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DEVELOPMENT OF ALTERNATIVE FUELS
FROM COAL-DERIVED SYNGAS

Quarterly Technical Progress Report No. 1
For The Period 1 October - 30 December 1990

Contractor

AIR PRODUCTS AND CHEMICALS, INC.
7201 Hamilton Blvd.
Allentown, PA 18195-1501

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DEVELOPMENT OF ALTERNATIVE FUELS
FROM COAL-DERIVED SYNGAS

Quarterly Technical Progress Report
1 October - 31 December 1990

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:

- Work on this program began under a Letter of Intent, from DOE/PETC; and the formal contract was in place by 15 November 1990. Considerable overlap exists in 1) the PDU (AFDU) engineering studies that were well underway as part of LPMEOH Part III (DE-AC22-87PC90005), and 2) the new fuels-from-syngas research which continues as part of the Oxygenated Fuels R&D program (DE-AC22-90PC89865). This overlap provides for a smooth, efficient transition from one program to the other.
- Project work on the Spring 1991 Enhanced Syngas Conversion (dimethyl ether) demonstration at the LaPorte AFDU continues. All remaining purchased material was placed on order with most material and equipment expected on-site by mid to late January 1991. A leasing agreement is being negotiated for the supply of CO₂ during the demonstration run. All required catalyst for the spring run was ordered.
- A site visit was made by members of the PSG Design team to layout the scope of work required to modify the unit for the demonstration run. Design packages are in progress and will be completed in mid-January. A piping Bill of Material was developed and long-lead piping materials were ordered.
- A final P&ID review meeting was conducted with minor changes noted and the Rev. 1 P&ID will be circulated in January.
- Environmental Engineering and Process Engineering continue to put together a new air exemption permit application. Air Products' original plan to operate under the existing exemption was rejected by the Texas Air Control Board due to recent court rulings in the state of Texas. This new application will be filed in January.

- Meetings were conducted with members of Research and Development, Project Management, Operations, and Project Engineering to confirm the operating objectives for LaPorte during the Alternative Fuels I (and II) campaigns. While the meetings did not result in complete definition of the program direction, action items resulted. These will serve to concentrate efforts on further definition of the products as well as the equipment configuration necessary to achieve these goals.
- Initial activities for the development of new fuels from dimethyl ether (Task 3.2) started in October with (1) ordering of a Bench Top Reactor System (BTRS) from Autoclave Engineers (delivery end of March 1991), (2) fabricating two micro-reactors for preliminary catalyst screening (completion end of February 1991), (3) preparing 30-35 catalysts with metals doped into oxide supports of various basicity, (4) establishing a model reaction (vinylation of methyl acetate with methanol to form methyl acrylate) to evaluate the catalyst performance and preparation procedure, and (5) submitting expected oxygenates from Task 3.2 to SWRI for blending with stock gasoline in order to determine Motor (M) and Research (R) octane numbers.
- Although a Milestone Schedule Status Report and a Milestone Log were prepared this quarter for program use, a definitive cost summary for the quarter is not yet available. We anticipate having a satisfactory version in place by the January/February Quarterly meeting.
- Discussions were held with DOE, Exxon, Mobil and UOP at the PETC Contractors Conference on the merits of carrying out a demonstration of Fischer-Tropsch technology at LaPorte. Exxon appears very interested and is considering both technical and financial contributions. DOE has indicated their commitment to a Fall '91 demonstration run and is considering increasing the available funds in the Alternative Fuels program.

Future Plans

- Accelerate and broaden the research programs aimed at producing higher ethers from 1) syngas/mixed alcohols, and 2) syngas/DME.
- Maintain the high level of engineering activities going into preparations for the High Syngas Conversion (DME) run planned for the LaPorte AFDU in Spring 1991.
- Continue discussions towards modifying the program so as to include demonstration of Fischer-Tropsch technology at the AFDU.

RESULTS AND DISCUSSION

TASK 1: ENGINEERING AND MODIFICATIONS

Hazards Review

A Preliminary Process Hazards Review (PrHR) meetings was conducted on 16 October 1990 with attenders from Process, Start-up, Project, and Safety Engineering groups. The purpose of the meeting was to highlight any major hazards and define any further areas of study. The scope of review was limited to the proposed Spring 1991 run. A report was prepared and is included as Appendix A. Several of the identified hazards have been addressed and the resolutions are documented below. A second hazards review meeting will be conducted in February 1991 (design verification review) with the purpose of (1) assuring that all of the hazard items identified in the PrHR have been properly addressed, and (2) outlining the agenda for an operational readiness inspection (ORI).

Refer to part C of the Preliminary Process Hazards Review Report (Appendix A) for the following items:

Item #3. Detailed line specifications specific to the process conditions dictated by the Spring 1991 run were developed. The specifications define all material design and composition requirements associated with the new piping system.

Item #8. A fitness for service analysis for the use of three existing vessels in a different service (vessel numbers 21.38, 22.14, and 22.18) was conducted, and the conclusions are documented in Appendix B (memo from J. C. Tafuri to D. M. Herron dated 4 December 1990).

P&ID Development

The P&ID was developed using the process flow diagram (see Figure 1) as a starting basis and defined in further detail through a matrix review iteration process. The review process included a matrix review meeting, the consolidation of notes onto a single copy, drafting, and distribution (after drafting) for further reviews.

The first phase was to develop a revision P (preliminary) version which included all major equipment items, the basic control logic, all major process lines, and most major manual and control valves. Next, a revision O version was developed which included the following in addition to the previous revision: all process line sizes; the detailed control logic; all in-line instruments; the preliminary tie-in and plant shutdown/interlock tables; and all valve, line, and insulation tag identifications. Lastly, a revision 1 version will be distributed in January 1991. The revision 1 version includes the following information in addition to the previous revision; relief valve headers, vent and drain locations; the completed tie-in and shutdown/interlock tables; final instrument and control information; and the results of an operability, start-up, and shutdown analysis.

