

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

**TECHNICAL PROGRESS REPORT NO. 17**

**For The Period**

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**and**

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**for the**

**Air Products Liquid Phase Conversion Company, L.P.**

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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 achieved a new milestone during the reporting period as the plant continued to operate through the longest continuous campaign to date (67 days) as of 30 September 1998.

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 monitored throughout the reporting period. The LPMEOH™ Demonstration Unit completed a 24-day stable period of operation on 14 July 1998 at a reactor temperature of 235°C and flowrate of the primary syngas feed (Balanced Gas) of approximately 700 KSCFH. Over this period, the rate of decline in catalyst activity was 0.2% per day at this condition. This performance was superior to the original target from the 4-month proof-of-concept run at the LaPorte Alternative Fuels Development Unit (AFDU) in 1988/89 (0.4% per day change in catalyst activity).

On 21 August 1998, a test at a reactor temperature of 250°C was initiated. Because of an outage of Eastman's water-gas shift reactor, a brief test on a 1:1 hydrogen to carbon monoxide ratio ( $H_2/CO$ ) syngas was performed on 24-26 August 1998 while the gas-phase methanol reactor was forced to shut down. The test at the higher reactor temperature was completed on 31 August 1998 when accelerated changes in the calculated value for the catalyst age were observed. Catalyst samples were taken before and after this operating test to determine if the changes in calculated performance can be correlated to changes in either the concentrations of catalyst poisons or in other catalyst physical properties.

During the week of 07 September 1998, three batches of fresh catalyst were activated and added to the LPMEOH™ Reactor, which brought the catalyst loading to slightly above the design value. The Balanced Gas flowrate was also increased to 800 - 850 KSCFH. For the remainder of the reporting period, the rate of change of catalyst activity during this period was 1.3% per day.

Catalyst slurry samples from the LPMEOH™ Reactor have been taken on a regular basis to correlate any change in unit performance with changes in the physical properties of the catalyst. Levels of arsenic have exceeded the concentrations measured on the initial charge of methanol synthesis catalyst from December of 1997. No correlation to date between the change in arsenic readings and catalyst performance has been identified. Sulfur has been measured at the analytical detection limit. Levels of iron and nickel have remained steady since the restart in December of 1997.

The pressure drop across the alternative gas sparger, which was designed by Air Products and installed into the LPMEOH™ Reactor prior to the restart of the LPMEOH™ Demonstration Unit in December of 1997, has shown a slight increase (1.0 psi) with time. One possible explanation is that the actual liquid head between the pressure taps is increasing with the higher catalyst loading. Once the steady-state slurry concentration in the reactor has been reached, the flow resistance will be monitored closely.

During the reporting period, a total of 5,422,626 gallons of methanol was produced at the LPMEOH™ Demonstration Unit. Since startup, over 25.7 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. The LPMEOH™ Demonstration Unit operated at 100% availability throughout the quarter and continues to operate at greater than 99% availability since being brought back onstream on 19 December 1997.

A meeting was held with the off-site catalyst reclaimer (Agmet) to review the handling of the spent catalyst slurry which was drained from the LPMEOH™ Reactor in November of 1997. It is anticipated that a solution to better optimize the materials handling issues will be developed at some minimal cost impact to the project; this will allow the reclaiming of the spent catalyst to continue.

During this quarter, planning, procurement, and test operations continued on the seven project sites selected for the off-site, product-use test program. A flexible fuel vehicle has completed over 3,400 miles of operation on fuel-grade methanol from inventory at the LaPorte AFDU. In a stationary turbine test, emissions testing was completed, and the concentration of nitrogen oxides was reduced from 25 ppm on Jet A fuel to less than 5 ppm on methanol. As part of the ongoing fuel cell test project, a proposal was submitted to conduct a small-scale reformer test to compare the behavior of chemical-grade methanol with fuel-grade methanol from the LPMEOH™ Demonstration Project.

During the reporting period, planning for a design verification test run of the Liquid Phase Dimethyl Ether (LPDME™) Process at the LaPorte AFDU continued. Air Products has been performing laboratory autoclave tests of samples of the 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 and commercial-scale production have not been resolved. As a result, the decision was made within the DOE's Liquid Fuels Program to delay the start of the LaPorte AFDU design verification test until the catalyst scale-up issues are resolved.

