# COMMERCIAL-SCALE DEMONSTRATION OF THE LIQUID PHASE METHANOL (LPMEOH™) PROCESS

## TECHNICAL PROGRESS REPORT NO. 22

**For The Period**

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**Prepared by**

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**and**

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**for the**
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**Prepared for the United States Department of Energy**
**National Energy Technology Laboratory**
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# Abstract

The Liquid Phase Methanol (LPMEOH™) Demonstration Project at Kingsport, Tennessee, is a $213.7 million cooperative agreement between the U.S. Department of Energy (DOE) and Air Products Liquid Phase Conversion Company, L.P. (the Partnership) to produce methanol from coal-derived synthesis gas (syngas). Air Products and Chemicals, Inc. (Air Products) and Eastman Chemical Company (Eastman) formed the Partnership to execute the Demonstration Project. The LPMEOH™ Process Demonstration Unit was built at a site located at the Eastman chemicals-from-coal complex in Kingsport.

The LPMEOH™ Demonstration Unit operated at 100% availability throughout the reporting period.

A major catalyst withdrawal and addition campaign was undertaken during the quarter to increase catalyst activity. After the addition of the final batch of catalyst, the total catalyst inventory was calculated to be 44,924 pounds.

During the balance of the quarter, the primary syngas feed (Balanced Gas) was supplied to the reactor at 680 KSCFH and the reactor pressure was set at 710 psig. Reactor temperature was held at 235°C throughout the reporting period.

There were two extended periods of operation at a reactor temperature of 235°C during which catalyst activity, as defined by the ratio of the rate constant at any point in time to the rate constant for freshly reduced catalyst (as determined in the laboratory autoclave), was calculated. During a 22-day continuous operating period which ended on 03 October 1999, a catalyst deactivation rate of 0.56% per day was achieved. A deactivation rate of 0.66% per day was calculated during a 23-day continuous operating period which ended on 07 November 1999. These deactivation results are slightly greater than the baseline deactivation rate from the 4-month proof-of-concept run at the LaPorte Alternative Fuels Development Unit (AFDU) in 1988/89 (this run was performed at 250°C).

On 02 December 1999, 45 KSCFH of a syngas stream which contains primarily carbon monoxide (Carbon Monoxide Gas or CO Gas) was introduced along with 675 KSCFH of Balanced Gas to achieve a ratio of hydrogen to carbon monoxide at the reactor inlet of 1:1. Reactor pressure was adjusted to 695 psig during periods of CO Gas addition to allow for proper control of the CO Gas. Operation at this condition continued until 11 December 1999. The catalyst performance met expectations for the quantity of methanol which was produced at these conditions; however, the operating period was not of sufficient length to calculate the rate of catalyst deactivation.

During the reporting period, analyses of catalyst and gas samples for changes in physical characteristics and levels of poisons have continued. Copper crystallite size measurements have shown an increase over time, which is an indication of catalyst aging. Levels of nickel (a known catalyst poison) have remained low and steady since the restart in December of 1997. As reported in Technical Progress Report No. 21, the adsorbents in the two catalyst

guard beds (the 10C-30 vessel, upstream of both the LPMEOH™ Demonstration Unit and the fixed-bed methanol plant, and the 29C-40 carbonyl guard bed) which treat Balanced Gas were changed in June of 1999; the 10C-30 was charged with arsine-removal adsorbent, and the 29C-40 was split between arsine and carbonyl removal materials. Initial results of batch sampling of the Balanced Gas stream demonstrated that the guard-bed system was effective in removing arsenic when it first came on-stream after the changeout. However, subsequent analysis confirmed that arsenic had broken through the guard-bed system within 2 to 3 months of initial operation. Although there is scatter in the data, the results of analyses of catalyst samples confirm this conclusion. In addition, sulfur is present on catalyst samples, and is increasing slowly with time. Work is underway to identify adsorbent materials for use in the 29C-40 guard bed to increase the removal efficiency of arsine and (if possible) sulfur from the Balanced Gas. The concentration of iron, although low (less than 200 ppmw), is increasing in the most recent samples. These results can be misleading, as contamination by iron from either piping or sample containers is possible. An assessment of the impact (if any) of the change in adsorbent materials in June of 1999 on the level of iron on the recent catalyst samples will be performed.

The original data acquisition system at the LPMEOH™ Demonstration Unit was replaced with a new system during the week of 08 November 1999. The original system was not Y2K compliant. The installation of the new system proceeded without any interruptions in gathering of plant data.

The performance of the gas sparger, which was designed by Air Products and installed into the LPMEOH™ Reactor prior to the restart of the LPMEOH™ Demonstration Unit in March of 1999, has met the expectations for pressure drop and reactor operation.

During the reporting period, a total of 4,804,902 gallons of methanol was produced at the LPMEOH™ Demonstration Unit. Since startup, about 47.6 million gallons of methanol has been produced. Eastman accepted all of this methanol for use in the production of methyl acetate, and ultimately cellulose acetate and acetic acid. No safety or environmental incidents were reported during this quarter.

During this quarter, planning, procurement, and test operations continued on three project sites selected for the off-site, product-use test program. Testing of stabilized methanol in a stationary gas turbine which generates low levels of nitrogen oxides ($NO_x$) was completed. Preliminary test results show that the emissions from the turbine fueled with stabilized methanol from the LPMEOH™ Demonstration Project are similar to those when fueled with natural gas. $NO_x$ emissions as low as 1 ppmv, corrected to 15% oxygen, were achieved at acceptable combustor CO emissions. A proposal was received from West Virginia University to allow additional time to complete the scope of work on testing of stabilized methanol in its stationary gas turbine. DOE accepted Air Products' recommendation to approve this no-cost extension to 01 April 2000. Testing has been performed to identify additives which can increase the lubricity of methanol to a value equal to that of Jet-A fuel. Construction of a second generation reformer test apparatus at the University of Florida is nearing completion. This will allow the evaluation of a high-temperature reformer catalyst as part of the ongoing activities to qualify stabilized methanol as a feedstock to a phosphoric acid fuel cell.

During the reporting period, the design verification test of the Liquid Phase Dimethyl Ether (LPDME) Process at the 10 TPD LaPorte AFDU was completed, using commercially produced catalysts. During this 25-day campaign, the reactor was operated at the same baseline conditions as the laboratory autoclave ($H_2$/CO = 0.5, 6,000 standard liters/hour-kg catalyst (oxide basis), 250°C, 750 psig reactor pressure). The primary objective of this test was to determine a tie-point between catalyst performance in the autoclave and the AFDU. The catalyst deactivation rate for both the methanol synthesis and dehydration catalysts was estimated to be 0.7% per day. This catalyst deactivation rate is lower than the 1.2% per day observed for both of the catalysts in the autoclave, and is only slightly higher than 0.5% per day rate achieved for the LPMEOH™ Process after the first 3 weeks of operation at during the 1988/89 testing at LaPorte. Hydrodynamic information was obtained at the baseline conditions by conducting a detailed survey of the reactor with radioactive tracer injections. The results from the design verification test will be used to update the economics of the LPDME Process and to support decision-making for future activities by the LPMEOH™ Demonstration Project in support in the scale-up of the LPDME technology.

A paper entitled “Direct Applications of Stabilized Methanol from the Liquid Phase Methanol (LPMEOH™) Process” was presented at the 16th Annual International Pittsburgh Coal Conference (11-15 October 1999). A presentation entitled “Liquid Phase Methanol (LPMEOH™) Project: Operating Experience Update” was given at the 1999 Gasification Technologies Conference (17-20 October 1999).

A letter was received from DOE stating that the most recent draft of Volume 1 - Public Design, of the Final Report for the LPMEOH™ Demonstration Project had satisfied the guidelines for preparation of the document. Work began to finalize the report.

Ninety-nine percent (99%) of the $38 million of funds forecast for the Kingsport portion of the LPMEOH™ Process Demonstration Project for the Phase 1 and Phase 2 tasks have been expended (as invoiced), as of 31 December 1999. Fifty-one percent (51%) of the $158 million of funds for the Phase 3 tasks have been expended (as invoiced), as of 31 December 1999.

# Table of Contents

## ACRONYMS AND DEFINITIONS

Acurex - Acurex Environmental Corporation (now ARCADIS Geraghty & Miller)
Air Products - Air Products and Chemicals, Inc.
AFDU - Alternative Fuels Development Unit - The “LaPorte PDU”
AFFTU - Alternative Fuels Field Trailer Unit
Balanced Gas - A syngas with a composition of hydrogen ($H_2$), carbon monoxide (CO), and carbon dioxide ($CO_2$) in stoichiometric balance for the production of methanol
Carbon Monoxide Gas - A syngas containing primarily carbon monoxide (CO); also called CO Gas
Catalyst Age ($\eta$ -eta) - the ratio of the rate constant at any point in time to the rate constant for a freshly reduced catalyst (as determined in the laboratory autoclave)
Catalyst Concentration - Synonym for Slurry Concentration
Catalyst Loading - Synonym for Slurry Concentration
CO Conversion - the percentage of CO consumed across the reactor
Crude Grade Methanol - Underflow from rectifier column (29C-20), defined as 80 wt% minimum purity; requires further distillation in existing Eastman equipment prior to use
DME - dimethyl ether
DOE - United States Department of Energy
DOE-NETL - The DOE's National Energy Technology Laboratory (Project Team)
DOE-HQ - The DOE's Headquarters - Coal Fuels and Industrial Systems (Project Team)
DTP - Demonstration Test Plan - The four-year Operating Plan for Phase 3, Task 2 Operation
DVT - Design Verification Testing
Eastman - Eastman Chemical Company
EIV - Environmental Information Volume
EMP - Environmental Monitoring Plan
EPRI - Electric Power Research Institute
FFV - flexible-fuel vehicle
Fresh Feed - sum of Balanced Gas, $H_2$ Gas, and CO Gas
Gas Holdup - the percentage of reactor volume up to the Gassed Slurry Height which is gas
Gassed Slurry Height - height of gassed slurry in the reactor
HAPs - Hazardous Air Pollutants
Hydrogen Gas - A syngas containing an excess of hydrogen ($H_2$) over the stoichiometric balance for the production of methanol; also called $H_2$ Gas
IGCC - Integrated Gasification Combined Cycle, a type of electric power generation plant
IGCC/OTM - An IGCC plant with a "Once-Thru Methanol" plant (the LPMEOH™ Process) added-on
Inlet Superficial Velocity - the ratio of the actual cubic feet of gas at the reactor inlet (calculated at the reactor temperature and pressure) to the reactor cross-sectional area (excluding the area contribution by the internal heat exchanger); typical units are feet per second
K - Sparger resistance coefficient (term used in calculation of pressure drop)
KSCFH - Thousand Standard Cubic Feet per Hour
LaPorte PDU - The DOE-owned experimental unit (PDU) located adjacent to Air Products’ industrial gas facility at LaPorte, Texas, where the LPMEOH™ Process was successfully piloted
LPDME - Liquid Phase DME Process, for the production of DME as a mixed coproduct with methanol
LPMEOH™ - Liquid Phase Methanol (the technology to be demonstrated)
M85 - a fuel blend of 85 volume percent methanol and 15 volume percent unleaded gasoline
MeOH - methanol
Methanol Productivity - the gram-moles of methanol produced per hour per kilogram catalyst (on an oxide basis)
MTBE - methyl tertiary butyl ether
MW - molecular weight, pound per pound mole
NEPA - National Environmental Policy Act
$NO_x$ - nitrogen oxides
OSHA - Occupational Safety and Health Administration

## ACRONYMS AND DEFINITIONS (cont'd)

$\rho$ - density, pounds per cubic foot
Partnership - Air Products Liquid Phase Conversion Company, L.P.
PDU - Process Development Unit
PFD - Process Flow Diagram(s)
ppbv - parts per billion (volume basis)
ppmv - parts per million (volume basis)
ppmw - parts per million (weight basis)
Project - Production of Methanol/DME Using the LPMEOH™ Process at an Integrated Coal Gasification Facility
psi - pounds per square inch
psia - pounds per square inch (absolute)
psig - pounds per square inch (gauge)
P&ID - Piping and Instrumentation Diagram(s)
Raw Methanol - sum of Refined Grade Methanol and Crude Grade Methanol; represents total methanol which is produced after stabilization
Reactor Feed - sun of Fresh Feed and Recycle Gas
Reactor O-T-M Conversion - percentage of energy (on a lower heating value basis) in the Reactor Feed converted to methanol (Once-Through-Methanol basis)
Reactor Volumetric Productivity - the quantity of Raw Methanol produced (tons per day) per cubic foot of reactor volume up to the Gassed Slurry Level
Recycle Gas - the portion of unreacted syngas effluent from the reactor "recycled" as a feed gas
Refined Grade Methanol - Distilled methanol, defined as 99.8 wt% minimum purity; used directly in downstream Eastman processes
SCF - Standard Cubic Feet
SCFH - Standard Cubic Feet per Hour
Slurry Concentration - percentage of weight of slurry (solid plus liquid) which is catalyst (on an oxide basis)
Sl/hr-kg - Standard Liter(s) per Hour per Kilogram of Catalyst
Syngas - Abbreviation for Synthesis Gas
Syngas Utilization - defined as the number of standard cubic feet of Balanced Gas plus CO Gas to the LPMEOH™ Demonstration Unit required to produce one pound of Raw Methanol
Synthesis Gas - A gas containing primarily hydrogen ($H_2$) and carbon monoxide (CO), or mixtures of $H_2$ and CO; intended for "synthesis" in a reactor to form methanol and/or other hydrocarbons (synthesis gas may also contain $CO_2$, water, and other gases)
Tie-in(s) - the interconnection(s) between the LPMEOH™ Process Demonstration Facility and the Eastman Facility
TPD - Ton(s) per Day
V - volumetric flowrate, thousand standard cubic feet per hour
VOC - volatile organic compound
WBS - Work Breakdown Structure
wt - weight

## Executive Summary

The Liquid Phase Methanol (LPMEOH™) Demonstration Project at Kingsport, Tennessee, is a $213.7 million cooperative agreement between the U.S. Department of Energy (DOE) and Air Products Liquid Phase Conversion Company, L.P. (the Partnership) to produce methanol from coal-derived synthesis gas (syngas). Air Products and Chemicals, Inc. (Air Products) and Eastman Chemical Company (Eastman) formed the Partnership to execute the Demonstration Project. The LPMEOH™ Process Demonstration Unit was designed, constructed, and is in operation at a site located at the Eastman chemicals-from-coal complex in Kingsport.

On 04 October 1994, Air Products and Eastman signed the agreements that would form the Partnership, secure the demonstration site, and provide the financial commitment and overall project management for the project. These partnership agreements became effective on 15 March 1995, when DOE authorized the commencement of Budget Period No. 2 (Modification No. A008 to the Cooperative Agreement). The Partnership has subcontracted with Air Products to provide the overall management of the project, and to act as the primary interface with DOE. As subcontractor to the Partnership, Air Products provided the engineering design, procurement, construction, and commissioning of the LPMEOH™ Process Demonstration Unit, and is providing the technical and engineering supervision needed to conduct the operational testing program required as part of the project. As subcontractor to Air Products, Eastman is responsible for operation of the LPMEOH™ Process Demonstration Unit, and for the interconnection and supply of syngas, utilities, product storage, and other needed services.

The project involves the operation of an 80,000 gallons per day (260 tons per day (TPD)) methanol unit utilizing coal-derived syngas from Eastman's integrated coal gasification facility. The new equipment consists of syngas feed preparation and compression facilities, the liquid phase reactor and auxiliaries, product distillation facilities, and utilities.