Figure 1

Specification/Design

The specification process was structured by the expected procurement durations and began with focus on major equipment items followed by in-line control valves, manual valves, and instrumentation. To date, all specification work is complete with the exception of any punchlist/start-up items.

To initiate the design process, a kickoff meeting was conducted, and the project's basic design execution strategy was established. Next, major equipment orientations and locations were fixed and used as a baseline for mechanical design work. A group site visit was conducted in early December with participants from the piping, instrument, and electrical design groups, as well as process and project engineering. The objective of the visit was to establish basic design strategies and to verify the accuracy of existing plant design documentation.

Following the site visit, detailed mechanical design (piping and structural) and civil design work was initiated and was 75% complete by 31 December 1990. Piping isometrics, equipment arrangement, structural steel, and isometrics, equipment arrangement, structural steel, and foundation packages will be completed in early January.

Concurrent with the initiation of mechanical design work, an instrument/electrical kickoff meeting was held, and schedule commitments were obtained for this work to be completed by 25 January 1991.

Procurement

Purchase orders were issued for all major equipment items (tag numbers 21.45, 21.80, and 28.40) as well as for the modifications to the 22.14 and 22.18 vessels. Orders were also placed for control valves, manual valves, safety valves, and other instrumentation. All orders placed were issued in accordance with Air Products normal procurement procedures.

Permitting

Efforts toward obtaining an approval to utilize the existing air exemption permit were redirected as a result of feedback from the Texas Air Control Board on our initial application. Recent court ruling in the state of Texas prohibited an acceptance of our application.

A fall-back plan was established, and our environmental, project, and process engineering team worked towards preparing a second permit application. This application will request an exemption be granted per the provisions of the Texas Air Control Board's Standard Exemption 106 (11 August 1989).

TASK 2: AFDU SHAKEDOWN, OPERATIONS, DEACTIVATION, AND DISPOSAL

No significant activity to report for the quarter. Activities on Shakedown (Task 2.1) will start in earnest at the AFDU during January.

Meanwhile the LaPorte AFDU shelter modification continued as funded and described in the overlapping program, No. DE-AC22-87PC90005.

TASK 3: RESEARCH PROGRAM

Task 3.1 New Fuels From Syngas

Much of the work anticipated under this subtask cannot start until the preliminary exploratory work in the Oxygenated Fuels R&D program (No. DE-AC22-90PC89865) is complete. This work focuses on the one-step synthesis of higher ethers and mixed alcohols from synthesis gas. Dehydration of C₂+ alcohols to C₄+ ethers is also featured.

As a result of the overlap, the initial activities under this program will not be reported until the February Quarterly Meeting.

Task 3.2 New Fuels From Dimethyl Ether (DME)

I. Overall 1QFY91 Objectives

Exploratory research for the synthesis of mixed ethers from DME has a set of objectives for 1QFY91. These are:

- laboratory reactor procurement and installation
- Process Hazards Review
- catalyst preparations
- catalyst evaluation on oxidative coupling and vinylation
- SWRI octane number (R and M) evaluation for oxygenates

II. Laboratory Reactor Procurement

- A. An order for a Model 900 Micro-Scale Bench-Top Reactor System (BTRS) was placed with Autoclave Engineers on 31 October 1990. Delivery of the system is scheduled for March 1991. The unit has a dual fixed-bed, tubular reactor equipped with mass flow controllers, HPLC pumps, heated oven for vaporization and mixing, gas/liquid separator and on-line GC. The system is also automated with a process controller (see Appendix C for general description). The physical location for the BTRS has been fitted with the necessary gas lines (N₂, D₂, H₂, He), house air and power requirements. Fabrication of the necessary table and racks for the BTRS is set for completion on 1 February 1991.
- B. In addition to the BTRS but for more near-term use, dual atmospheric gas-phase tubular reactors were reviewed with a PrHR and fabrication initiated. These reactors are designed for initial screening of catalysts prepared for DME coupling and vinylation experiments. A process flow diagram for the dual tubular reactors is in Appendix D. Complete fabrication is scheduled for January 1991 with system shakedown planned for February 1991.

C. For immediate use and very preliminary experiments, an existing gas phase reactor system was modified for on-line analysis to start the catalyst screening with a model probe reaction (see IV-b).

III. Catalyst Preparations

A general procedure was adopted for the preparation of redox metal ions doped on oxide supports. The preparation sequence consisted of impregnation of metal salt solutions (H_2O , CH_3OH or CH_3CN/H_2) on pellets (12-20 mesh) or powder, drying at $100^\circ C$, wafer disk formation from powders, sieving, and calcination at $400^\circ C$ for 1 hr. Table 1 summarizes the catalysts prepared in 10 g quantities for initial screening experiments on oxidative coupling of DME and vinylation of DME.

Table 1
Catalyst Preparations

<u>Support</u>	<u>Metal</u>	<u>% Metal By Wt.</u>
MgO	Sn, Mn, Fe	3 and 9
	Cu, Cr	3
	Rh, Ru, Ir, Pt	1
CaO	Sn, Mn, Fe	3 and 9
	Cu, Cr, Ni	3
SrO	Sn, Fe	3
BaO	Sn	3
La ₂ O ₃	Sn, Cr, Cu, Fe, Mn	3
ZrO ₂	Sn, Cr	3
TiO ₂ (anatase)	Sn, Fe, Mn	3
TiO ₂ (rutile)	Sm, Fe, Mn	3

IV. Catalyst Evaluation

A. Thermodynamics

Thermodynamics using ideal gas properties for reactants and products give the following ΔG_{rxn} at 473K. The primary products of the proposed chemistries to be studied are all favored thermodynamically.