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 30 September 1998. Twenty-eight percent (28%) of the \$158 million of funds for the Phase 3 tasks have been expended (as invoiced), as of 30 September 1998.

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## ACRONYMS AND DEFINITIONS

Acurex	-	Acurex Environmental Corporation
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 <sub>2</sub> ), carbon monoxide (CO), and carbon dioxide (CO <sub>2</sub> ) 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-FETC	-	The DOE's Federal Energy Technology Center (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 <sub>2</sub> 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 <sub>2</sub> ) over the stoichiometric balance for the production of methanol; also called H <sub>2</sub> 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
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)
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	-	sum 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
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 <sub>2</sub> ) and carbon monoxide (CO), or mixtures of H <sub>2</sub> and CO; intended for "synthesis" in a reactor to form methanol and/or other hydrocarbons (synthesis gas may also contain CO <sub>2</sub> , 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 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 achieved a new milestone during the reporting period as the plant continued to operate through the longest continuous campaign to date (67 days) as of 30 September 1998.

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 monitored throughout the reporting period. The LPMEOH™ Demonstration Unit completed a 24-day stable period of operation on 14 July 1998 at a reactor temperature of 235°C and flowrate of the primary syngas feed (Balanced Gas) of approximately 700 KSCFH. Over this period, the rate of decline in catalyst activity was 0.2% per day at this condition. This performance was superior to the original target

from the 4-month proof-of-concept run at the LaPorte AFDU in 1988/89 (0.4% per day change in catalyst activity). Additional plant operation in August at similar conditions resulted in a rate of decline in catalyst activity of 0.4 - 0.5% per day.

On 21 August 1998, a test at a reactor temperature of 250°C was initiated in order to check the catalyst activity and approximate the catalyst life at the temperature used during the majority of the 1997 operating year. Because of an outage of Eastman's water-gas shift reactor, a brief test on a 1:1 hydrogen to carbon monoxide ration ( $H_2/CO$ ) syngas was performed on 24-26 August 1998 while the gas-phase methanol reactor was forced to shut down. The test at the higher reactor temperature was completed on 31 August 1998 when accelerated changes in the calculated value for the catalyst age were observed. Catalyst samples were taken before and after this operating test to determine if the changes in calculated performance can be correlated to changes in either the concentrations of catalyst poisons or in other catalyst physical properties.

During the week of 07 September 1998, three batches of fresh catalyst were activated and added to the LPMEOH™ Reactor, which brought the catalyst loading to slightly above the design value. For the remainder of the reporting period, the rate of change of catalyst activity during this period was 1.3% per day.

Catalyst slurry samples from the LPMEOH™ Reactor have been taken on a regular basis to correlate any change in unit performance with changes in the physical properties of the catalyst. Samples have continued to show an increase in arsenic loading, with levels in excess of the concentrations measured on the initial charge of methanol synthesis catalyst from December of 1997. No correlation to date between the change in arsenic readings and catalyst performance has been identified. Sulfur has been measured at the analytical detection limit. Levels of iron and nickel have remained steady since the restart in December of 1997.

The performance of the alternative gas sparger, which was designed by Air Products and installed into the LPMEOH™ Reactor prior to the restart of the LPMEOH™ Demonstration Unit in December of 1997, was monitored. During the reporting period, the gas sparger has shown a slight increase in flow resistance with time. The magnitude of this change is an increase of about 1.0 psi in the pressure drop. One possible explanation is that the actual liquid head between the pressure taps is increasing with the higher catalyst loading. Once the steady-state slurry concentration in the reactor has been reached, the flow resistance will be monitored closely for any continuing changes.

During the reporting period, a total of 5,422,626 gallons of methanol was produced at the LPMEOH™ Demonstration Unit. Since startup, over 25.7 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. The LPMEOH™ Demonstration Unit operated at 100% availability throughout the quarter and continues to operate at greater than 99% availability since being brought back onstream on 19 December 1997.