The technology to be demonstrated is the product of a cooperative development effort by Air Products and DOE in a program that started in 1981. Developed to enhance electric power generation using integrated gasification combined cycle (IGCC) technology, the LPMEOH™ Process is ideally suited for directly processing gases produced by modern day coal gasifiers. Originally tested at the Alternative Fuels Development Unit (AFDU), a small, DOE-owned experimental unit in LaPorte, Texas, the technology provides several improvements essential for the economic coproduction of methanol and electricity directly from gasified coal. This liquid phase process suspends fine catalyst particles in an inert liquid, forming a slurry. The slurry dissipates the heat of the chemical reaction away from the catalyst surface, protecting the catalyst and allowing the methanol synthesis reaction to proceed at higher rates.

At the Eastman chemicals-from-coal complex, the technology is integrated with existing coal gasifiers. A carefully developed test plan will allow operations at Eastman to simulate electricity demand load-following in coal-based IGCC facilities. The operations will also demonstrate the enhanced stability and heat dissipation of the conversion process, its reliable on/off operation, and its ability to produce methanol as a clean liquid fuel without additional upgrading. An off-site, product-use test program will be conducted to demonstrate the suitability of the methanol product as a transportation fuel and as a fuel for stationary applications for small modular electric power generators for distributed power.

The four-year operating test phase and off-site product-use test program will demonstrate the commercial viability of the LPMEOH™ Process and allow utilities to evaluate the application of this technology in the coproduction of methanol with electricity. A typical commercial-scale IGCC coproduction facility, for example, could be expected to generate 200 to 350 MW of electricity, and to also manufacture 45,000 to 300,000 gallons per day of methanol (150 to 1,000 TPD). A successful demonstration at Kingsport will show the ability of a local resource (coal) to be converted in a reliable (storable) and environmentally preferable way to provide the clean energy needs of local communities for electric power and transportation.

This project may also demonstrate the production of dimethyl ether (DME) as a mixed coproduct with methanol if laboratory- and pilot-scale research and market verification studies show promising results. If implemented, the DME would be produced during the last six months of the four-year demonstration period. DME has several commercial uses. In a storable blend with methanol, the mixture can be used as a peaking fuel in gasification-based electric power generating facilities, or as a diesel engine fuel. Blends of methanol and DME can be used as chemical feedstocks for synthesizing chemicals, including new oxygenated fuel additives.

The project was reinitiated in October of 1993, when DOE approved a site change to the Kingsport location. DOE conditionally approved the Continuation Application to Budget Period No. 2 (Design and Construction) in March of 1995 and formally approved it on 01 June 1995 (Modification No. M009). After approval, the project initiated Phase 1 - Design - activities. Phase 2 - Construction - activities were initiated in October of 1995. The project required review under the National Environmental Policy Act (NEPA) to move to the construction phase. DOE prepared an Environmental Assessment (DOE/EA-1029), and subsequently a Finding of No Significant Impact (FONSI) was issued on 30 June 1995. The Cooperative Agreement was modified (Modification No. A011) on 08 October 1996, authorizing the transition from Budget Period No. 2 (Design and Construction) to the final Budget Period (Commissioning, Start-up, and Operation). This modification provides the full $213,700,000 of authorized funding, with 56.7% participant cost share and 43.3% DOE cost share.

The LPMEOH™ Demonstration Unit operated at 100% availability throughout the reporting period.

A major catalyst withdrawal and addition campaign was undertaken during the quarter to increase catalyst activity. A series of four withdrawals were conducted on 08 and 09 November 1999. This was followed by four catalyst additions which were activated and added between 12 November and 19 November 1999. After the addition of the fourth batch of catalyst, the total catalyst inventory was calculated to be 44,924 pounds.

During the balance of the quarter, the primary syngas feed (Balanced Gas) was supplied to the reactor at 680 KSCFH and the reactor pressure was set at 710 psig. Reactor temperature was held at 235°C throughout the reporting period.

There were two extended periods of operation at a reactor temperature of 235°C during which catalyst activity was measured to track catalyst deactivation during the quarter. An overall deactivation rate of 0.56% per day was calculated for the period 11 September 1999 to 03 October 1999 (22 days). An overall deactivation rate of 0.66% per day was calculated for the period 13 October 1999 to 07 November 1999 (23 days). These deactivation results are slightly greater than the baseline deactivation rate from the 4-month proof-of-concept run at the LaPorte AFDU in 1988/89 (this run was performed at 250°C).

On 02 December 1999, 45 KSCFH of a syngas stream which contains primarily carbon monoxide (Carbon Monoxide Gas or CO Gas) was introduced along with 675 KSCFH of Balanced Gas to achieve a ratio of hydrogen ($H_2$) to CO in the reactor inlet of 1:1. Reactor pressure was adjusted to 695 psig during periods of CO Gas addition to allow for proper control of the CO Gas. Operation at this condition continued until 11 December 1999. The catalyst performance met expectations for the quantity of methanol which was produced at these conditions; however, the operating period was not of sufficient length to calculate the rate of catalyst deactivation.

During the reporting period, analyses of catalyst and gas samples for changes in physical characteristics and levels of poisons have continued. Copper crystallite size measurements have shown an increase over time, which is an indication of catalyst aging. Levels of nickel (a known catalyst poison) have remained low and steady since the restart in December of 1997. As reported in Technical Progress Report No. 21, the adsorbents in the two catalyst guard beds (the 10C-30 vessel, upstream of both the LPMEOH™ Demonstration Unit and the fixed-bed methanol plant, and the 29C-40 carbonyl guard bed) which treat Balanced Gas were changed in June of 1999; the 10C-30 was charged with arsine-removal adsorbent, and the 29C-40 was split between arsine and carbonyl removal materials. Initial results of batch sampling of the Balanced Gas stream demonstrated that the guard-bed system was effective in removing arsenic when it first came on-stream after the changeout. However, subsequent analysis confirmed that arsenic had broken through the guard-bed system within 2 to 3 months of initial operation. Although there is scatter in the data, the results of analyses of catalyst samples confirm this conclusion. In addition, sulfur is present on catalyst samples, and is increasing slowly with time. Work is underway to identify adsorbent materials for use in the 29C-40 guard bed to increase the removal efficiency of arsine and (if possible) sulfur from the Balanced Gas. The concentration of iron, although low (less than 200 ppmw), is increasing in the most recent samples. These results can be misleading, as contamination by iron from either piping or sample containers is possible. An assessment of the impact (if any) of the change in adsorbent materials in June of 1999 on the level of iron on the recent catalyst samples will be performed.

The original data acquisition system at the LPMEOH™ Demonstration Unit was replaced with a new system during the week of 08 November 1999. The original system was not Y2K compliant. The installation of the new system proceeded without any interruptions in gathering of plant data.

The performance of the gas sparger, which was designed by Air Products and installed into the LPMEOH™ Reactor prior to the restart of the LPMEOH™ Demonstration Unit in March of 1999, was monitored. The performance to date has met the design expectations for pressure drop and reactor operation.

During the reporting period, a total of 4,804,902 gallons of methanol was produced at the LPMEOH™ Demonstration Unit. Since startup, about 47.6 million gallons of methanol has been produced. Eastman accepted all of this methanol for use in the production of methyl acetate, and ultimately cellulose acetate and acetic acid. No safety or environmental incidents were reported during this quarter.

During this quarter, planning, procurement, and test operations continued on three project sites selected for the off-site, product-use test program. Testing of stabilized methanol in a stationary gas turbine which generates low levels of nitrogen oxides ($NO_x$) was completed. Preliminary test results show that the emissions from the turbine fueled with stabilized methanol from the LPMEOH™ Demonstration Project are similar to those when fueled with natural gas. $NO_x$ emissions as low as 1 ppmv, corrected to 15% oxygen, were achieved at acceptable combustor CO emissions. A proposal was received from West Virginia University to allow additional time to complete the scope of work on testing of stabilized methanol in its stationary gas turbine. DOE accepted Air Products' recommendation to approve this no-cost extension to 01 April 2000. Testing has been performed to identify additives which can increase the lubricity of methanol to a value equal to that of Jet-A fuel. Construction of a second generation reformer test apparatus at the University of Florida is nearing completion. This will allow the evaluation of a high-temperature reformer catalyst as part of the ongoing activities to qualify stabilized methanol as a feedstock to a phosphoric acid fuel cell.

During the reporting period, the design verification test of the Liquid Phase Dimethyl Ether (LPDME) Process at the LaPorte AFDU was completed. Commercial viability of the LPDME Process was successfully evaluated at the 10 TPD scale, using commercially produced catalysts. The plant was operated for 25 days on stream to compare catalyst aging in an 18-inch diameter slurry bubble column with that in a laboratory autoclave. The catalyst life study was extended in favor of a planned process variable study to obtain additional data on catalyst aging. Hydrodynamic information was obtained at the baseline conditions by conducting a detailed survey of the reactor with radioactive tracer injections. The tracer data will be analyzed as part of the Hydrodynamic Program with DOE's Liquid Fuels Program.

The deactivation rate for both the catalysts was calculated to be 0.7% per day. This result is lower than the 1.2% per day which had been calculated for both the methanol synthesis and dehydration catalysts during experiments in the autoclave. The rate of deactivation is slightly higher than 0.5% per day rate which was achieved for the LPMEOH™ Process after 3 weeks of operation at LaPorte in 1988/89. The methanol productivity remained relatively constant throughout the run, while the DME productivity showed a slight decline. These trends are consistent with observations from the laboratory. The standard error for the methanol catalyst deactivation rate was high (0.25% per day) due to initial scatter in the data. The scatter decreased significantly after problems in the sampling and analytical system were discovered and resolved at 350 hours on stream. The dehydration catalyst activity data have better statistics, with a standard error of 0.06% per day.

The methanol synthesis catalyst was activated successfully with an expected reductant uptake. The initial productivities of methanol and DME were higher than the laboratory. The DME production rate started at 5.1 TPD and declined to 4.1 TPD over the 25 days on stream, while the methanol production showed a scatter within the range of 3.1 to 3.8 TPD throughout the run.

The reactor operated in a stable hydrodynamic regime as determined by the presence of a uniform temperature profile and gas hold-up. Differential pressure measurements along the reactor resulted in a calculated gas hold-up of about 42 vol% gas hold-up and a catalyst slurry concentration of 36 wt%.

The initial start-up was very quick with the baseline condition reached in 12 hours after the introduction of syngas. A re-start after a syngas outage only took 4 hours. This further demonstrates the ease and flexibility of the slurry technology.

The 1999 design verification test of the LPDME Process at the LaPorte AFDU represents a significant step forward in the development of the technology. The 0.7% per day rate of catalyst deactivation which was achieved during this campaign is a large improvement over the 4% per day rate of deactivation which was calculated from autoclave studies prior to the initial test of the LPDME Process at the LaPorte AFDU in 1991. The results from the design verification test will be used to update the economics of the LPDME Process and to support decision-making for future activities by the LPMEOH™ Demonstration Project in support in the scale-up of the LPDME technology.

A paper entitled “Direct Applications of Stabilized Methanol from the Liquid Phase Methanol (LPMEOH™) Process” was presented at the 16th Annual International Pittsburgh Coal Conference (11-15 October 1999). A presentation entitled “Liquid Phase Methanol (LPMEOH™) Project: Operating Experience Update” was given at the 1999 Gasification Technologies Conference (17-20 October 1999).

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## A. Introduction

The Liquid Phase Methanol (LPMEOH™) demonstration project at Kingsport, Tennessee, is a $213.7 million cooperative agreement between the U.S. Department of Energy (DOE) and Air Products Liquid Phase Conversion Company, L. P. (the Partnership). Air Products and Chemicals, Inc. (Air Products) and Eastman Chemical Company (Eastman) formed the Partnership to execute the Demonstration Project. A demonstration unit producing 80,000 gallons per day (260 TPD) of methanol was designed, constructed, and is operating at a site located at the Eastman chemicals-from-coal complex in Kingsport. The Partnership will own and operate the facility for the four-year demonstration period.

This project is sponsored under the DOE's Clean Coal Technology Program, and its primary objective is to “demonstrate the production of methanol using the LPMEOH™ Process in conjunction with an integrated coal gasification facility.” The project will also demonstrate the suitability of the methanol produced for use as a chemical feedstock or as a low-sulfur dioxide, low-nitrogen oxides alternative fuel in stationary and transportation applications. The project may also demonstrate the production of dimethyl ether (DME) as a mixed coproduct with methanol, if laboratory research, design verification testing, and market verification studies show promising results. If implemented, the DME would be produced during the last six months of the four-year demonstration period.

The LPMEOH™ Process is the product of a cooperative development effort by Air Products and the DOE in a program that started in 1981. It was successfully piloted at a 10-TPD rate in the DOE-owned experimental unit at Air Products' LaPorte, Texas, site. This demonstration project is the culmination of that extensive cooperative development effort.

## B. Project Description

The demonstration unit, which occupies an area of 0.6 acre, is integrated into the existing 4,000-acre Eastman complex located in Kingsport, Tennessee. The Eastman complex employs approximately 8,600 people. In 1983, Eastman constructed a coal gasification facility utilizing Texaco technology. The synthesis gas (syngas) generated by this gasification facility is used to produce carbon monoxide and methanol. Both of these products are used to produce methyl acetate and ultimately cellulose acetate and acetic acid. The availability of this highly reliable coal gasification facility was the major factor in selecting this location for the LPMEOH™ Process Demonstration. Three different feed gas streams (hydrogen gas or $H_2$ Gas, carbon monoxide gas or CO Gas, and the primary syngas feed known as Balanced Gas) are diverted from existing operations to the LPMEOH™ Demonstration Unit, thus providing the range of coal-derived syngas ratios (hydrogen to carbon monoxide) needed to meet the technical objectives of the demonstration project.

For descriptive purposes and for design and construction scheduling, the project has been divided into four major process areas with their associated equipment:

- *Reaction Area* - Syngas preparation and methanol synthesis reaction equipment.
- *Purification Area* - Product separation and purification equipment.
- *Catalyst Preparation Area* - Catalyst and slurry preparation and disposal equipment.
- *Storage/Utility Area* - Methanol product, slurry, and oil storage equipment.

The physical appearance of this facility closely resembles the adjacent Eastman process plants, including process equipment in steel structures.

- *Reaction Area*

The reaction area includes feed gas compressors, catalyst guard beds, the reactor, a steam drum, separators, heat exchangers, and pumps. The equipment is supported by a matrix of structural steel. The most salient feature is the reactor, since with supports, it is approximately 84-feet tall.

- *Purification Area*

The purification area features two distillation columns with supports; one is approximately 82-feet tall, and the other 97-feet tall. These vessels resemble the columns of the surrounding process areas. In addition to the columns, this area includes the associated reboilers, condensers, air coolers, separators, and pumps.

- *Catalyst Preparation Area*

The catalyst preparation area consists of a building with a roof and partial walls, in which the catalyst preparation vessels, slurry handling equipment, and spent slurry disposal equipment are housed. In addition, a hot oil utility system is included in the area.

- *Storage/Utility Area*

The storage/utility area includes two diked lot-tanks for methanol, two tanks for oil storage, a slurry holdup tank, a trailer loading/unloading area, and an underground oil/water separator. A vent stack for safety relief devices is located in this area.

