LIQUID PHASE METHANOL LAPORTE PDU:
MODIFICATION, OPERATION, AND SUPPORT STUDIES

Quarterly Technical Progress Report No. 4

DOE/PC/90005--T59

DE92 019206

For The Period 1 April - 30 June 1988

Contractor

AIR PRODUCTS AND CHEMICALS, INC.
Allentown, PA 18195

and

Subcontractor to Air Products

CHEM SYSTEMS INC.
Tarrytown, NY 10591

D. M. Brown - Air Products Program Manager
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10 August 1988

Prepared for the United States Department of Energy
Under Contract No. DE-AC22-87PC90005
Contract Period 9 April 1987 - 9 October 1989

I. CONTRACT OBJECTIVE CHANGES:

None.

II. TECHNICAL APPROACH CHANGES:

The work under this contract will be to implement and test certain process improvements identified through the engineering studies completed under DOE Contract DE-AC22-85PC80007, to demonstrate the capability of long-term catalyst activity maintenance, and to perform process and design engineering work that is generic to a scaled-up Liquid Phase Methanol (LPMEOH)* facility. A series of process development unit (PDU) runs will be performed to extend the testing of the process improvements. A parallel research program will be conducted to enhance the LPMEOH technical data base to improve the likelihood of commercialization of the LPMEOH process.

Task 1 - LaPorte PDU Engineering and Modification

This task and the research work and process engineering studies conducted under Contract DE-AC22-85PC80007 complement each other. The results of the previous contract studies led to the preparation of preliminary process engineering specifications for several economically prudent concepts that are expected to improve the prospects for the successful advancement of LPMEOH technology.

To improve data accuracy and reliability during PDU operations and to maintain the high on-stream factor of the LaPorte PDU over a long period of operation, modifications will be made within the instrumentation, piping, and process/mechanical systems.

The work for this task is being conducted under the following subtasks; the following accomplishments have been made during this reporting quarter:

Subtask 1.1 - Engineering

The process control computer (DEC PDP-11/73) and the gas chromatograph interface computer (HP-1000A) were delivered. The AIM-III software was installed on the PDP. Applications and communications programs were written, and debugging of the systems began. The computer deck for the PDU heat and material balances for the equipment evaluation phase of the PDU operations were issued. Work began on the development of the operating procedures for 2-phase gas holdup tests, catalyst reduction, and equipment evaluation runs.

A flowcheck of the newly installed piping was completed. Air Products Process Engineering group developed responses to the action items from the design hazards review notes. An operational readiness inspection was held in June, 1988.

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A study was conducted by Air Products Engineering Technology group to determine the effect gas holdup has as a function of position within the LPMEOH reactor. See Attachment 1 for the report. In addition, the Engineering Technology group interacted with the University of Western Ontario, a subcontractor to Air Products, to understand the progress of the work on the fiber-optic bubble detection probe being developed for the LPMEOH program. Because of concerns about the status of the work, a number of tests must be completed prior to considering installing the probes in the PDU.

The gas and slurry sparger as-built drawings were reviewed; minor modifications to the hole pattern were recommended to improve the uniformity of gas distribution from the gas sparger.

No further work is envisioned for this subtask.

Subtask 1.2 - LaPorte PDU Modification

The new piping, steel and vessels were installed. Pressure testing, x-ray inspection, and insulation work was completed. Installation of new instruments and wiring was finalized. Commissioning and checkout of new and existing valves and instruments was accomplished.

No further work is envisioned for this subtask.

Task 2 - LaPorte PDU Shakedown, Operations, Deactivation and Disposal

Air Products will provide regular on-site and home office technical assistance to the LaPorte PDU operation. Overall operating manpower and direct supervision of the operations will be supplied by the Air Products Operations Department.

Subtask 2.1 - LaPorte PDU Shakedown

Training of the new operators began. The new nuclear density gauge was calibrated using the empty reactor, nitrogen at various pressures, and process oil C-1 at various temperatures. Two phase gas holdup tests with process oil C-1 and nitrogen over a wide range of operating conditions were completed. Preliminary data analysis indicates a more linear axial gas holdup profile and an overall slightly higher gas holdup compared to what had been observed in the old reactor system. Work began on two-phase gas holdup with CO-rich gas in conjuction with carbonyl surveys. These surveys are important to confirm low (<10 ppb) levels of nickel and iron carbonyl, known to be effective methanol catalyst poisons. Both wet chemical and a new GC analytical method were used to measure carbonyl levels at various points in the PDU, confirming <10 ppb present throughout. The new slurry sampling lines were installed and checked out. In addition, the analytical equipment was commissioned. Delivery of the F21/0E75-44 (standard) and the F21/0E75-43 (alternate) catalyst was received.

Task 3 - Research Program

To strengthen the data base of the LPMEOH technology, research is being conducted in parallel with the PDU engineering and construction efforts. This work will address alternate liquid media studies, effects of CO_2 in CO-rich synthesis gas, optimization of in-situ catalyst reduction and storage, catalyst poison studies, fundamental kinetic modelling, testing alternate commercial catalysts, and field testing of new guard-bed materials for catalyst poisons. In addition to the research work, each subtask includes data evaluation which will be done through the use of the data base generated under Contracts DE-AC22-81PC30019 and DE-AC22-85PC80007. Tests will be performed primarily using CO-rich synthesis gas. The work accomplished during this quarter is as follows:

Subtask 3.1 - Alternate Liquid Media Studies

The study of alternate liquid media undertaken during Contract DE-AC22-85PC80007 has been expanded to build upon the results from that contract. Key liquid properties have been identified and tests have been conducted to discover which liquids provide the most satisfactory in-situ reduction and catalyst activity (see Final Report of DE-AC22-85PC80007).