(1) Oxidative coupling

$$\Delta G_{\text{rxn.}} = -45.6 \text{ Kcal per mol}$$

(2) Vinylation

$$\Delta G_{\text{rxn.}} = -58.0 \text{ Kcal per mol}$$

or

$$\Delta G_{\text{rxn.}} = -14.8 \text{ Kcal per mol}$$

B. Model Probe Reaction

A model reaction was chosen to probe catalyst activity and selectivity. In addition, the model reaction would give information on the catalyst preparation procedures. The first model reaction chosen was the oxidative addition of methanol to acetone to form methyl vinyl ketone (MVK). The

reactor in II-C described above was used in these studies. Instead of on-line gas sampling, the liquid product(s) was collected at the exit of the reactor. A series of catalysts were screened, and the results are summarized in Table 2.

Table 2

Conversion of Methanol and Acetone

<u>Catalyst</u>	Acetone Conversion		Selectivity to C ₄ + Oxygenates (wt. %)						
	<u>IPA</u>	<u>C₄+</u>	<u>MVK</u>	<u>MEK</u>	<u>C₄</u>	<u>C₅</u>	<u>C₆</u>	<u>C₇, C₈</u>	<u>C₉±</u>
3% Sn/MgO	4	17	14	22	38	8	7	47	1
9% Sn/MgO	0	12	24	34	60	8	7	24	1
3% Sn/CaO	9	9	14	22	53	9	5	32	1
3% Sn/TiO ₂	0	5	71	7	78	2	7	12	0

5% methanol, 5% acetone in nitrogen: 80 sccm,
1 grams catalyst, 400°C

Mass spectroscopy of the products of this reaction showed that the majority of the components were the products from the aldol condensation of the acetone, MVK, and methyl ethyl ketone (MEK). Hydrogenation of acetone to isopropyl alcohol (IPA) and vinyl compounds to saturated ketones occurs by either hydrogen transfer or gaseous hydrogen formed during dehydrogenation of methanol to formaldehyde. The complicated product spectrum limits the utility of this reaction as a model reaction, but initial results show the effect of a basic support (aldol condensation of acetone to C₆+ products). In addition, these and other catalysts tested gave similar results as literature data on the oxidative addition of methanol to acetone. Therefore, credence is given to the catalyst preparation procedures.

The second model reaction examined was the oxidative addition of methanol to methyl acetate to form methyl acrylate. Initial

results show that the reactivity of methyl acetate for oxidative addition is much lower than for acetone. Results are shown in Table 3. This reaction is also complicated by the formation of both methanol and acetone from methyl acetate especially over the catalysts with basic supports.

Table 3

Conversion of Methanol and Methyl Acetate

<u>Catalyst</u>	<u>Conv.</u>	<u>Esters</u>		<u>Selectivity (wt. %)</u>					
		<u>MA</u>	<u>MP</u>	<u>MMA</u>	<u>MiB</u>	<u>ACE</u>	<u>C₄-C₆</u>	<u>C₇±</u>	<u>Unkn.</u>
3% Sn/MgO	1.2	20	10	1	2	50	4	1	12
3% Sn/CaO	2.7	1	6	1	5	71	9	4	3
3% Sn/TiO ₂	1.9	23	3	0	1	25	12	0	36

<u>MA</u> :	methyl acrylate	<u>MP</u> :	methyl propionate
<u>MMA</u> :	methyl methacrylate	<u>MiB</u> :	methyl isobutyrate
<u>ACE</u> :	acetone	<u>C₄-C₆</u> :	ketones
<u>C₇±</u> :	higher esters and/or ketones		
<u>Unkn</u> :	Unknown		

5% methanol, 5% methyl acetate in nitrogen: 80 sccm,
2 grams catalyst, 400°C

C. Octane Numbers

Southwest Research Institute (SWRI) has been contacted to measure Reid vapor pressure, Motor and Research octane numbers on expected oxygenates from this program. The first set of mixture properties was based on a stock gasoline with an Rvp of 9 psi and $(R + M)/2$ of 92.9. Oxygenates of methyl acetate, dimethoxyethane and MTBE (control) gave blending $(R + M)/2$ of 95, 43 and 115 at 8.1%, 9.8%, and 11.0% by weight, respectively. The initial gasoline should have had a $(R + M)/2$ of 86-87 instead of 92.9. Therefore another set of oxygenates has been submitted for properties. These pending results will assess reproducibility of the tests and better define the blending characteristics of the oxygenates.

Task 3.1 Catalyst Poison Studies

With the attention being given to preparations for the Spring 1991 operations at the LaPorte AFDU, the start of this activity has been delayed until January 1991.

TASK 5: PROGRAM MANAGEMENT

Task 5.1 Planning and Reports

Monthly reports for October and November 1990 were prepared and submitted to DOE. A Milestone Schedule Status Report and Milestone Log were both prepared for ongoing contract use. Although monthly cost summaries are being collected for this project, work is continuing on obtaining the best format for their presentation. It is our intention to have the cost summary in acceptable form by late January when the program Management Plan should issue. The cost summary will also be addressed at the next Quarterly meeting, scheduled for early February 1991.

A paper entitled "Syntheses of DME and Alternative Fuels in the Liquid Phase from Coal-derived Gas" was presented by B. L. Bhatt at DOE's Indirect Liquefaction Contractors' Review Meeting in Pittsburgh. The paper was well received and generated significant interest.

Task 5.2 Management Activities

The DOE Annual Contractor's Review meeting, held in Pittsburgh in November, was attended by members of Process and R&D. This meeting allowed contractors in the Oxygenated fuels and Fischer-Tropsch synthesis programs to present progress reports (Air Products presented results of the DME laboratory work). A number of informal discussions were also conducted between members of DOE/Air Products and EXXON, Mobil and UOP to describe the technical objectives of a proposed demonstration of Fischer-Tropsch at the LaPorte AFDU. Discussions also focused on technical and financial support for this program. EXXON appears the most interested and is considering both technical (analytical methods, for example), as well as financial contributions towards this demonstration (which is planned for late 1991). DOE-PETC continues to demonstrate enthusiasm towards a Fischer-Tropsch demonstration in FY 92.