## C. Process Description

The LPMEOH™ Demonstration Unit is integrated with Eastman's coal gasification facility. A simplified process flow diagram is included in Appendix A. Syngas is introduced into the slurry reactor, which contains a slurry of liquid mineral oil with suspended solid particles of catalyst. The syngas dissolves through the mineral oil, contacts the catalyst, and reacts to form methanol. The heat of reaction is absorbed by the slurry and is removed from the slurry by steam coils. The methanol vapor leaves the reactor, is condensed to a liquid, sent to the distillation columns for removal of higher alcohols, water, and other impurities, and is then stored in the day tanks for sampling before being sent to Eastman's methanol storage. Most of the unreacted syngas is recycled back to the reactor with the syngas recycle compressor, improving cycle efficiency. The methanol will be used for downstream feedstocks and in off-site, product-use testing to determine its suitability as a transportation fuel and as a fuel for stationary applications in the power industry.

## D. Results and Discussion

The project status is reported by task, covering those areas in which activity took place during the reporting period. Major accomplishments during this period are as follows:

### *D.1 Off-Site Testing (Product-Use Demonstration)*

Discussion

The product-use test program, developed in 1992 to support the demonstration at the original Cool Water Gasification Facility site, became outdated due in large part to changes within the power and chemical industries. This original product test program under-represented new utility dispersed electric power developments, and possibly new mobile transport engine developments. The updated product-use test program attempts for broader market applications and for commercial fuels comparisons. The objective of the product-use test program is to demonstrate commercial market applications for the “as produced” methanol as a replacement fuel and as a fuel supplement. Fuel economics will be evaluated for the “as produced” methanol for use in municipal, industrial, and utility applications and as fuel supplements for gasoline, diesel, and natural gas. These fuel evaluations will be based on the U.S. energy market needs projected during the 1998 to 2018 time period when the LPMEOH™ technology is expected to be commercialized.

The product-use test program has been developed to enhance the early commercial acceptance of central clean coal technology processing facilities, coproducing electricity and methanol to meet the needs of the local community. One of the advantages of the LPMEOH™ Process for coproduction from coal-derived syngas is that the as-produced, stabilized (degassed) methanol product is of unusually high quality (e.g. less than 1 wt% water) which may be suitable for the premium fuel applications. When compared to conventional methanol synthesis processes, cost savings (10 to 15%) of several cents per gallon of methanol can be achieved in coproduction facilities, if the suitability of the stabilized product as a fuel can be demonstrated. The applications (for example, as a hydrogen source for fuel cells, and as a clean transportable, storable fuel for dispersed power) will require testing of the product to confirm its suitability. Chemical feedstock applications will also be tested as warranted.

A limited quantity (up to 400,000 gallons) of the methanol product as produced from the demonstration unit is being made available for product-use tests. Product-use tests are targeted for an approximate 18 to 30-month period, and commenced during the first year of demonstration operations. An initial inventory of approximately 12,000 gallons of stabilized methanol was produced at LPMEOH™ Demonstration Unit in February of 1998 to supply the needs of the product-use test program; due to the pre-1998 timing for certain tests, methanol was shipped from the inventory held at the LaPorte AFDU. Air Products, ARCADIS Geraghty & Miller (formerly Acurex Environmental Corporation), and the DOE have worked together to select the projects to be included in the off-site, product-use test program.

Activity during this quarter

During an evaluation period, eight sites involving a variety of product-use tests were selected to participate in this task. In a letter to the DOE dated 31 July 1997, Air Products formally recommended that seven of the eight projects had been defined in sufficient detail so that final planning and implementation should begin. DOE accepted Air Products' recommendation to proceed with the seven projects in August of 1997. The sites and project titles are listed in Appendix B-1. The eighth project, which involved the testing of a water/naphtha/methanol emulsion as a transportation fuel, was removed from the Product-Use Test Program during a review meeting between DOE, Air Products, and ARCADIS Geraghty & Miller.

All of the remaining product-use test projects are at varying phases of project planning, equipment procurement, and execution; two projects have been completed. Methanol produced from carbon monoxide (CO)-rich syngas at the LaPorte AFDU has been shipped to three of the project sites. Appendices B-2 through B-5 contain summary reports from the approved active projects. Highlights from these reports include:

ARCADIS Geraghty & Miller Flexible-Fuel Vehicle (FFV) - The draft final report for this project was submitted to Air Products (no update in this reporting period).

Stationary Turbine for Nitrogen Oxide ($NO_x$) Control - Testing for this project was completed at Alzeta Corporation during November of 1999. Preliminary test results show that the emissions from the low-$NO_x$ gas turbine combustor fueled with stabilized methanol from the LPMEOH™ Demonstration Project are similar to those when fueled with natural gas. $NO_x$ emissions as low as 1 ppmv, corrected to 15% oxygen, were achieved at acceptable combustor CO emissions. A final report is under review by ARCADIS Geraghty & Miller.

West Virginia University (WVU) Stationary Gas Turbine - A proposal was received from WVU to allow additional time to complete the scope of work on testing of stabilized methanol in a stationary gas turbine. DOE accepted Air Products' recommendation to approve this no-cost extension to 01 April 2000. Testing has been performed to identify additives which can increase the lubricity of methanol to a value equal to that of Jet-A fuel. A final choice of additives which will be used during emission testing on the gas turbine will be made following lubricity testing of a less expensive, commercial methanol racing additive.

Aircraft Ground Equipment Emulsion - Testing of stabilized methanol as an emulsion fuel in a 110 horsepower flight line generator at Tyndall Air Force Base, Florida was suspended due to the loss of funding from other sources. A draft of this report was continuing to undergo review at ARCADIS Geraghty & Miller as of the end the reporting period.

University of Florida Fuel Cell - The construction of the second generation methanol steam reforming rig is well underway. Construction on one side of the apparatus has been completed. The superheater and reformer must still be installed on the second parallel rig. A high-temperature reformer catalyst, with an operating range of 350°C to 450°C, was acquired. This will allow the evaluation of a high-temperature reformer catalyst as part of the ongoing activities to qualify stabilized methanol from the LPMEOH™ Demonstration Project as a feedstock to a phosphoric acid fuel cell. Catalyst activation will commence following the completion of construction and shakedown activities.

West Virginia University Tri-Boro Bus - The draft final report for this project was submitted to Air Products (no update in this reporting period).

Florida Institute of Technology Bus & Light Vehicle - The final report on testing of stabilized methanol as a transportation fuel at the Florida Institute of Technology was received. DOE accepted Air Products' recommendation to provide stabilized methanol from the LPMEOH™ Process Demonstration Unit for use as part a new contract between the Institute and the Florida Energy Office. Air Products will receive copies of the reports which are submitted to the state of Florida.

## *D.2 DME Design Verification Testing*

Discussion

The first decision milestone, on whether to continue with dimethyl ether (DME) Design Verification Testing (DVT), was targeted for 01 December 1996. This milestone was relaxed to July of 1997 to allow time for further development of the Liquid Phase Dimethyl Ether (LPDME) catalyst system. DVT is required to provide additional data for engineering design and demonstration decision-making. The essential steps required for decision-making are: a) confirm catalyst activity and stability in the laboratory, b) develop engineering data in the laboratory, and c) confirm market(s), including fuels and chemical feedstocks.

Prior work in this task included a recommendation to continue with DME DVT and Market Economic Studies. Ongoing activity is focusing on Laboratory R&D and preparations for the design verification test run at the LaPorte AFDU.

### ***1997 DME DVT Recommendation***

DOE issued a letter dated 31 July 1997 accepting Air Products' recommendation to continue with the design verification testing to coproduce DME with methanol, and to proceed with planning a design verification test run at the LaPorte AFDU. A copy of the recommendation (dated 30 June 1997) is included in Appendix C-1. The recommendation was based on the results of the Market Economic Studies and on the LPDME catalyst system R&D work, and is summarized in the following.

The Market Economic Studies show that the LPDME Process should have a significant economic advantage for the coproduction of DME with methanol for local markets. The studies show that the market applications for DME are large. DME is an ultra clean diesel fuel; and an 80% DME mixture with methanol and water is now being developed and tested by others. DME is a key intermediate in a commercial syngas-to-gasoline process, and is being developed as an intermediate for other chemicals and fuels. An LPDME catalyst system with reasonable long-term activity and stability has been developed from the laboratory R&D work.

Based upon the potential size of the markets and the promise of the LPDME catalyst system, design verification planning for the LaPorte AFDU was recommended. A summary of the DME DVT recommendation is:

- Planning for a DME DVT run at the LaPorte AFDU, in conjunction with other DOE Liquid Fuels Programs, should be initiated. Test plans, budgets, and a schedule for these LaPorte AFDU tests are under development. Up to $875,000 of Clean Coal Technology Program budget support from the LPMEOH™ Project budget could be made available to support a suitable LPDME test run at LaPorte.

- An implementation decision, made mutually by the DOE's Clean Coal Technology Program (DE-FC22-92PC90543) LPMEOH™ project participants, and by the DOE's Liquid Fuels Program (DE-FC22-95PC93052) project participants, will be made in order to finalize the schedule for testing at LaPorte.

LPDME is not applicable to hydrogen ($H_2$)-rich syngas; and it is unlikely that a substantive LPDME demonstration will be recommended for Kingsport. Therefore, a convincing case that the test-run on CO-rich syngas at LaPorte will lead to successful commercialization must be made, prior to approving the final test-run plan. The strategy for commercialization must present the technical logic to combine the results of the following two areas:

1) catalyst performance (productivity, selectivity, and life) for the LPDME catalyst system under CO-rich syngas from the design verification testing at the LaPorte AFDU; and

2) reactor performance (methanol catalyst activity and life, hydrodynamics, and heat transfer) from the LPMEOH™ Process Demonstration Unit at Kingsport.

The 1997 DME DVT recommendation summarizes the catalyst targets, experimental results, and the corresponding economics for a commercially successful LPDME catalyst.

### *Market Economic Studies*

Work on the feasibility study for the coproduction of DME and methanol with electric power has been completed. The product DME would be used as a domestic liquid cooking fuel, to replace imported Liquid Petroleum Gas, for China and the Pacific Rim regions. The results are included in the 1997 DME recommendation in Appendix C-1.

### *Laboratory R&D - Background*

Initially, synthesis of DME concurrently with methanol in the same reactor was viewed as a way of overcoming the syngas conversion limitations imposed by equilibrium in the LPMEOH™ Process. Higher syngas conversion would provide improved design flexibility for the coproduction of power and liquid fuels from an IGCC facility. The LPDME Process concept seemed ideally suited for the slurry-based liquid phase technology, since the second reaction (methanol to DME) could be accomplished by adding a second catalyst with dehydration activity to the methanol-producing reactor. Initial research work determined that two catalysts, a methanol catalyst and an alumina-based dehydration catalyst, could be physically mixed in different proportions to control the yield of DME and of methanol in the mixed product. These two commercially available catalysts comprise the LPDME catalyst system. Previously, proof-of-concept runs, in the laboratory and at the AFDU, confirmed that a higher syngas conversion could be obtained when a mixture of DME and methanol is produced in the liquid phase reactor.

Subsequent catalyst activity-maintenance experiments have shown the catalyst system utilized in the proof-of-concept run experienced relatively fast deactivation compared to the LPMEOH™ process catalyst system. Further studies of the LPDME catalyst deactivation phenomenon, initially undertaken under the DOE's Liquid Fuels Program (Contract No. DE-FC22-95PC93052), was continued under this Task 1.5.3 through Fiscal Year 1996, and is now again being continued under the DOE Liquid Fuels Program. This LPDME catalyst deactivation research has determined that an interaction between the methanol catalyst and the dehydration catalyst is the cause of the loss of activity. Parallel research efforts--a) to determine the nature of the interaction; and b) to test new dehydration catalysts--was undertaken. In late 1995, the stability of the LPDME catalyst system was greatly improved, to near that of an LPMEOH™ catalyst system, when a new aluminum-based (AB) dehydration catalyst was developed. This new AB catalyst development showed that modification of the LPDME catalyst system could lead to long life.

Air Products performed laboratory autoclave tests of samples of the AB dehydration catalyst from the commercial catalyst manufacturer (Engelhard). The results to date have not been consistent, indicating that all issues related to catalyst scale-up have not been resolved. As a result, the decision was made within the DOE’s Liquid Fuels Program to delay the start of the AFDU design verification test. Changes to the commercial production procedure were made, and additional batches of dehydration catalyst were made and tested. These tests did not yield the desired catalyst aging characteristics.

During an earlier reporting period, a set of experiments was performed on a commercially available dehydration catalyst to compare this material with the AB dehydration catalyst.

These results showed that the desired catalyst life could be achieved with a commercially available dehydration catalyst at a 10-20% reduction in system productivity (primarily a reduction in the selectivity to DME).

### *LPDME Design Verification Test - Background*

At a review meeting for the DOE's Liquid Fuels Program on 09 June 1999, members of the LPMEOH™ Project Team from Air Products and DOE were given an update on the activities regarding the status of catalyst development and the economics for the LPDME Process. The participants agreed that the next test for the LPDME Process at the LaPorte AFDU should be treated as an interim campaign, with the primary objective being the determination of a tie-point between catalyst performance in the autoclave and the pilot plant scale.

Following this meeting, a formal recommendation to proceed with the interim campaign at the LaPorte AFDU was issued by Air Products to DOE. A copy of this letter (dated 06 August 1999) is included in Appendix C-2. The objectives for this campaign, as stated in this recommendation, are:

1) Determine commercial viability of the LPDME Process on a 10 TPD scale, using commercially produced catalysts.
2) Obtain information to correlate scale-up of catalyst aging from the laboratory autoclave to the slurry bubble column.
3) Conduct process variable testing at conditions of potential commercial interest.
4) Perform experiments to better understand the hydrodynamics of the slurry bubble column.

DOE issued a letter dated 10 August 1999 accepting accepted Air Products' recommendation to proceed with DME DVT activities at the LaPorte AFDU.

During a Project Review Meeting on 15-16 September 1999, DOE agreed with recommendations which were made by Air Products regarding the run plan; the finalized version is presented in Table D.2-1. The first portion of the campaign was to be dedicated to studying catalyst life at the reactor conditions which have been studied extensively in the autoclave. For the remainder of the operating days, the plan called for process variable scans to be performed at conditions which may be of interest for both coproduction with electric power and high conversion of syngas to DME and methanol. Nuclear tracer scans to study reactor hydrodynamics were planned at two of the test conditions.

#### LaPorte AFDU Process Description

The process flow diagrams for the equipment used as part of the LPDME design verification test at the LaPorte AFDU are shown in Appendix D. The operation of the plant is described as follows:

# Table D.2-1

**FINAL RUN PLAN**

**DME RUN AT THE LAPORTE AFDU - OCTOBER / NOVEMBER 1999**

| Run No. | No. of Days | Comment | Gas Type | Reactor Pressure psia | Reactor Temp. deg F | Space Vel. sl/kg-hr | React. Fd. lbmol/hr | Inlet Sup. Vel. ft/sec | Slurry wt% oxide | Methanol Production TPD | DME Production TPD |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **MEOH + DEHYDRATION CATALYST (% MEOH CAT = 95%)** | | | | | | | | | | | |
| | 1 | Catalyst Loading | | | | | | | | | |
| AF-A13 | 1 | Reduction | 3% H2 in N2 | 82 | | 800 | 32 | 0.62 | 35 | | |
| AF-R17.1 | 18 | Life Study + Tracer1 (on-stream Day 18) | Shell | 765 | 482 | 6000 | 248 | 0.56 | 35.9 | 3.5 | 4.8 |
| AF-R17.2 | 1.5 | Low Space Velocity | Shell | 765 | 482 | 3100 | 128 | 0.29 | 34.6 | 1.1 | 4.2 |
| AF-R17.3 | 1.5 | Stoch. Feed | 1:1 H2/CO | 765 | 482 | 6000 | 248 | 0.56 | 35.1 | 8.5 | 4.0 |
| AF-R17.4 | 2.5 | High Velocity + Tracer2 (on-stream Day 23) | Shell | 765 | 482 | 8000 | 331 | 0.75 | 36.5 | 5.0 | 5.1 |
| AF-R17.5 | 1.5 | High Concentration | Shell | 765 | 482 | 8000 | 331 | 0.75 | 40 | 5.0 | 5.1 |
| TOTAL | 27 | | | | | | | | | | |

$H_2$, CO, carbon dioxide ($CO_2$), and nitrogen ($N_2$) are blended and compressed in the 01.10 feed gas compressor. This stream then mixes with recycle gas and additional $H_2$ from a high pressure pipeline to obtain the desired syngas composition and flow. The reactor feed then bypasses a booster compressor, as the operating conditions for the test were all within the capacity of the feed gas compressor. The syngas is then fed to the 21.11 feed/product economizer, which preheats the feed against the reactor effluent. The stream bypasses a steam preheater and is introduced at the bottom of the 27.20 high pressure slurry reactor.