A meeting was held with the off-site catalyst reclaimer (Agmet) to review the handling of the spent catalyst slurry which was drained from the LPMEOH™ Reactor in November of 1997.

The processing of this material is ongoing; however, the reclaimer is having difficulty with the mineral oil phase. Several ideas to limit the total free liquid were discussed, and parallel testing has begun in Eastman's laboratories and at Agmet's facilities. It is anticipated that a solution to better optimize the materials handling issues will be developed at some minimal cost impact to the project; this will allow the reclaiming of the spent catalyst to continue.

During this quarter, planning, procurement, and test operations continued on the seven project sites selected for the off-site, product-use test program. A flexible fuel vehicle has completed over 3,400 miles of operation on fuel-grade methanol from inventory at the LaPorte AFDU. In a stationary turbine test, emissions testing was completed, and the concentration of nitrogen oxides was reduced from 25 ppm on Jet A fuel to less than 5 ppm on methanol. As part of the ongoing fuel cell test project, a proposal was submitted to conduct a small-scale reformer test to compare the behavior of chemical-grade methanol with fuel-grade methanol from the LPMEOH™ Demonstration Project.

During the reporting period, planning for a design verification test run of the Liquid Phase Dimethyl Ether (LPDME™) Process at the LaPorte AFDU continued. Air Products has been performing laboratory autoclave tests of samples of the 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 and commercial-scale production have not been resolved. As a result, the decision was made within the DOE's Liquid Fuels Program to delay the start of the LaPorte AFDU design verification test. Once the catalyst scale-up issues are resolved, a new date for the start of the campaign at the LaPorte AFDU will be selected.

The final version of the Demonstration Technology Start-up Report was submitted to DOE.

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 30 September 1998. Twenty-eight percent (28%) of the \$158 million of funds for the Phase 3 tasks have been expended (as invoiced), as of 30 September 1998.

## **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- 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.

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 12,000 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<sub>2</sub> 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

Eight sites involving a variety of product-use tests have been 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, involving the testing of a water/naphtha/methanol emulsion as a transportation fuel, is awaiting final project definition.

A review of the status of the product-use test projects is scheduled with DOE, Air Products, and the program participants on 14 October 1998 in Morgantown, WV. The meeting agenda is included in Appendix B-2.

All of the remaining product-use test projects have begun planning and equipment procurement. Methanol produced from carbon monoxide (CO)-rich syngas at the LaPorte AFDU has been shipped to three of the project sites. Appendix B-3 through B-6 contain summary reports from the approved active projects. Highlights from these reports include:

Acurex Flexible Fuel Vehicle (FFV) - The FFV has completed a 3,400 mile trial on M85 made from methanol supplied from the inventory at the LaPorte AFDU. The FFV has accumulated 2,100 miles on M85 made from chemical-grade methanol. The data show comparable fuel economy for both fuels. Emissions of CO, NO<sub>x</sub>, and nonmethane hydrocarbon were below the California emissions standards for both fuels.

Stationary Turbine for Volatile Organic Carbon (VOC) Control - AlliedSignal has submitted a proposal to support this project via testing on a full-scale 500-kW turbine at their Phoenix, AZ test facility. Additional cost share is required before the project can be initiated.

West Virginia University (WVU) Stationary Gas Turbine - After initial operating problems, the testing on the stationary gas turbine was completed. Of particular interest on the emissions testing is the reduction in nitrogen oxide levels from 25 ppm on Jet A fuel to 5 ppm on methanol. Methanol from inventory at the LaPorte AFDU was being used in this program. A final report is being prepared.

Aircraft Ground Equipment Emulsion - A draft test plan was prepared, and the necessary equipment to prepare the emulsion was assembled. Initial testing is scheduled to begin on 10 November 1998.

University of Florida Fuel Cell - A proposal was submitted to Air Products to conduct a small-scale reformer test to compare the behavior of chemical-grade methanol with fuel-grade methanol from the LPMEOH™ Demonstration Project.

West Virginia University Tri-Boro Bus - Work has continued on preparation of the final report for this project (no update in this reporting period).