During the work in this subtask, ten candidate liquids were screened based on their physical properties. The key properties are Vap. Press./Temperature compatibility with LPMEOH conditions, and the absence of unsaturated hydrocarbons. Samples from four different suppliers were requested and autoclave testing was conducted on five of these candidates. Except for MOBIL SHF61, the other four candidates demonstrated acceptable compatibility with the standard catalyst as shown by the usual activity test. Drakeol 10 from PENRECO is recommended for LaPorte for its slightly higher B.pt. than the other three (see pg. 23, Supplemental Report). All work has been completed except for data evaluation and report preparation

Subtask 3.2 - Effects of CO_2 in CO-Rich Gas

Carbon dioxide contained in synthesis gas is known to play a key role in the formation and maintenance of the active sites for methanol synthesis. The literature indicates there is an optimal CO_2 concentration ratio for vapor phase methanol synthesis, and it is likely that a similar optimum exists for the liquid phase synthesis. Previous work conducted at Air Products has provided information at concentrations of 4, 8 and 13 volume % CO_2 in CO-rich gas, holding CO and H_2 concentrations constant. The results show that an optimum productivity exists between 8 and 13 vol % CO_2

In the current contract, additional experiments are planned to more fully understand the effect of changing CO_2 in typical Texaco gasifier effluent on the performance of a LPMEOH unit.

Specifically, as shown in Table 3.2.1, gas mixes simulating different degrees of CO_2 removal from a Texaco CO-rich gas will be used for the tests. In addition, gas typical of that leaving a Shell gasifier is included in the program to provide another data point of commercial interest. Since water and CO_2 are closely related through the water gas shift reaction, some water addition experiments will be studied to complete the investigation of CO_2 effects.

Work accomplished thus far in this area is considered to be of a potentially patentable nature. Details of the work conducted are included in the Supplementary Report.

Subtask 3.4 - Catalyst Poisons Studies

The work in this subtask is to screen adsorbents as guard-bed materials for the removal of poisons from synthesis gas. The work which was begun during the last quarter on adsorbent E to serve as a "throwaway" adsorbent for sulfur removal was continued this quarter. At a temperature 400°F and 90 psig CO_2 total pressure, adsorbent E was able to reduce the carbonyl sulfide (COS) concentration from an initial concentration of 156 ppmv COS to ~1 ppmv.

Further studies were conducted for COS removal by using adsorbent L at 75°F and 90 psig CO_2 pressure. This adsorbent is somewhat similar to the previously tested adsorbent F, except that this new adsorbent has a higher capacity for COS at methanol reaction conditions. The results of the testing of adsorbent L are contained in the Supplementary Report.

The screening of seven adsorbents for removal of trace hydrogen chloride (HCl) from a 90 psig CO_2 gas stream at 75°F was conducted (see pg. 23, Supplemental Report). HCl concentrations were measured using the FT-IR detector. Table 3.4-1 shows the adsorbents evaluated and their corresponding capacities. Adsorbents A-2 and L showed the highest HCl capacities.

The adsorbent screening task has now been completed. The preferred adsorbents for each of the five poisons will be further evaluated under Subtask 3.8, to investigate their efficacy in the presence of other impurities.

TABLE 3.2.1

GASES FOR CO2 EFFECT STUDIES

Gas	CO, mole %	H2, mole %	CO2, mole %	N2, mole %	Comment
A	51	35	13	1	CO-rich gas, Texaco Gasifier
B	54	37	8	1	CO-rich gas, with CO2 removal
C	56.3	38.7	4	1	CO-rich gas, with CO2 removal
D	58.7	40.3	0	1	CO-rich gas, with CO2 removal
E	48	33	18	1	CO-rich gas, with CO2 addition
F	66	30	3	1	Shell Gasifier
G	57.5	39.5	2	1	CO-rich gas, with CO2 removal

Table 3.4-1

Adsorbent Screening for Trace HCl Removal
(75°F and 90 psig CO_2 pressure)

Designation	Equilibrium HCl Capacities (mmole/g) nADS @ 5ppmv	Equilibrium HCl Capacities (mmole/g) nADS @ 20ppmv
A-1	0.08	0.25
A-2	1.75	2.70
B	0.39	0.80
G-2	0.90	1.50
G-3	0.22	0.85
J	0.14	0.37
L	7.44	--

(I.D. - see pg. 23)

Subtask 3.7 - Alternate Catalyst Life Test

Based on recommendations from Subtasks 3.1 and 3.6, the selected liquid and the alternate commercial catalyst will be subjected to a life test in the autoclave for a period of up to 40 days.

During this quarter, a 15 wt% slurry (25 grams of F21/0E75-43 catalyst and 142 grams of oil C-1) was activated in-situ to begin the life test The test conditions were 250°C, 750 psig, 5400 Sl/hr/kg-catalyst space velocity using CO-rich gas. After 44 days of testing (1050 hours) the methanol productivity was 18.3 gmol/hr-kg. Figure 3.7-1 summarizes the results as both the productivity and the exit methanol concentrations were plotted against time on synthesis gas. A linear deactivation rate of 0.0016% per hour has been estimated. This rate of decline compares favorably against the rate of decline for the standard F21/0E75-35 catalyst which was reported as 0.0024% per hour in the Final Report of the prior contract (DE-AC22-85PC80007).