The syngas flows upward through the slurry of catalyst and mineral oil as the reaction proceeds. The mineral oil acts as a temperature moderator and a heat removal medium, transferring the heat of reaction from the catalyst surface via the liquid slurry to a heat transfer oil in an internal tubular heat exchanger. The 27.20 bubble-column reactor measures 50-feet long (flange-to-flange) and 18-inches inside diameter. The design slurry level is 40 feet; the remaining volume is used as disengagement space between vapor and catalyst slurry. The reactor contains an internal heat exchanger consisting of twelve ¾-inch U-tubes which occupy about 8% of the reactor cross-sectional area. In addition, thirteen thermocouples spaced 4-feet apart measure the longitudinal temperature profile. A nuclear density gauge, mounted on an external hoist mechanism, spans the space occupied by the internal exchanger to measure slurry level and gas holdup.

The methanol and DME products pass through the reactor freeboard with the unconverted syngas, and the gross reactor effluent cools against the feed in the 21.11 economizer. The bulk of the catalyst slurry which is entrained in the effluent plus the condensed oil from the syngas are returned to the bottom of the reactor by the 10.52.02 pumps. The vapor leaving the 21.11 passes through the 27.14 entrained oil separator to capture the remainder of the entrained oil which is present in the syngas stream. The stream which contains the unreacted syngas, methanol, and DME is chilled against cooling water in the 21.30 hairpin exchangers, and passes into the 22.10 separator where any liquid products (methanol, water, trace higher alcohols) collect. The liquids flash to near atmospheric pressure in the 22.11 degasser and collect in the 22.15 low pressure separator before passing on to the 22.16 day tank and eventually a trailer for storage.

To minimize the amount of gas sent to the flare, most of the syngas leaving the 22.10 separator is recycled to the reactor. Since $CO_2$ is a byproduct of the chemistry (via the water-gas shift reaction), it is necessary to remove $CO_2$ from the 22.10 vapor outlet before recycling this stream. The closed-loop $CO_2$ removal system uses methanol to preferentially absorb the $CO_2$ from the syngas.

The vapor from the 22.10 separator cools against returning $CO_2$-lean syngas in the 21.10 gas-gas economizer. This stream is then fed into the bottom of the 07.10 absorber and contacts against chilled methanol introduced at the top of the column. The $CO_2$-lean syngas leaves the top of the absorber and is warmed to ambient temperatures in the 21.10 gas-gas economizer before being recompressed in the 01.20 recycle compressor. A small portion of this gas is purged to flare to prevent the buildup of inerts.

The $CO_2$-rich liquid collects in the bottom of the 07.10 absorber, de-pressurizes across a valve, and heats up against returning methanol in the 21.45 hairpin exchangers. This liquid then passes into the top of the 07.20 stripper where it is reboiled to remove the dissolved gases such as $CO_2$ and DME. The overhead cooling water condenser reduces the amount of methanol solvent lost in the overhead stream, which goes to flare. The liquid from the bottom of the 07.20 stripper cools in the 21.45 exchangers prior to recompression in the 10.80 pump. The methanol then chills against liquid $CO_2$ in the 21.80 kettle evaporator before recycling to the top of the 07.10 absorber.

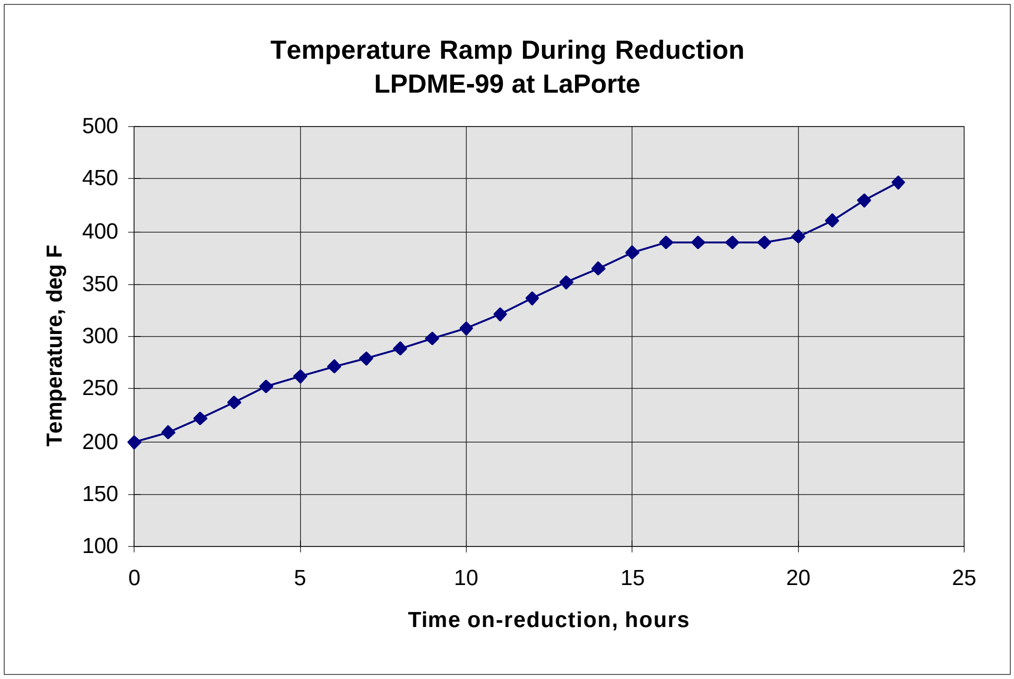
The syngas from the 22.10 separator will include equilibrium amounts of methanol, water, and other hydrocarbons which will build up in the methanol solvent. Methanol is also lost as vapor in the overhead stream from the 07.20 stripper. As a result, the $CO_2$ removal system operates in an unsteady state as the composition of the solvent changes. Since this change affects the level of $CO_2$ removal, the system includes a solvent purge and fresh methanol makeup lines.

### *LPDME Design Verification Test - October/November 1999*

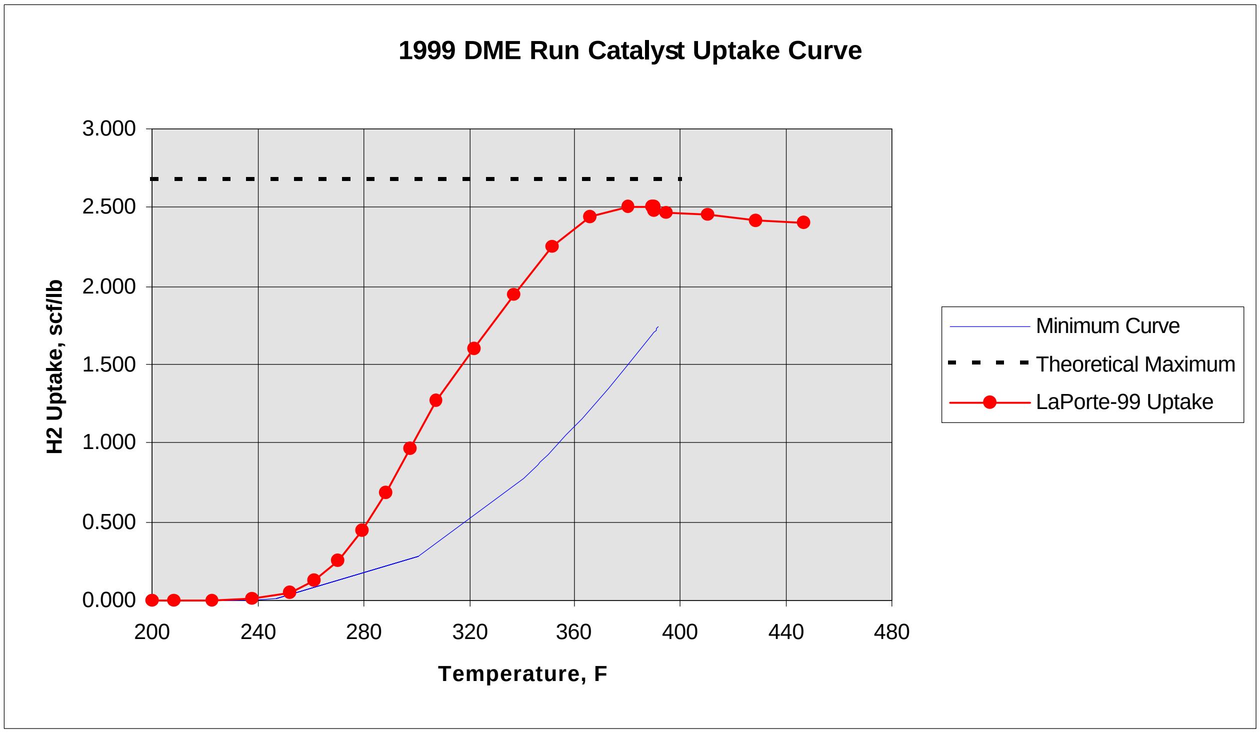
The LPDME design verification test at the LaPorte AFDU was started during the reporting period. Calibration of the nuclear density gauge on the reactor was completed in early October of 1999. A function test of the $CO_2$ removal system revealed no major problems; several pressure relief valves were removed and sent for maintenance, as the valves lifted at pressures below their respective set pressures. Set-up of the AFDU was completed and carbonyl burnout (a hot function test with syngas, but in the absence of catalyst) was started on 8 October 1999. By 10 October 1999, levels of iron and nickel carbonyl, both known catalyst poisons, were both well below the maximum allowable concentration to which methanol synthesis catalyst can be exposed (10 ppbv). Syngas was then removed from the plant, and the plant was purged and drained in preparation for start-up.

A 35 wt% oxide catalyst slurry was mixed in the slurry preparation tank. The recipe called for 1,747 pounds of mineral oil, 894 pounds of methanol synthesis catalyst, and 47 pounds of dehydration catalyst. The proportion of two catalysts corresponded to a 95:5 methanol to dehydration catalyst ratio. The slurry was heated and agitated in the slurry preparation tank for about two hours, after which the slurry was transferred to the reactor by using pressurized nitrogen. Catalyst reduction began at 1800 on 11 October 1999. The reduction gas (3 vol% $H_2$ in $N_2$) was set at 12,400 SCFH with the reactor pressure at 67 psig; these were the same conditions as those used in earlier testing in the laboratory autoclave. The temperature ramp was then started and proceeded from 200°F to 464°F (see Figure D.2-1). The catalyst activation appeared normal, as shown in Figure D.2-2, and reached a cumulative uptake of reductant which was very close to the theoretical maximum value of 2.68 standard cubic feet (SCF) $H_2$ per pound of catalyst (on an oxide basis). The activation was essentially complete at 390°F or 17-hours on stream. The uptake curve is plotted against a minimum curve which was developed to ensure successful activation of the methanol synthesis catalyst; the rate of increase of reactor temperature was controlled to ensure that the cumulative uptake of reductant was always above the minimum curve.

## Figure D.2-1



## Figure D.2-2



Nuclear density gauge measurements taken at a reactor temperature of 392°F indicated a calculated average gas hold-up of 36.8 vol% with a catalyst concentration of 40.1 wt%.

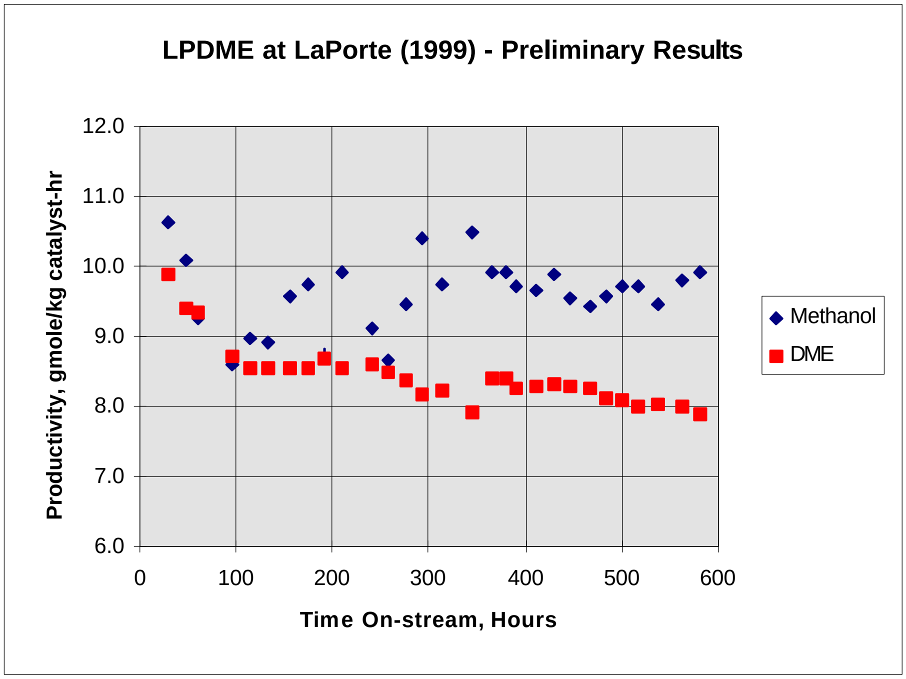
Catalyst activation was completed at 1800 on 12 October 1999 and syngas was brought in the reactor at 1930. The start-up with syngas was smooth and the operating conditions for the catalyst life study ($H_2$/CO=0.5, 6,000 sl/hr-kg, 750 psig, 482°F) were reached within 12 hours after the introduction of syngas. Stable reactor temperature and pressure were achieved. The reactor feed composition was then fine tuned and a mass balance period began at 1600 on 13 October 1999. The methanol synthesis and dehydration catalysts appear to have good initial activity, with DME and methanol productivity slightly exceeding expectations. This confirmed that the catalyst activation was proper. The DME production rate was estimated to be about 5 TPD compared to an expectation of 4.8 TPD, while the methanol production rate was 3.6 TPD vs 3.5 TPD expected. Calculations based on differential pressure measurements indicated the catalyst concentration in the reactor was about 36 wt% with a gas hold-up of between 41 and 42 vol%.

A 13-hour outage was experienced on 15 October 1999 due to an interruption in the syngas supply. The AFDU was put in a stand-by mode (nitrogen flow through the reactor at a lower temperature). The syngas became available just before midnight on 15 October 1999 and the plant was brought back to the baseline condition in 8 hours.