Florida Institute of Technology Bus & Light Vehicle - A second light vehicle was acquired during the reporting period, and both vehicles were operated extensively. Initial emissions tests on the light vehicle and the bus were received. Fuel-grade methanol from the LPMEOH™ Demonstration Project was used to operate the vehicles.

## **D.2 Commercialization Studies**

### Discussion

Several areas have been identified for development to support specific commercial design studies. These include: a) product purification options; b) feed gas impurity removal options; c) catalyst addition/withdrawal options; and d) plant design configuration options. Plant sizes in the range of 300 TPD to 1,800 TPD and plant design configurations for the range from 20% up to 70% syngas conversion will be considered. The Kingsport demonstration unit design and costs will be the basis for value engineering work to focus on specific cost reduction targets in developing the initial commercial plant designs.

The Process Economics Study - Outline has been prepared to provide guidance for the overall study work. The four part outline is included in Appendix C. This Outline addresses several needs for this Task 1.5.2 Commercialization Study:

- a) to provide process design guidance for commercial plant designs.
- b) to meet the Cooperative Agreement's technical objectives requirement for comparison with gas phase methanol technology. This preliminary assessment will help set demonstration operating goals, and identify the important market opportunities for the liquid phase technology.
- c) to provide input to the Demonstration Test Plan (Task 2.3).
- d) to provide input to the Off-Site Testing (Task 1.4) product-use test program.

### Recent Activities

- Part One of the Outline - "Coproduction of Methanol" has been written for release as a Topical Report. Comments from DOE on the 31 March 1997 draft of the Topical Report "Economic Analysis - LPMEOH™ Process as an Add-on to IGCC for Coproduction" were incorporated and sent to DOE on 06 July 1998. Additional comments were received from DOE, and a new update was sent to DOE on 24 September 1998.
- Part Two of the Outline - "Baseload Power and Methanol Coproduction", has been incorporated into the paper, "Fuel and Power Coproduction - The Liquid Phase Methanol (LPMEOH™) Process Demonstration at Kingsport ", that was presented at the DOE's Fifth Annual Clean Coal Technology Conference in January of 1997.
- Part Three of the Outline - "Coproduction for Intermediate Electric Load Following", has been incorporated into the paper, "Dispatchable IGCC Facilities: Flexibility through Coproduction", that was presented at POWER-GEN EUROPE '97 in June of 1997.
- Part Four of the Outline - "Methanol Fuel Applications", was used as the basis to update the product-use test program (Task 1.4).



### ***D.3 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. The DME Milestone Plan, showing the DVT work and the decision and implementation timing, is included in Appendix D.

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.

#### ***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 D. 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 test 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 should now be developed. 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 time to meet the schedule for testing at LaPorte.

LPDME™ is not applicable to hydrogen (H<sub>2</sub>)-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 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 continued. 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 to date, are included in the DME recommendation in Appendix D.

### ***Laboratory R&D***

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. 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 runs 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. During this quarter, laboratory work continued on developing an LPDME™ catalyst system based on the AB series of catalysts.

#### *Summary of Laboratory Activity and Results*

- Air Products has been performing laboratory autoclave tests of samples of the 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 design verification test at the LaPorte AFDU. Changes to the commercial production procedure were made, and additional batches of dehydration catalyst will be made and tested beginning in October of 1998. Once the catalyst scale-up issues are resolved, a new date for the start of the campaign at the LaPorte AFDU will be selected.

#### **D.4 LPMEOH™ Process Demonstration Facility - Methanol Operation**

Table D.4-1 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 5,422,626 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 safety or environmental incidents were reported during this quarter.

The LPMEOH™ Demonstration Unit achieved a new milestone during the reporting period as the plant extended the longest continuous operating campaign to date (67 days as of 30 September 1998). The LPMEOH™ Demonstration Unit operated at 100% availability throughout the quarter and continues to operate at greater than 99% availability since being brought back onstream on 19 December 1997. Appendix F, Table 1 contains the summary of outages for the LPMEOH™ Demonstration Unit during this quarter.



