites which are oxygen ions.[2]

The adsorption of the alcohol to the surface occurs through hydrogen bonds between the alcohol hydroxyl group and the surface hydroxyl group and oxide ion.[3] At this point it is believed that the reaction scheme is slightly different depending on the structure of the alcohol.[3] The schemes proposed are based on the fact that the alumina contains only weak to moderate acidic sites and thus the reaction can be compared to dehydration in dilute aqueous acids. Taft et al.[4] found that tertiary alcohols abstract the hydrogen from the acid forming a carbonium ion basically free of covalently bonded water. Less stable secondary carbonium ions were found to be stabilized by specific interaction with two water molecules indicating a more concerted mechanistic character.[5] Dostrovsky and Klein[6] determined that oxygen exchange with primary alcohols in dilute acid solution occurred through a concerted mechanism and not by way of a carbonium ion.

The mechanism of dehydration for a primary alcohol such as isobutanol occurs through abstraction of the β-hydrogen of the alcohol by the surface oxide ion with subsequent cleavage of the alcohol hydroxyl group forming water and a surface oxide ion.[7] This mechanism has been concluded through a number of experimental observations. Knozinger[8] found that if aluminum hydroxide (which exposes solely hydroxyl groups at the surface) is used as the catalyst, there is complete inactivity for the dehydration of tertiary butanol. However, if the catalyst is heated such that the trihydroxide losses water to form the monohydroxide resulting as well in the formation of oxygen and aluminum ions, the dehydration reaction is observed. This indicates that other surface sites must take part in the formation of olefins. It has also been shown that selective poisoning of the Lewis acid sites by pyridine does not significantly alter the dehydration of alcohols.[8] Roca et al.[9] on the other hand have verified the participation of basic sites by poisoning experiments with tetracyanoethylene.

The rate limiting step during the dehydration reaction has been studied by Knozinger and Scheglila.[10] By examining primary kinetic isotope effects for the dehydration of tertiary, secondary, and iso-butanol in the gas phase, they determined that deuteration of the hydroxyl group does not cause an isotope effect and thus excludes the hydroxyl proton from any rate determining participation. This result also excludes the desorption of water as being rate determining at least in the case where the water is adsorbed by hydrogen bonds to hydroxyl or deuteroxyl surface groups. The kinetic isotope effect for β-carbon deuteration was greatest for the primary isobutanol and least for tertiary butanol. At temperatures below 200 C, they believe that all three alcohols exhibit E 2-like behavior, but as the temperature is raised the mechanism for tertiary alcohol shifts to E 1-like. An E2 reaction mechanism involves a single transition state in which the base pulls a proton away from the carbon while the hydroxide ion simultaneously departs allowing the double bond to form. The E1 reaction mechanism however, involves two steps whereby the alcohol undergoes cleavage of the hydroxyl ion with formation of a carbonium ion. This carbonium ion then loses a proton to the base to form the alkene. The results presented by Knozinger and Scheglila[10] reaffirm the mechanisms postulated earlier by Pines and Manassen[3] for the dehydration of tertiary, secondary, and primary alcohols on weak acid sites.

The mechanism for dehydration is not the same for all alcohols. Arai et al.[11] found while studying the dehydration of ethanol that at low temperatures (T<135 C) the major product desorbed from the alumina catalyst was diethyl ether. At higher temperatures they found a decrease in ether formation and an increase in ethylene formation. They postulated that the ether was formed by reaction of two nearby surface ethoxides. The presence of the surface ethoxides was verfied through IR studies. Knozinger and Kohne[12] however, found ethylene to be produced only above 250 C during ethanol dehydration. They believed that the ethylene was formed directly from dehydration as well as through decomposition of the ether. As the temperature was increased, the ether composition decreased significantly. The difference between the two findings is most likely a result of slight variations in the catalyst as well as the fact that Knozinger and Kohne performed continuous operation while Arai et al. performed batch experiments. Knozinger and Kohne proposed that the ether formed by reaction of an adsorbed alcohol with a surface ethoxide. They found a similar behavior for straight-chained alcohols up to n-hexanol; however, the temperature range in which ether could be isolated as the only product decreased with increasing chain length. They were also unable to detect any ether as a dehydration product of the branched butanols. This appears to be due to the instability of the alkoxide of the branched butanols. Surface alkoxides were detected by IR spectroscopy for the ether-forming alcohols whereas no surface alkoxide could be detected for the olefin-forming alcohols.[2] Thus it appears that the dehydration of isobutanol over alumina occurs through the concerted mechanism proposed by Pines and Haag.[7]

The E 2-like mechanism for dehydration of primary and secondary alcohols has been fairly well accepted. It is the transition state during the dehydration of the alcohol which appears to still be in question. Pillai and Pines[13] as well as Kibby et al.[14] had determined that alcohol dehydration on γ-alumina occurs as the trans-elimination of the elements of water. It has also been found that when formation of the cis- and trans- isomers is possible, the cis-olefin forms preferentially.[2,3,7] From the results of selectivity studies, Schwab and Schwab-Agallidis[15] proposed that the dehydration proceeded in pores and crevices of the catalyst. This view was also taken by Pines and Manassen[3] and Pines and Pillai[16] on the assumption that acidic and basic sites would be located on opposite sides of the pore. This scheme would indicate a reaction controlled by diffusion which has never been observed for alumina. Knozinger et al.[17] proposed that the alcohol molecule adsorbed onto the surface exercises as a whole vibrational motions, such that the $O\text{-}C_{\alpha}\text{-}C_{\beta}\text{-}H$ plane inclines to the surface. This would lead to the sterically more favorable conformation where bulky substituents are farthest away from the surface leading to preferential cis formation. Sedlacek and Kraus[18] have determined from quantum chemical modelling using the adsorbed state proposed by Knozinger et al.[17] that anti-elimination is the more energetically favorable path on the alumina surface. Sedlacek[19] was also able to explain the significant preference for cis-olefin formation by taking into account geometric and electronic factors.

It appears that an E2 reaction mechanism is followed for the dehydration of isobutanol on alumina. According to Pines and Haag[7] as well as Knozinger and Scheglila[10], it appears that pure β-H elimination occurs to form the primary dehydration product. This olefin product may then readsorb onto the strong acid sites where it may undergo isomerization. It is also assumed that oligermization occurs on these strong acid sites when the olefin is readsorbed. This most likely can be avoided by either running at lower conversions so as to avoid the olefin concentration from building up to a point where the probability of readsorption becomes high or by selectively poisoning the strong acid sites. Running at lower conversions was proposed due to the observed increase in isomer composition with increased contact time. It is also possible that at higher temperatures (T>300 C) γ-H elimination may occur with sebsequent migration of the hydrogen or methyl group forming a number of isomers.[20]

DEHYDRATION CATALYSTS AND REACTION CONDITIONS:

The information presented in this section has been divided into subsections according to the type of catalyst used for the dehydration reaction, namely: aluminas, zeolites, metal phosphates and sulfates, and oxides. According to the literature, alumina is a widely used catalyst for the dehydration of alcohols. Because of this, the information regarding alumina has been organized according to the structure of the alcohol (mixed alcohols, 2-methyl-1-alkanols, and isoamyl alcohol) used in the reaction so as to provide only that information which is most relavent in regard to the dehydration of isobutanol. The type of reactor and reaction conditions used by the various authors is also discussed as well as any pertinent information with respect to catalyst fouling and competitive side reactions.

A. ALUMINA:

The surface of alumina contains both acidic and basic sites. These acidic sites range in strength from strong to weak. Pines and Pillai[21] found that by modifying alumina with ammonia it was possible to produce relatively pure primary β-H dehydration products from a number of alcohols such as 3,3-dimethyl-1-butanol without significant quantities of their isomers. Pines and Haag[7] found that by incorporating small amounts of sodium (0.001% - 1.5% weight) into the alumina, the activity for dehydration decreased as the sodium content increased, however the more significant finding was that the activity for isomerization decreased substantially. According to the findings of Pines and Haag,[22] aluminas without alkali contain a substantial number of strong acid sites; aluminas prepared from alkali aluminates contain a large number of weak acid sites; and aluminas impregnated with alkali-base contain a reduced number of acidic sites without an appreciable change in the strength distribution. When the alumina is impregnated with alkali base, it is quite possible that if the base concentration is low and the solute is nonselectively adsorbed, the solution may be depleted of solute before the pores are filled. This would lead to the nonpreferential decrease in acid sites. The fact that both isomerization and dehydration decrease on impregnation of an alkali-base could result from adsorption of the base on the aluminum ions as well as sodium exchange with the surface hydroxyl protons.

1. MIXED ALCOHOLS:

Several patents have been issued which describe the use of an alumina catalyst for dehydration of alcohols. Hofstadt et al.[23] suggested using an alumina catalyst impregnated with LiOH, KOH, or NaOH with alkali metal concentrations of 0.1 to 1.5 wt.%. for the dehydration of C_4-C_6 alcohols produced from a synthesis gas. An undisclosed alumina catalyst was proposed by Reichl[24] for the dehydration of a mixed alcohol stream produced from synthesis gas. Reichle[25] used a high-purity (alkoxide derived) γ-alumina with low impurity levels impregnated with metal nitrates for the dehydration of normal alcohols to high-purity α-olefins. The metal ion consisted of Ba, K, Rb, or Cs with a concentration on the doped catalyst of 0.05-2.0 wt.%. Reichle suggests a low impurity alumina most likely so that the poisoning can be controlled solely through impregnation with the metal nitrates. Alvila et al.[26] proposed the use of a commercially available (Harshaw) aluminum oxide catalyst for the dehydration of a stream of mixed butanols. The proportion of straight-chained: branched alcohols was 1.3:1. The preparation of α-olefins in high selectivity from fatty alcohols was described by Voeste and Buchold.[27] In their process, they used a γ-alumina doped with NH_3 to dehydrate the alcohols while inhibiting any isomerization. Min'ko and Timofeev[28] described a pilot facility which uses an aluminum oxide catalyst treated with 0.25% KOH for the dehydration of several normal alcohols and isoamyl alcohol. They found that using this catalyst they could produce 1-hexene with 90-95% selectivity.

The above mentioned dehydration reactions were carried out in packed bed reactors. The reaction conditions used were temperatures ranging from 300-500 C and pressures ranging from 0.5 to 1 atmosphere. The LHSV (liquid hourly space velocity) were on the order of 1-4 liters of alcohol feed per liter of catalyst per hour. These conditions were utilized to obtain a product stream which consisted of a high selectivity for the primary olefin.

2. ISOBUTANOL OR 2-METHYL-1-ALKANOLS:

The dehydration of isobutanol was performed by Kim et al.[29] using an aluminum oxide catalyst doped with 1.5-2% $Ca(H_2PO_4)_2$ to inhibit skeletal isomerization. The reaction was carried out at temperatures of 300-400 C and GHSV of 300-2500 providing contact times of 5 seconds or less. They found that the yield of isobutylene could be raised from 80% to 96% by modifying the alumina catalyst. It was determined by Kim et al.[30] that by carrying out the reaction in a fluidized bed reactor they were able to obtain results which were similar to those obtained in a fixed bed reactor.

Several patents were issued on the use of modified alumina as a dehydration catalyst for 2-methyl-1-alkanols whereby the modified alumina produces a higher yield of the 2-methyl-1-olefin. Specific increases in the product selectivity or yield were not always stated. Shioyama[31] proposed using a zinc aluminate catalyst which is prepared by mixing equimolar portions of γ-alumina and zinc oxide in a ball mixer and then processed to produce the final physical form. Results were obtained which were similar to those using a sodium modified alumina, but the zinc aluminate had a wider temperature range over which the maximum olefin yield was produced. He also determined that the zinc aluminate was more effective than simple mixtures of zinc oxide and alumina. Resofszki et al.[32] studied the dehydration reaction using a solid solution of iron oxide and aluminum oxide prepared by spray-decomposing the aqueous solution of the nitrates at 500 C. They found that the addition of 1-10 mole% of iron oxide caused a sharp decrease in the acidity of the catalyst as well as total inactivity for skeletal isomerization. A zinc aluminate catalyst was also suggested by John[33]. However, John used a γ-alumina which was impregnated with an aqueous zinc salt solution producing an alumina carrier with zinc aluminate on its surface. With this zinc aluminate he was able to obtain 1-pentene with better than 90% selectivity. Drake[34] proposed the use of an alumina treated by soaking it in a solution of an organic carboxylic acid and a diluent to produce 2-methyl-1-butene with a selectivity of 85-95%. The amount of carboxylic acid used in the treatment of the silica can range from about 0 01-0.1 g per gram of alumina. An alumina catalyst which was modified simply by heat treatment was utilized by Drake[35] for the dehydration of branched alcohols. According to his process, a mixed boehmite (aluminum oxide-hydroxide)/chi-alumina catalyst is heated to about 550 C for several hours under a stream of nitrogen. The result is a relatively pure chi-alumina which shows high selectivities for the primary dehydration products without subsequent isomerization.

The above discussed catalysts were utilized for the dehydration reaction of branched alcohols to their corresponding olefins. The reactions were carried out in fixed bed reactors over a temperature range of 250-450 C and pressures of 1-7 atmospheres. The alcohol was introduced to the reactor at a WHSV ranging from 0.1 to 20 grams of alcohol feed per gram of catalyst per hour along with an inert carrier gas flow of 40-50 liters per hour.