OPEN ITEMS:

None

ATTACHMENTS:

Milestone Schedule Status Report

Milestone Log

Appendix A Preliminary Process Hazards Review: March 1991 DME
Run - AFDU, LaPorte, Texas

Appendix B Memorandum, Tafuri to Herron: LaPorte AFDU
Operations in Spring 1991 - Materials Review

Appendix C Product Specifications for Model 900 Micro-Scale Bench-Top
Reactor System - Autoclave Engineers

Appendix D Laboratory: Process Flow Diagram

M I L E S T O N E L O G

Report Date: 31 December 1990

Contract No. DE-AC22-91PC90018

<u>Ident. No.</u>	<u>Description</u>	<u>Planned Completion Date</u>	<u>Actual Completion Date</u>	<u>Comments</u>
1.1	Detailed Engineering and Procurement	Apr 92		
1.2	AFDU Modifications	Oct 92		
2.1	AFDU Shakedown	Apr 91		
2.2	AFDU Operations	Jul 93		
2.3	AFDU Reactivation, Deactivation and Disposal	Sep 93		
3.1	New Fuels from Syngas	Oct 92		Delayed Start (complete Oxy. Fields R&D Program)
3.2	New Fuels from DME	May 93		On Schedule
3.3	Catalyst Poisons Studies	Oct 92		Delayed Start
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		

Milestone Schedule Status Report
(In lieu of DOE Form F1332.3)
Development of Alternative Fuels from Coal-Derived Syngas

DE-AC22-91PC90018

Reporting Period: October -- December 1990

Memorandum

Appendix A

To: Distribution Dept./Loc.:
 From: M.R. Jocsak Dept./Ext.: Project Eng./3848
 Date: 18 December 1990
 Subject: Preliminary Process Hazards Review Report: March 1991 DME
 Run - Alternative Fuels Development Unit, LaPorte, TX

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 R.L. Williams
 M.K. Wolk

Please find attached a copy of the Preliminary Process Hazards Review for the March '91 DME run of the Alternative Fuels Development Unit (AFDU) in LaPorte, TX. The review was conducted on 16 October 1990 in accordance with Engineering Procedure R-4.

Please contact me if you have any questions or comments.

 Michael R. Jocsak

MRJ/003

PRELIMINARY PROCESS HAZARDS REVIEW
Alternative Fuels Development Unit (AFDU)

March 1991 Run (DME)

LaPorte, Texas

16 October 1990

Review Team

S. Cronauer	Process Engineering
S. DeWire	Start-Up Engineering
J. R. Hamilton	Start-Up Engineering
D. M. Herron	Process Engineering
M. R. Jocsak	Project Engineering
G. A. Peters	PSG Engineering Safety
D. W. Studer	Process Engineering
R. L. Williams	Project Engineering

Preliminary Process Hazards Review
Alternative Fuels Development Unit (AFDU)
March 1991 Run (DME)
LaPorte, Texas

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Appendices

- I. Process Flow Diagram
- II. Operating Run Schedule, Tables 1a and 1b
- III. Simulation Work Results, Tables 2a-2d
- IV. Table - Comparison of CO Conversion
- V. Table - Comparison of Syngas Conversion
- VI. Reactivity Grid

Preliminary Process Hazards Review
Alternative Fuels Development Unit (AFDU)
March 1991 Run (DME)
LaPorte, Texas

A. INTRODUCTION

A Preliminary Process Hazards Review (PrHR) was conducted for the proposed March 1991 run [dimethyl ether (DME) production] of the Alternative Fuels Development Unit (AFDU) located in LaPorte, TX. The March 1991 run will require modifications and additions to the existing Liquid Phase Methanol (LEMeOH) Process Development Unit (PDU) that has been operated by APCI under various Department of Energy (DOE) contracts for the last ten (10) years. A new contract will be obtained with the DOE to authorize the required work to perform the March 1991 run as well as future runs for other alternative fuel products.

The purpose of the PrHR was to highlight any major hazards and to define any areas of further study. The scope of review was limited to the March 1991 run. Refer to the PrHR published on 22 May 1990 for highlights and recommendations of the proposed "major" modifications of the PDU including reactor train modifications, new distillation and refrigeration areas, and a new storage area.

Since the existing plant has been operated for various periods of time for the last ten (10) years with the required hazards reviews conducted in accordance with accepted procedures, a complete review of the existing plant was not conducted. Only a review of modifications to the existing plant as well as new equipment and processes was done.

B. PROCESS DESCRIPTION

The operating plan for the 1991 run of the Alternative Fuels Development Unit has been formulated. The intention of this run is to demonstrate higher conversion levels of syngas by coproducing dimethyl ether and methanol. Verification of our lab and simulation results is also desired. The operating period will last approximately 2-3 weeks.

A simplified flowsheet of the LaPorte AFDU is attached (Appendix I). This arrangement will recover DME with a purity of 65% without the use of fractionation equipment. The necessary fractionation equipment for higher purity will be added to the facility before the nine month run in FY92/93.

Pure CO and H₂ will be mixed with the recycle stream to achieve the desired reactor inlet composition. The combined stream will then be warmed against the reactor outlet in 21.10 and sent to the reactor. After reacting, the effluent will be cooled and passed through two vessels to recover entrained oil.

After further cooling in 21.30 A&B, most of the methanol and water will be recovered from the reactor effluent in the 22.10 separator. (The MeOH and water composition in the vapor line of 22.10 is approximately 0.9 and 0.2 mole%, respectively.) The vapor take-off line from the 22.10 will then be cooled to 0°F, the low temperature achieved with the use of a CO₂ kettle evaporator.

Seventy percent of the DME and 20 percent of the CO₂ in the reactor effluent will be liquified and knocked out in 22.14. The remaining vapor will be rewarmed by cross exchange in 21.38. A portion of this vapor will then be sent to flare and the remainder recycled. The liquid take-off from the 22.14 will be let down in pressure. To minimize vaporization in the storage tank, this stream will be heated to ambient temperature in 21.45 A&B. The vapor produced will be removed in the phase separator, 22.18, and sent to flare. The liquid will be sent to storage.