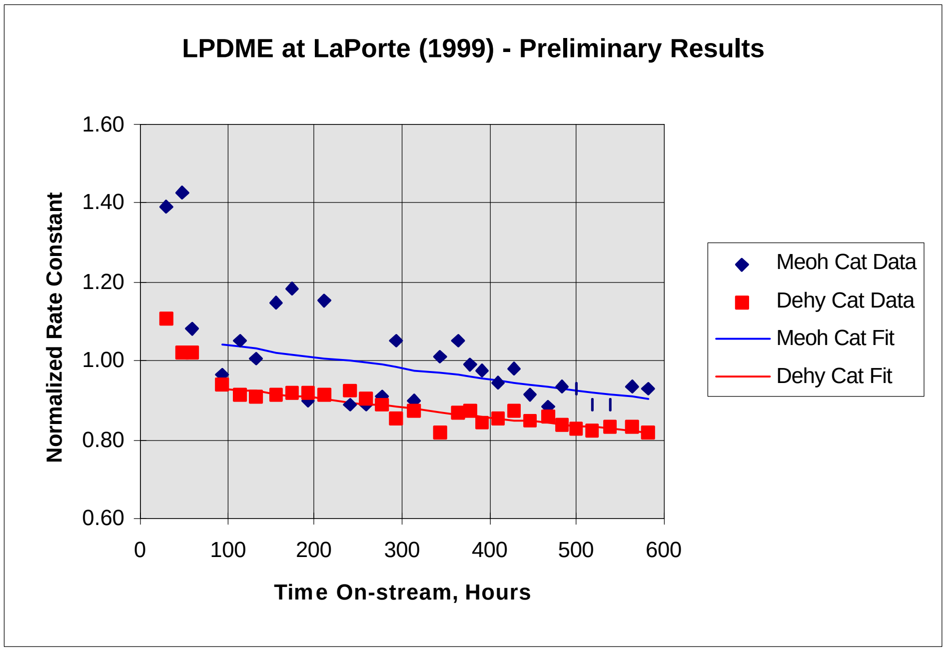
Over the first 320 hours of operation (ending on 27 October 1999), several material balances were generated during this period to track the catalyst performance. The rate of catalyst deactivation can be expressed by the ratio of the rate constant at any time to the rate constant immediately after catalyst activation (as determined in the laboratory autoclave); this can be applied to both the methanol synthesis and dehydration catalysts. Preliminary results on catalyst productivities and the normalized rate constants are shown in Figures D.2-3 and D.2-4. After the initial aging period, the rate of catalyst deactivation of both catalysts appeared to be stabilizing, but there was significant scatter in the data. The initial deactivation rate appeared high for the methanol synthesis catalyst (2% per day) with a very high standard error of 1.2% per day; for the dehydration catalyst, a deactivation rate of 0.6% per day with a 0.2% per day standard error was calculated. For reference, the rate of deactivation for both the methanol synthesis and dehydration catalysts in the autoclave is 1.2% per day. Upon troubleshooting the analytical system, two problems were discovered (a programming error within the gas chromatographs, and insufficient heat tracing and insulation within the sampling system) which resulted in an underreporting of the concentration of methanol in the effluent stream from the reactor. These problems were fixed within two days. Based upon the scatter in the data associated with catalyst activity, Air Products recommended that operating time at the baseline condition should be continued until Wednesday 3 November 1999. DOE accepted this recommendation. In order to stay within the budget, the process variable study was eliminated. An extensive tracer study was still scheduled to be performed.

Operations continued at the baseline conditions into early November. At that point, the cumulative time on stream was 500 hours. The data from the slurry bubble column at the LaPorte AFDU appeared to follow the same trends which were observed in the laboratory,

## Figure D.2-3



## Figure D.2-4



with somewhat higher conversions of $H_2$ and CO than those measured in the autoclave. The methanol productivity of the LPDME catalyst system remained relatively constant, while the DME productivity showed a slight decline. The scatter in data (see Figures D.2-3 and D.2-4) decreased significantly after the GC and the sampling problems were resolved (at 350 hours on stream). At this point, the deactivation rate for both the methanol synthesis and dehydration catalysts was estimated at 0.7% per day. This is lower than the 1.2% per day rate which was achieved in the autoclave, and only slightly higher than 0.5% per day rate which was calculated during the first 500 hours of the 4-month proof-of-concept run for the LPMEOH™ Process which was performed at the LaPorte AFDU in 1988/89. Due to the initial scatter in the calculation of the production rate of methanol (which was related to the sampling and analytical problems described above), the standard error at this point was still high for the methanol catalyst (0.34% per day).

As planned, an extensive tracer study was conducted at the baseline condition to evaluate gas, liquid and solid mixing. DOE accepted Air Products' recommendation to use the remainder of the operating time to continue the catalyst life study at the expense of gaining process and tracer data at a second condition. The catalyst life study was continued for two more days after completion of the tracer work. Overall, the LaPorte AFDU was operated for approximately 600 hours during this design verification test. The standard error for the calculated rate constant for both the methanol synthesis and hydration catalysts was lowered as a results of the additional data which was gathered; there was no change in the calculated deactivation rates. Following a shut-down test conducted to get a better estimate of the gas hold-up, the LaPorte AFDU was shut down at 1000 on 6 November 1999. The slurry was cooled down under a nitrogen flow and then drained from the reactor.

The following is a summary of the accomplishments of the run:

- Commercial viability of the LPDME Process was successfully evaluated on a 10 TPD scale, using commercially produced catalysts. The plant was operated for 25 days on stream to compare catalyst aging in a pilot scale slurry bubble column with that in a laboratory autoclave. The catalyst life study was extended in favor of a planned process variable study to obtain additional data on catalyst aging. Hydrodynamic information was obtained at the baseline conditions by conducting a detailed survey of the reactor with radioactive tracer injections.

- The deactivation rate for both the catalysts was calculated to be 0.7% per day. This result is lower than the 1.2% per day which had been calculated for both the methanol synthesis and dehydration catalysts during experiments in the autoclave. The rate of deactivation is slightly higher than 0.5% per day rate which was achieved for the LPMEOH™ Process after 3 weeks of operation at LaPorte in 1988/89. The methanol productivity remained relatively constant throughout the run, while the DME productivity showed a slight decline. These trends are consistent with observations from the laboratory. The standard error for the methanol catalyst deactivation rate was high (0.25% per day) due to initial scatter in the data. The scatter decreased significantly after problems in the sampling and analytical system were discovered and resolved at 350 hours on stream. The dehydration catalyst activity data have better statistics, with a standard error of 0.06% per day.

- The methanol synthesis catalyst was activated successfully with an expected reductant uptake. The initial productivities of methanol and DME were higher than the laboratory. The DME production rate started at 5.1 TPD and declined to 4.1 TPD over the 25 days on stream, while the methanol production showed a scatter within the range of 3.1 to 3.8 TPD throughout the run.

- The reactor operated in a stable hydrodynamic regime as determined by the presence of a uniform temperature profile and gas hold-up. Differential pressure measurements along the reactor resulted in a calculated gas hold-up of about 42 vol% gas hold-up and a catalyst slurry concentration of 36 wt%.

- Preliminary mass balance calculations indicate good closure.

- The initial start-up was very quick with the baseline condition reached in 12 hours after the introduction of syngas. A re-start after a syngas outage only took 4 hours. This further demonstrates the ease and flexibility of the slurry technology.

- Gas, liquid, and solid phase mixing was studied at the baseline conditions using radioactive materials. A large quantity of data was collected using 34 detectors around the reactor. Several repeat injections were made during the gas and liquid injections to evaluate variability with time. A sample of dehydration catalyst was doped with manganese oxide and irradiated; this material was injected at four different locations to observe the mixing patterns of the dehydration catalyst. Both short term and long term observations of irradiated dehydration catalyst suggest no settling in the reactor. A post-run inspection of the reactor bottom head did not show any settled catalyst, in contrast to the large quantity of dehydration catalyst which was found at the bottom after the 1991 DME test run at the LaPorte AFDU. The tracer data will be analyzed as part of the Hydrodynamic Program with DOE’s Liquid Fuels Program.

- The 1999 design verification test of the LPDME Process at the LaPorte AFDU represents a significant step forward in the development of the technology. The 0.7% per day rate of catalyst deactivation which was achieved during this campaign is a large improvement over the 4% per day rate of deactivation which was calculated from autoclave studies prior to the initial test of the LPDME Process at the LaPorte AFDU in 1991.

The results from the design verification test will be used to update the economics of the LPDME Process and to support decision-making for future activities by the LPMEOH™ Demonstration Project in support in the scale-up of the LPDME technology.

### *D.3 LPMEOH™ Process Demonstration Unit - Methanol Operation*

Table D.3-1 contains the summary table of performance data for the LPMEOH™ Demonstration Unit during the reporting period. These data represent daily averages, typically from a 24-hour material balance period, and those days with less than 12 hours of stable operation are omitted. Appendix E contains samples of the detailed material balance reports which are representative of the operation of the LPMEOH™ Demonstration Unit during the reporting period.

During the reporting period, a total of 4,804,902 gallons of methanol was produced at the LPMEOH™ Demonstration Unit. Eastman accepted all of this methanol for use in the production of methyl acetate, and ultimately cellulose acetate and acetic acid. No environmental incidents or injuries were reported during this quarter.

The LPMEOH™ Demonstration Unit operated at 100% availability throughout the reporting period. Six syngas outages were the only operating interruptions experienced. Appendix F, Table 1 contains the summary of outages for the LPMEOH™ Demonstration Unit during this quarter.

Catalyst Life (eta) - October - December 1999

The “age” of the methanol synthesis catalyst can be expressed in terms of a dimensionless variable eta ($\eta$), which is defined as the ratio of the rate constant at any time to the rate constant for freshly reduced catalyst (as determined in the laboratory autoclave). Appendix F, Figure 1 plots log $\eta$ versus days onstream from the restart in March 1999 to the end of the reporting period. Since catalyst activity typically follows a pattern of exponential decay, the plot of log $\eta$ is fit to a series of straight lines, with step-changes whenever fresh catalyst was added to the reactor.

A major catalyst withdrawal and addition campaign was undertaken during the quarter to increase catalyst activity. A series of four withdrawals were conducted on 08 and 09 November 1999. This was followed by four catalyst additions which were activated and added between 12 November and 19 November 1999. After the addition of the fourth batch of catalyst, the total catalyst inventory was calculated to be 44,924 pounds.

During the balance of the quarter, Balanced Gas at 680 KSCFH was supplied to the reactor and the reactor pressure was set at 710 psig. Reactor temperature was held at 235°C throughout the reporting period.

There were two extended periods of operation at a reactor temperature of 235°C during which catalyst activity was measured to track catalyst deactivation during the quarter. An overall deactivation rate of 0.56% per day was calculated for the period 11 September 1999 to 03 October 1999 (22 days). An overall deactivation rate of 0.66% per day was calculated for the period 13 October 1999 to 07 November 1999 (23 days). These deactivation results are slightly greater than the baseline deactivation rate from the 4-month proof-of-concept run at the LaPorte AFDU in 1988/89 (this run was performed at 250°C).