3. ISOAMYL ALCOHOL:

Two studies have been performed on the dehydration of 3-methyl-1-butanol to provide information for optimal pilot plant operation. The studies were concerned with determination of a catalyst and reaction conditions which would produce a product stream with a high yield of 3-methyl-1-butene and low concentrations of product isomers. Drake et al.[36] of the Phillips Petroleum Co. found that a base treated gamma alumina inhibited the formation of product isomers. The pilot plant utilized a packed bed reactor operating at about 300 C core temperature and a pressure of approximately 3 atmospheres. The alcohol feed was varied from 1.0-1.5 LHSV resulting in a product yield of greater than 85% 3-methyl-1-butene. It should be noted that the product yield dropped to about 70-75% when the unit was run on a lower purity feed. Nitrogen was used as a carrier gas for the alcohol feed. Early tests on the catalyst life revealed that approximately 1000 pounds of 3-methyl-1-butene were produced per pound of catalyst. The second pilot plant operation was described by Timofeev et al.[37] Their process relied on a γ-alumina impregnated with 0.25 wt.% KOH. The dehydration was carried out at approximately 380 C with an alcohol feed of 4 liters per liter of catalyst per hour. Under these conditions, they were able to obtain a product selectivity of about 70%.

B. ZEOLITES AND AMORPHOUS ALUMINOSILICA:

Several experimental studies have been carried out in which silica-alumina catalysts of various compositions have been used for the dehydration of isobutyl alcohol. Weisz and co-workers[38] looked at the molecular shape selective dehydration of the isomeric butanols on Ca-zeolites 5A and 10X. They found that approximately 100% conversion of the isobutanol could be obtained at 300 C on the 10X catalyst, but that negligible conversion occurred for the dehydration on the 5A. This implies that the isobutanol is excluded from the crystal interior of the zeolite 5A. Normal butanol was dehydrated to about the same extent on both. No analysis of the butene products was presented. Amorphous aluminosilica gels and zeolites having chemical compositions corresponding to that of type X zeolite were used for the dehydration of isobutanol by Levchuk and Dzis'ko.[39] Running the reaction at 310 C they determined that the conversion could be increased by lowering the space velocity; however, they also found a corresponding increase in the concentration of polymeric products. Over the range of space velocities used, normal butene isomers constituted approximately 20-30% of the product stream. Samples with low sodium content were found to decrease in activity quite rapidly with time. This could result from oligomer formation within the pores and their inability to diffuse out. Their results showed that at low conversions the rate of dehydration as well as isomerization were independent of the alcohol conversion, but both became dependent with increasing conversion. They also found a linear decay of both rates with increasing sodium content.

Makarova et al.[40,41] performed limited experiments on the dehydration of isobutanol on H-ZSM-5. Their reaction conditions were 100-150 C, 1 atmosphere pressure, and low conversions (<10%) such that the reaction was zero order with respect to isobutanol. They did not provide an analysis of the product stream butene isomer composition. IR studies were performed to determine a possible reaction scheme. They believe that the reaction occurs through formation of a surface alkoxide which reacts with the alcohol to form a hydrogen bonded ether. This ether, restricted from diffusing out of the channel intersection, decomposes to form a butene and an alcohol molecule. Under conditions of higher conversion or interupted alcohol flow, they found a significant increase in oligomer formation. They postulate this to arise from interaction of the butene with the highly reactive alkoxide as the butene is diffusing through the pore.

C. METAL PHOSPHATES AND SULFATES:

Hofstadt et al.[23] suggested using either an aluminum phosphate or a calcium phosphate as the dehydration catalyst for a mixed alcohol stream. However, they stated that they preferred using an aluminum oxide or calcium phosphate, $Ca_3(PO_4)_2$, as the dehydration catalyst so that secondary reactions (condensation and polymerization) could be suppressed. A phosphorous rich hydroxyapatite catalyst $Ca_9(HPO_4)(PO_4)_5OH$ was investigated by Kibby et al.[14,42] for the dehydration reaction of several alcohols. They found that upon dehydration of isobutanol they were able to obtain about 90% isobutene with 10% normal butenes. The reaction was carried out at 300-400 C and low conversions such that the reaction was zero order with respect to the alcohol concentration. The calcium rich form of this catalyst, $Ca_{10}(PO_4)_6(OH)_2$ makes it a suitable catalyst for alcohol dehydrogenation. Brett et al.[43] states that the dehydration reaction is catalyzed by the acidic phosphate hydrogen. Clearfield and Thakur[44] studied the dehydration of cyclohexanol using a zirconium phosphate catalyst. They found the catalyst to be very selective toward the dehydration reaction with little activity for isomerization or dehydrogenation. The reaction was performed over a temperature range of 300-400 C and they determined that the dehydration data fit a first order rate equation. Clearfield and Thakur also proposed that the primary active sites are the monohydrogen phosphate protons with a possible secondary active site being of the Lewis acid type.

A sulfate modified zirconia catalyst was proposed by Klier et al.[45] as a possible catalyst for the dehydration of isobutanol. They found that when a mixture of isobutanol and methanol were charged to the reactor, the catalyst proved to be efficient and highly selective for the production of isobutene with methanol dehydration suppressed. However, no work has been done to study solely the dehydration reaction of isobutanol with this catalyst. Thorton and Gates[46] studied the dehydration of isobutyl alcohol using a poly(styrene-divinylbenzene) matrix containing sulfate groups as the catalyst. The reaction was performed at approximately 100 C giving a mixture of butene isomers and isobutane formation at low substrate partial pressures. The reaction was accompanied by about a 20% decrease in rate over tens of hours of operation resulting from a catalyst which became covered in a dark, sticky tar. The catalyst deactivation was not observed with either isopropyl or sec-butyl alcohols. According to Knozinger,[20] it is believed that the dehydration of alcohols on ion exchange resins occurs through oxonium or carbonium ion intermediates.

D. OXIDE CATALYSTS:

Schwab and Schwab-Agallidis[15] studied the dehydration of ethanol to ethylene on a number of oxide catalysts (ZnO, TiO_2, Cr_2O_3, γ-Al_2O_3, CeO_3, and ThO_2) and found that the product stream from the alumina and thoria catalysts consisted of better than 90% ethylene. Canesson and Blanchard[47] found that on dehydration of secondary alcohols over thoria a high selectivity was shown for the formation of the 1-alkene. They proposed that the reaction proceeds as a syn-elimination occurring by an E1cB pathway. A reaction occurring by an E1cB mechanism involves the loss of a proton from the alcohol to the base with formation of a negatively charged carbanion which then losses the hydroxide ion in a separate step to yield the alkene. Studying the possibility of γ-H eliminations from certain alcohols during the course of dehydration at 300-350 C, Siddhan and Narayanan[48] found that thoria showed very little propensity for γ-eliminations whereas the products obtained from alumina doped with sodium exhibited a significant contribution from γ-eliminations. It should also be noted that alumina exhibited a much higher activity for the dehydration of alcohols such as 3-methyl-1-pentanol than did thoria.

The dehydration of isobutanol was observed by Kotsarenko and Malysheva[49] using binary compounds of the type aM_mO_n $(1-a)SiO_2$, where M=Al, Ga, Zr, Be, and Y as catalysts. The reactions were carried out over the temperature range of 275-350 C using a circulation-flow method with a circulation rate of 800 liters per hour. They found that with increasing alcohol concentration, the order of the reaction changed from first to zero on all of the catalysts. The results of their experiments showed that isobutylene made up about 60-70 mole% of all the butylenes formed for all of the binary compounds. They also found that a gamma-alumina sample produced about 95% isobutylene. No indication as to the chemical composition of the alumina was given. Results for the isomerization of an isobutylene feed showed that alumina and the binary compounds of Be and Y were inactive for this reaction. From their results they concluded that the dehydration reaction of isobutanol on the binary oxides occurs through a carbonium ion mechanism leading to a high rate of normal olefins. Davis[50] looked at the dehydration of branched secondary and tertiary alcohols over aluminum and molybdenum oxide at temperatures of 180-275 C. For certain alcohols (i.e. 2,2-dimethyl-3-pentanol) it was found that molybdena produced a significant quantity of products which resulted from skeletal isomerization whereas the alumina did not. Davis postulated that the skeletal isomerization resulted from the dehydration step and not from a secondary reaction. The acidity and basicity of a number of metal oxides were investigated by Gervasini and Auroux.[51] The catalysts were tested for the decomposition of isopropanol to propene and acetone. While it is difficult to make any conclusions about the use of these catalysts for the dehydration of isobutanol, there are a few points that should be mentioned. They found that the oxides of Mo and W gave propene in the temperature range of 400-430 K while those of Al, Nb, Ta, Ti, and Zr were active in the temperature range of 430-490 K. This would indicate that MoO_3 and WO_3 possess stronger acid sites than the other oxides. However, it should be noted that MoO_3 and WO_3 also gave acetone, an undesired product in the dehydration reaction, at lower temperatures.

DEHYDRATION IN A SLURRY REACTOR:

Some work has been undertaken in the use of liquid phase reaction technology for the dehydration of tertiary butyl alcohol (TBA). A patent issued to Dockner and Krug[52] describes a process in which a feed of TBA and nitrogen are passed into a packed quartz tube filled with vacuum gas oil (boiling point 400 C) containing about 5% resin catalyst. The reaction is carried out at 205 C giving 97% yield isobutene. Abraham and Prescott[53] discuss the processes utilized by several companies for the dehydration of tertiary butanol to isobutene. According to the authors, Cities Service dissolves the TBA and a p-toluene sulfonic acid catalyst in a reaction medium of xylene. The isobutylene is removed as a gas and the water separates out and is removed continuously. Nippon, Asashi, and Maruzen use powdered resin catalysts in a stirred reactor for their processes. It must be noted that the patents referenced by Abraham and Prescott could not be located as cited in their article.

THERMODYNAMICS:

Calculations were made to determine the heat of reaction as well as the change in the Gibbs free energy upon dehydration of isobutanol to form isobutene and water. The heat of reaction at 298 C and 1 atmosphere is 8.16 kcal/mole and the Gibbs free energy change is -0.64 kcal/mole. The entropy change was determined to be 24.1 cal/mole K. The heat of reaction was also calculated at 300 C with its value being 8.75 kcal/mole. Thus, the reaction is endothermic and will require the process to be run at elevated temperatures in order to obtain good conversions. Klotz[54] performed some equilibrium calculations for the dehydration reaction and found that the equilibrium favors almost 100% conversion in the temperature range of 100-300 C and that it was only slightly shifted toward isobutanol at elevated pressures up to 52 atmospheres. The adiabatic temperature drop for the reaction was also determined by Klotz[55]. He found that at inlet conditions of 1 atmosphere and 200 C the temperature dropped to 77 C for 100% conversion while for an inlet temperature of 300 C the temperature dropped to 130 C. The temperature drop for the low inlet condition is controlled by the condensation of water in the reactor.

CONCLUSIONS:

From the information that has been gathered on the dehydration of alcohols, and in particular 2-methyl-1-alkanols, it appears that the catalysts best suited for the dehydration of isobutanol would be a treated alumina or possibly just a less pure gamma-alumina, a phosphate or sulfate modified zirconia, or a calcium phosphate. The literature indicates that the reaction should be run at temperatures ranging from about 300 to 400 C and at pressures around atmospheric. From the thermodynamics it is seen that the reaction is endothermic and requires the higher temperatures in order to obtain reasonable conversion of the isobutanol. According to the literature, the majority of the work has been performed in packed bed reactors; however, some of the TBA dehydration processes indicate that a slurry phase reactor should provide the proper conditions for an efficient and economic isobutanol dehydration process. It was difficult to make any reasonable conclusions in regard to the catalyst life expectancy. It appears that a catalyst which does not possess strong acid sites such that isomerizations do not occur should also inhibit other side reactions from occurring which lead to carbon formation on the catalyst surface.

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B. E. Latshaw

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APPENDIX 4

MATERIAL BALANCE SHEETS

FOR

A. RUN #11782-58 (GROUND-UP K3-110)

&

B. RUN #11782-63 (POWDER K3-110, LAPORTE BATCH)

A. Run #11782-58 (Ground-up K3-110)

Texaco Gas
Methanol Synthesis

LIQUID PHASE METHANOL SYNTHESIS

APCI STIRRED AUTOCLAVES

RUN # :11782-58A
OIL TYPE :SONTEX 100 (Drakeol 10)
OIL WEIGHT : 121.79 GM
CATALYST :BASF K3-110 (210 mesh)
INLET FLOW : 146.61 L/HR
PRESSURE : 754.10 PSIG
GHSV : 4836.84 L/KG-HR

DATE :02/28/92
HOURS ON STREAM : 25.00 HRS
STIR SPEED : 1200.00 RPM
TOTAL CAT LOADING: 30.31 GM
OUTLET FLOW : 121.54 L/HR
TEMPERATURE : 250.00 C

	INLET CONC %	FLOW L/HR	OUTLET CONC %	FLOW L/HR	DELTA FLOW L/HR	FLOW GMOL/HR
H2	36.45	53.44	23.57	28.65	-24.79	-1.11
N2	1.08	1.58	1.19	1.45	-0.14	-0.01
CH4	0.00	0.00	0.01	0.01	0.01	0.00
CO	46.33	67.92	45.66	55.49	-12.43	-0.55
CO2	13.46	19.73	16.79	20.41	0.67	0.03
H2O	0.00	0.00	0.00	0.00	0.00	0.00
MEOH	0.00	0.00	9.16	11.14	11.14	0.50
DME	0.00	0.00	0.14	0.17	0.17	0.01
MeFormate	0.00	0.00	0.09	0.11	0.11	0.01
ETOH	0.00	0.00	0.07	0.09	0.09	0.00
TOTALS	97.32	142.68	96.69	117.51	-25.17	-1.12

HYDROGEN CONVERSION : 46.39 MOLE %
CARBON MONOXIDE CONVERSION : 18.30 MOLE %
CARBON DIOXIDE CONVERSION : -3.41 MOLE %

CARBON RECOVERY : 100.15 %
HYDROGEN RECOVERY : 97.19 %
OXYGEN RECOVERY : 100.58 %
NITROGEN RECOVERY : 91.34 %

METHANOL PRODUCTIVITY : 16.40 GMole/HR-KG (172)