All autoclave work has been completed. The only remaining work is the preparation of the reports.

Subtask 3.8 - Catalyst Poisons Field Test Unit

Work in this subtask is intended to test guard bed materials for the removal of catalyst poisons at an actual coal gasifier site. During this quarter, Air Products personnel visited with EPRI personnel at Wilsonville, Alabama to discuss thoughts and ideas on collecting synthesis gas from Cool Water in a tube-trailer for tests in the Air Products laboratory. Because of difficulties in being able to pressurize the Cool Water gas to a preferred high pressure (i.e. 2000 psig), the design of the field test unit will be modified to permit operation at 450 psig. The modification consists of reducing the size of the adsorbers from 2" diameter to 3/4" diameter. By making this modification, the mass flowrate through the 3/4" adsorption unit using 450 psig gas will be the same as the flowrate through the 2" adsorption unit using 2000 psig gas.

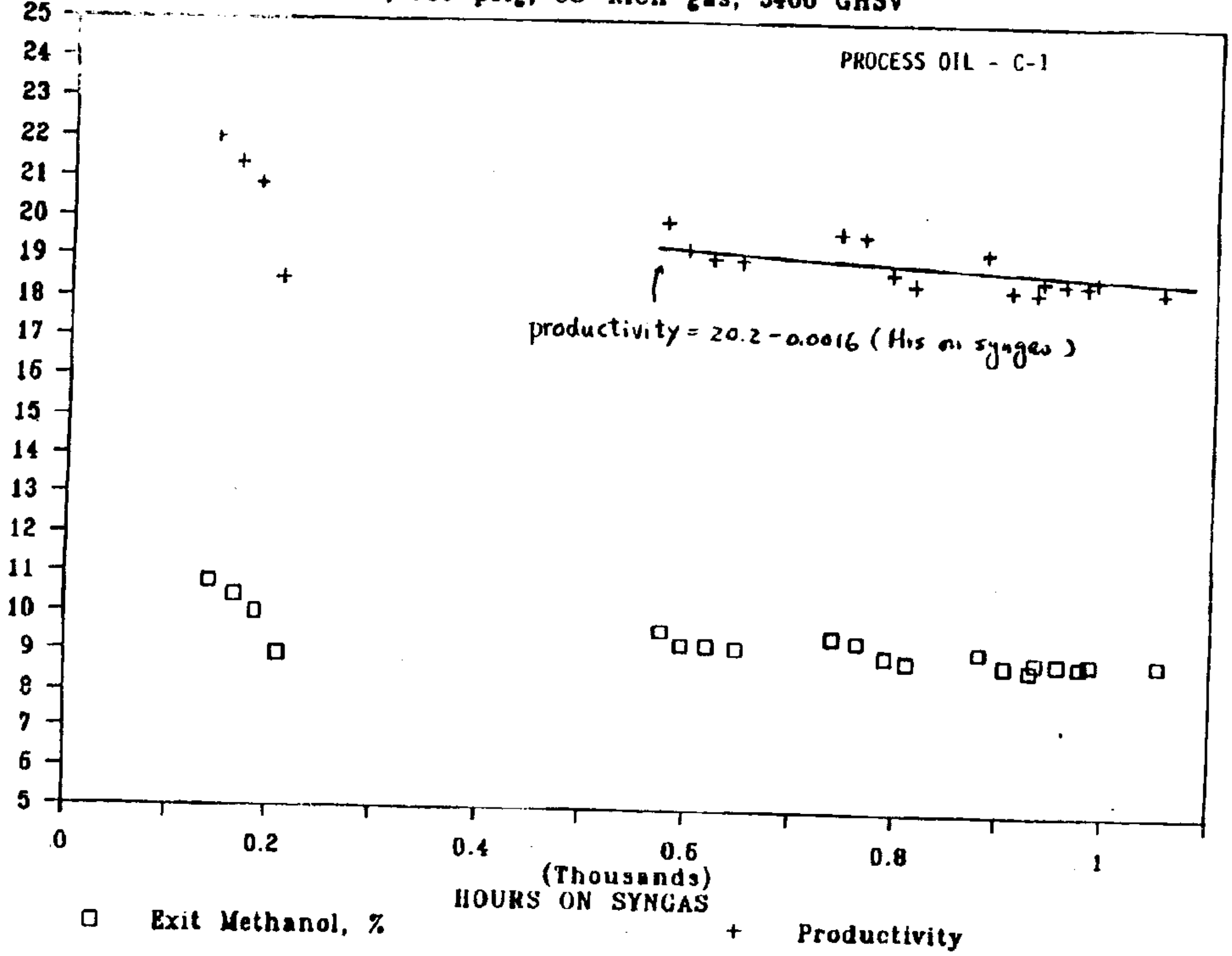
Arrangements are being made with an outside testing laboratory to analyze the gas as it is being collected in the tube trailer. Upon arrival at the Air Products laboratories, the gas will again be analyzed to ensure that any poisons in the gas have not plated out on the walls of the tube trailer during transport.

A box trailer has been identified to house the test unit. This trailer is currently undergoing safety inspections. Hazard review studies are currently being conducted by the Air Products research team to assure the safety of the operation.

FIGURE 3.7-1

AGING OF F21/OE75-43 IN 300CC AUTOCLAVE

250°C, 750 psig, CO-RICH gas, 5400 GHSV



Materials of construction for the test unit have been procured and construction will begin upon completion of the hazards reviews.