**Table D.4-1. Data Summary for LPMEOH™ Demonstration Unit (continued)**

Case	Date	Days Onstream	Gas Type	Temp (Deg C)	Pres. (psig)	Fresh Feed (KSCFH)	Recycle Gas (KSCFH)	Reactor Feed (H <sub>2</sub> 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 ft <sup>2</sup> F)	Sparger dP (psi)	Sparger Resistance ('K')
10	9-Sep-98	263	Balanced	235	710	692	2,085	3.75	71.5	0.65	4320	43.6	39.4	49.0	38,000	0.39	37.9	20.7	41.0	202.6	13.91	0.099	202	5.30	5.89
10	10-Sep-98	264	Balanced	235	713	783	2,043	3.88	74.8	0.65	4093	44.6	41.9	52.5	40,650	0.44	43.9	23.4	40.7	231.1	14.83	0.105	200	5.48	5.93
10	11-Sep-98	265	Balanced	235	711	796	2,003	4.29	57.6	0.65	3834	45.2	41.8	54.0	42,900	0.51	51.1	25.0	39.7	240.8	14.64	0.106	206	5.56	6.08
10	12-Sep-98	266	Balanced	235	710	837	1,950	4.00	69.6	0.65	3837	44.3	40.4	54.5	42,900	0.52	50.0	25.9	40.1	250.6	15.24	0.109	202	5.71	6.09
10	13-Sep-98	267	Balanced	235	710	851	1,920	3.91	71.9	0.64	3811	43.4	40.0	56.0	42,900	0.54	50.7	26.8	39.8	256.4	15.60	0.109	199	6.16	6.53
10	15-Sep-98	269	Balanced	235	710	853	1,884	4.04	81.6	0.64	3767	42.8	39.6	57.0	42,900	0.53	51.4	26.5	40.4	253.2	15.41	0.106	198	5.60	6.35
10	16-Sep-98	270	Balanced	235	710	848	1,857	4.25	89.6	0.63	3730	40.9	39.3	61.0	42,900	0.53	53.0	26.4	40.9	248.8	15.14	0.097	193	5.20	6.11
10	17-Sep-98	271	Balanced	235	710	834	1,868	4.07	83.3	0.63	3730	40.8	39.6	61.5	42,900	0.51	50.8	26.2	41.0	244.4	14.87	0.094	191	5.33	5.97
10	18-Sep-98	272	Balanced	235	710	849	1,851	4.00	91.6	0.63	3728	41.9	40.3	59.5	42,900	0.51	50.6	26.4	41.1	247.8	15.09	0.099	195	5.37	6.03
10	19-Sep-98	273	Balanced	235	710	835	1,865	3.87	90.1	0.63	3733	42.9	39.8	57.0	42,900	0.49	48.7	26.1	41.0	244.5	14.88	0.102	196	5.42	5.98
10	20-Sep-98	274	Balanced	235	710	837	1,855	3.92	89.9	0.63	3702	42.0	39.3	58.5	42,900	0.49	49.7	26.3	41.0	244.8	14.90	0.099	193	5.43	6.14
10	21-Sep-98	275	Balanced	235	710	840	1,905	3.84	92.8	0.64	3775	43.5	40.7	56.5	42,900	0.48	47.9	25.8	41.0	245.9	14.96	0.103	196	5.50	6.04
10	22-Sep-98	276	Balanced	235	710	845	1,901	3.77	93.8	0.64	3779	44.1	40.5	55.0	42,900	0.48	47.2	25.8	41.2	246.5	15.00	0.107	201	5.57	6.08
10	23-Sep-98	277	Balanced	235	710	847	1,913	3.80	96.3	0.64	3798	42.1	41.2	60.0	42,900	0.48	47.3	25.7	41.1	247.3	15.05	0.098	197	5.66	6.23
10	24-Sep-98	278	Balanced	235	710	850	1,900	3.78	108.8	0.64	3764	41.5	41.2	61.5	42,900	0.46	46.5	25.4	42.0	242.6	14.77	0.094	195	5.71	6.42
10	25-Sep-98	279	Balanced	235	710	828	1,897	3.78	99.1	0.63	3747	42.3	40.5	59.0	42,900	0.45	45.9	25.1	41.8	237.7	14.47	0.096	197	5.61	6.27
10	26-Sep-98	280	Balanced	235	710	818	1,883	3.74	99.3	0.63	3721	43.2	40.6	57.0	42,900	0.44	45.5	25.0	41.8	234.7	14.29	0.098	195	5.83	6.52
10	27-Sep-98	281	Balanced	234	710	814	1,872	3.78	103.5	0.62	3698	43.8	38.1	53.5	42,900	0.44	45.7	24.9	42.0	232.9	14.18	0.104	205	5.59	6.36
10	28-Sep-98	282	Balanced	235	710	813	1,841	3.86	101.4	0.62	3661	43.0	40.1	57.0	42,900	0.44	46.8	25.1	42.2	231.5	14.10	0.097	193	5.54	6.42
10	29-Sep-98	283	Balanced	234	710	811	1,871	3.74	104.4	0.62	3685	44.8	39.9	53.0	42,900	0.43	44.9	24.7	42.4	229.5	13.97	0.103	199	6.00	6.82
10	30-Sep-98	284	Balanced	235	710	815	1,871	3.69	112.0	0.62	3691	43.2	41.0	57.5	42,900	0.42	44.0	24.5	42.6	229.6	13.98	0.095	199	5.80	6.68