NOTE: Reduction done with dilute syn gas.

```
=======================================================================
Software Version: 3.2 <0E01>
Sample Name  : 300cc-1                   Time          : 2/28/92   5:42 PM
Sample Number: 300cc   #1                Study         : alcohols research
Operator     : seg

Instrument    : 950-1  ALCOHOLS  GC      Channel : A     A/D mV Range : 1000
AutoSampler   : NONE
Rack/Vial     : 0/0

Interface Serial # : 9212551066   Data Acquisition Time: 2/28/92  5:27 PM
Delay Time      : 0.00   min.
End Time        : 15.00  min.
Sampling Rate   : 5.0000   pts/sec

Raw Data File   : c:\2700\data1\059a004.raw
Result File     : c:\2700\data1\059a004.rst
Instrument File: c:\2700\methods\alcohols.ins
Process File    : c:\2700\methods\alcohols.prc
Sample File     : c:\2700\methods\alcohols.smp
Sequence File   : C:\2700\SEQUENCE\ALCOHOLS.seq

Inj. Volume     : 1 MOL%                 Area Reject       : 0.00
Sample Amount   : 1.0000                 Dilution Factor   : 1.00

=======================================================================


                                 ALCOHOLS

Peak  Time      Area     Area  Norm. Area BL    Amount        Component
  #   [min]  [uV*sec]    [%]      [%]           [ppm]           Name
-----------------------------------------------------------------------
  1   0.723    1528.71   0.21     0.21 BV        0.0000
  2   0.774     633.29   0.09     0.09 VB       60.8212   METHANE
  3   0.991   17085.81   2.36     2.36 BB     1470.7085   DIMETHYL ETHER
  4   1.109  668060.69  92.36    92.36 BV    91190.3750   METHANOL
  5   1.318    8128.98   1.12     1.12 VB      937.1200   METHYLFORMATE
  6   1.539   12418.00   1.72     1.72 BB      797.0054   ETHANOL
  7   2.454    2927.99   0.41     0.41 BB      179.8903   METHYL ACETATE
  8   3.144    5192.41   0.72     0.72 BB      200.6799   1-PROPANOL
  9   4.660    3353.78   0.46     0.46 BB       89.1717   ISOBUTANOL
 10   5.407    1852.24   0.26     0.26 BB       50.7410   1-BUTANOL
 11   6.376     747.10   0.10     0.10 BB        0.0000
 12   6.745     662.04   0.09     0.09 BB       14.2106   2-METHYL-1-BUTANOL
 13   7.253     719.20   0.10     0.10 BB       15.8368   1-PENTANOL
-----------------------------------------------------------------------
             723310.31 100.00   100.00       95006.5625
```

Basis 100 moles liquid

LIQUID PHASE SHIFT

APCI STIRRED AUTOCLAVES

RUN # 11782-58B
OIL TYPE SONTEX 100 (Drakeol 10)
OIL WEIGHT 121.78 GM
CATALYST BASF K3-110 (210 mesh)
INLET FLOW 153.61 SL/HR
PRESSURE 467.30 PSIG
GHSV (DRY) 5067.96 SL/KG-HR (6106.5)
H2O INJECTION RATE: 27.00 ML/HR
H2O/CO RATIO IN FEED 0.44

DATE : 02/29/92
HOURS ON STREAM : 49.00 HRS
STIR SPEED : 1200.00 RPM
CATALYST LOADING: 30.31 GM
OUTLET FLOW : 183.27 SL/HR
TEMPERATURE : 252.10 DEG C
Keq = 83.54
33.60 sl/hr Exit water= 2.42 sl/hr

	INLET CONC %	FLOW L/HR		OUTLET CONC %	FLOW L/HR	DELTA FLOW L/HR	FLOW GMOL/HR
H2	37.74	57.97	31.38	46.94	86.03	28.06	1.25
N2	1.05	1.61	0.87	0.86	1.58	-0.04	0.00
CH4	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO	49.56	76.13	41.21	23.22	42.56	-33.57	-1.50
CO2	10.04	15.42	8.35	25.43	46.61	31.18	1.39
H2O	0.00	0.00	18.19	1.32	2.42	2.42	0.11
MEOH	0.00	0.00	0.00	0.92	1.69	1.69	0.08
DME	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MeFormate	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ETOH	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL	98.39	151.14	100.00	98.69	180.87	29.73	1.33

CARBON MONOXIDE CONVERSION : 44.10 MOLE %
CARBON DIOXIDE YIELD : 40.96 MOLE %
HYDROGEN YIELD : 36.85 MOLE %
water conversion : 92.81%
CARBON RECOVERY : 99.23 %
HYDROGEN RECOVERY : 100.30 %
OXYGEN RECOVERY : 99.52 %
NITROGEN RECOVERY : 97.72 %

Pco2*Ph2/Pco*PH2O: inlet= 0.35 exit= 38.99
equilirium H2O conversion= 0.9648 1.18 sl/hr

NOTE: Reduction done with dilute syn gas.
moles of water converted= 17.5471
83.54

```
                    LIQUID PHASE SHIFT

                   APCI STIRRED AUTOCLAVES


RUN #        11782-58C                   DATE               : 02/29/92
OIL TYPE     SONTEX 100 (Drakeol 10)     HOURS ON STREAM :       51.25 HRS
OIL WEIGHT      121.78 GM                STIR SPEED         :  1200.00 RPM
CATALYST     BASF K3-110 (210 mesh)      CATALYST LOADING:      30.31 GM
INLET FLOW      294.44 SL/HR             OUTLET FLOW        :  349.52 SL/HR
PRESSURE        468.20 PSIG              TEMPERATURE        :  248.20 DEG C
GHSV (DRY)     9714.44 SL/KG-HR (117:6 ) Keq =        89.42
H2O INJECTION RATE:       49.00 ML/HR      60.98 sl/hr  Exit water=     8.58 sl/hr
H2O/CO RATIO IN FEED       0.42

                INLET                         OUTLET                        DELTA
               CONC     FLOW                  CONC     FLOW           FLOW     FLOW
                 %      L/HR                    %      L/HR           L/HR    GMOL/HR
              -------  -------               -------  -------        -------  -------

H2             37.74    111.12     31.69      42.95    150.12          39.00     1.74
N2              1.05      3.09      0.88       0.83      2.90          -0.19    -0.01
CH4             0.00      0.00      0.00       0.00      0.00           0.00     0.00
CO             49.56    145.93     41.61      27.01     94.41         -51.52    -2.30
CO2            10.04     29.56      8.43      23.45     81.96          52.40     2.34
H2O            0.00       0.00     17.39       2.45      8.58           8.58     0.38
MEOH            0.00      0.00      0.00       0.22      0.77           0.77     0.03
DME             0.00      0.00      0.00      0.00       0.00           0.00     0.00
MeFormate       0.00      0.00      0.00      0.00       0.00           0.00     0.00
ETOH            0.00      0.00      0.00      0.00       0.00           0.00     0.00

TOTAL          98.39    289.70    100.00      96.91    338.74          49.03     2.19

             CARBON MONOXIDE CONVERSION :          35.31 MOLE %
             CARBON DIOXIDE YIELD       :          35.91 MOLE %
             HYDROGEN YIELD             :          26.72 MOLE %
             water conversion           :         85.93%
             CARBON RECOVERY            :         100.94 %
             HYDROGEN RECOVERY          :          98.60 %
             OXYGEN RECOVERY            :         104.17 %
             NITROGEN RECOVERY          :          93.83 %

             Pco2*Ph2/Pco*PH2O=  inlet=     0.37          exit=        15.20
             equilirium H2O conversion=    0.9682      1.94 sl/hr

NOTE:        Reduction done with dilute syn gas.
             moles of water converted=     16.835
                                            89.42
```

LIQUID PHASE SHIFT

APCI STIRRED AUTOCLAVES

RUN # 11782-54D
OIL TYPE SONTEX 100 (Drakeol 10)
OIL WEIGHT 121.78 GM
CATALYST BASF K3-110
INLET FLOW 150.97 SL/HR
PRESSURE 456.70 PSIG
GHSV (DRY) 4980.87 SL/KG-HR (6089.5)
H2O INJECTION RATE: 22.00 ML/HR
H2O/CO RATIO IN FEED 0.29

DATE : 03/01/92
HOURS ON STREAM : 72.75 HRS
STIR SPEED : 1200.00 RPM
CATALYST LOADING: 30.31 GM
OUTLET FLOW : 171.39 SL/HR
TEMPERATURE : 250.40 DEG C
Keq = 86.04
27.38 sl/hr Exit water= 1.43 sl/hr
94.77%

	INLET CONC %	FLOW L/HR		OUTLET CONC %	FLOW L/HR	DELTA FLOW L/HR	FLOW GMOL/HR
H2	29.62	44.72	25.85	39.38	67.49	22.78	1.02
N2	0.97	1.46	0.85	0.83	1.42	-0.04	0.00
CH4	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO	62.69	94.64	54.71	39.51	67.72	-26.93	-1.20
CO2	3.18	4.80	2.78	17.94	30.75	25.95	1.16
H2O	0.00	0.00	15.82	0.83	1.43	1.43	0.06
MEOH	0.00	0.00	0.00	0.79	1.35	1.35	0.06
DME	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MeFormate	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ETOH	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL	96.46	145.63	100.00	99.28	170.17	24.54	1.10

CARBON MONOXIDE CONVERSION : 28.45 MOLE %
CARBON DIOXIDE YIELD : 27.42 MOLE %
HYDROGEN YIELD : 24.07 MOLE %
water conversion : 94.77%
CARBON RECOVERY : 100.38 %
HYDROGEN RECOVERY : 99.99 %
OXYGEN RECOVERY : 100.63 %
NITROGEN RECOVERY : 97.14

Pco2*Ph2/Pco*PH2O: inlet= 0.08 exit= 21.42
equilirium H2O conversion= 0.9857 0.39 sl/hr

NOTE: reduction done with dilute syn gas.
moles of water converted= 15.5987
86.04

LIQUID PHASE SHIFT

APCI STIRRED AUTOCLAVES

RUN #	11782-58E		DATE	: 03/01/92
OIL TYPE	SONTEX 100 (Drakeol 10)		HOURS ON STREAM	: 75.00 HRS
OIL WEIGHT	121.78 GM		STIR SPEED	: 1200.00 RPM
CATALYST	BASF K3-110		CATALYST LOADING	: 30.31 GM
INLET FLOW	150.97 SL/HR		OUTLET FLOW	: 198.10 SL/HR
PRESSURE	460.10 PSIG		TEMPERATURE	: 250.80 DEG C
GHSV (DRY)	4980.87 SL/KG-HR		Keq =	85.45
H2O INJECTION RATE:	41.00 ML/HR		51.02 sl/hr	Exit water: 7.23 sl/hr
H2O/CO RATIO IN FEED	0.54			

	INLET CONC %	FLOW L/HR		OUTLET CONC %	FLOW L/HR	DELTA FLOW L/HR	FLOW GMOL/HR
H2	29.62	44.72	22.74	44.33	87.82	43.10	1.92
N2	0.97	1.46	0.74	0.72	1.43	-0.04	0.00
CH4	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO	62.69	94.64	48.13	26.02	51.55	-43.10	-1.92
CO2	3.18	4.80	2.44	24.53	48.59	43.79	1.96
H2O	0.00	0.00	25.95	3.65	7.23	7.23	0.32
MEOH	0.00	0.00	0.00	0.31	0.61	0.61	0.03
DME	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MeFormate	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ETOH	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL	96.46	145.63	100.00	99.56	197.23	51.60	2.30

CARBON MONOXIDE CONVERSION : 45.54 MOLE %
CARBON DIOXIDE YIELD : 46.27 MOLE %
HYDROGEN YIELD : 45.54 MOLE %
water conversion : 85.83%
CARBON RECOVERY : 101.32 %
HYDROGEN RECOVERY : 108.84 %
OXYGEN RECOVERY : 105.95 %
NITROGEN RECOVERY : 97.40

Pco2*Ph2/Pco*PH2O= inlet= 0.04 exit= 11.45
equilirium H2O conversion= 0.9738 1.34 sl/hr

NOTE: reduction done with dilute syn gas.
moles of water converted= 25.27
85.43

LIQUID PHASE SHIFT

APCI STIRRED AUTOCLAVES

8

RUN # 11782-5[illegible]Fx
OIL TYPE SONTEX 100 (Drakeol 10)
OIL WEIGHT 121.78 GM
CATALYST BASF K3-110
INLET FLOW 153.41 SL/HR
PRESSURE 468.20 PSIG
GHSV (DRY) 5061.48 SL/KG-HR (6170)
H2O INJECTION RATE: 27.00 ML/HR
H2O/CO RATIO IN FEED 0.46

DATE : 03/02/92
HOURS ON STREAM : 91.50 HRS
STIR SPEED : 1200.00 RPM
CATALYST LOADING: 30.31 GM
OUTLET FLOW : 184.28 SL/HR
TEMPERATURE : 250.00 DEG C
Keq = 86.65
33.60 sl/hr Exit water= 5.44 sl/hr

	INLET CONC %	FLOW L/HR		OUTLET CONC %	FLOW L/HR	DELTA FLOW L/HR	FLOW GMOL/HR
H2	37.62	57.71	30.93	46.70	86.06	28.34	1.27
N2	1.01	1.55	0.83	0.83	1.53	-0.02	0.00
CH4	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO	47.72	73.21	39.24	23.45	43.21	-30.00	-1.34
CO2	13.37	20.51	10.99	26.41	48.67	28.16	1.26
H2O	0.00	0.00	18.01	2.95	5.44	5.44	0.24
MEOH	0.00	0.00	0.00	0.45	0.83	0.83	0.04
DME	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MeFormate	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ETOH	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL	99.72	152.98	100.00	100.79	185.74	32.76	1.46