Flexibility will be built into the unit design to allow investigation of the best scheme for cleaning the coal gas. Temperature (up to 500°F) and pressure (up to 1000 psig) will be the principal variables used in the study.

Task 4 - Chem Systems' Engineering and PDU Support Program

To expand the process design and evaluation studies begun under Contracts DE-AC22-81PC30019 and DE-AC22-85PC80007, further work in these areas is being conducted by Chem Systems as a subcontractor to Air Products. This work addresses: 1) process sensitivity for enhancing the viability of the LPMEOH technology, while using the latest data from the LaPorte PDU and Air Products' laboratories for both once-through and all-methanol commercial base cases; 2) updating literature surveys; and 3) developing a standardized methodology for LPMEOH reactor design and evaluation. The following accomplishments have been made during this reporting period:

Subtask 4.1/4.2 - Process Design Evaluation Studies

The objective of this subtask is the conceptualization of LPMEOH process flowschemes, development of commercial-scale process designs, economic evaluations of the commercial designs, and optimization through parametric sensitivity studies. Results of these analyses are used to guide the research and development program in the most economic direction.

CO-Rich Evaluation

The CO-rich evaluation consists of updating LPMEOH process case studies performed under previous contracts and developing vapor-phase cases with commercial or developmental technologies for comparison. The following is an overview of the vapor phase cases currently being evaluated and the LPMEOH process base case presented in Quarterly Technical Progress Report No. 3.

Liquid Phase Methanol Base Case Design

The LPMEOH base-case design was configured to fit into an intermediate-sized Texaco-based Integrated Gasification Combined Cycle (IGCC) facility design originally producing 658 MW of electricity at 20°F ambient temperature. A radiant plus convective design was chosen as the basis because of its high thermal efficiency. No supplemental firing was included for higher ambient conditions.

Insertion of a LPMEOH unit between the acid gas removal system and the gas turbine generator, as shown in Figure 4.1-1, requires that the gasification pressure be raised from a nominal 600 psig to