# Table D.3-1.  Data Summary for LPMEOH™ Demonstration Unit

| Case | Date | Days Onstream | Gas Type | Temp (Deg C) | Pres. (psig) | Fresh Feed (KSCFH) | Recycle Gas (KSCFH) | Reactor Feed (H2:CO) | Purge Gas (KSCFH) | Inlet Sup. Velocity (ft/sec) | Space Velocity (l/hr-kg) | Slurry Conc. (wt% ox) | Gas Holdup (vol%) | Gassed Slurry Hgt (ft) | Catalyst Inventory (lb) | Catalyst Age (eta) | CO Conv. (%) | Reactor O-T-M Conv. (%) | Syngas Util. (SCF/lb) | Raw MeOH Production (TPD) | Catalyst MeOH Prod. (gmol/hr-kg) | Reactor Vol. Prod. (TPD/Cu ft) | U Overall (BTU/hr ft2 F) | Sparger dP (psi) | Sparger Resistance ("K") |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 11 | 1-Oct-99 | 650 | Balanced | 235 | 710 | 771 | 2,031 | 2.90 | 103.1 | 0.65 | 3559 | 43.3 | 30.9 | 53.0 | 46,488 | 0.326 | 33.4 | 22.2 | 42 | 220.5 | 12.38 | 0.099 | 184 | 4.39 | 4.39 |
| 11 | 2-Oct-99 | 651 | Balanced | 234 | 710 | 767 | 2,019 | 3.06 | 103.0 | 0.64 | 3515 | 43.2 | 30.8 | 53.0 | 46,488 | 0.328 | 34.7 | 22.2 | 42.1 | 218.9 | 12.29 | 0.098 | 187 | 4.14 | 4.40 |
| 11 | 3-Oct-99 | 652 | Balanced | 234 | 710 | 763 | 2,025 | 2.97 | 104.0 | 0.64 | 3522 | 43.5 | 30.2 | 52.0 | 46,488 | 0.325 | 33.5 | 21.9 | 42.1 | 217.3 | 12.21 | 0.099 | 186 | 4.18 | 4.40 |
| 11 | 6-Oct-99 | 655 | Balanced | 235 | 710 | 699 | 2,065 | 3.21 | 72.6 | 0.64 | 3495 | 42.7 | 30.6 | 54.0 | 46,488 | 0.313 | 34.4 | 21.2 | 40.5 | 206.9 | 11.61 | 0.091 | 184 | 3.98 | 4.34 |
| 11 | 7-Oct-99 | 656 | Balanced | 235 | 710 | 745 | 2,039 | 2.92 | 98.0 | 0.65 | 3528 | 42.6 | 30.4 | 54.0 | 46,488 | 0.309 | 32.3 | 21.4 | 42.1 | 212.4 | 11.93 | 0.094 | 180 | 4.20 | 4.37 |
| 11 | 8-Oct-99 | 657 | Balanced | 235 | 711 | 765 | 1,991 | 3.05 | 122.6 | 0.64 | 3484 | 43.4 | 33.5 | 54.5 | 46,488 | 0.311 | 33.5 | 21.5 | 43.4 | 211.5 | 11.88 | 0.092 | 180 | 4.01 | 4.42 |
| 11 | 9-Oct-99 | 658 | Balanced | 235 | 711 | 770 | 1,996 | 3.00 | 125.1 | 0.64 | 3488 | 43.3 | 30.1 | 53.5 | 46,488 | 0.314 | 33.3 | 21.7 | 43.3 | 213.3 | 11.98 | 0.095 | 185 | 4.05 | 4.40 |
| 11 | 10-Oct-99 | 659 | Balanced | 234 | 710 | 766 | 2,021 | 2.76 | 118.5 | 0.64 | 3526 | 43.3 | 30.3 | 52.5 | 46,488 | 0.309 | 31.1 | 21.5 | 43.2 | 212.6 | 11.94 | 0.096 | 186 | 4.35 | 4.38 |
| 11 | 13-Oct-99 | 662 | Balanced | 235 | 710 | 646 | 2,097 | 3.08 | 64.2 | 0.63 | 3465 | 44.2 | 30.0 | 50.5 | 46,488 | 0.284 | 31.4 | 19.9 | 40.4 | 191.7 | 10.76 | 0.090 | 189 | 4.08 | 4.37 |
| 11 | 14-Oct-99 | 663 | Balanced | 235 | 711 | 669 | 2,092 | 3.10 | 80.6 | 0.64 | 3480 | 43.9 | 30.5 | 51.5 | 46,488 | 0.279 | 31.3 | 19.9 | 41.6 | 193.2 | 10.80 | 0.089 | 184 | 4.04 | 4.38 |
| 11 | 16-Oct-99 | 665 | Balanced | 235 | 710 | 663 | 2,049 | 3.18 | 85.9 | 0.63 | 3423 | 43.3 | 29.5 | 52.0 | 46,488 | 0.276 | 31.7 | 19.7 | 42.1 | 189.1 | 10.62 | 0.087 | 180 | 3.82 | 4.34 |
| 11 | 17-Oct-99 | 666 | Balanced | 235 | 710 | 654 | 2,034 | 3.04 | 79.3 | 0.62 | 3407 | 43.6 | 29.1 | 51.0 | 46,488 | 0.273 | 30.7 | 19.8 | 41.4 | 189.5 | 10.64 | 0.088 | 185 | 3.84 | 4.45 |
| 11 | 18-Oct-99 | 667 | Balanced | 234 | 711 | 675 | 2,037 | 3.36 | 110.0 | 0.63 | 3417 | 44.1 | 29.5 | 50.5 | 46,488 | 0.275 | 32.3 | 19.4 | 43.4 | 186.5 | 10.47 | 0.088 | 189 | 3.59 | 4.34 |
| 11 | 19-Oct-99 | 668 | Balanced | 234 | 710 | 665 | 2,088 | 2.88 | 95.4 | 0.64 | 3486 | 45.0 | 30.6 | 49.5 | 46,488 | 0.264 | 28.5 | 19.1 | 42.6 | 187.5 | 10.53 | 0.090 | 183 | 4.02 | 4.33 |
| 11 | 20-Oct-99 | 669 | Balanced | 234 | 710 | 682 | 2,063 | 3.27 | 122.8 | 0.63 | 3442 | 44.9 | 29.7 | 49.0 | 46,488 | 0.264 | 30.9 | 19.0 | 44.4 | 184.4 | 10.35 | 0.090 | 189 | 3.64 | 4.36 |
| 11 | 21-Oct-99 | 670 | Balanced | 234 | 710 | 682 | 2,066 | 3.15 | 122.8 | 0.63 | 3461 | 45.4 | 29.4 | 48.0 | 46,488 | 0.261 | 30.0 | 19.0 | 44.3 | 184.8 | 10.37 | 0.092 | 195 | 3.76 | 4.33 |
| 11 | 22-Oct-99 | 671 | Balanced | 234 | 710 | 674 | 2,050 | 3.01 | 120.3 | 0.63 | 3439 | 45.5 | 29.7 | 48.0 | 46,488 | 0.259 | 29.1 | 19.0 | 44.3 | 182.6 | 10.26 | 0.091 | 193 | 3.87 | 4.28 |
| 11 | 23-Oct-99 | 672 | Balanced | 234 | 710 | 675 | 2,078 | 2.91 | 125.6 | 0.64 | 3478 | 46.2 | 30.0 | 47.0 | 46,488 | 0.251 | 27.7 | 18.6 | 44.8 | 180.9 | 10.16 | 0.092 | 188 | 3.95 | 4.29 |
| 11 | 24-Oct-99 | 673 | Balanced | 234 | 710 | 683 | 2,093 | 2.89 | 139.0 | 0.64 | 3507 | 46.5 | 29.3 | 46.0 | 46,488 | 0.245 | 27.1 | 18.2 | 45.4 | 180.4 | 10.13 | 0.094 | 191 | 3.92 | 4.29 |
| 11 | 25-Oct-99 | 674 | Balanced | 235 | 710 | 684 | 2,059 | 2.88 | 139.8 | 0.64 | 3494 | 45.9 | 30.2 | 47.5 | 46,488 | 0.241 | 26.8 | 18.1 | 45.9 | 178.7 | 10.04 | 0.090 | 185 | 3.98 | 4.37 |
| 11 | 26-Oct-99 | 675 | Balanced | 235 | 710 | 659 | 2,066 | 3.06 | 129.9 | 0.63 | 3438 | 45.9 | 28.5 | 46.5 | 46,488 | 0.237 | 27.8 | 18.0 | 45.4 | 174.1 | 9.78 | 0.089 | 187 | 3.78 | 4.38 |
| 11 | 27-Oct-99 | 676 | Balanced | 234 | 710 | 659 | 2,042 | 3.13 | 133.9 | 0.63 | 3420 | 45.4 | 28.8 | 47.5 | 46,488 | 0.239 | 28.0 | 17.8 | 45.9 | 172.2 | 9.68 | 0.086 | 186 | 3.66 | 4.38 |
| 11 | 29-Oct-99 | 678 | Balanced | 235 | 711 | 648 | 2,035 | 2.95 | 116.8 | 0.62 | 3387 | 43.1 | 30.4 | 53.0 | 46,488 | 0.238 | 27.3 | 18.1 | 44.6 | 174.5 | 9.80 | 0.078 | 187 | 3.66 | 4.45 |
| 11 | 31-Oct-99 | 680 | Balanced | 235 | 711 | 660 | 2,019 | 2.76 | 123.3 | 0.62 | 3387 | 43.4 | 30.0 | 52.0 | 46,488 | 0.243 | 26.2 | 18.1 | 45 | 175.9 | 9.89 | 0.081 | 184 | 3.81 | 4.45 |
| 11 | 1-Nov-99 | 681 | Balanced | 235 | 710 | 567 | 2,042 | 2.97 | 61.7 | 0.61 | 3312 | 43.8 | 28.8 | 50.5 | 46,488 | 0.253 | 26.9 | 17.7 | 40.7 | 167.1 | 9.38 | 0.079 | 182 | 3.51 | 4.48 |
| 11 | 2-Nov-99 | 682 | Balanced | 235 | 711 | 566 | 2,136 | 2.98 | 49.2 | 0.63 | 3419 | 45.3 | 30.8 | 49.0 | 46,488 | 0.248 | 27.2 | 18.0 | 39.8 | 170.0 | 9.56 | 0.083 | 199 | 3.79 | 4.29 |
| 11 | 3-Nov-99 | 683 | Balanced | 234 | 710 | 537 | 2,175 | 3.02 | 38.1 | 0.63 | 3470 | 43.9 | 31.8 | 52.5 | 46,488 | 0.233 | 26.7 | 17.4 | 39.2 | 164.8 | 9.24 | 0.075 | 207 | 3.99 | 4.28 |
| 11 | 6-Nov-99 | 686 | Balanced | 235 | 710 | 624 | 2,027 | 3.11 | 112.1 | 0.61 | 3353 | 42.9 | 30.0 | 53.0 | 46,488 | 0.244 | 27.0 | 17.3 | 45.1 | 166.3 | 9.35 | 0.075 | 187 | 3.43 | 4.45 |
| 11 | 7-Nov-99 | 687 | Balanced | 235 | 710 | 616 | 2,060 | 2.92 | 101.1 | 0.62 | 3386 | 43.2 | 30.1 | 52.5 | 46,488 | 0.246 | 25.9 | 17.4 | 43.8 | 168.7 | 9.48 | 0.076 | 185 | 3.61 | 4.44 |
| 11 | 9-Nov-99 | 689 | Balanced | 234 | 711 | 529 | 2,171 | 2.57 | 112.6 | 0.63 | 4407 | 42.0 | 31.2 | 43.5 | 36,124 | 0.24 | 18.9 | 13.9 | 46.4 | 136.8 | 9.89 | 0.075 | 195 | 3.87 | 4.41 |
| 11 | 10-Nov-99 | 690 | Balanced | 234 | 711 | 529 | 2,144 | 2.52 | 114.9 | 0.62 | 4375 | 42.4 | 30.4 | 42.5 | 36,124 | 0.236 | 18.5 | 13.8 | 47.1 | 134.7 | 9.75 | 0.076 | 192 | 3.89 | 4.41 |
| 11 | 11-Nov-99 | 691 | Balanced | 234 | 712 | 557 | 2,140 | 2.51 | 128.3 | 0.62 | 4411 | 43.6 | 29.4 | 40.0 | 36,124 | 0.247 | 19.0 | 14.1 | 47.9 | 139.6 | 10.10 | 0.083 | 215 | 3.91 | 4.38 |
| 11 | 12-Nov-99 | 692 | Balanced | 235 | 712 | 594 | 2,140 | 2.98 | 73.6 | 0.63 | 4215 | 41.9 | 32.2 | 47.0 | 38,324 | 0.29 | 26.7 | 17.6 | 41.8 | 172.0 | 11.71 | 0.087 | 185 | 3.89 | 4.39 |
| 11 | 13-Nov-99 | 693 | Balanced | 235 | 712 | 596 | 2,130 | 2.90 | 75.8 | 0.63 | 4200 | 41.9 | 32.8 | 47.5 | 38,324 | 0.288 | 26.2 | 17.6 | 42 | 171.9 | 11.71 | 0.086 | 186 | 3.94 | 4.40 |
| 11 | 14-Nov-99 | 694 | Balanced | 235 | 711 | 660 | 2,030 | 3.74 | 64.3 | 0.62 | 3890 | 40.8 | 32.9 | 52.5 | 40,524 | 0.361 | 37.6 | 20.9 | 40.5 | 195.7 | 12.60 | 0.089 | 180 | 3.50 | 4.33 |
| 11 | 15-Nov-99 | 695 | Balanced | 235 | 711 | 667 | 2,091 | 3.37 | 68.2 | 0.64 | 3992 | 41.7 | 38.9 | 55.5 | 40,524 | 0.34 | 34.1 | 20.6 | 40.4 | 197.9 | 12.73 | 0.085 | 163 | 3.80 | 4.33 |
| 11 | 17-Nov-99 | 697 | Balanced | 235 | 705 | 784 | 2,161 | 1.44 | 68.8 | 0.7 | 4115 | 42.4 | 36.2 | 54.5 | 42,724 | 0.421 | 21.3 | 22.5 | 40.2 | 233.9 | 14.27 | 0.102 | 177 | 6.75 | 4.34 |
| 11 | 20-Nov-99 | 700 | Balanced | 235 | 710 | 807 | 2,050 | 3.31 | 77.6 | 0.66 | 3727 | 41.0 | 32.8 | 57.5 | 44,924 | 0.413 | 40.6 | 24.7 | 40.1 | 241.7 | 14.03 | 0.100 | 172 | 4.45 | 4.38 |
| 11 | 21-Nov-99 | 701 | Balanced | 235 | 710 | 808 | 1,994 | 3.61 | 78.2 | 0.65 | 3660 | 40.1 | 27.1 | 55.0 | 44,924 | 0.417 | 43.4 | 24.8 | 40.1 | 241.8 | 14.04 | 0.105 | 177 | 3.83 | 4.26 |
| 11 | 24-Nov-99 | 704 | Balanced | 225 | 700 | 577 | 2,157 | 2.86 | 24.7 | 0.61 | 3488 | 40.8 | 30.4 | 55.5 | 44,924 | 0.408 | 29.9 | 20.0 | 38.2 | 181.1 | 10.50 | 0.078 | 165 | 4.05 | 4.45 |
| 11 | 30-Nov-99 | 710 | Balanced | 235 | 710 | 756 | 2,104 | 3.40 | 86.1 | 0.65 | 3688 | 43.7 | 30.2 | 50.0 | 44,924 | 0.362 | 38.5 | 23.0 | 40.8 | 220.5 | 12.91 | 0.106 | 164 | 4.20 | 4.35 |
| 11 | 1-Dec-99 | 711 | Balanced | 235 | 710 | 755 | 2,092 | 3.27 | 78.9 | 0.66 | 3739 | 43.5 | 31.7 | 51.5 | 44,924 | 0.346 | 36.2 | 22.5 | 41.1 | 220.7 | 12.81 | 0.102 | 165 | 4.33 | 4.36 |
| 21 | 2-Dec-99 | 712 | Destec | 235 | 695 | 722 | 2,157 | 1.06 | 96.9 | 0.69 | 3816 | 45.5 | 33.6 | 45.5 | 44,924 | 0.368 | 15.9 | 19.8 | 42.6 | 203.4 | 11.81 | 0.099 | 158 | 7.28 | 4.38 |
| 21 | 3-Dec-99 | 713 | Destec | 235 | 695 | 722 | 2,140 | 1.00 | 99.1 | 0.69 | 3802 | 44.8 | 33.3 | 50.0 | 44,924 | 0.372 | 15.4 | 19.5 | 42.9 | 202.1 | 11.75 | 0.096 | 153 | 7.26 | 4.35 |
| 21 | 4-Dec-99 | 714 | Destec | 234 | 695 | 723 | 2,115 | 1.06 | 98.0 | 0.68 | 3783 | 45.4 | 31.2 | 47.5 | 44,924 | 0.382 | 16.5 | 20.3 | 41.8 | 208.0 | 12.09 | 0.104 | 166 | 7.08 | 4.35 |
| 21 | 5-Dec-99 | 715 | Destec | 235 | 695 | 715 | 2,121 | 1.00 | 97.0 | 0.68 | 3770 | 44.0 | 33.0 | 51.5 | 44,924 | 0.381 | 15.8 | 20.0 | 41.9 | 204.7 | 11.90 | 0.095 | 160 | 7.18 | 4.33 |
| 21 | 8-Dec-99 | 718 | Destec | 235 | 695 | 730 | 2,112 | 1.03 | 120.6 | 0.69 | 3813 | 44.7 | 32.9 | 50.0 | 44,924 | 0.37 | 15.5 | 19.5 | 43.1 | 203.2 | 11.81 | 0.097 | 184 | 7.05 | 4.29 |
| 21 | 9-Dec-99 | 719 | Destec | 234 | 696 | 703 | 2,127 | 1.02 | 107.5 | 0.68 | 3797 | 45.2 | 32.0 | 48.5 | 44,924 | 0.346 | 14.9 | 18.7 | 43.3 | 194.9 | 11.34 | 0.096 | 148 | 7.06 | 4.29 |
| 21 | 10-Dec-99 | 720 | Destec | 234 | 697 | 703 | 2,127 | 1.00 | 112.5 | 0.68 | 3766 | 46.0 | 32.6 | 47.5 | 44,924 | 0.353 | 15.0 | 18.9 | 43.2 | 195.7 | 11.37 | 0.098 | 151 | 6.92 | 4.32 |
| 11 | 16-Dec-99 | 726 | Balanced | 235 | 710 | 662 | 1,925 | 4.44 | 107.7 | 0.59 | 3323 | 40.5 | 25.7 | 53.0 | 44,924 | 0.325 | 41.3 | 20.4 | 43.4 | 183.2 | 10.63 | 0.082 | 170 | 2.80 | 4.62 |
| 11 | 17-Dec-99 | 727 | Balanced | 235 | 710 | 659 | 1,942 | 4.08 | 76.3 | 0.6 | 3398 | 37.5 | 24.3 | 58.5 | 44,924 | 0.329 | 40.3 | 21.1 | 41.1 | 192.2 | 11.16 | 0.083 | 179 | 3.18 | 4.54 |
| 11 | 18-Dec-99 | 728 | Balanced | 235 | 710 | 665 | 1,933 | 3.98 | 77.6 | 0.6 | 3390 | 38.1 | 23.3 | 56.5 | 44,924 | 0.329 | 40.1 | 21.3 | 41.3 | 193.0 | 11.21 | 0.081 | 176 | 3.24 | 4.48 |
| 11 | 19-Dec-99 | 729 | Balanced | 235 | 710 | 658 | 1,936 | 3.86 | 75.3 | 0.6 | 3389 | 40.0 | 28.9 | 56.5 | 44,924 | 0.321 | 38.9 | 21.1 | 41.4 | 190.7 | 11.08 | 0.080 | 170 | 3.32 | 4.47 |
| 11 | 20-Dec-99 | 730 | Balanced | 235 | 710 | 731 | 1,953 | 3.24 | 94.6 | 0.62 | 3511 | 39.9 | 25.3 | 54.0 | 44,924 | 0.326 | 35.4 | 22.0 | 42.3 | 207.3 | 12.04 | 0.091 | 177 | 3.75 | 4.41 |
| 11 | 22-Dec-99 | 732 | Balanced | 235 | 710 | 698 | 2,060 | 3.02 | 81.2 | 0.64 | 3622 | 41.6 | 32.1 | 55.5 | 44,924 | 0.297 | 31.6 | 20.9 | 41.5 | 202.1 | 11.72 | 0.087 | 172 | 4.11 | 4.47 |
| 11 | 23-Dec-99 | 733 | Balanced | 235 | 710 | 724 | 1,992 | 3.24 | 104.9 | 0.63 | 3566 | 41.7 | 30.4 | 54.0 | 44,924 | 0.303 | 33.8 | 21.2 | 42.8 | 202.8 | 11.77 | 0.089 | 177 | 3.79 | 4.46 |
| 11 | 24-Dec-99 | 734 | Balanced | 235 | 710 | 721 | 1,996 | 3.18 | 102.8 | 0.63 | 3572 | 42.3 | 31.4 | 53.5 | 44,924 | 0.3 | 33.1 | 21.1 | 42.8 | 202.2 | 11.73 | 0.090 | 177 | 3.80 | 4.46 |
| 11 | 25-Dec-99 | 735 | Balanced | 235 | 710 | 727 | 2,005 | 3.01 | 103.4 | 0.64 | 3604 | 43.0 | 33.2 | 53.5 | 44,924 | 0.297 | 31.8 | 21.1 | 42.5 | 205.2 | 11.90 | 0.091 | 177 | 3.92 | 4.47 |
| 11 | 26-Dec-99 | 736 | Balanced | 235 | 710 | 738 | 1,946 | 3.31 | 135.4 | 0.62 | 3508 | 43.0 | 30.7 | 51.5 | 44,924 | 0.3 | 33.2 | 20.6 | 44.8 | 196.7 | 11.42 | 0.091 | 173 | 3.47 | 4.49 |
| 11 | 27-Dec-99 | 737 | Balanced | 235 | 710 | 719 | 1,981 | 3.29 | 117.0 | 0.63 | 3538 | 42.5 | 30.0 | 52.0 | 44,924 | 0.296 | 33.5 | 20.8 | 43.6 | 198.0 | 11.49 | 0.091 | 177 | 3.65 | 4.44 |
| 11 | 28-Dec-99 | 738 | Balanced | 235 | 710 | 742 | 1,964 | 3.05 | 125.6 | 0.63 | 3561 | 42.0 | 35.5 | 57.5 | 44,924 | 0.297 | 32.3 | 21.3 | 43.8 | 203.2 | 11.79 | 0.084 | 168 | 3.87 | 4.42 |
| 11 | 29-Dec-99 | 739 | Balanced | 235 | 710 | 695 | 2,017 | 3.16 | 96.6 | 0.63 | 3569 | 42.7 | 30.3 | 52.0 | 44,924 | 0.288 | 32.1 | 20.6 | 42.6 | 196.0 | 11.37 | 0.090 | 180 | 3.88 | 4.41 |
| 11 | 31-Dec-99 | 741 | Balanced | 235 | 710 | 723 | 1,999 | 3.04 | 114.1 | 0.63 | 3567 | 42.0 | 28.5 | 52.0 | 44,924 | 0.291 | 31.6 | 20.8 | 43.6 | 199.2 | 11.56 | 0.091 | 174 | 4.04 | 4.62 |