CARBON MONOXIDE CONVERSION : 40.97 MOLE %
CARBON DIOXIDE YIELD : 38.46 MOLE %
HYDROGEN YIELD : 38.72 MOLE %
water conversion : 83.80%
CARBON RECOVERY : 98.92 %
HYDROGEN RECOVERY : 105.97 %
OXYGEN RECOVERY : 101.75 %
NITROGEN RECOVERY : 98.71

Pco2*Ph2/Pco*PH2O= inlet= 0.48 exit= 17.80
equilirium H2O conversion= 0.9602 1.34 sl/hr

NOTE: reduction done with dilute syn gas.
moles of water converted= 17.29
86.68

```
                    LIQUID PHASE SHIFT

                  APCI STIRRED AUTOCLAVES


RUN #        11782-58G                     DATE               : 03/02/92
OIL TYPE     SONTEX 100 (Drakeol 10)       HOURS ON STREAM :      91.50 HRS
OIL WEIGHT     121.78 GM                   STIR SPEED         :  1200.00 RPM
CATALYST     BASF K3-110                   CATALYST LOADING:      30.31 GM
INLET FLOW     297.10 SL/HR                OUTLET FLOW        :  358.92 SL/HR
PRESSURE       473.20 PSIG                 TEMPERATURE        :  250.80 DEG C
GHSV (DRY)   9801.97 SL/KG-HR  11,978      Keq =         85.45
H2O INJECTION RATE:        53.00 ML/HR        65.96 sl/hr  Exit water:    18.13 sl/hr
H2O/CO RATIO IN FEED        0.46

                                                                        DELTA
               INLET                        OUTLET                      FLOW     FLOW
               CONC     FLOW                CONC     FLOW               L/HR     GMOL/HR
                %       L/HR                 %       L/HR
             -------  -------             -------  -------            -------  -------

H2             38.00   112.90    31.08     44.77   160.69              47.79     2.13
N2              1.02     3.03     0.83      0.83     2.98              -0.05     0.00
CH4             0.00     0.00     0.00      0.00     0.00               0.00     0.00
CO             47.88   142.25    39.17     26.18    93.96             -48.29    -2.16
CO2            13.15    39.07    10.76     24.21    86.89              47.83     2.14
H2O           0.00       0.00    18.16      5.05    18.13              18.13     0.81
MEOH            0.00     0.00     0.00      0.10     0.36               0.36     0.02
DME             0.00     0.00     0.00    0.00       0.00               0.00     0.00
MeFormate       0.00     0.00     0.00    0.00       0.00               0.00     0.00
ETOH            0.00     0.00     0.00    0.00       0.00               0.00     0.00

TOTAL         100.05   297.25   100.00    101.14   363.01              65.77     2.94

            CARBON MONOXIDE CONVERSION :              33.94 MOLE %
            CARBON DIOXIDE YIELD       :              33.62 MOLE %
            HYDROGEN YIELD             :              33.60 MOLE %
            water conversion           :             72.51%
            CARBON RECOVERY            :              99.94 %
            HYDROGEN RECOVERY          :             110.26 %
            OXYGEN RECOVERY            :             106.14 %
            NITROGEN RECOVERY          :              98.30

            Pco2*Ph2/Pco*PH2O:  inlet=      0.47           exit=          8.20
            equilirium H2O conversion=    0.9595      2.67 sl/hr

NOTE:       reduction done with dilute syn gas.
            moles of water converted=    17.4237
                                          85.45
```

LIQUID PHASE SHIFT

APCI STIRRED AUTOCLAVES

RUN #	11782-58H	DATE	: 03/03/92
OIL TYPE	SONTEX 100 (Drakeol 10)	HOURS ON STREAM	: 117.25 HRS
OIL WEIGHT	121.78 GM	STIR SPEED	: 1200.00 RPM
CATALYST	BASF K3-110	CATALYST LOADING	: 30.31 GM
INLET FLOW	297.13 SL/HR	OUTLET FLOW	: 336.61 SL/HR
PRESSURE	458.70 PSIG	TEMPERATURE	: 250.90 DEG C
GHSV (DRY)	9803.15 SL/KG-HR (11,445.5)	Keq =	85.30

49.78 sl/hr Exit water: 9.20 sl/hr

H2O INJECTION RATE: 40.00 ML/HR

H2O/CO RATIO IN FEED 0.26

	INLET CONC %	FLOW L/HR		OUTLET CONC %	FLOW L/HR	DELTA FLOW L/HR	FLOW GMOL/HR
H2	30.85	91.67	26.27	39.11	131.65	39.98	1.79
N2	0.92	2.73	0.78	0.81	2.73	-0.01	0.00
CH4	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO	65.45	194.47	55.73	44.53	149.89	-44.58	-1.99
CO2	3.46	10.28	2.95	15.11	50.86	40.58	1.81
H2O	0.00	0.00	14.27	2.73	9.20	9.20	0.41
MEOH	0.00	0.00	0.00	0.16	0.54	0.54	0.02
DME	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MeFormate	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ETOH	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL	100.68	299.15	100.00	102.45	344.87	45.71	2.04

CARBON MONOXIDE CONVERSION	:	22.92 MOLE %
CARBON DIOXIDE YIELD	:	20.87 MOLE %
HYDROGEN YIELD	:	20.56 MOLE %
water conversion	:	81.53%
CARBON RECOVERY	:	98.31 %
HYDROGEN RECOVERY	:	104.01 %
OXYGEN RECOVERY	:	100.66 %
NITROGEN RECOVERY	:	99.74

Pco2*Ph2/Pco*PH2O: inlet= 0.10 exit= 4.86

equilirium H2O conversion= 0.9865 0.67 sl/hr

NOTE: reduction done with dilute syn gas.

moles of water converted= 14.0726

85.32

LIQUID PHASE SHIFT

APCI STIRRED AUTOCLAVES

RUN # 11782-58I
OIL TYPE SONTEX 100 (Drakeol 10)
OIL WEIGHT 121.78 GM
CATALYST BASF K3-110
INLET FLOW 294.44 SL/HR
PRESSURE 476.40 PSIG wet
GHSV (DRY) 9714.44 SL/KG-HR (11357)
H2O INJECTION RATE: 40.00 ML/HR
H2O/CO RATIO IN FEED 0.26

DATE : 03/03/92
HOURS ON STREAM : 120.50 HRS
STIR SPEED : 1200.00 RPM
CATALYST LOADING: 30.31 GM
OUTLET FLOW : 339.05 SL/HR
TEMPERATURE : 275.60 DEG C
Keq = 56.59
49.78 sl/hr Exit water= 4.67 sl/hr

	INLET CONC %	INLET FLOW L/HR		OUTLET CONC %	OUTLET FLOW L/HR	DELTA FLOW L/HR	DELTA FLOW GMOL/HR
H2	30.85	90.84	26.24	39.19	132.87	42.04	1.88
N2	0.92	2.71	0.78	0.81	2.75	0.04	0.00
CH4	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO	65.45	192.71	55.66	43.18	146.40	-46.31	-2.07
CO2	3.46	10.19	2.94	16.31	55.30	45.11	2.01
H2O	0.00	0.00	14.38	1.38	4.67	4.67	0.21
MEOH	0.00	0.00	0.00	0.72	2.44	2.44	0.11
DME	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MeFormate	0.00	0.00	0.00	0.00	0.00	0.00	0.00
ETOH	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL	100.68	296.45	100.00	101.59	344.43	47.98	2.14

CARBON MONOXIDE CONVERSION : 24.03 MOLE %
CARBON DIOXIDE YIELD : 23.41 MOLE %
HYDROGEN YIELD : 21.81 MOLE %
water conversion : 90.62%
CARBON RECOVERY : 100.61 %
HYDROGEN RECOVERY : 103.75 %
OXYGEN RECOVERY : 101.79 %
NITROGEN RECOVERY : 101.38

Pco2*Ph2/Pco*PH2O= inlet= 0.10 exit= 10.75
equilirium H2O conversion= 0.9797 1.01 sl/hr

NOTE: reduction done with dilute syn gas.
mole of water converted= 14.09
56.59

B. Run #11782-63 (Powder K3-110, LaPorte Batch)

LaPorte Catalyst K3-110
(shipped from Germany)

LIQUID PHASE METHANOL SYNTHESIS

APCI STIRRED AUTOCLAVES

RUN #	:11782-63A	DATE	:03/25/92
OIL TYPE	:SONTEX 100 (DRAKEOL 10)	HOURS ON STREAM	: 19.00 HRS
OIL WEIGHT	: 121.92 GM	STIR SPEED	: 1200.00 RPM
CATALYST	:BASF K3-110 (LOT #453 8263)	TOTAL CAT LOADING	: 31.11 GM
INLET FLOW	: 173.04 L/HR	OUTLET FLOW	: 142.28 L/HR
PRESSURE	: 748.04 PSIG	TEMPERATURE	: 250.00 C
GHSV	: 5563.09 L/KG-HR		

	INLET CONC %	INLET FLOW L/HR	OUTLET CONC %	OUTLET FLOW L/HR	DELTA FLOW L/HR	DELTA FLOW GMOL/HR
H2	37.65	65.15	24.49	34.84	-30.31	-1.35
N2	1.09	1.89	1.27	1.81	-0.08	-0.00
CH4	N/A	0.00	0.01	0.01	0.01	0.00
CO	49.30	85.31	48.61	69.16	-16.15	-0.72
CO2	13.52	23.40	16.92	24.07	0.68	0.03
H2O	N/A	0.00	N/A	0.00	0.00	0.00
MEOH	N/A	0.00	9.76	13.89	13.89	0.62
DME	N/A	0.00	0.08	0.11	0.11	0.01
MeFormate	N/A	0.00	0.13	0.18	0.18	0.01
ETOH	N/A	0.00	0.08	0.11	0.11	0.01
TOTALS	101.56	175.74	101.35	144.20	-31.54	-1.41

HYDROGEN CONVERSION : 46.52 MOLE %
CARBON MONOXIDE CONVERSION : 18.93 MOLE %
CARBON DIOXIDE CONVERSION : -2.90 MOLE %

CARBON RECOVERY : 99.32 %
HYDROGEN RECOVERY : 97.77 %
OXYGEN RECOVERY : 99.77 %
NITROGEN RECOVERY : 95.80 %

METHANOL PRODUCTIVITY : 19.93 GMole/HR-KG

NOTE: Reduction done with dilute syn gas.

```
===================================================================================
Software Version: 3.2 <OEG1>
Sample Name   : 300cc-1                      Time          : 3/25/92  11:39 AM
Sample Number: 300cc  #1                     Study         : alcohols research
Operator      : seg

Instrument    : 950-1  ALCOHOLS  GC          Channel : A     A/D mV Range : 1000
AutoSampler   : NONE
Rack/Vial     : 0/0

Interface Serial # : 9212551066   Data Acquisition Time: 3/25/92  11:23 AM
Delay Time       : 0.00   min.
End Time         : 15.00  min.
Sampling Rate    : 5.0000   pts/sec

Raw Data File    : c:\2700\data1\085a004.raw
Result File      : c:\2700\data1\085a004.rst
Instrument File: c:\2700\methods\alcohols.ins
Process File     : c:\2700\methods\alcohols.prc
Sample File      : c:\2700\methods\alcohols.smp
Sequence File    : C:\2700\SEQUENCE\ALCOHOLS.seq

Inj. Volume      : 1 MOL%                     Area Reject        : 0.00
Sample Amount    : 1.0000                     Dilution Factor    : 1.00

===================================================================================

                                  ALCOHOLS
===================================================================================
                               C1-C6 MIXED ALCOHOLS
===================================================================================

Peak  Time     Area     Area  Norm. Area BL     Amount        Component
 #    [min]  [uV*sec]   [%]      [%]            [ppm]           Name
-----------------------------------------------------------------------------------

 1   0.725    1464.64   0.18      0.18 BV     140.6647    METHANE
 2   0.776     618.96   0.08      0.08 VB      27.5824    ETHANE
 3   0.996    8534.80   1.04      1.04 BB     891.6980    DIMETHYL ETHER
 4   1.107  739286.06  90.08     90.08 BV   97394.9453    METHANOL
 5   1.324   10206.25   1.24      1.24 VB    1293.2148    METHYLFORMATE
 6   1.532   14601.78   1.78      1.78 BB     893.6423    ETHANOL
 7   2.462    3520.77   0.43      0.43 BB     209.4092    METHYL ACETATE
 8   3.101    7573.34   0.92      0.92 BB     277.8900    1-PROPANOL
 9   4.043    1165.58   0.14      0.14 BB       0.0000
10   4.638    3414.21   0.42      0.42 BB      85.6162    ISOBUTANOL
11   5.325    4538.05   0.55      0.55 BB     123.5396    1-BUTANOL
12   5.986    1467.64   0.18      0.18 BB      36.5261    METHYL ISOBUTYRATE
13   6.374    1270.50   0.16      0.16 BB       0.0000
14   6.676    1753.13   0.21      0.21 BB      35.7360    2-METHYL-1-BUTANOL
15   7.134    2566.10   0.31      0.31 BB      51.7179    1-PENTANOL
16   7.602    1133.76   0.14      0.14 BB       0.0000
17   7.997     756.80   0.09      0.09 BB       0.0000
18   8.168    1083.43   0.13      0.13 BB      21.0583    2-METHYL-1-PENTANOL
19   8.656    2198.12   0.27      0.27 BB      50.6085    1-HEXANOL
20   9.534    1101.59   0.13      0.13 BB       0.0000
21   9.997    1416.86   0.17      0.17 BB       0.0000
22  10.373     632.33   0.08      0.08 BB       0.0000
```