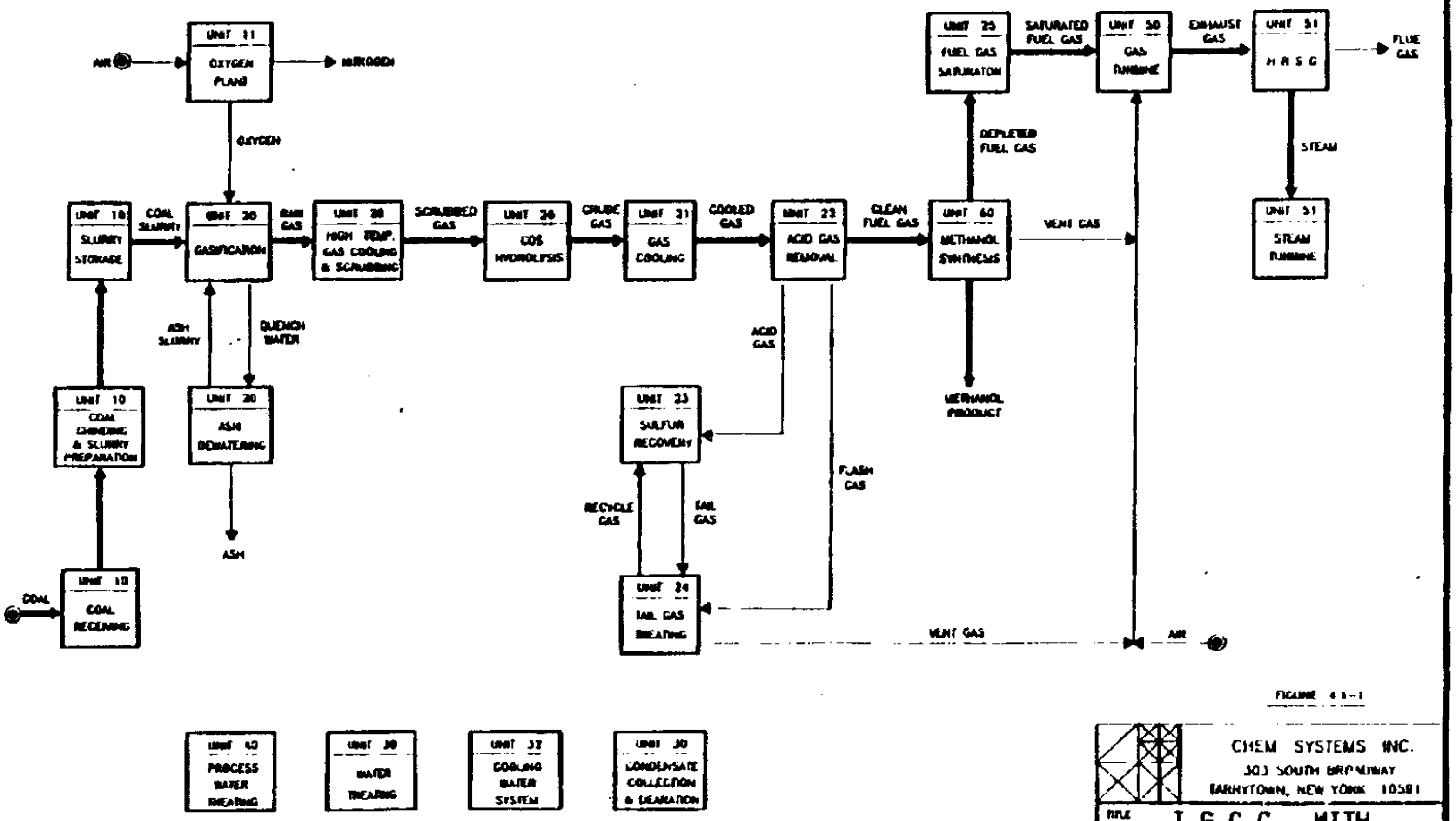


FIGURE 4.1-1

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TITLE
I G C C WITH
LIQUID PHASE
METHANOL COPRODUCTION

PROJECT NO. 8183

950 psig to accommodate an average pressure of 765 psia in the methanol synthesis reactors without intermediate synthesis gas compression. A carbonyl sulfide (COS) hydrolysis unit must be added between the raw gas scrubbing and the acid gas removal steps to convert carbonyl sulfide into hydrogen sulfide. Methanol feed gas must be heated and sent to guard beds for removal of carbonyls, sulfur compounds, and other potential poisons prior to entering the liquid-phase synthesis reactors. Unconverted synthesis gas must be cooled to condense the methanol, reheated, and expanded to 390 psia before being sent to the fuel gas saturator. The saturated fuel gas is combusted in the gas turbine, and generates power. Additional power is recovered from the steam turbine attached to the heat recovery steam generation (HRSG) unit. Total electricity production is 533.3 MW, and fuel methanol production is 977.6 tons per day. On a mid-1987 basis, the costs plus 6 percent discounted cash flow (DCF) return for synthesis, methanol and electricity were $5.19 per MM BTU, 49.0 cents per gallon and 5.00 cents per KWH, respectively.

Vapor Phase Alcohol Design

A once-through vapor phase alcohol design is being developed on the basis of the composite data presented in Quarterly Technical Progress Report No. 1. This vapor phase scenario utilizes a developmental higher alcohol technology where approximately 15 percent of the product is composed of oxygenates other than methanol. The process configuration, shown in Figure 4.1-2, is quite similar to that required for the LPMEOH design. The major difference in the higher alcohol design is the need to lower the carbon dioxide concentration in the synthesis gas to only 1 percent. This is accomplished by adding CO_2 removal to the acid gas removal unit. The excess CO_2 is ejected at atmospheric pressure, however, in order not to waste any contained synthesis gas components, the CO_2 is recompressed to 390 psia and reinjected into the depleted fuel gas after expansion. Thus the CO_2 acts as a diluent in the gas turbine by directly replacing compressed air.

Conventional Vapor-Phase Design

A conventional vapor-phase methanol design is also being developed for comparison with the once-through LPMEOH and vapor-phase alcohol designs. In this case, a portion of the synthesis gas is shifted to a balanced gas composition before entering the methanol synthesis unit which includes recycle of unreacted hydrogen and carbon monoxide. The process configuration, shown in Figure 4.1-3 is quite different from the other two designs. Most of the synthesis gas from gasification and radiant cooling passes through a conventional train consisting of convective cooling, gas scrubbing and cooling, sulfur removal and expansion prior to fuel gas saturation and combustion in the gas turbine. The remaining synthesis gas, approximately 20 percent of the total stream, is