On 02 December 1999, CO Gas was introduced with the Balanced Gas to achieve a 1:1 $H_2$/CO reactor inlet feed composition. Reactor pressure was adjusted to 695 psig during periods of CO Gas addition to allow for proper control of the CO Gas. Approximately 45 KSCFH of CO Gas was introduced with approximately 675 KSCFH of Balanced Gas for this CO-rich feed case. Operation at this condition continued until 11 December 1999. The catalyst performance met expectations for the quantity of methanol which was produced at these conditions; however, the operating period was not of sufficient length to calculate the rate of catalyst deactivation. CO-rich demonstration cases will be restarted as soon as sufficient CO Gas becomes available.

During the reporting period, analyses of catalyst and gas samples for changes in physical characteristics and levels of poisons have continued. Appendix F, Table 2 summarizes the results to date. Copper crystallite size measurements have shown an increase over time, which is an indication of catalyst aging. Levels of nickel (a known catalyst poison) have remained low and steady since the restart in December of 1997. As reported in Technical Progress Report No. 21, the adsorbents in the two catalyst guard beds (the 10C-30 vessel, upstream of both the LPMEOH™ Demonstration Unit and the fixed-bed methanol plant, and the 29C-40 carbonyl guard bed) which treat Balanced Gas were changed in June of 1999; the 10C-30 was charged with arsine-removal adsorbent, and the 29C-40 was split between arsine and carbonyl removal materials. Initial results of batch sampling of the Balanced Gas stream demonstrated that the guard-bed system was effective in removing arsenic when it first came on-stream after the changeout. However, subsequent analysis confirmed that arsenic had broken through the guard-bed system within 2 to 3 months of initial operation. Although there is scatter in the data, the results of analyses of catalyst samples confirm this conclusion. The most recent concentration of arsenic on the methanol synthesis catalyst is 1,400 ppmw. In addition, sulfur is present at about 300 ppmw, and is increasing slowly with time. Work is underway to identify adsorbent materials for use in the 29C-40 guard bed to increase the removal efficiency of arsine and (if possible) sulfur from the Balanced Gas. The concentration of iron, although low (less than 200 ppmw), is increasing in the most recent samples. These results can be misleading, as contamination by iron from either piping or sample containers is possible. An assessment of the impact (if any) of the change in adsorbent materials in June of 1999 on the level of iron on the recent catalyst samples will be performed.

The original data acquisition system at the LPMEOH™ Demonstration Unit was replaced with a new system during the week of 08 November 1999. The original system was not Y2K compliant. This replacement system will allow for continued data collection and reporting in support of the overall demonstration project's goals. The installation of the new system proceeded without any interruptions in gathering of plant data.

### Sparger Resistance

The performance of the gas sparger continues to meet the design expectations for pressure drop and reactor operation. Appendix F, Figure 2 plots the average daily sparger resistance coefficient for the period following the installation during the March 1999 outage. The data for this plot, along with the corresponding average pressure drop, are also included in Table

D.3-1. The flow resistance will continue to be monitored in order to determine the changes in performance with operating time.

## *D.4 Planning and Administration*

The Milestone Schedule Status Report and the Cost Management Report, through the period ending 31 December 1999, are included in Appendix G. These two reports show the current schedule, the percentage completion and the latest cost forecast for each of the Work Breakdown Structure (WBS) tasks. Ninety-nine percent (99%) of the $38 million of funds forecast for the Kingsport portion of the LPMEOH™ Process Demonstration Project for the Phase 1 and Phase 2 tasks have been expended (as invoiced), as of 31 December 1999. Fifty-one percent (51%) of the $158 million of funds for the Phase 3 tasks have been expended (as invoiced), as of 31 December 1999.

The monthly reports for October, November, and December were submitted. These reports include the Milestone Schedule Status Report, the Project Summary Report, and the Cost Management Report.

A paper entitled "Direct Applications of Stabilized Methanol from the Liquid Phase Methanol (LPMEOH™) Process" was presented at the 16th Annual International Pittsburgh Coal Conference (11-15 October 1999). A presentation entitled "Liquid Phase Methanol (LPMEOH™) Project: Operating Experience Update" was given at the 1999 Gasification Technologies Conference (17-20 October 1999).

A letter was received from DOE stating that the most recent draft of Volume 1 - Public Design, of the Final Report for the LPMEOH™ Demonstration Project had satisfied the guidelines for preparation of the document. Work began to finalize the report.

## E. Planned Activities for the Next Quarter

- Continue to analyze catalyst slurry samples and reactor performance data to determine causes for deactivation of methanol synthesis catalyst.
- Continue executing Phase 3, Task 2.1 Methanol Operation per the Demonstration Test Plan. Focus activities on increasing catalyst activity, performing additional testing on CO-rich syngas, and monitoring the performance of the gas sparger in the reactor.
- Identify new adsorbent materials for use in the 29C-40 guard bed within the LPMEOH™ Demonstration Unit to increase the removal efficiency of arsine and sulfur. Complete assessment of changes in levels of iron on catalyst samples.
- Provide DOE with an analysis of catalyst samples and an assessment of the results of the LPDME design verification test at the LaPorte AFDU.
- Continue execution of the Off-Site, Product-Use Test Program (Phase 1, Task 1.4).

- Conduct a Project Review Meeting with DOE.

## F. Conclusion

The LPMEOH$^{TM}$ Demonstration Unit operated at 100% availability throughout the reporting period.

A major catalyst withdrawal and addition campaign was undertaken during the quarter to increase catalyst activity. A series of four withdrawals were conducted on 08 and 09 November 1999. This was followed by four catalyst additions which were activated and added between 12 November and 19 November 1999. After the addition of the fourth batch of catalyst, the total catalyst inventory was calculated to be 44,924 pounds.

During the balance of the quarter, Balanced Gas at 680 KSCFH was supplied to the reactor and the reactor pressure was set at 710 psig. Reactor temperature was held at 235°C throughout the reporting period.

There were two extended periods of operation at a reactor temperature of 235°C during which catalyst activity was measured to track catalyst deactivation during the quarter. An overall deactivation rate of 0.56% per day was calculated for the period 11 September 1999 to 03 October 1999 (22 days). An overall deactivation rate of 0.66% per day was calculated for the period 13 October 1999 to 07 November 1999 (23 days). These deactivation results are slightly greater than the baseline deactivation rate from the 4-month proof-of-concept run at the LaPorte AFDU in 1988/89 (this run was performed at 250°C).

On 02 December 1999, 45 KSCFH of CO Gas was introduced along with 675 KSCFH of Balanced Gas to achieve a 1:1 $H_2$/CO reactor inlet feed composition. Reactor pressure was adjusted to 695 psig during periods of CO Gas addition to allow for proper control of the CO Gas. Operation at this condition continued until 11 December 1999. The catalyst performance met expectations for the quantity of methanol which was produced at these conditions; however, the operating period was not of sufficient length to calculate the rate of catalyst deactivation.

During the reporting period, analyses of catalyst and gas samples for changes in physical characteristics and levels of poisons have continued. Copper crystallite size measurements have shown an increase over time, which is an indication of catalyst aging. Levels of nickel (a known catalyst poison) have remained low and steady since the restart in December of 1997. As reported in Technical Progress Report No. 21, the adsorbents in the two catalyst guard beds (the 10C-30 vessel, upstream of both the LPMEOH™ Demonstration Unit and the fixed-bed methanol plant, and the 29C-40 carbonyl guard bed) which treat Balanced Gas were changed in June of 1999; the 10C-30 was charged with arsine-removal adsorbent, and the 29C-40 was split between arsine and carbonyl removal materials. Initial results of batch sampling of the Balanced Gas stream demonstrated that the guard-bed system was effective in removing arsenic when it first came on-stream after the changeout. However, subsequent analysis confirmed that arsenic had broken through the guard-bed system within 2 to 3 months of initial operation. Although there is scatter in the data, the results of analyses of catalyst samples confirm this conclusion. In addition, sulfur is present on catalyst samples, and is increasing slowly with time. Work is underway to identify adsorbent materials for use in the 29C-40 guard bed to increase the removal efficiency of arsine and (if possible) sulfur from the Balanced Gas. The concentration of iron, although low (less than 200 ppmw), is increasing in the most recent samples. These results can be misleading, as contamination by iron from either piping or sample containers is possible. An assessment of the impact (if any) of the change in adsorbent materials in June of 1999 on the level of iron on the recent catalyst samples will be performed.

The original data acquisition system at the LPMEOH™ Demonstration Unit was replaced with a new system during the week of 08 November 1999. The original system was not Y2K compliant. The installation of the new system proceeded without any interruptions in gathering of plant data.

The performance of the gas sparger, which was designed by Air Products and installed into the LPMEOH™ Reactor prior to the restart of the LPMEOH™ Demonstration Unit in March of 1999, was monitored. The performance to date has met the design expectations for pressure drop and reactor operation.

During the reporting period, a total of 4,804,902 gallons of methanol was produced at the LPMEOH™ Demonstration Unit. Since startup, about 47.6 million gallons of methanol has been produced. Eastman accepted all of this methanol for use in the production of methyl acetate, and ultimately cellulose acetate and acetic acid. No safety or environmental incidents were reported during this quarter.

During this quarter, planning, procurement, and test operations continued on three project sites selected for the off-site, product-use test program. Testing of stabilized methanol in a low-$NO_x$ stationary gas turbine was completed. Preliminary test results show that the emissions from the turbine fueled with stabilized methanol from the LPMEOH™ Demonstration Project are similar to those when fueled with natural gas. $NO_x$ emissions as low as 1 ppmv, corrected to 15% oxygen, were achieved at acceptable combustor CO emissions. A proposal was received from WVU to allow additional time to complete the scope of work on testing of stabilized methanol in its stationary gas turbine. DOE accepted Air Products’ recommendation to approve this no-cost extension to 01 April 2000. Testing has been performed to identify additives which can increase the lubricity of methanol to a value equal to that of Jet-A fuel. Construction of a second generation reformer test apparatus at the University of Florida is nearing completion. This will allow the evaluation of a high-temperature reformer catalyst as part of the ongoing activities to qualify stabilized methanol as a feedstock to a phosphoric acid fuel cell.

During the reporting period, the design verification test of the LPDME Process at the LaPorte AFDU was completed. Commercial viability of the LPDME Process was successfully evaluated at the 10 TPD scale, using commercially produced catalysts. The plant was operated for 25 days on stream to compare catalyst aging in a pilot scale slurry bubble column with that in a laboratory autoclave. The catalyst life study was extended in favor of a planned process variable study to obtain additional data on catalyst aging. Hydrodynamic information was obtained at the baseline conditions by conducting a detailed survey of the reactor with radioactive tracer injections. The tracer data will be analyzed as part of the Hydrodynamic Program with DOE's Liquid Fuels Program.

The deactivation rate for both the catalysts was calculated to be 0.7% per day. This result is lower than the 1.2% per day which had been calculated for both the methanol synthesis and dehydration catalysts during experiments in the autoclave. The rate of deactivation is slightly higher than 0.5% per day rate which was achieved for the LPMEOH™ Process after 3 weeks of operation at LaPorte in 1988/89. The methanol productivity remained relatively constant throughout the run, while the DME productivity showed a slight decline. These trends are consistent with observations from the laboratory. The standard error for the methanol catalyst deactivation rate was high (0.25% per day) due to initial scatter in the data. The scatter decreased significantly after problems in the sampling and analytical system were discovered and resolved at 350 hours on stream. The dehydration catalyst activity data have better statistics, with a standard error of 0.06% per day.

The methanol synthesis catalyst was activated successfully with an expected reductant uptake. The initial productivities of methanol and DME were higher than the laboratory. The DME production rate started at 5.1 TPD and declined to 4.1 TPD over the 25 days on stream, while the methanol production showed a scatter within the range of 3.1 to 3.8 TPD throughout the run.

The reactor operated in a stable hydrodynamic regime as determined by the presence of a uniform temperature profile and gas hold-up. Differential pressure measurements along the reactor resulted in a calculated gas hold-up of about 42 vol% gas hold-up and a catalyst slurry concentration of 36 wt%.

The initial start-up was very quick with the baseline condition reached in 12 hours after the introduction of syngas. A re-start after a syngas outage only took 4 hours. This further demonstrates the ease and flexibility of the slurry technology.