9593

#11782-63a

19 hrs on-stream

1.0153e5

```
                    LIQUID PHASE METHANOL SYNTHESIS

                       APCI STIRRED AUTOCLAVES


RUN #       :11782-63b                 DATE             :03/26/92
OIL TYPE    :SONTEX 100 (DRAKEOL 10)   HOURS ON STREAM  :   43.00 HRS
OIL WEIGHT  :  121.92 GM               STIR SPEED       : 1200.00 RPM
CATALYST    :BASF K3-110 (LOT #453 8263)TOTAL CAT LOADING:   31.11 GM
INLET FLOW  :  173.04 L/HR             OUTLET FLOW      :  143.65 L/HR
PRESSURE    :  749.90 PSIG             TEMPERATURE      :  250.10 C
GHSV        : 5563.09 L/KG-HR


                 INLET                 OUTLET                  DELTA
                 CONC     FLOW         CONC     FLOW           FLOW     FLOW
                  %       L/HR          %       L/HR           L/HR     GMOL/HR
                -------  -------      -------  -------        -------  -------


H2               37.45    64.80        24.59    35.32         -29.48    -1.32
N2                1.04     1.80         1.24     1.78          -0.02    -0.00
CH4              N/A       0.00         0.01     0.01           0.01     0.00
CO               48.92    84.65        48.21    69.25         -15.40    -0.69
CO2              13.58    23.50        16.95    24.35           0.85     0.04
H2O              N/A       0.00        N/A       0.00           0.00     0.00
MEOH             N/A       0.00         9.27    13.32          13.32     0.59
DME              N/A       0.00         0.08     0.11           0.11     0.01
MeFormate        N/A       0.00         0.11     0.16           0.16     0.01
ETOH             N/A       0.00         0.08     0.11           0.11     0.00

TOTALS          100.99   174.75       100.54   144.42         -30.33    -1.35

                HYDROGEN CONVERSION        :        45.49 MOLE %
                CARBON MONOXIDE CONVERSION :        18.19 MOLE %
                CARBON DIOXIDE CONVERSION  :        -3.62 MOLE %

                CARBON RECOVERY            :        99.58 %
                HYDROGEN RECOVERY          :        97.18 %
                OXYGEN RECOVERY            :       100.12 %
                NITROGEN RECOVERY          :        98.98 %

                METHANOL PRODUCTIVITY      :        19.11 GMole/HR-KG

NOTE:        Reduction done with dilute syn gas.
```

```
AutoSampler    : NONE
Rack/Vial      : 0/0

Interface Serial # : 9212551066    Data Acquisition Time: 3/26/92  11:40 AM
Delay Time         : 0.00   min.
End Time           : 15.00  min.
Sampling Rate      : 5.0000   pts/sec

Raw Data File    : c:\2700\data1\086a004.raw
Result File      : c:\2700\data1\086a004.rst
Instrument File: c:\2700\methods\alcohols.ins
Process File     : c:\2700\methods\alcohols.prc
Sample File      : c:\2700\methods\alcohols.smp
Sequence File    : C:\2700\SEQUENCE\ALCOHOLS.seq
                                                    Area Reject      : 0.00
Inj. Volume      : 1 MOL%                           Dilution Factor  : 1.00
Sample Amount    : 1.0000
==========================================================================
==========================================================================

                                ALCOHOLS
==========================================================================
==========================================================================
                           C1-C6 MIXED ALCOHOLS
==========================================================================
==========================================================================

                                                     Component
Peak  Time     Area     Area  Norm. Area BL   Amount    Name
 #    [min]  [uV*sec]   [%]      [%]          [ppm]
------------------------------------------------------------------------
 1    0.726    1351.34  0.18    0.18 BV     129.7832   METHANE
 2    0.777     498.66  0.07    0.07 VB      22.2215   ETHANE
 3    0.995    7743.01  1.02    1.02 BB     808.9733   DIMETHYL ETHER
 4    1.101  704323.81 92.32   92.32 BV   92788.9531   METHANOL
 5    1.321    8648.12  1.13    1.13 VB    1095.7876   METHYLFORMATE
 6    1.528   12480.61  1.64    1.64 BB     763.8251   ETHANOL
 7    2.464    2810.04  0.37    0.37 BB     167.1365   METHYL ACETATE
 8    3.103    6163.11  0.81    0.81 BB     226.1440   1-PROPANOL
 9    4.046     983.46  0.13    0.13 BB      15.5200   HEXANE
10    4.639    2593.26  0.34    0.34 BB      65.0296   ISOBUTANOL
11    5.325    3568.56  0.47    0.47 BB      97.1471   1-BUTANOL
12    5.983    1157.23  0.15    0.15 BB      28.8008   METHYL ISOBUTYRATE
13    6.375     902.34  0.12    0.12 BB       0.0000
14    6.676    1207.66  0.16    0.16 BB      24.6172   2-METHYL-1-BUTANOL
15    7.131    1862.44  0.24    0.24 BB      37.5362   1-PENTANOL
16    8.166     645.84  0.09    0.09 BB      12.5530   2-METHYL-1-PENTANOL
17    8.656    1341.27  0.18    0.18 BB      30.8809   1-HEXANOL
18    9.535     545.34  0.07    0.07 BB       0.0000
19    9.997     691.44  0.09    0.09 BB       0.0000
20   10.778     554.31  0.07    0.07 BB       0.0000
21   11.933    1558.77  0.20    0.20 BB       0.0000
22   12.403     356.21  0.05    0.05 BB       0.0000



23   13.017     929.47  0.12    0.12 BB       0.0000
------------------------------------------------------------------------
             762916.25 100.00  100.00      96314.9141
```

96.30

#11782-63b

43 hrs. on-stream

LIQUID PHASE SHIFT

APCI STIRRED AUTOCLAVES

RUN # :11782-63c
OIL TYPE :SONTEX 100 (DRAKEOL 10)
OIL WEIGHT : 121.92 GM
CATALYST :BASF K3-110 (LOT #453 8263)
INLET FLOW : 173.04 SL/HR
PRESSURE : 452.70 PSIG
GHSV (DRY) : 5562.20 SL/KG-HR
H2O INJECTION RATE: 30.00 ML/HR;
H2O/CO RATIO IN FEED: 0.45

DATE : 03/26/92
HOURS ON STREAM : 48.25 HRS
STIR SPEED : 1200 RPM
CATALYST LOADING: 31.11 GM
OUTLET FLOW : 211.49 SL/HR
TEMPERATURE : 250.70 DEG C
Equil. Const. : 85.868
37.33 sl/hr;
Exit Water, sl/hr= 3.16

	INLET DRY Dry CONC %	INLET DRY FLOW L/HR	Inlet Wet Conc. %	OUTLET DRY dry CONC %	OUTLET DRY FLOW L/HR	Outlet Wet Conc. %	DELTA FLOW L/HR	FLOW GMOL/HR
H2	37.18	64.34	30.48	45.42	96.06	45.06	31.72	1.42
N2	1.01	1.75	0.83	0.86	1.82	0.85	0.07	0.00
CH4	n/a	0.00	0.00	n/a	0.00	0.00	0.00	0.00
CO	47.86	82.82	39.24	24.16	51.10	23.96	-31.72	-1.42
CO2	14.35	24.83	11.76	27.90	59.01	27.67	34.18	1.53
H2O	n/a	0.00	17.69	n/a	0.00	1.48	0.00	0.00
MEOH	n/a	0.00	0.00	0.99	2.09	0.98	2.09	0.09
DME	n/a	0.00	0.00	n/a	0.00	0.00	0.00	0.00
MeFormate	n/a	0.00	0.00	n/a	0.00	0.00	0.00	0.00
ETOH	n/a	0.00	0.00	n/a	0.00	0.00	0.00	0.00
TOTAL	100.40	173.73	100.00	99.33	210.08	100.00	36.34	1.62

CARBON MONOXIDE CONVERSION : 38.30 MOLE %
CARBON DIOXIDE YIELD : 41.27 MOLE %
HYDROGEN YIELD : 38.31 MOLE %
Water Conversion : 91.54 %

CARBON RECOVERY : 104.23 %
HYDROGEN RECOVERY : 104.12 %
OXYGEN RECOVERY : 104.12 %
NITROGEN RECOVERY : 104.07 %

NOTE: Reduction done withdilute syn.gas

RUN #	OPERATION	DURATION
CATALYST ACTIVATION		
AF-A2	Activation of 550# of K3-110 catalyst	2.0 days
LPM DEMONSTRATION		
AF-R4	Methanol synthesis w/K3-110	6.5
	Drain reactor to 275# of catalyst (oxide basis)	0.5
LPS DEMONSTRATION		
AF-R5 .1	Texaco Gas, SV=10000, H2:CO=1:1	2.0
.2	Texaco Gas, SV=10000, H2:CO=2:1	1.0
.3	Texaco Gas, SV= 6000, H2:CO=2:1	1.0
.4	Texaco Gas, SV= 6000, H2:CO=1:1	1.0
	Change-out methanol in CO2 removal section	0.5
AF-R5 .5	Shell Gas, SV=7000, H2:CO=2:1	1.0
.6	Shell Gas, SV=7000, H2:CO=1:1	1.0
.7	Shell Gas, SV=4000, H2:CO=1:1	1.0
.8	Shell Gas, SV=4000, H2:CO=2:1	1.0
	Prepare for once-through operation	0.5
AF-R5 .9	H2 Lean Gas, SV=6000, H2:CO=2:1	1.0
.10a	POX Gas, SV=6000, H2:CO=20:1	1.0
.10b	POX Gas, SV=6000, H2:CO=40:1	1.0
	TOTAL	22.0

SV is space velocity expressed as sL/kg-hr. Runs R5.6, R5.7, and R5.10b are optional and will be carried-out if the schedule can be maintained. The feed gas compositions to be used are presented in Table 2.

TABLE 2: Feed Gas Compositions for Spring '92 LPS Demonstration

Component:	H2	CO	CO2	N2
Shell Gas	31.0	65.0	3.0	1.0
Texaco Gas	35.0	51.0	13.0	1.0
H2 Lean Gas	1.5	72.0	13.4	13.1
POX Gas	60.7	37.7	1.6	0.0

APPENDIX 5

MEETING NOTES OF PARTNERS' MEETING IN PITTSBURGH; MARCH 19 – 20, 1992

Air Products and Chemicals, Inc.
7201 Hamilton Boulevard
Allentown, PA 18195-1501

Telephone (215) 481-4911
Telex: 847416
Fax: (215) 481-5900

AIR PRODUCTS

31 March 1992

Mr. Gary J. Stiegel
Project Manager
Liquid Fuels Division
Pittsburgh Energy Technology Center
US Department of Energy
PO Box 10940
MS 922-H
Pittsburgh, PA 15236

Dear Gary:

Attached please find:

- Our notes on the Partners' Meeting at Pittsburgh on March 19-20.
- A summary of follow-up discussion with Dr. Fred Tungate, UCI regarding catalyst preparation for F-T demonstration at LaPorte.
- A summary of follow-up discussion with Dr. Rocco Fiato, Exxon regarding starting wax at LaPorte.
- Information on Drakeol-10.
- A Proposed Run Plan for the F-T demonstration in July 92.

Timely comments from everyone on the distribution list are welcome.

Yours truly,

B. L. Bhatt

Dr. Bharat L. Bhatt
Senior Principal Process Engineer
PSG Process Engineering
(215) 481-5995

cc: Dr. Udaya Rao
Project Manager
Liquid Fuels Division
Pittsburgh Energy Technology Center
US Department of Energy
PO Box 10940
MS 922-H
Pittsburgh, PA 15236

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Project Development Department
UOP Inc
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Des Plains, IL 60017-5017

Dr. Dennis M. Brown
Technology Manager
Methanol and Alternative Fuels
Air Products and Chemicals, Inc
7201 Hamilton Blvd.
Allentown, PA 18195-1501

Mr. Keijo Kinnari
Staff Engineer
Research and Development
Statoil
PO Box 300
N-4001 Stavanger
Norway

Dr. Rocco Fiato, Exxon
Research Manager
Exxon Research & Engineering Co.
180 Park avenue
Florham Park, NJ 07932

NOTES FROM MEETING

Page One Of One

DATE OF MEETING	WEEKDAY	TIME STARTED	TIME ENDED	LOCATION
3/19/92-3/20/92	Thursday & Friday	8:30 AM 8:30 AM	5:00 PM 12:00 Noon	Holiday Inn Airport, Pittsburgh

SUBJECT AND/OR PURPOSE
Fischer-Tropsch Partners Meeting

ITEM NO.	RESPONSIBLE PERSON (INITIALS)	TARGET DATE	DISCUSSION
1.			The partners agreed to include the following individuals at any future meetings or discussions as non-financial contributing attendees. Each will bring different areas of expertise to the group. They are: • Dr. Norman Carr- Statoil Consultant- hydrodynamics expert • Dr. Fred Tungate- UCI catalyst developer • Prof. Drago Bukur- Texas A&M research scientist- catalyst testing capability; DOE FT advisor
	UOP		UOP noted that they may need to sign a secrecy agreement with Dr. Fred Tungate/UCI. Dr. Carr joined the meetings after lunch on Thursday. Dr. David Gray from Mitre was attending as DOE's FT advisor.
2.	APCI		The possibility of including Rentech in the LaPorte planning was discussed at several points during the meeting. Since Rentech is in a partnership with Fuelco and Houser Chemical, this complicates the matter. They are also busy trying to solve problems in their own unit at this time. It was suggested that Bob Senn or Dennis Brown of APCI contact Rentech and determine if they are available to provide insight into possible startup problems, with limited legal problems.
	Statoil		In place of possibly using Rentech's 1.6" bubble column reactor, Statoil offered to run a few tests in a 2" bubble column reactor once we have decided LaPorte operating conditions, the catalyst, and the wax starting material. This will provide an intermediate data point between the autoclaves and the LaPorte reactor. However, this test will not be in the decision scheme for LaPorte; it will be a parallel effort.
3			The partners agreed that they would prefer to run low alpha (0.70-0.78) cases at LaPorte this year. However, this was a change from our original objectives to make as much wax as possible. The reasons for preferring low α operations include: • higher chance of success for our first run • minimize our dependence on the catalyst/wax separation equipment to achieve maximum days on stream