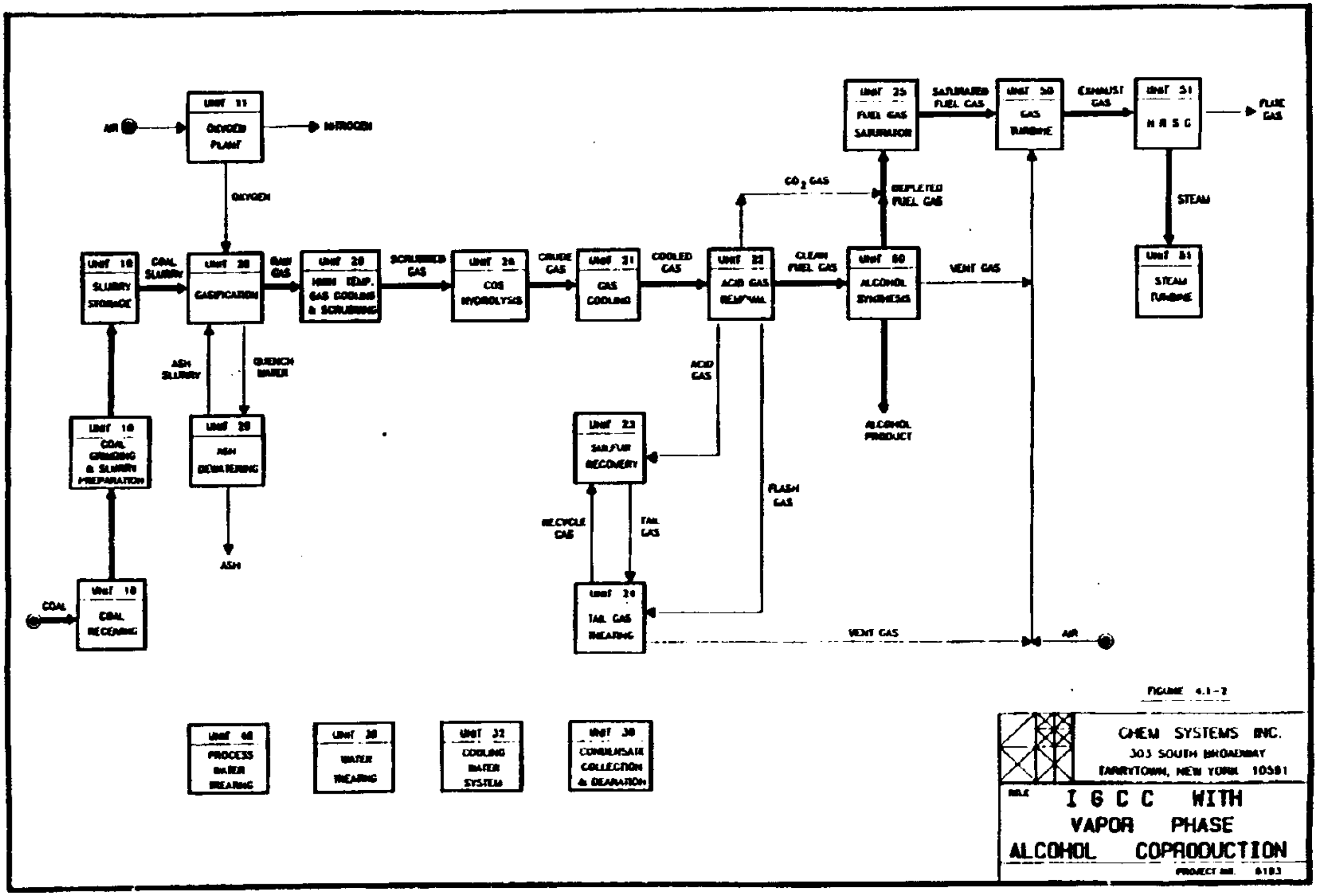

FIGURE 4.1-2

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TITLE I G C C WITH VAPOR PHASE ALCOHOL COPRODUCTION

PROJECT NO. 6183

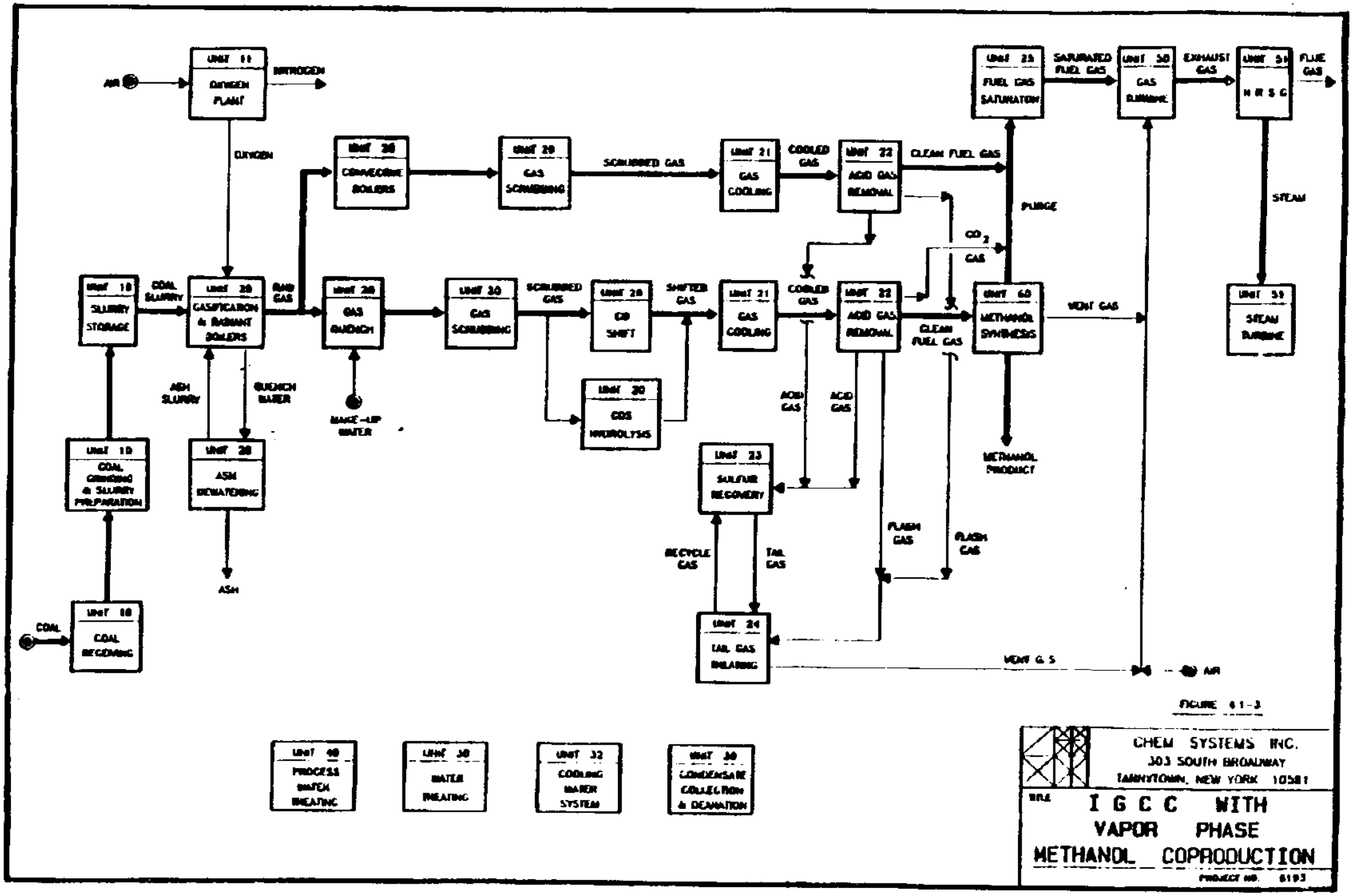

FIGURE 41-3

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TITLE I G C C WITH
VAPOR PHASE
METHANOL COPRODUCTION

PROJECT NO. 6193

quenched and scrubbed to provide the proper level of water vapor for the shift unit. Part of this gas is shifted while the remainder by-passes the shift unit to provide a balanced H_2/CO ratio for methanol synthesis. The by-passed gas is sent through a COS hydrolysis unit to convert carbonyl sulfide to hydrogen sulphide (H_2S) which is readily removed in the acid gas removal unit. This is unnecessary on the portion passing through CO shift since the shift catalyst will accomplish the same task. Following shift, the combined gas stream is cooled and sent to acid gas removal where, in addition to sulfur removal, a portion of the carbon dioxide is adsorbed to create the proper balance ratio for methanol synthesis.

As in the once-through vapor phase alcohol design, the rejected CO_2 is recompressed and combined with fuel gas entering the saturation unit. Meanwhile, the balanced synthesis gas ($H_2/CO \sim 2.0$) is sent to methanol production where it is combined with recycle and passes through the fixed bed reactor. A small purge is taken from the recycle stream to prevent buildup of inerts. A purge is also sent to the saturation unit.

Reactor Conditions

Some of the major design assumptions forming the basis for the three methanol production cases are summarized in Table 4.1-1. The two vapor phase cases are being designed to yield fuel alcohol products as nearly equivalent to the LPMEOH case as possible on a higher heating value basis. Power production in the vapor phase designs is based solely on the resulting energy balances and may, therefore, differ from that produced in the LPMEOH design.