In Technical Progress Report No. 16, rapid changes were reported in the pressure-drop profile within the LPMEOH™ Reactor, as well as in the pressure of the steam system which provides cooling to the LPMEOH™ Reactor. Over a 12-hour period, the liquid level in the LPMEOH™ Reactor dropped about six feet with little appreciable change in overall pressure drop, indicating a decrease in the gas holdup. Shortly thereafter, the steam pressure (as measured by two independent transmitters and confirmed by a temperature measurement device) increased over a 4-hour period. Since the productivity of the catalyst did not change during either of these transients, the change in steam pressure caused the calculated heat transfer coefficient for the internal heat exchanger to increase. However, the new value of the heat transfer coefficient at the end of the event exceeded even the original startup value for the clean system. The pressure drop across the gas sparger remained steady during the changes in the other measurements. Over several weeks at the beginning of the present reporting period, the gas holdup in the reactor returned to the historical values measured since the catalyst concentration reached about 38 wt% in April of 1998, but the calculated heat transfer coefficient continued to exceed the design value. Work is continuing to identify the causes of both of these changes in reactor operation.

Operations focused on resolution of key issues identified during prior operating periods.

#### Catalyst Life ( $\eta$ ) - July - September 1998

The “age” of the methanol synthesis catalyst can be expressed in terms of a dimensionless variable  $\eta$ , 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 December of 1997 through 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.

On 14 July 1998 the LPMEOH™ Demonstration Unit completed a 24-day period of stable operation at a reactor temperature of 235°C and Balanced Gas flowrate of approximately 700 KSCFH. Throughout this period, the rate of decline in catalyst activity averaged 0.2% per day. This performance was superior to the original target from the 4-month proof-of-concept run at the LaPorte AFDU in 1988/89 (0.4% per day decrease in catalyst activity). A syngas outage terminated the test; however, this was the only shutdown of any kind during the quarter.

When the syngas supply was restored eleven days later, the Balanced Gas flowrate was set at about 630 KSCFH. The calculated value of  $\eta$  exhibited a large negative step-change during the shutdown, and catalyst samples from before and after the event are being analyzed for clues about the cause of activity loss. This feature is clearly visible in Figure 1 of Appendix F, just past 200 days onstream. A batch of fresh catalyst was activated and added to the LPMEOH™ Reactor on 01 August 1998, bringing the catalyst loading to 87% of design. At the same time, the Balanced Gas flowrate was raised to 700 KSCFH. The rate of decline in catalyst activity during the period 01 August to 21 August 1998 was 0.2 - 0.3% per day.