Equipment Modifications

The following modifications are necessary to the AFDU to achieve the above process.

1. The facility will remain essentially unchanged through 22.10. The cooling water flow direction through the 21.30 will be reversed.
2. A line will be tied into the vapor take-off of 22.10. This line will be split and directed to two parallel exchangers (21.38 and 21.45). The split will be varied to control the temperature of 22.18. One exchanger, 21.38, is currently on site. This shell and tube exchanger was previously used as 21.10. Two hairpin exchangers in series (21.45 A&B) need to be acquired.

3. A kettle evaporator will be added to the facility. This kettle will boil carbon dioxide to cool the reactor effluent to 0°F. Level controllers and temperature indicators are necessary to provide adequate refrigeration control.
4. The old guard beds will be employed as phase separators 22.14 and 22.18. These vessels will be installed in their original location. Control valves are needed on each to maintain level. A pressure control valve will also be needed on the 22.18.
5. The vapor take-off of 22.14 will pass through the shell side of 21.38. This stream will then be tied into the existing recycle loop.
6. A storage tank for the crude DME product will be required.

Operating Schedule

Attached is a detailed schedule of the operating run (Appendix II). This schedule describes the different process conditions that are to be investigated. These conditions will verify the optimum ratio of MeOH to alumina catalyst over a range of space velocities. Each run is allotted 36 hours of nominal running time. This period includes eight hours per condition to line out. More time has been allotted to the first condition. Experience from LaPorte suggests five days are necessary to line out the plant with a totally new catalyst charge.

To determine the level of methanol catalyst activity, the initial condition at LaPorte will be pure methanol production. Upon completion of the run, the system will be depressurized. Alumina will be added to obtain a MeOH catalyst to alumina ratio of 14:1. The facility will then be restarted at a space velocity of 5,000 SI/kg-hr, total cat. Thirty-six hours of data will be collected at this condition. More alumina will then be added to decrease the catalyst ratio to 4.33:1. Two space velocities, 5,000 and 9,000, will be run at this catalyst charge. Time permitting, a trial will be run with MeOH cat./alumina = 3.0. The facility will then be shut down and the vessels inspected.

As mentioned, the goal of the '91 campaign is to demonstrate higher levels of syngas conversion by coproducing DME and MeOH. However, to avoid constraints in product storage and disposal, the facility's overall production will be nominally 1,000 gallons of DME product (65% purity). After the desired amount is recovered, any further product will be flashed, vaporized, and sent directly to flare.

Anticipated Results

Appendix III presents the key results of the simulation work. Of importance are the reactor inlet and outlet conditions, the syngas conversion, the fraction of MeOH catalyst to total catalyst, and the weight fraction of catalyst in the oil slurry.

A comparison of carbon monoxide conversion at different space velocities and ratios of catalysts is included in Appendix IV. As illustrated, coproducing DME with methanol more than doubles the CO conversion compared to pure methanol production.

The increased conversion is also supported by Appendix V. This plot compares the syngas conversion with catalyst ratios at various space velocities. (Note that syngas conversion is defined as the conversion of CO plus hydrogen.) For the space velocities of interest, syngas conversion can be increased by 50% if DME is coproduced with methanol.

C. HAZARDS REVIEW

The following are the hazards identified during the Preliminary Hazards Review Meeting and the recommended follow-up action.

<u>Hazard</u>	<u>Recommendation/Follow-Up</u>
(The first six (6) items listed below pertain to existing plant equipment.)	
1. Runaway reaction in the 27.10 reactor vessel caused by a loss of oil flow or fin fan in the utility oil loop.	1. Although the catalyst composition will be different from previous runs, it was determined that the existing high temperature shutdowns should provide sufficient protection. The appropriate high temperature shutdown setpoints on the existing switches need to be determined by Process Engineering but will probably be the same as was used for previous runs.
2. Personnel exposure to the new alumina catalyst that will be used in the 27.10 reactor.	2. The existing procedures for catalyst reduction, handling of catalyst, and sampling will apply and should be utilized.
3. Equipment or piping system corrosion or damage caused by material incompatibilities due to the presence of DME and larger quantities of CO ₂ and water in the system downstream of 27.10 reactor. DME is a solvent.	3. Review material composition requirements of existing equipment, piping, gaskets, o-rings, etc.
4. Rupture of 22.10 separator vessel caused by deterioration of vessel walls from corrosion that may have occurred during previous operating runs. The vessel is carbon steel construction.	4. Measure the wall thickness of vessel to determine if any corrosion has taken place. Project Engineering will initiate.
5. Improper disposal of methanol from the storage tank after the run is complete. The methanol composition will contain larger quantities of CO ₂ and water and may include DME	5. This is an environmental issue. Address the potential options for disposal of the methanol and determine if any new risks exist. Project Engineering will initiate.

Hazard	Recommendation/Follow-Up
<p>6. An operability concern was identified with the recycle compressor and the potential for exposing its suction side to low temperatures due to a failure of the new CO₂ exchanger's (21.80) temperature control system.</p>	<p>6. Although this concern was not identified as a hazard, these follow-up items were recommended:</p> <ul style="list-style-type: none"> a) Determine the need and appropriate setpoint for a low temperature alarm on the compressor's suction line. b) Review the compressor material compatibilities at low operating temperatures.
<p>7. Carry over of alumina catalyst into equipment (new and existing) downstream of 27.10 reactor could cause a reaction.</p>	<p>7. Review the reactivity grid. Process Engineering</p>
<p>8. Damage or rupture of the 22.14 separator vessel caused by the presence of cold gas into the vessel as a result of a failure of the pressure control system on the CO₂ exchanger (21.80). The vessel is 1-1/4 Cr - 1/2 Mo construction.</p>	<p>8. A review of the temperature/pressure capabilities of the equipment downstream needs to be performed considering the short duration of the proposed run. A low temperature protection system may have to be installed in accordance with results from previous fault trees developed for similar systems.</p> <p>In addition to the 22.14 vessel, other equipment located downstream (21.38, 22.18, DME storage tank) could be exposed to the low temperatures.</p>
<p>9. Liquid carryover from the 22.18 separator vessel vent to downstream equipment due to a failure of the vessel's LIC.</p>	<p>9. The thermal effects of introducing liquid to the knock-out pot which is located downstream of the vapor outlet nozzle on the 22.18 should be reviewed.</p>