Work is continuing on the vapor phase cases. Upon completion of the designs, economics will be developed on a basis similar to that presented for the LPMEOH case in Quarterly Technical Progress Report No. 3.

All-Methanol Evaluations

The all-methanol evaluations consist of developing a commercial base case LPMEOH process design and evaluation. The base case design will be compared to commercial vapor-phase processes. Process sensitivity analyses will be performed to determine the most likely areas for improvement which can be used to guide the ongoing research and development effort.

Overview

The search for an all-methanol scenario for the LPMEOH process that will be technically and economically competitive with commercial vapor-phase processes was completed. A conceptual flowsheet based on high pressure operation and two LPMEOH reactors in series with minimal recycle was developed. This scenario is depicted in simplified form in Figure 4.1-4. This design would have per pass

TABLE 4.1-1

SUMMARY OF ALCOHOL REACTOR DESIGN ASSUMPTIONS

	OTM LPMEOH	OTA VPA (Developmental)	Recycle VPM (Conventional)
Alcohol produced			
T/D	977.6	895.9	982.0
MM Btu/D	18,833.4	18,345.5	18,833.4
Composition of product (Wt. %)			
MeOH	97.66	84.28	98.29
EtOH	0.37	6.86	-
PrOH	0.33	3.07	-
BuOH	-	3.53	-
EtAc	-	1.25	-
Pentane	-	0.06	-
H_2O	1.35	0.73	1.71
CO_2	0.24	0.22	-
Oil	0.05	-	-
Gas to alcohol synthesis, MMSCFD	383.71	340.23	76.74
Feed gas composition (vol %)			
H_2	37.64	42.21	67.20
CO	49.08	54.55	28.07
CO_2	11.13	0.85	3.11
H_2O	0.01	0.01	-
N_2	0.91	1.01	0.82
CH_4	0.10	0.11	0.11
Ar	1.13	1.26	0.69
Alcohol synthesis			
Temperature (°F)	482	545	510
Pressure (psia)	765	795	735
Space velocity (L/h-kg cat)	8,000	3,900	9,050
Recycle ratio (volume basis)	-	-	4-6:1
CO conv./pass (%)	13.2	13.6	39.9