NOTES FROM MEETING
CONTINUATION

ITEM NO.	RESPONSIBLE PERSON (INITIALS)	TARGET DATE	DISCUSSION
			• DOE was interested in using the wax product in their other programs which include catalyst/wax separation. However, since APCI proposed a second Fischer-Tropsch run in 1993, they were willing to forego significant wax production until the second run and concentrate on reactor performance and days on stream.
4.	Catalyst Choice Committee	3/24/92	A high α catalyst has been developed by Fred Tungate/UCI for the summer '92 operations. Much discussion focused on the means available to either develop a low α catalyst or determine operating conditions with the present catalyst that would produce a low α product distribution. The partners agreed they were willing to accept a delay of 1 month in the schedule, but not a 2 month or longer delay. Two phone conversations with Fred Tungate were held by a sub-group of the partners. Tungate felt he could make a low α catalyst by a minor change in the formulation of the catalyst and without changing the silica binder. He will give a sub-committee of the partners (B.L. Bhatt/R. Fiato) his schedule for making this change on March 23 or 24.
	UOP		The α of the present catalyst has yet to be determined. UOP will report back when their analysis is complete.
5.	UOP	4/1/92	As an alternative to a different catalyst formulation, it was suggested that the α may drop a sufficient amount by raising the operating temperature by 20°C. The partners have no data on the present catalyst at different temperatures. There is data on other catalysts which show varying degrees of α's dependency on temperature. However, it was stated that although increasing the temperature may decrease the fraction of products as wax, it could cause increased activity, with the result being the same (or higher) amount of wax product. The partners agreed that on 3/23/92, UOP will begin a test with the high α catalyst. They will activate the catalyst using their previous activation method, use the same liquid medium, run for a few days at their regular operating temperature of 265 °C to establish a baseline conversion rate, and then increase the reactor temperature to 285 °C. Run conditions are 290 psig and 2400 space velocity. Following the operation at these conditions, LaPorte base conditions of 200 psig, 2500 space velocity and 265°C will be investigated.

NOTES FROM MEETING
CONTINUATION

ITEM NO.	RESPONSIBLE PERSON (INITIALS)	TARGET DATE	DISCUSSION
6.			Another method discussed for lowering the catalyst α was desurfacing the present catalyst by pretreating it with steam. Desurfacing the catalyst will reduce the sites available for the longer chain hydrocarbons to grow. However, Rocco Fiato stated that by pretreating the catalyst in a H_2, N_2, steam mixture would deactivate the catalyst by roughly 50%. The partners agreed that such a reduction in catalyst activity would not be acceptable.
7.	Exxon		Since low α conditions will result in a longer turnover period for the LaPorte reactor, the partners felt that the starting slurry medium was more important than in a high α run, where reactor turnover would occur rapidly. Rocco Fiato will investigate what wax starting material Exxon could provide for the operations. The closer the starting wax is to an FT product, the more legal work will be required by Exxon to allow its use. Therefore, legal matters may require us to use Drakeol as our starting medium.
	Wax Starting Medium Committee		A sub-committee of Bharat Bhatt, Rocco Fiato, Udaya Rao and Hemant Gala was identified to chose the starting medium. They will inform the other partners of their choice and their reasons.
			If a solid Exxon wax is provided, a partial charge of Drakeol would be used to preheat the equipment while the wax was being melted externally with steam coils. The liquid would then be added to the Drakeol.
8.	DOE		A discussion of the CAER's test results using Drakeol with the UCI catalyst indicated that most participants felt that the poor CO conversions seen by CAER may have been the result of the unit (for example, no gas sparger) or the conditions, rather than the Drakeol (no controls were run). Udaya Rao will have an X-ray analysis done on both the spent CAER catalyst and some spent catalyst tested by UOP.
9.	APCI		Bharat Bhatt presented the gas analysis points we are planning to use and the use of DOE methods to do the gas analysis. Since operating decisions will be made based on the on line gas analysis, duplicate analysis will be done on the gas samples. This will involve altering the new FID analyzer and one of the new TCD gas analyzers.

ITEM NO.	RESPONSIBLE PERSON (INITIALS)	TARGET DATE	DISCUSSION
	DOE/APCI		It was further agreed that Joe Hackett of DOE/PETC would spend one week at LaPorte, during the startup, training the APCI analytical technician in the DOE gas sampling methods. After the first week, APCI will provide two analytical technicians.
10.	DOE/APCI/ Shell		On line hydrocarbon analysis cannot be done for this run since the LaPorte lab is too remote from the sample points and it is likely that the hydrocarbons will condense in the sample lines. DOE suggested that to install their hydrocarbon analysis methods at the LaPorte facility in time for the run would be extremely difficult, due to the different analytical computer setup. The partners agreed that batch hydrocarbon liquid, aqueous, and wax samples will be priority shipped to PETC for analysis and they will fax the results back to LaPorte. This should allow for a 48 hour turnaround time on liquid and wax analysis. Two samples per day <u>each</u> of the liquid hydrocarbon, wax, and aqueous cuts will be analyzed. This plan may be modified when Shell joins the discussions, since they have previously offered analytical capabilities. PETC has the capabilities to analyze C_{15}-C_{45} hydrocarbons and intends to archive all samples received from LaPorte for future re-analysis.
	Exxon		Exxon offered to analyze a <u>limited</u> number of representative wax samples from the run. Their analytical capabilities include C_{10}-$C_{10,000}$.
			An analytical sub-committee was identified for future decisions which included Curt White (DOE Analytical Group), Hemant Gala (UOP), Bharat Bhatt (APCI), and Rocco Fiato (Exxon).
11.	UOP/DOE/ Exxon/APCI		A "dry run" of the analytical methods will be conducted using the products made from the UOP autoclave high temperature test. UOP will forward to both PETC and Exxon samples of the hydrocarbon liquid and wax. They will also send to PETC an aqueous product sample. With the gas analysis from UOP, the partners will try to piece together a Schultz-Flory α distribution. In addition, PETC will send a sample of their typical hydrocarbon and wax reports to Bharat Bhatt, so APCI can the LaPorte data acquisition system.

ITEM NO.	RESPONSIBLE PERSON (INITIALS)	TARGET DATE	DISCUSSION
12.	ALL		Some areas of operations which will require further action from the partners include: • Due to the expected exotherm, it is desirable that the LaPorte reactor only be preheated to 240°C during catalyst activation. Heat of reaction will then increase the temperature further. UOP currently does catalyst activation at 280°C. Any effects on catalyst activity of introducing syngas at the lower temperature will need to be quantified before the run. • The amount of aromatics which the present catalyst makes must be quantified before the LaPorte run so that the appropriate safety precautions may be taken. • Ed Heydorn (APCI) will investigate how the analytical samples can be shipped to PETC for analysis. The equivalent of MSDS's will be required, as may special packaging or ground transportation, instead of air. • Each partner must let APCI know what quantity of each product cut they want at the end of the run. This will affect APCI storage and therefore, APCI safety/hazard analysis. • The concept of lowering the operating pressure to increase the superficial velocity through the reactor was discussed. Currently, APCI intends to run LaPorte at 200 psig and 400 psig.
13.			Bharat Bhatt presented the results from the cross flow filter tests. The results were disappointing, but APCI has incorporated a gravity settling method into the system so that the filters will see a less concentrated slurry than was tested. No additional tests are planned with the filters since it would require an additional 10 to 12 lbs of reduced catalyst, which is not available. The first set of tests were done with the catalyst oxide. It is known that the reduced catalyst properties are much different than that of the oxide.
14.			The reactor feed gas will have a H_2/CO ratio of 0.7 and will contain no CO_2.

NOTES FROM MEETING
CONTINUATION

ITEM NO.	RESPONSIBLE PERSON (INITIALS)	TARGET DATE	DISCUSSION
15.			The partners identified their criteria of success: • high number of days on stream • good catalyst activity- CO conversion at least 50% • stable bubble column reactor performance • good correlation of catalyst performance between the autoclaves and the LaPorte reactor Criterion identified as not being required for a successful run included: • clean wax product • % filtration catalyst recovery

Follow-up Discussion with Dr. Fred Tungate (UCI) regarding Catalyst Preparation

After the partners' meeting on March 19-20, follow-up discussions were held by Dr. Bharat Bhatt (APCI) and Dr. Rocco Fiato (Exxon) with Dr. Fred Tungate (UCI) regarding the catalyst preparation for the F-T run at LaPorte. UCI has agreed to prepare two different low alpha catalysts on a small scale by end April. One batch will made with about 1% K_2O and 1.6% SiO_2, starting with potassium silicate. This requires a minimum change from the current method of producing high alpha catalyst which also uses potassium silicate as starting material (5.9% K_2O and 9.7% SiO_2). The K_2O to SiO_2 ratio would remain the same. The second batch would involve adding extra SiO_2 from another source making up to 5% SiO_2. The second batch will be a back-up catalyst, in case the first batch has less than acceptable physical properties due to lower silica content. Both the samples would be tested for physical properties such as attrition resistance by UCI. UOP will quickly activity test the catalyst selected from the two in early May. By mid-May, a decision will be made on whether to proceed with a high or a low alpha catalyst. UCI has blocked out pilot plant time to prepare 2000 lbs of the selected catalyst between mid-May and mid-June. Thus, the catalyst would be prepared in time for the July run as scheduled. Dr. Udaya Rao (DOE) and Dr. Hemant Gala (UOP) were consulted during the discussions and they are in agreement with the above plans.

Follow-up Discussion with Dr. Rocco Fiato (Exxon) regarding Starting Wax

Follow-up discussions were held by Dr. Bharat Bhatt (APCI) with Dr. Rocco Fiato (Exxon) regarding the supply of the starting wax for the LaPorte F-T run. For Exxon to supply their process wax, they would need to restrict access to their wax and would require those with the access to sign a non-disclosure agreement with them. However, since starting wax would end up with the product wax, it would be very difficult to limit access to the starting wax. Also, with the run coming up in about three months, there is not enough time to get legal agreements in place. Exxon offered Isopar, which is a C_{20}-C_{30} saturated isoparaffin liquid. In absence of availability of wax, APCI would rather use Drakeol-10, which has been extensively successfully used at LaPorte for LPMEOH and LPDME. Drakeol-10 is a C_{16}-C_{38} saturated hydrocarbon liquid which includes straight chain and branched paraffins as well as naphthenic compounds. Dr. Rocco Fiato agrees with the plan of using Drakeol-10. The catalyst performance would be independent of starting medium so long as it does not contain any contaminants. Dr. Udaya Rao (DOE) and Dr. Hemant Gala (UOP) were consulted during the discussions and they are in agreement with our plans of using Drakeol-10. Drakeol-10 will be used by UOP in future tests after a catalyst decision has been made. Information on Drakeol-10 is given below.

Information on Drakeol-10

Drakeol-10 is a white mineral oil, manufactured by Penreco. It contains C_{16}-C_{38} saturated straight chain and branched paraffins as well as naphthenic hydrocarbons. Some relevant physical properties of Drakeol-10 are given in Table 1. Results of a simulated distillation (ASTM D2887-73) to check for the oil's stability are shown in Figure 1. A calibration curve using n-alkanes as a standard to identify carbon numbers quantitatively is given in Figure 2. C_{25} is the maximum ingredient of the oil. The autoclave spent sample shows only a slight decrease in the light ends ($< C_{20}$). Density, viscosity, thermal conductivity and heat capacity of Drakeol-10 as function of temperature are given in Figures 3-6.

Proposed Run Plan

The proposed run plan as discussed at the partners' meeting is summarized in Table 2. The plan was accepted by the partners. About 780 lbs of catalyst and 210 gallons of Drakeol-10 will be loaded in the reactor to make about 35 wt% slurry. The catalyst will be activated using 0.7 H_2/CO syngas at 2000 nl/hr-kg Fe, 150 psig and 280°C for about 12-16 hours. About 1% N_2 will be added to the syngas as an internal standard. The inlet gas velocity of about 0.23 ft/sec will be sufficient for adequate mixing. Expanded slurry height of 20 ft, which is maximum, will be maintained throughout the run. The decline in CO_2 and rise in CH_4 content of the product gas will be monitored and when they level off, the operating conditions will be changed to Run No. 1.

Run No. 1

The baseline run will be conducted with 0.7 H_2/CO syngas (1% N_2) at 2500 nl/hr-kg Fe, 200 psig and 265°C. It is estimated that the reactor will contain about 490-500 lbs of catalyst during the run; the remaining catalyst will be in the slurry holding tank and the cross-flow filter system. The slurry concentration in the reactor will be about 26 wt%. The inlet gas velocity will be about 0.14 ft/sec, which is the minimum velocity required for adequate mixing. Run No. 1 will be continued for 10 days to check for stabilization of the catalyst performance. The conditions of Run No. 1 will be repeated for 4 days after Run No. 3 to check for any catalyst deactivation.

Run No. 2

Following Run No. 1, the space velocity will be doubled to 5000 nl/hr-kg Fe at 200 psig and 265°C to study the effect of space velocity. The inlet gas velocity will be about 0.27 ft/sec. These conditions will be maintained for 3 days.

Run No. 3

The reactor pressure will then be doubled to 400 psig at 5000 nl/hr-kg Fe and 265°C to study the effect of reactor pressure. The inlet gas velocity will be back to about 0.14 ft/sec. Run at these conditions will be continued for 3 days.