Since the catalyst deactivation now seemed satisfactory during steady periods at 235°C, reactor temperature was raised to 250°C on 21 August 1998 to check catalyst activity and life at the temperature used during most of the 1997 operating campaign. As expected, the calculated value for  $\eta$  showed a step-change increase of about 20% with the change in reactor temperature; this result provided additional confirmation to the observation in Technical Progress Report No. 16 that the kinetic model tends to underpredict the rate constant at lower operating temperature. Soon after, because of an outage of Eastman's water-gas shift reactor, a brief test on a 1:1 H<sub>2</sub>/CO syngas was performed on 24-26 August 1998; during this period, the gas-phase methanol reactor was unable to process this syngas stream and was forced to shut down. Catalyst performance dropped significantly during this period, but it is not yet known whether the decline was related to the 250°C operating temperature or the gas supply transient. This feature is clearly visible in Figure 1 of Appendix F, at about 250 days onstream. Again, catalyst samples from before and after the transient are being compared to determine the cause of this change. On September 1, the reactor temperature was decreased back to 235°C to minimize further activity loss before significantly increasing catalyst loading during the second week of September.

During the week of 07 September 1998, three batches of fresh catalyst were activated and added to the LPMEOH™ Reactor, which brought the catalyst loading to slightly above the design value. The Balanced Gas flowrate was also increased with the addition of each catalyst charge; through the remainder of the reporting period, rates have averaged between 800 KSCFH and 850 KSCFH. Through the same period, methanol production rates averaged 243 TPD at 235°C. The current combination of conditions (catalyst loading, catalyst age, feed flow, production, etc.) is as close as the plant has come so far to matching the overall design. The rate of change of catalyst activity during this period was 1.3% per day, which is consistent with the higher deactivation rates seen before with significant quantities of fresh catalyst.

Analyses of catalyst samples for changes in physical characteristics and levels of poisons have continued. Appendix F, Table 2 summarizes the results to date. Samples have continued to show an increase in arsenic loading, with levels in excess of the concentrations measured on the initial charge of methanol synthesis catalyst from 1997. No correlation between the change in arsenic levels and plant performance has been identified to date. Sulfur has been measured at the analytical detection limit. Copper crystallite size measurements have shown an increase in the most recent samples; tests which utilize other analytical equipment are planned to verify this change in crystallite size. Levels of iron and nickel have remained low and steady since the restart in December of 1997.

### Sparger Resistance

As reported in earlier Technical Progress Reports, flow resistance through the gas sparger of the LPMEOH™ Reactor had been stabilized using a continuous flush of condensed oil and entrained slurry from the 29C-05 secondary oil knock-out drum and 29C-06 cyclone. These streams are gravity-drained back to the reactor through a flush connection at the gas inlet line to the reactor, thus eliminating a batch-transfer operation which had been used during prior operation. The flow rate of the flush is equivalent to the average rate of liquid traffic in the reactor loop (1 to 2 gallons per minute).

This technique was first applied to a clean sparger at the restart of operations on 19 December 1997. Appendix F, Figure 2 plots the average daily sparger resistance coefficient since then. The data for this plot, along with the corresponding average pressure drop, are included in Table D.4-1. This parameter will continue to be closely monitored for any change in flow resistance.

Since the extended shutdown in July, the gas sparger has shown a slight increase in flow resistance with time. This change reflects an increase of about 1 psi in the measured pressure drop, and may be related to increased liquid head between the pressure taps because of higher catalyst loading. However, the increase has been gradual throughout this period, as opposed to step-change behavior corresponding to catalyst additions. Once the steady-state slurry concentration in the reactor has been reached, the flow resistance will be monitored closely for any continuing changes. Condensed and entrained oil and catalyst continue to be gravity-drained back to the reactor. During the next reporting period, a trial of an automatic level control system for the reactor is planned so that a steady-state value can be maintained as the limitations of catalyst loading in the reactor are approached.

#### Catalyst Reclaiming

During the reporting period, the off-site catalyst reclaimer (Agmet) reported their initial results with handling of the spent catalyst slurry drained from the LPMEOH™ Reactor in November of 1997. Processing of this material is ongoing; however, the reclaimer is having difficulty with the mineral oil phase. Agmet is presently blending the spent slurry with other materials in a ratio that limits the total free liquid. The remainder of the initial shipment of spent slurry from Kingsport will be processed in this manner. A meeting between Eastman, Air Products, and Agmet was held on 18 August 1998 at the reclaiming facility to review the handling issues and identify ways to improve the process. Several ideas were discussed, and parallel testing has begun in Eastman's laboratories and at Agmet's facilities. It is anticipated that a solution to better optimize the materials handling issues will be developed at some minimal cost impact to the project; this will allow the reclaiming of the spent catalyst to continue.