Hazard	Recommendation/Follow-Up
10. More excessive equipment or piping overpressurization due to the presence of a different fluid composition. (The addition of DME.)	10. Review the sizing of existing relief devices and establish criteria for relief devices on new equipment. Process Engineering/Start-Up
11. Methanol storage tank fire.	11. The existing fire protection system should be adequate. The incremental DME levels in the methanol poses no additional fire risks that cannot be handled by existing equipment.
12. DME storage tank fire (external) caused from a leak, overfill, or open drain valve.	12. Review the plant design layout with regard to the location of DME storage tank and methanol storage tank. Review the need for additional fire protection systems.

Figure 1

Table 1a
CO2 Refrigerant Requirements

	Days	Hours	Refrigerant (gpm)	CO2 req'd
Carbonyl Burnout Mar 10: 0600 -- Mar 15: 0600	5	120	0	0
Catalyst Activation Mar 15: 0600 -- Mar 18: 0600	3	72	0	0
All MeOH Mar 18: 0600 -- Mar 23: 0600	5	120	0	0
Alumina add'n Mar 23: 0600 -- 1800		12	0	0
5,000 SV; 93.3 FLARE Mar 23: 1800 -- Mar 25: 0600	3.5	84	0.33	1662
Alumina add'n Mar 25: 0600 -- 1800		12	0	0
5,000 SV; 81.3 COLLECT Mar 25: 1800 -- Mar 26: 1400		36 20	1.48	1774
FLARE Mar 26: 1400 -- Mar 27: 0600		16	0.45	431
9,000 SV; 81.3 FLARE Mar 27: 0600 -- Mar 28: 1800		36	0.99	2138
Total Gallons of CO2 Req'd				6006

Table 1b
HYCO Requirements

	Days	Hours	MoVhr H2	SCFH H2	MoVhr CO	SCFH CO	MoVhr N2	SCFH N2
Carbonyl Burnout Mar 10: 0600 -- Mar 15: 0600	5	120	0.0	0	7.0	2513	0.0	0
Catalyst Activation Mar 15: 0600 -- Mar 18: 0600	3	72	1.2	431	1.8	646	92.0	33028
All MeOH Mar 18: 0600 -- Mar 23: 0600	5	120	31.1	11165	19.3	6929	0.5	180
Alumina add'n Mar 23: 0600 -- 1800		12	0.0	0	0.0	0	0.0	0
5,000 SV; 93.3 FLARE Mar 23: 1800 -- Mar 25: 0600	3.5	84	47.0	16873	42.8	15365	0.3	97
Alumina add'n Mar 25: 0600 -- 1800		12	0.0	0	0.0	0	0.0	0
5,000 SV; 81.3 COLLECT Mar 25: 1800 -- Mar 26: 1400		36 20	46.6	16729	42.7	15329	0.2	72
FLARE Mar 26: 1400 -- Mar 27: 0600		16	46.6	16729	42.7	15329	0.2	72
9,000 SV; 81.3 FLARE Mar 27: 0600 -- Mar 28: 1800		36	49.5	17774	40.2	14439	0.2	54
Total				4030263		3541665		2412222

Table 2a

Space Velocity = 5000 sL/kg-hr, total cat.

MeOH Cat/Alumina = 14

(To be Flared)

	Net Feed from HYCO (vapor)	Reactor Inlet (vapor)	Reactor Outlet (vapor)	To Flare (vapor)	To MeOH Storage (liquid)	Net Product to Storage (liquid)
P (psia)	165	815	750	20	20	20
T (F)	100	380	482	75	85	85
Flow						
Mole/hr	90.0	218.7	168.4	33.1	6.6	0.0
TPD	15.6	54.0	54.0	13.2	2.3	0.0
SCFH*	32329	78533	60471	11873	N/A	0.0
gpm	N/A	N/A	N/A	N/A	0.46	0.0
mole% H ₂	52.2	35.7	20.9	12.7	0.0	0.0
mole% CO	47.5	52.0	48.2	30.6	0.0	0.0
mole% N ₂	0.3	1.0	1.3	0.8	0.0	0.0
mole% CO ₂	0.0	9.5	16.8	22.7	0.2	0.0
mole% MeOH	0.0	0.02	4.1	5.8	74.1	0.0
mole% DME	0.0	1.7	7.7	26.9	3.1	0.0
mole% H ₂ O	0.0	0.003	1.0	0.5	22.6	0.0

Total Run Time (hr)	36
Syngas Conversion	40.0
Wt% Catalyst in Slurry	36
Reactor Velocity (ft/sec)	0.34
CO ₂ Refrigerant Req'd (gals)	1662

NOTE: The discrepancy in the overall mass balance is attributed to the convergence loop in the process simulation.

* SCFH uses a conversion of 359.03 scf/lbmol

Table 2b

Space Velocity = 5000 sL/kg-hr, total cat.