Catalyst Loading

The catalyst loading in the above plan is based on the use of high alpha catalyst, requiring significant catalyst-wax separation. The initial loading may be reduced if our efforts to prepare a low alpha catalyst are successful. Lower wax production will mean lower catalyst inventory outside the reactor. The reactor slurry concentration will remain the same.

Table 1

Drakeol-10 Physical Properties

Average Molecular Weight	366
Distillation (ASTM D1160), °C	
IBP	283
10%	353
50%	407
90%	481
Specific Gravity, g/ml	
25°C	0.849
Hydrocarbon Type (PONA) % Paraffinic/Naphthenic	65/35
Surface Tension, DYNE/CM	
25°C	30
Viscosity, CP	
25°C	31.2
Pour Point, °C	-7
Flash Point, °C	185

Table 2

RUN PLAN FOR F-T SYNTHESIS

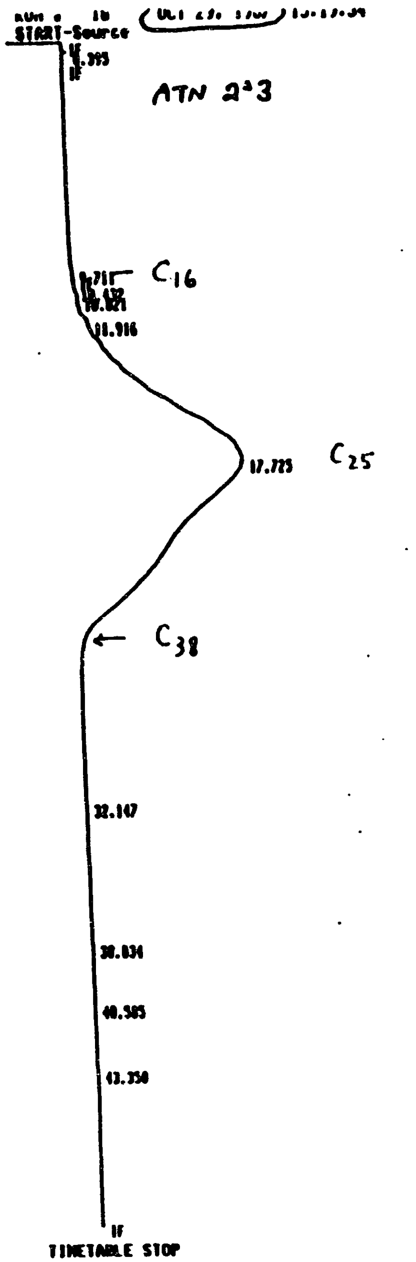
SYNGAS COMP. = 0.7 H_2/CO, ~~2% CO_2~~, 1% N_2
EXPANDED SLURRY HT = 20 FT (MAX)

RUN NO.	SPACE VEL. NL/KG-FE-HR	RX PRS. PSIG	RX TEMP. DEG C	NO. OF DAYS ON-STREAM	CATALYST CONC, WT%	LIN. GAS VEL (IN), FT/SEC	LIN. GAS VEL (OUT), FT/SEC	CO CONV. %	S-F ALPHA	WAX GPD	LIQ HC GPD	WATER GPD
ACTIVATION	2000	150	280	1	35	0.23						
1	2500	200	265	10+4	26	0.14	0.09	58	0.95	164	74	47
									0.90	118	117	47
									0.85	55	149	47
2	5000	200	265	3	26	0.27	0.19	47	0.95	255	120	77
									0.90	171	193	77
									0.85	65	243	77
3	5000	400	265	3	26	0.14	0.09	59	0.95	349	125	94
									0.90	241	219	94
									0.85	125	286	94

FIGURE 1 - Simulated Distillation of Drakeol 10 Oil

Drakeol 10 , Fresh

% OFF	BOILING POINT(F)
INITIAL BOILING POINT=	580.360 F
5	649.224
10	677.546
15	696.054
20	709.503
25	721.079
30	731.727
35	741.155
40	750.165
45	759.043
50	768.401
55	777.994
60	787.673
65	798.207
70	809.684
75	822.190
80	836.360
85	853.096
90	872.686
95	894.496
FINAL BOILING POINT =	932.06 F



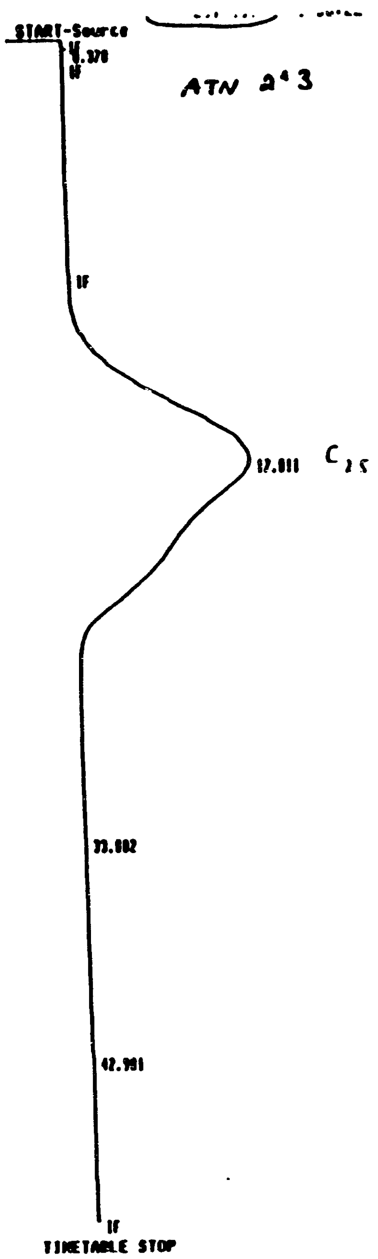
TIMETABLE STOP

Error storing signal to A1056A7087.BHA

Drakeol 10, Spent
(Run # 9397-19)

SAMPLE ID:
SONTEX 100 RUN 9397-19

% OFF	BOILING POINT(F)
INITIAL BOILING POINT=	627.106 F
5	673.921
10	695.211
15	709.479
20	720.972
25	731.403
30	740.630
35	749.200
40	757.920
45	766.909
50	775.962
55	784.011
60	794.276
65	804.597
70	815.037
75	828.035
80	841.600
85	858.096
90	876.430
95	897.452
FINAL BOILING POINT =	933.904 F



TIMETABLE STOP

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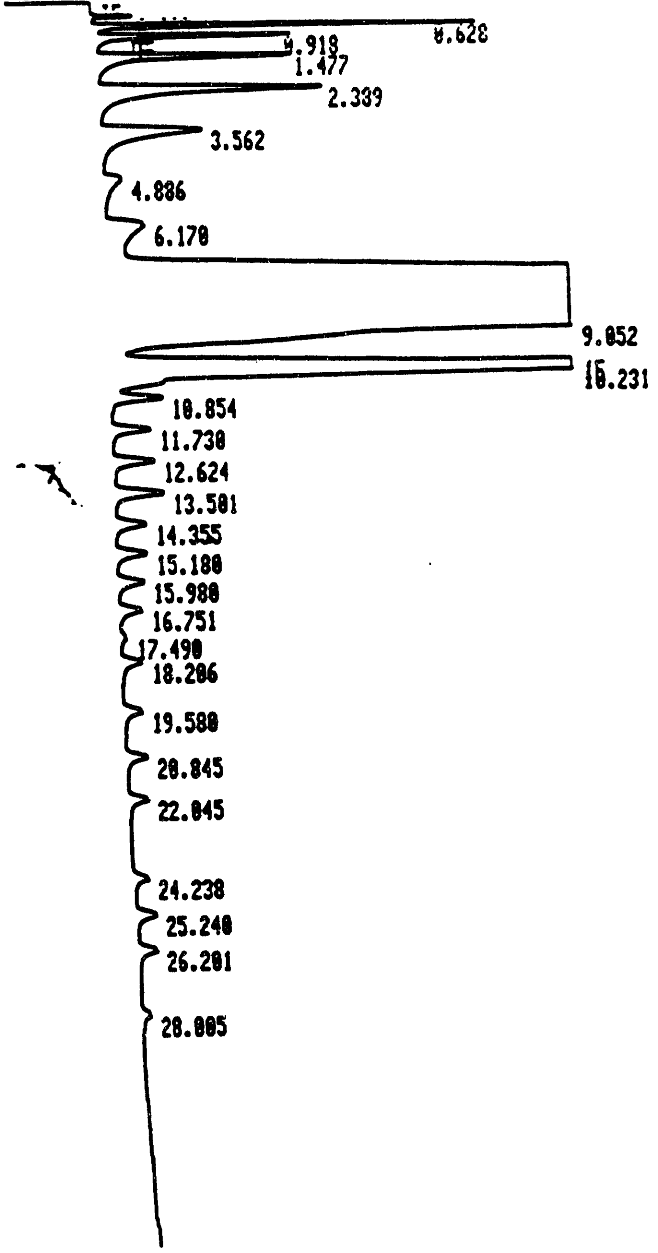
FIGURE 2 - Calibration Curve

```
*  RUN #   30      NOV  2, 1987  10:27:51
START-Source
```

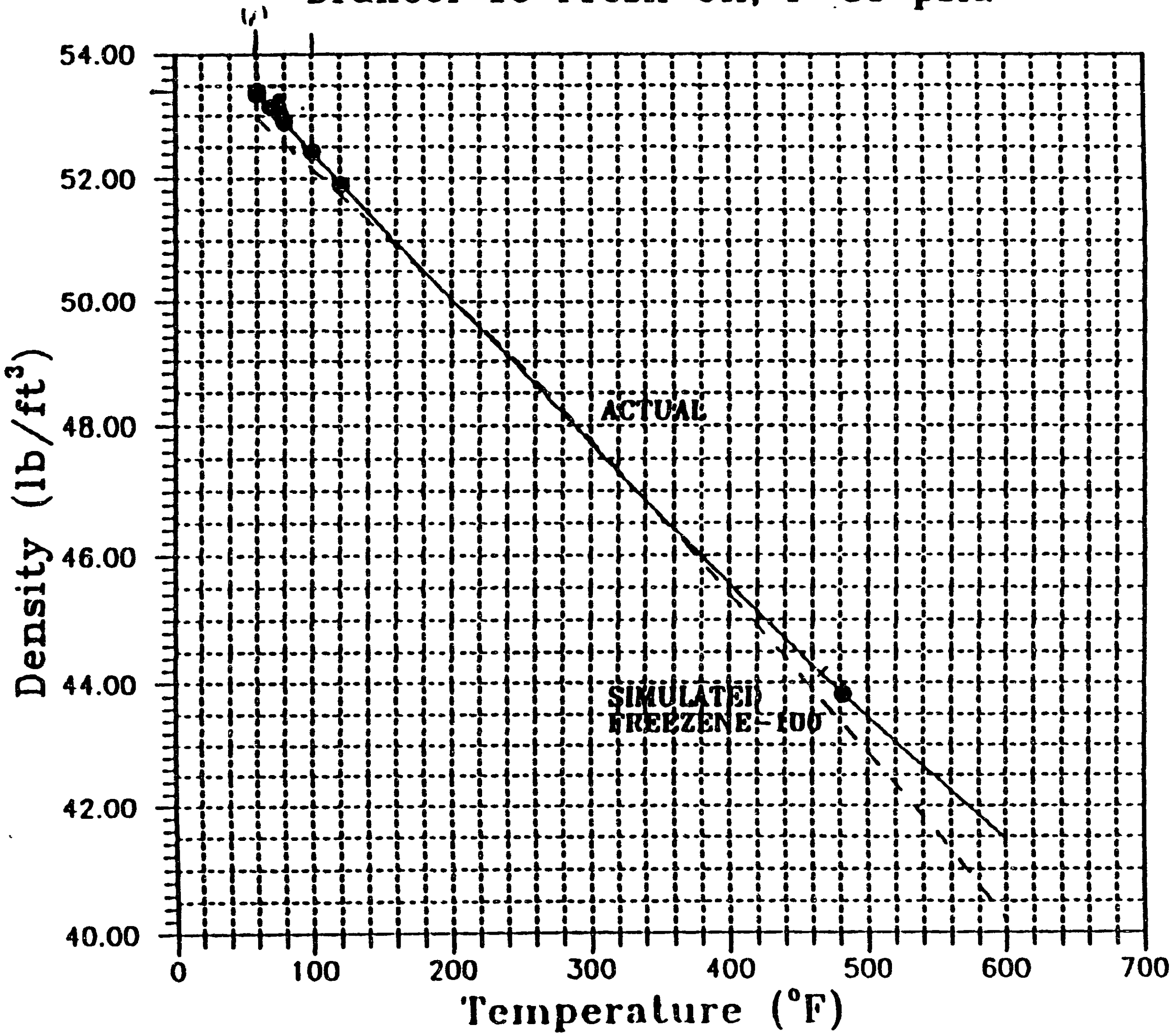


```
STOP

Closing signal file B:Q56F71A7.BNC

RUN#    30          NOV  2, 1987  10:27:51

SIGNAL FILE: B:Q56F71A7.BNC
```

```
CAL#      RT       LV     AMT         AMT/AREA
  1      0.636     1 1.0000E+00   2.0032E-04
  2      0.940     1 1.0000E+00   9.1617E-05
  3      1.524     1 1.0000E+00   5.8343E-05
  4      2.464     1 1.0000E+00   2.5201E-05
  5      3.653     1 1.0000E+00   3.4171E-05
  6      4.984     1 1.0000E+00   2.9069E-05
  7      6.284     1 1.0000E+00   3.2380E-0
  8      7.590     1 1.0000E+00   1.6522E-07
  9      9.830     1 1.0000E+00   1.6096E-07
 10     10.960     1 1.0000E+00   1.1920E-0
 11     11.844     1 1.0000E+00   1.2240E-0
 12     12.739     1 1.0000E+00   1.2550E-0
 13     13.615     1 1.0000E+00   1.3094E-0
 14     14.468     1 1.0000E+00   1.2376E-0
 15     15.296     1 1.0000E+00   1.2878E-0
 16     16.095     1 1.0000E+00   1.8818E-0
 17     16.868     1 1.0000E+00   6.9798E-0
 18     17.624     1 1.0000E+00   6.9798E-0
 19     18.327     1 1.0000E+00   1.2035E-0
 20     19.691     1 1.0000E+00   1.3235E-0
 21     20.964     1 1.0000E+00   1.2464E-
 22     22.162     1 1.0000E+00   1.1039E-0
 23     24.366     1 1.0000E+00   9.5611E-0
 24     25.365     1 1.0000E+00   8.7827E-0
 25     26.331     1 1.0000E+00   8.4904E-0
 26     27.380     1 1.0000E+00   1.0000E+0

CAL#    NAME
  1   C7
  2   C8
  3   C9
  4   C10
  5   C11
  6   C12
  7   C13
  8   C14
  9   C16
 10   C17
 11   C18
 12   C19
 13   C20
 14   C21
 15   C22
 16   C23
 17   C24
 18   C25
 19   C26
 20   C28
 21   C30
 22   C32
 23   C36
 24   C38
 25   C40
 26   C44
```