The 1999 design verification test of the LPDME Process at the LaPorte AFDU represents a significant step forward in the development of the technology. The 0.7% per day rate of catalyst deactivation which was achieved during this campaign is a large improvement over the 4% per day rate of deactivation which was calculated from autoclave studies prior to the initial test of the LPDME Process at the LaPorte AFDU in 1991. The results from the design verification test will be used to update the economics of the LPDME Process and to support decision-making for future activities by the LPMEOH™ Demonstration Project in support in the scale-up of the LPDME technology.

A paper entitled "Direct Applications of Stabilized Methanol from the Liquid Phase Methanol (LPMEOH™) Process" was presented at the 16th Annual International Pittsburgh Coal Conference (11-15 October 1999). A presentation entitled "Liquid Phase Methanol (LPMEOH™) Project: Operating Experience Update" was given at the 1999 Gasification Technologies Conference (17-20 October 1999).

A letter was received from DOE stating that the most recent draft of Volume 1 - Public Design, of the Final Report for the LPMEOH™ Demonstration Project had satisfied the guidelines for preparation of the document.  Work began to finalize the report.

Ninety-nine percent (99%) of the $38 million of funds forecast for the Kingsport portion of the LPMEOH™ Process Demonstration Project for the Phase 1 and Phase 2 tasks have been expended (as invoiced), as of 31 December 1999.  Fifty-one percent (51%) of the $158 million of funds for the Phase 3 tasks have been expended (as invoiced), as of 31 December 1999.

# APPENDICES

## APPENDIX A - SIMPLIFIED PROCESS FLOW DIAGRAM

# APPENDIX B - OFF-SITE TESTING (DEFINITION AND DESIGN)

**Appendix B-1 - Summary Table of Seven Test Sites**

**Quarterly Reports:**

**Appendix B-2 - ARCADIS Projects (two pages):**
- **Aircraft Ground Equipment Emulsion**
- **Stationary Turbine for $NO_x$ Control**

**Appendix B-3 - West Virginia University Stationary Gas Turbine (three pages)**
**Appendix B-4 - University of Florida Fuel Cell (eleven pages)**
**Appendix B-5 - Florida Institute of Technology (twenty-nine pages)**

# APPENDIX C - DME DESIGN VERIFICATION TESTING

## Appendix C-1 - 1997 DME Design Verification Testing Recommendation
(fourteen pages)

## Appendix C-2 - Recommendation to Proceed with Fall 1999 Test at LaPorte AFDU
(nine pages)

# APPENDIX D - SIMPLIFIED PROCESS FLOW DIAGRAM - LAPORTE AFDU

# APPENDIX E - SAMPLES OF DETAILED MATERIAL BALANCE REPORTS

# APPENDIX F - RESULTS OF DEMONSTRATION UNIT OPERATION

**Table 1 - Summary of LPMEOH™ Demonstration Unit Outages - October/December 1999**
**Table 2 - Summary of Catalyst Samples - Second Catalyst Batch**

**Figure 1 - Catalyst Age (η): August - December 1999**
**Figure 2 - Sparger Resistance Coefficient vs. Days Onstream (August 1999 - December 1999)**

# Table 1
# Summary of LPMEOH™ Demonstration Unit Outages - October/December 1999

| Operation Start | Operation End | Operating Hours | Shutdown Hours | Reason for Shutdown |
|---|---|---|---|---|
| 10/1/99 00:00 | 10/6/99 02:25 | 122.4 | 3.6 | Syngas Outage |
| 10/6/99 06:00 | 10/11/99 22:30 | 136.5 | 15.5 | Syngas Outage |
| 10/12/99 14:00 | 11/19/99 01:00 | 899.0 | 32.3 | Syngas Outage |
| 11/20/99 09:20 | 11/27/99 17:15 | 175.9 | 38.3 | Syngas Outage |
| 11/29/99 07:30 | 12/11/99 07:30 | 288.0 | 114.5 | Syngas Outage |
| 12/16/99 02:00 | 12/30/99 12:30 | 346.5 | 6.0 | Syngas Outage |
| 12/30/99 18:30 | 12/31/99 23:59 | 29.5 | | End of Reporting Period |

| | |
|---|---|
| Total Operating Hours | 1997.8 |
| Syngas Available Hours | 1997.8 |
| **Plant Availability, %** | **100.00** |

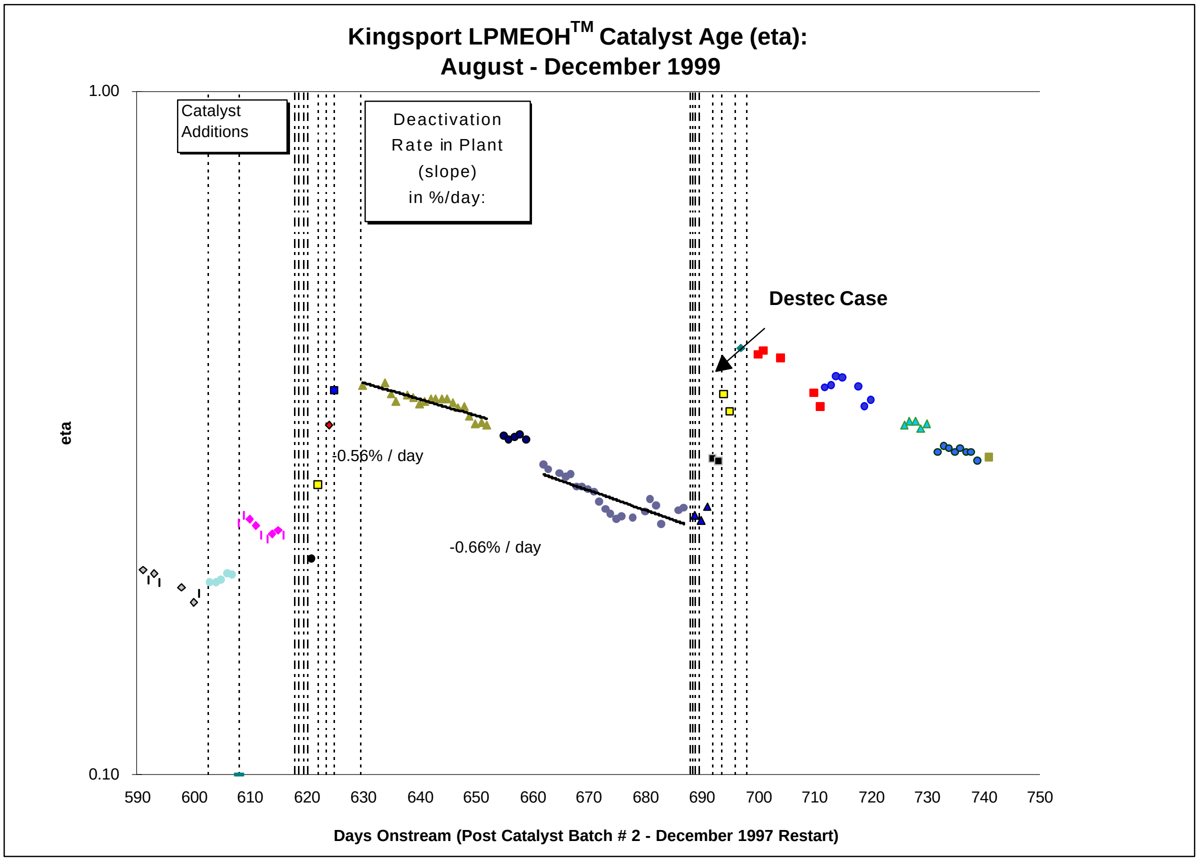
# Table 2
# Summary of Catalyst Samples - Second Catalyst Batch

| Sample | Identity | XRD | | BET | Analytical (ppmw) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Cu | ZnO | m2/g | Fe | Ni | S | As | Cl |
| K9804-1 | Reduction Sample 4/2/98 - Alternative Catalyst | 72.5 | 84.9 | 105 | 23 | 11 | <=110 | <=12 | |
| K9712-1 | Transfer sample from 29D-02 to Reactor | 95.3 | 74 | | 362 | 47.2 | 66.7 | 10.2 | nd |
| K9712-2 | Reactor Sample Day 1 | 100 | 123.8 | 75 | 92.1 | <=18 | <=167 | <50 | nd |
| K9712-3 | Reactor Sample Day 4 | 130.9 | 64 | | | | | | |
| K9712-4 | Reactor Sample Day 10 | 126.8 | 73.3 | 73 | 126 | <=22 | <=127 | <50 | nd |
| K9801-2 | Reactor Sample 1/26/98 | 132.05 | 98.3 | | 63.5 | 39.5 | 42.7 | 29.2 | <100 |
| K9802-1 | Reactor Sample 2/3/98 | 141.1 | 91.5 | | | | | | |
| K9802-2 | Reactor Sample 2/9/98 | 158.1 | 113 | | | | | | |
| K9802-3 | Reactor Sample 2/15/98 | 145.7 | 91 | | 67.1 | 36 | <=97 | 209 | |
| K9802-4 | Reactor Sample 2/23/98 | 176.8 | 114.5 | | | | | | |
| K9803-2 | Reactor Sample 3/10/1998 | 154.3 | 95.8 | 44 | 61.4 | 35.8 | <=94 | 408 | |
| K9803-4 | Reactor Sample 3/29/98 | 169.6 | 87.9 | | | | | | |
| K9804-2 | Reactor Sample 4/14/98 | 152.4 | 89.3 | | 81.7 | 30.8 | <=170 | 615 | |
| K9805-2 | Reactor Sample 5/11/98 | 219.2 | 109.6 | | 73.15 | 35.85 | 163 | 538 | |
| K9606-2 | Reactor Sample 6/16/98 | 272.3 | 117.2 | | 86.4 | 31.1 | 220 | 1110 | |
| K9807-2 | Reactor Sample 7/8/98 | 263.2 | 108.6 | | 88.7 | 27.6 | 277 | 1045 | |
| K9807-3 | Reactor Sample 7/29/98 | 412* | 112 | | 93.25 | 30.95 | 209 | 1620 | |
| K9807-4 | Reactor Sample 8/14/98 | 353.9* | 124 | | 121.5 | 37.1 | 213.5 | 1215 | |
| K9809-1 | Reactor Sample 9/24/98 | 347.4 | 129.8 | | 69.6 | 29.8 | 326 | 1149 | |
| K9810-1 | Reactor Sample 10/5/98 | 331.1 | 130.4 | | | | | | |
| K9811-2 | Reactor Sample 11/25/98 | 293.9 | | | 57.3 | 23.4 | 264 | 1400 | <100 |
| K9812-1 | Reactor Sample 12/29/98 | 283.1 | | | 72.3 | 20.4 | 260 | 1300 | <100 |
| K9901-1 | Reactor Sample 1/15/99 | 252.5 | 61.4 | | | | | | |
| K9902-1 | Reactor Sample 2/17/99 | 474.7 | 133.6 | | 82.6 | 22.2 | 385 | 1490 | <300 |
| K9904-3 | Reactor Sample 4/27/99 | 417.8 | 110.4 | 15 | 131 | 18.2 | 348 | 1460 | <30 |
| K9906-1 | Reactor Sample 6/1/99 | 517 | 105 | 43 | 109 | 19.7 | 316 | 1680 | 40 |
| K9907-1 | Reactor Sample 7/13/99 | 446 | 116 | 59 | 175 | 19.7 | 488 | 1810 | 30 |
| K9908-2 | Reactor Sample 8/31/99 | 632 | 117 | 56 | 161 | 15.1 | 406 | 1470 | 50 |
| K9909-2 | Reactor Sample 9/21/99 | 357 | 109 | 64 | 132 | 11.2 | 253 | 1050 | nd |
| K9910-2 | Reactor Sample 10/19/99 | 135 | 94 | 55 | 157 | 15.4 | 343 | 1270 | 30 |
| K9911-1 | Reactor Sample 11/4/99 | | | | 184 | 12.8 | 335 | 1580 | na |
| K9912-1 | Reactor Sample 12/8/99 | 797 | 121 | 60 | 167 | 13.9 | 248 | 1400 | 40 |

Notes:

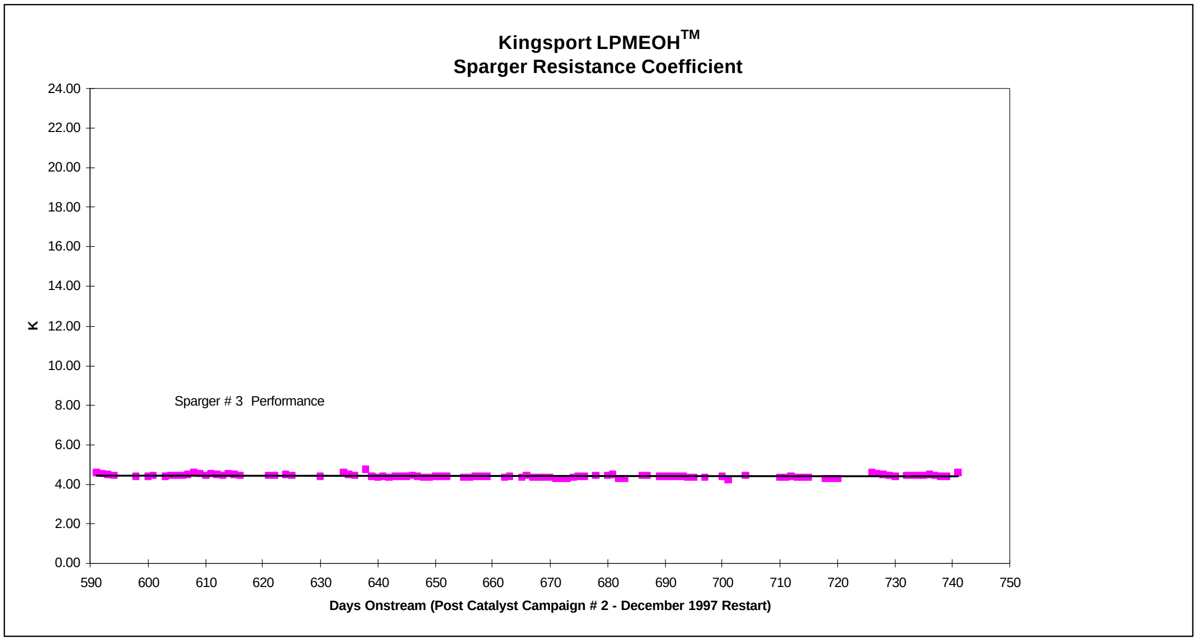
1) nd = none detected
2) * - these values represent re-analysis of the sample as compared to Technical Progress Report no. 17
3) na = data not available

# Figure 1



Kingsport LPMEOH™ Catalyst Age (eta):
August - December 1999
1.00
0.10
eta
Catalyst Additions
Deactivation Rate in Plant (slope) in %/day:
-0.56% / day
-0.66% / day
Destec Case
590
600
610
620
630
640
650
660
670
680
690
700
710
720
730
740
750
Days Onstream (Post Catalyst Batch # 2 - December 1997 Restart)

# Figure 2


Kingsport LPMEOHTM
Sparger Resistance Coefficient
K
24.00
22.00
20.00
18.00
16.00
14.00
12.00
10.00
8.00
6.00
4.00
2.00
0.00
Sparger # 3 Performance
590
600
610
620
630
640
650
660
670
680
690
700
710
720
730
740
750
Days Onstream (Post Catalyst Campaign # 2 - December 1997 Restart)

# APPENDIX G - MILESTONE SCHEDULE STATUS AND COST MANAGEMENT REPORTS