MeOH Cat/Alumina = 4.33

(To be Collected)

	Net Feed from HYCO (vapor)	Reactor Inlet (vapor)	Reactor Outlet (vapor)	To Flare (vapor)	To MeOH Storage (liquid)	Net Product to Storage (liquid)
P (psia)	165	815	750	20	20	160
T (F)	100	381	482	53	85	85
Flow						
Mole/hr	89.5	223.3	170.7	26.9	4.4	6.0
TPD	15.6	56.4	56.4	11.4	1.4	3.0
SCFH*	32141	80159	61231	9671	N/A	N/A
gpm	N/A	N/A	N/A	N/A	0.27	0.70
mole% H ₂	52.1	35.0	20.2	11.2	0.0	0.0
mole% CO	47.7	51.0	46.0	27.6	0.0	0.1
mole% N ₂	0.2	1.0	1.3	0.8	0.0	0.0
mole% CO ₂	0.0	11.3	20.0	33.1	0.1	9.3
mole% MeOH	0.0	0.01	2.2	0.7	51.4	21.4
mole% DME	0.0	1.7	8.9	26.6	3.1	65.5
mole% H ₂ O	0.0	0.006	1.3	0.1	45.4	3.7

Total Run Time (hr)	20
Syngas Conversion	41.3
Wt% Catalyst in Slurry	38
Reactor Velocity (ft/sec)	0.34
CO ₂ Refrigerant Req'd (gals)	1774

NOTE: The discrepancy in the overall mass balance is attributed to the convergence loop in the process simulation.

* SCFH uses a conversion of 359.03 scf/lbmol

Table 2c

Space Velocity = 5000 sL/kg-hr, total cat.
 MeOH Cat./Alumina = 4.33
 (To be Flared)

	Net Feed from HYCO (vapor)	Reactor Inlet (vapor)	Reactor Outlet (vapor)	To Flare (vapor)	To MeOH Storage (liquid)	Net Product to Storage (liquid)
P (psia)	165	815	750	15	20	15
T (F)	100	381	482	75	85	85
Flow						
Mole/hr	89.5	223.3	170.7	33.0	4.4	0.0
TPD	15.6	56.4	56.4	14.4	1.4	0.0
SCFH*	32141	80159	61281	11840	N/A	N/A
gpm	N/A	N/A	N/A	N/A	0.27	0.00
mole% H ₂	52.1	35.0	20.2	9.1	0.0	0.0
mole% CO	47.7	51.0	46.0	22.6	0.0	0.0
mole% N ₂	0.2	1.0	1.3	0.6	0.0	0.0
mole% CO ₂	0.0	11.3	20.0	28.7	0.1	0.0
mole% MeOH	0.0	0.01	2.2	4.5	51.4	0.0
mole% DME	0.0	1.7	8.9	33.7	3.1	0.0
mole% H ₂ O	0.0	0.006	1.3	0.8	45.4	0.0
Total Run Time (hr)				16		
Syngas Conversion				41.3		
Wt% Catalyst in Slurry				38		
Reactor Velocity (ft/sec)				0.34		
CO ₂ Refrigerant Req'd (gals)				431		

NOTE: The discrepancy in the overall mass balance is attributed to the convergence loop in the process simulation.

* SCFH uses a conversion of 359.03 scf/lbmol

Table 2d

Space Velocity = 9000 sL/kg-hr, total cat.

MeOH Cat/Alumina = 4.33

(To be Flared)

	Net Feed from HYCO (vapor)	Reactor Inlet (vapor)	Reactor Outlet (vapor)	To Flare (vapor)	To MeOH Storage (liquid)	Net Product to Storage (liquid)
P (psia)	165	815	750	20	20	20
T (F)	100	385	482	76	85	85
Flow						
Mole/hr	89.9	325.8	272.2	29.1	6.8	0.5
TPD	14.8	83.2	83.2	12.5	2.2	0.2
SCFH*	32269	116987	97746	10440	N/A	0.0
gpm	N/A	N/A	N/A	N/A	0.42	0.04
mole% H ₂	55.1	34.6	24.4	10.3	0.0	0.0
mole% CO	44.8	50.5	47.9	21.9	0.0	0.0
mole% N ₂	0.2	1.0	1.2	0.5	0.0	0.0
mole% CO ₂	0.0	11.9	16.8	25.0	0.1	0.2
mole% MeOH	0.0	0.02	2.3	7.0	54.4	66.7
mole% DME	0.0	2.1	6.3	34.6	2.8	2.9
mole% H ₂ O	0.0	0.006	1.2	0.6	42.8	30.2
Total Run Time (hr)				36		
Syngas Conversion				26.9		
Wt% Catalyst in Slurry				35		
Reactor Velocity (ft/sec)				0.48		
CO ₂ Refrigerant Req'd (gals)				2138		

NOTE: The discrepancy in the overall mass balance is attributed to the convergence loop in the process simulation.

* SCFH uses a conversion of 359.03 scf/lbmol

Figure 2
 Comparison of CO Conversion
 Mixed DME/MeOH vs. MeOH
 (P=750 psia, T=250° C)

Figure 3
 Comparison of Syngas Conversion
 Mixed DME/MeOH vs. MeOH
 (P=750 psia, T=250° C)

LEGEND

○	01.3% MeOH Cat
□	03.3% MeOH Cat
●	100% MeOH Cat

REACTIVITY GRID

[illegible]

COMPONENT LIST FOR ALT FUELS I - SPRING 91 RUN

PRIMARY COMPONENTS		HPLC		METHANOL ANALYSIS FROM LP-III			
hydrogen		H2	-252.8				
carbon monoxide		CO	-191.5				
carbon dioxide		CO2	-78.5				
nitrogen		N2	-195.8				
methanol		MeOH	64.8				
dimethyl ether		DME	-24.8				
water		H2O	100				
Pentico oil		Poil	range				
TRACE COMPONENTS							
methane		C1					
ethanol		EtOH	78.4				
propanol		PrOH	97.2				
C4+ alcohols		ROH					
methylacetate		MeAc	57.8				
methylformate		MeFm	31.5				
methyl-ethylketone		MEK	79.6				
POSSIBLE BYPRODUCTS							
R1-O-R2 Ethers		ROR					(methyl ethyl ether)
R1O-OR2 Esters		ROOR					(methyl acetate, ethyl acetate)
Acetals		RORO					
Nickel Carbonyl		Ni(CO)4					
Iron Carbonyl		Fe(CO)5					
Carbon		C					
CATALYST							
BASF S3 86		S386					
Catapal Gamma Alumina		Al2O3					
MATERIALS							
304/316 stainless		SS					
CrMo		CrMo					
carbon steel		CS					
gaskets							
lub oil		l oil					