DENSITY vs. TEMPERATURE

Drakeol 10 Fresh Oil, P=85 psia



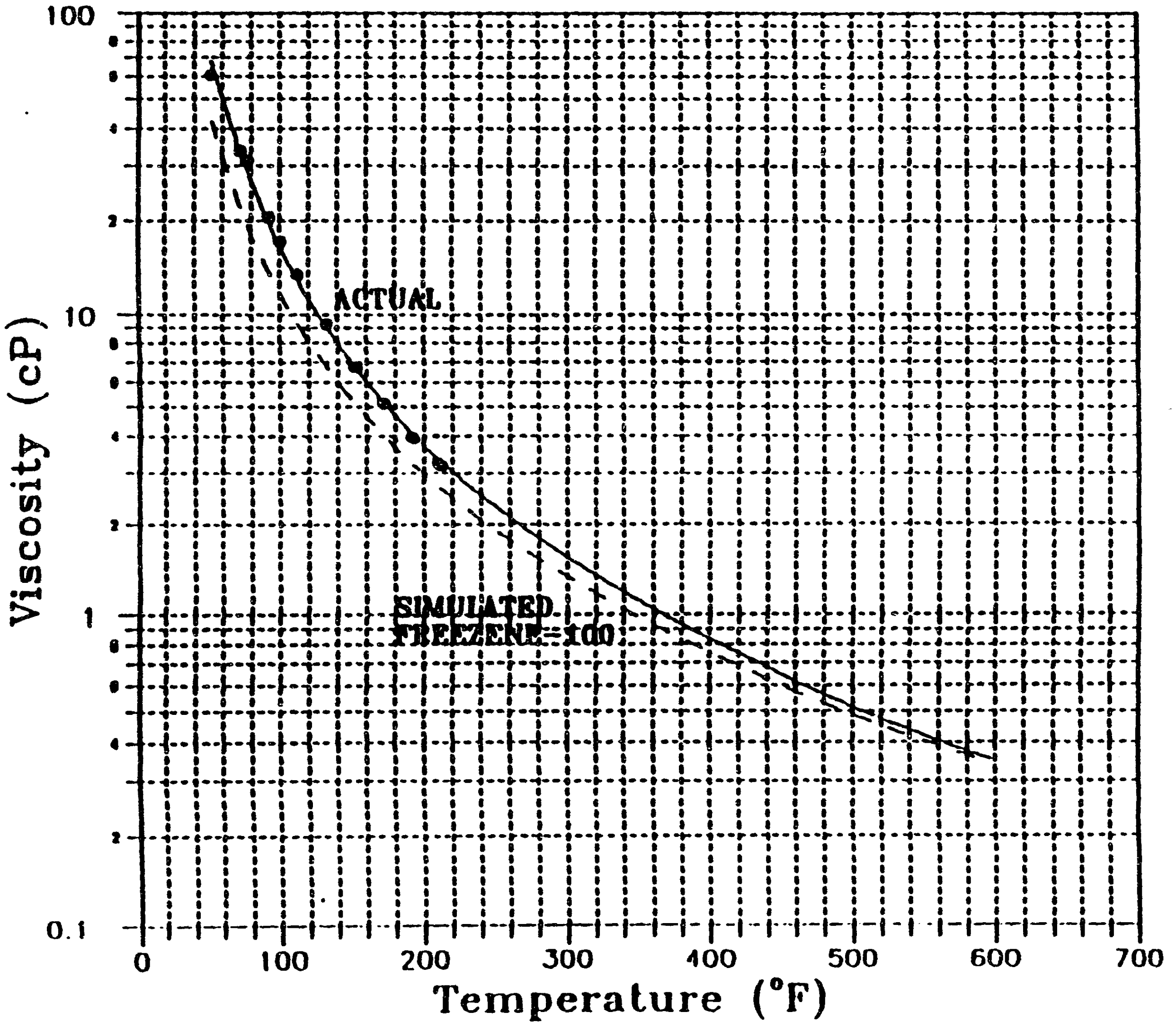
$Y = 4.914e-6X^2 - 0.02534X + 54.00$ Actual

$Y = -6.817e-6X^2 - 0.01910X + 54.13$ Simulated

FIGURE 3

VISCOSITY vs. TEMPERATURE

Drakeol 10 Fresh Oil, P=85 psia



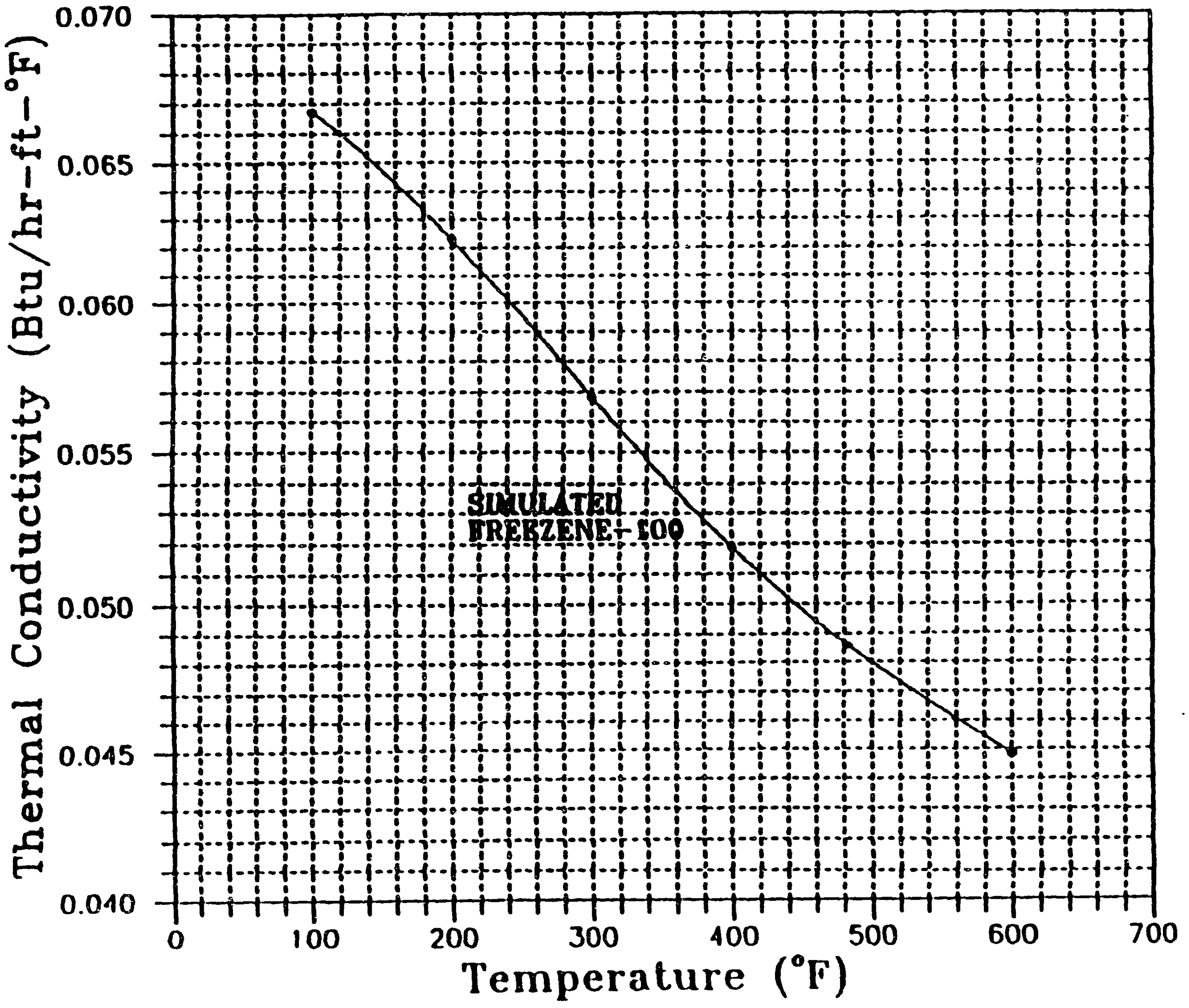
$Y = 339000 \cdot X^{-2.166}$ Actual

$Y = 103500 \cdot X^{-1.974}$ Simulated

FIGURE 4

CONDUCTIVITY vs. TEMPERATURE

Drakeol 10 Fresh Oil, P=85 psia

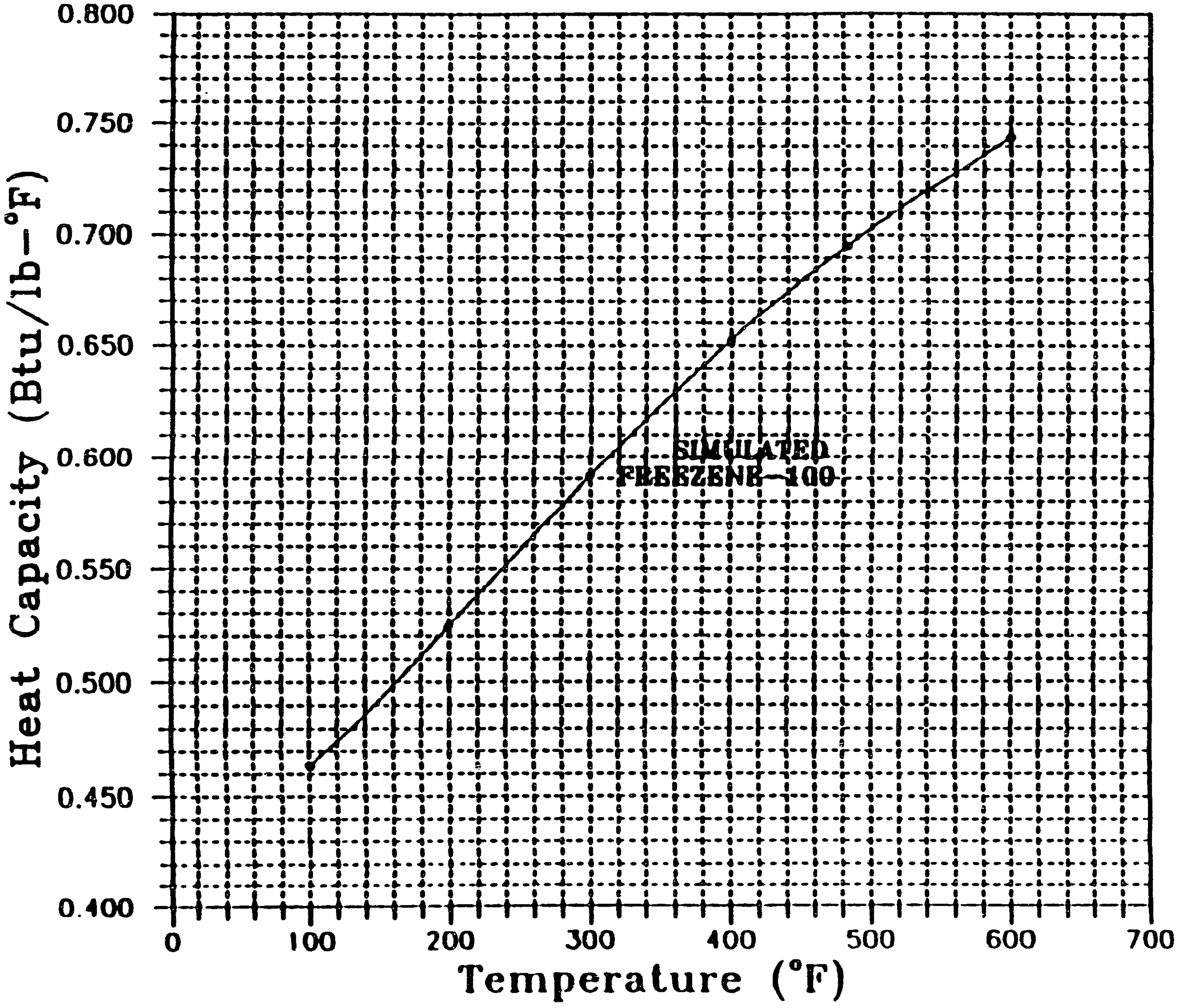


$Y = -3.035e-13X^4 + 6.050e-10X^3 - 3.207e-7X^2 + 1.470e-5X + 0.06787$

FIGURE 5

HEAT CAPACITY vs. TEMPERATURE

Drakeol 10 Fresh Oil, P=85 psia



$Y = 2.012E-12X^4 - 4.520e-0X^3 + 2.357e-0X^2 + 1.013e-4X + 0.4201$

FIGURE 6

DATE
FILMED

5/12/93