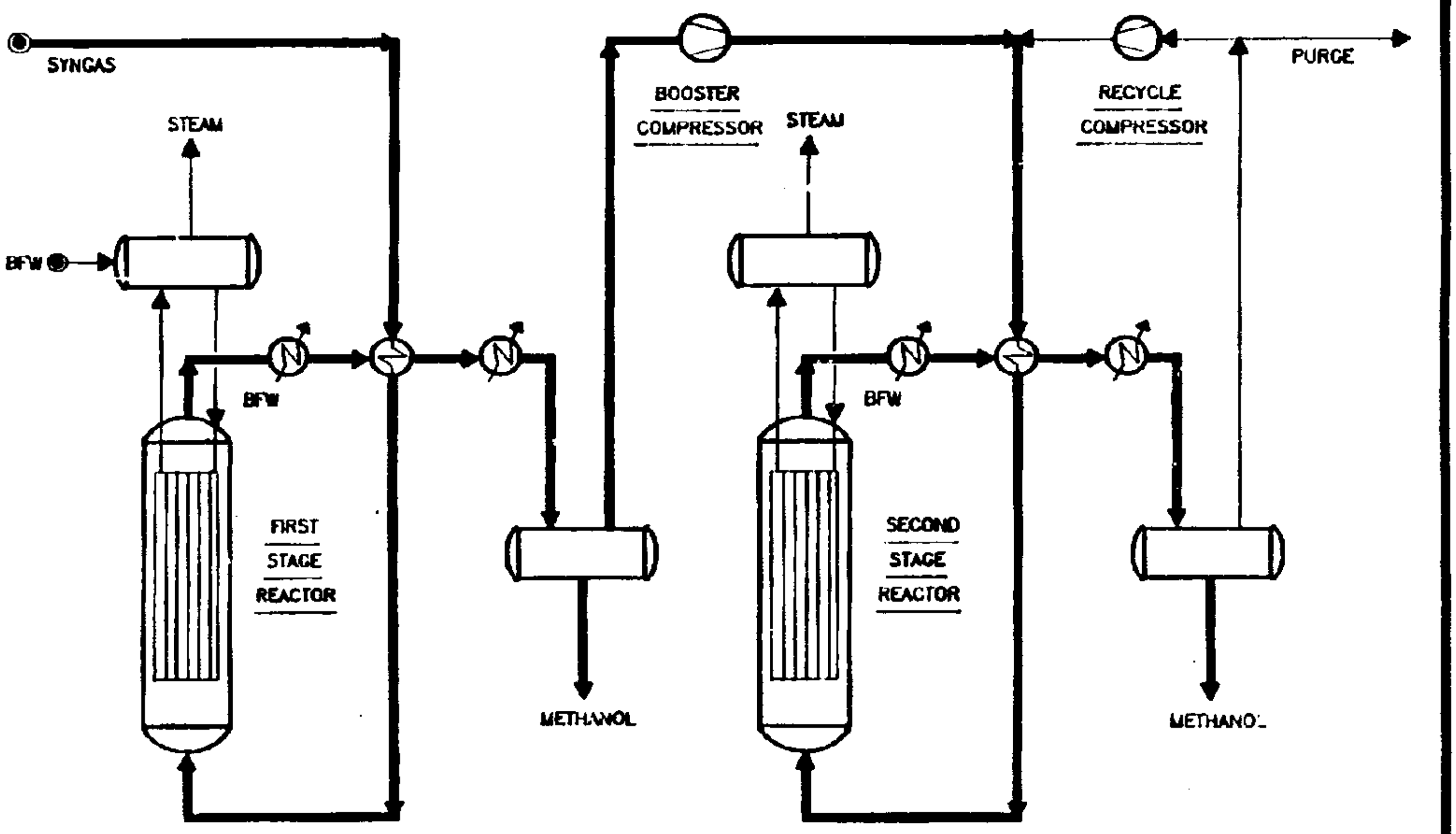

FIGURE 4.1-4

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TITLE
TWO-STAGE HIGH PRESSURE
LPMEOH PROCESS

PROJECT NO. 6193

conversions approximately triple those encountered in vapor-phase processes, thus, taking maximum advantage of the ability of the LPMEOH reactor to adsorb large quantities of the heat of reaction. The net result is potential for a single-train system producing 5,000 tons per day of methanol.

A design has been developed based on natural gas feed and partial oxidation to achieve the design synthesis gas composition. The first methanol synthesis stage, operating at a pressure of 1,500 psia, converts approximately half the synthesis gas to methanol. Carbon dioxide removal is used between the two LPMEOH reactors to adjust the gas composition for more efficient utilization. After carbon dioxide removal, the unconverted gas is further compressed to 2,200 psia and sent to the second stage. Unconverted gas form the second-stage effluent is recycle in combination with fresh feed to the second-stage in order to obtain high overall carbon efficiencies.

The two-stage system has the following features.

- Selective conversion of CO in a once-through, first-stage reactor.
- Conversion of the remainder of the gas in a second-stage reactor operating at conditions that favor the conversion of CO_2.

Of course, methanol synthesis at the pressures required for very high per pass conversions as utilized in this conceptual design has not yet been tested in the LPMEOH program.

This natural gas-based design is being reinterpreted into one based on coal gasification with partial CO shift and CO_2 removal as necessary. Economics of this design will be used to determine whether the concept of two large-scale high-pressure reactors is competitive with vapor phase technologies. If so, a recommendation for laboratory verification of high pressure LPMEOH operation with balances gas would be forthcoming.

4.3/4.4 CSI LaPorte Support

This subtask was initiated in the latter part of the reporting period, coinciding with shakedown operations at the PDU.

4.5/4.6 CSI Program Management

A quarterly review meeting, held on 23 June 1988 in LaPorte was attended by Chem Systems personnel. All monthly and quarterly reporting requirements during the period were satisfied.

Task 5 - Air Products Program Management Activities

Subtasks 5.1/5.2 - Reports

The 3rd Quarterly Report (1 January - 31 March 1988) and the Monthly Technical Progress Reports for April and May 1988 were issued.

Subtasks 5.3/5.4 - Management Activities

Provided general input to design and research tasks. A paper entitled "Recent LPMEOH Process Research and Field Modifications for the LaPorte Program" was presented at the 13th Annual Conference on Fuel Sciences and Conversion in May 1988. Also during May, Air Products presented research recommendations for future coal liquefaction programs in a meeting addressing "Assessment of Coal Liquefaction Research Needs". The meeting was sponsored by the Science Applications International Corp on behalf of DOE.

The quarterly review meeting was conducted in LaPorte on June 23, 1988.

III. OPEN ITEMS

None

IV. SUMMARY STATUS ASSESSMENT AND FORECAST:

None

V. ATTACHMENTS

1. Milestone Schedule Status Report and Milestone Log for the 1 April - 30 June 1988 period are submitted herewith. Similar reports for the previous individual months had been submitted as required by the Contract.
2. J. H. Frey interoffice memorandum to R. F. Weimer, dated 22 April 1988, subject, "Liquid Phase Methanol Column: Gas Holdings as a Function of Position".