SUM 100.000 3.113 100.000

PRIMARY REACTIONS

1 SHIFT	$\text{CO} + \text{WA} \rightarrow \text{CO}_2 + \text{H}_2$
2 METHANOL	$\text{CO} + 2 \text{H}_2 \rightarrow \text{MeOH}$
3 DME	$2 \text{MeOH} \rightarrow \text{DME} + \text{WA}$
4 HIGHER ALCOHOLS	$x \text{CO} + y \text{H}_2 \rightarrow \text{ROH} + \text{WA}$
5 MIXED ETHERS	$\text{R}_1\text{OH} + \text{R}_2\text{OH} \rightarrow \text{R}_1\text{-O-R}_2 + \text{WA}$
6 ACETATES	$\text{CO} + \text{R}_1\text{-O-R}_2 \rightarrow \text{R}_1\text{-CO-OR}_2$
7 ACETALS	$\text{KETONE} + 2 \text{ROH} \rightarrow \text{ACETAL} + \text{WA}$
8 HYDROGENOLYSIS	$\text{R}_1\text{-O-R}_2 + \text{H}_2 \rightarrow \text{R}_1\text{OH} + \text{R}_2\text{OH}$
9 TRANS-ESTERIFICATION	$\text{R}_1\text{-O-R}_2 + \text{R}_3\text{OH} \rightarrow \text{R}_1\text{-O-R}_3 + \text{R}_2\text{OH}$
10 HYDROLYSIS	$\text{R}_1\text{-O-R}_2 + \text{WA} \rightarrow \text{R}_1\text{COOH} + \text{R}_2\text{OH}$
11 CONDENSATION	$\text{R}_1\text{OH} \rightarrow \text{R}_1\text{olefin} + \text{H}_2$
12 CARBOXYLS	$\text{M} + x \text{CO} \rightarrow \text{M}(\text{CO})_x \quad \text{Ni}(\text{CO})_4 \quad \text{Fe}(\text{CO})_5$
13 BOURBOUARD	$2 \text{CO} \rightarrow \text{C} + \text{CO}_2$
14 METHANATION	$\text{CO} + 3 \text{H}_2 \rightarrow \text{CH}_4 + \text{WA}$
15 PEROXIDE	$\text{R}_1\text{-O-R}_2 + \text{O} \rightarrow \text{R}_1\text{-OO-R}_2 \quad (\text{CH}_3 \rightarrow \text{CH}_2, \text{CH}_3 \cdot \& \cdot \text{C} \cdot \rightarrow \text{no})$
16 AMMONIA	$\text{R}_2 + 3 \text{H}_2 \rightarrow 2 \text{NH}_3$
17 HYDROLYSIS	$\text{MeFm} + \text{H}_2\text{O} \rightarrow \text{MeOH} + \text{FORMIC ACID}$

SECONDARY REACTIONS

Memorandum

Appendix B

① 0-2-1200
AIR PRODUCTS

To: D. M. Herron

Dept./Loc.: PSG - Process

From: J. C. Tafuri

Dept./Ext.: PSG Technology/7687

Date: 4 December 1990

Subject: Laporte AFDU Operation in Spring of 91 - Materials Review

cc: G. Broadhurst
R. L. Williams
G. A. Peters

I have carried out a fitness for services analysis of the three vessels described in your memo to me dated 6 November 1990, and have concluded that these vessels are satisfactory for both the expected operating conditions and also the worst upset conditions (i.e., 1000 psig and -70°F).

The fitness for service analysis considered the following factors;

1. The C2.60 vessels were 100% radiographed and the vessels were post weld heat treated.
2. The C2.06 vessels and 21.10 exchanger shells have reasonably good fracture toughness down to -100°F.
3. The subject low temperature operating conditions will be limited to two-two week operating periods only.
4. While we do not expect any problems with these vessels it would be prudent to limit operator exposure during the first cooldown.

J. C. Tafuri

51601/jmk

MODEL 900
MICRO-SCALE BENCH-TOP REACTOR SYSTEM

EXECUTIVE SUMMARY AND PRICING

Autoclave Engineers Micro-Scale Bench-Top Reaction Systems (Micro-BTRS^R) are designed to provide the laboratory researcher with an instrument to evaluate the kinetics and chemistry of catalytic and noncatalytic processes. Their small scale permits lower costs for catalysts, feed materials, product disposal, and operation. The reduced system volume also means reduced containment of hazardous materials. All systems are capable of safe, long term, unattended operation.

In order to achieve reproducible performance from a bench scale system, care must be taken to ensure that maximum control is provided for all process variables. Through a combination of individually heated components and spacious ovens, all valves and tubing are heated to provide a well defined flow path for the process fluid. This design not only improves the characterization of the fluids, but it enhances the overall smooth performance of the system and increases greatly the system's reproducibility.

This modularly expandable, dual reactor, continuous flow reaction system is designed to provide computer-supervised control over multiple, pre-programmed experiments. System temperatures, flow rates, and digital operations are programmable with menu-driven software, complete with failsafes for unattended operation.

The base system includes two electronic mass flow controllers, two liquid metering pumps, and a heated mixer/vaporizer for the controlled introduction of reactants to the reactor. Reactor temperatures up to 650°C are easily obtained. A back pressure regulator permits operation of the system at pressures up to 1500 psig.

All process valves and tubing are isothermally maintained at temperatures up to 280°C to insure a single reactant phase. A thermostated gas/liquid separator insures that only a gaseous phase reaches the back pressure regulator and sampling valve. The High Performance Gas Chromatograph features a Hydrogen Transfer System packed column for analysis of C1-C5, and capillary column for analysis up to C25. The sampling valves are thermostated to achieve reproducible results.

Base Model 900 Micro-BTRS^R including Training, Installation and Warranty:

F.O.B. Erie, PA

PROCESS FLOW DIAGRAM

**DATE
FILMED**

01/03/92