#### 29G-01 Condensed Oil Circulation Pumps

In late September, the 29G-01 condensed oil circulation pumps were started up for the first time under operating conditions. These pumps have a screw-type design similar to the original 29G-03 oil makeup pumps which failed to meet operating requirements at startup in the spring of 1997. Commissioning results were encouraging, including shaft rotation and seal integrity, but the 29G-01 pumps also failed to produce the required flow and head under normal operating conditions. An assessment of alternative pump designs will be performed.



## ***D.5 Planning and Administration***

A project review meeting was held in Allentown on 26 and 27 August 1998. The meeting focused on reviewing the performance of the demonstration unit since the restart in December of 1997. Also covered was a review of the status of the catalyst development work for the upcoming LPDME™ design verification test at the LaPorte AFDU. The meeting agenda, extracts from the meeting handouts, and the meeting notes are included in Appendix G.

The Milestone Schedule Status Report and the Cost Management Report, through the period ending 30 September 1998, are included in Appendix H. 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 30 September 1998. Twenty-eight percent (28%) of the \$158 million of funds for the Phase 3 tasks have been expended (as invoiced), as of 30 September 1998.

The monthly reports for July, August, and September were submitted. These reports include the Milestone Schedule Status Report, the Project Summary Report, and the Cost Management Report.

A paper entitled " Liquid Phase Methanol (LPMEOH™) Project Operating Experience" was submitted for presentation at the Gasification Technologies Conference in San Francisco, California on 04-07 October 1998.

A presentation on the LPMEOH™ Demonstration Project was made at an Energy Performance Workshop for the Chemical and Pulp and Paper Industries (01-02 September 1998), which was sponsored by the DOE's Office of Energy Efficiency and Renewable Energy.

Comments were received from DOE on the draft topical report entitled "Design and Fabrication of the First Commercial-Scale LPMEOH™ Reactor." An updated revision was prepared and submitted to DOE on 01 September 1998. Comments from DOE are being incorporated into a final version.

A draft topical report entitled "Alternative Fuels Field Test Unit Support to Kingsport LPMEOH™ Demonstration Unit - December 1997 - January 1998" was prepared and routed for review within Air Products.

The Demonstration Technology Start-up Report was submitted to DOE.

## **E. Planned Activities for the Next Quarter**

- Continue to analyze catalyst slurry samples and gas samples 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 concentration in the LPMEOH™ Reactor to determine the maximum slurry concentration (Test 9 of Test Plan).
- Resume preparations for a LPDME™ design verification test run at the LaPorte AFDU pending the completion of the production of the dehydration catalyst.
- Continue execution of the Off-Site, Product-Use Test Program (Phase 1, Task 1.4).
- Submit the draft topical report on the operation of the Alternative Fuels Field Test Unit to DOE.

## **F. Conclusion**

The LPMEOH™ Demonstration Unit achieved a new milestone during the reporting period as the plant continued to operate through the longest continuous campaign to date (67 days) as of 30 September 1998.

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 monitored throughout the reporting period. The LPMEOH™ Demonstration Unit completed a 24-day stable period of operation on 14 July 1998 at a reactor temperature of 235°C and Balanced Gas flowrate of approximately 700 KSCFH. Over this period, the rate of decline in catalyst activity was 0.2% per day at this condition. This performance was superior to the original target from the 4-month proof-of-concept run at the LaPorte AFDU in 1988/89 (0.4% per day change in catalyst activity). Additional plant operation in August at similar conditions resulted in a rate of decline in catalyst activity of 0.4 - 0.5% per day.

On 21 August 1998, a test at a reactor temperature of 250°C was initiated in order to check the catalyst activity and approximate the catalyst life at the temperature used during the majority of the 1997 operating year. Because of an outage of Eastman's water-gas shift reactor, a brief test on a 1:1 H<sub>2</sub>/CO syngas was performed on 24-26 August 1998 while the gas-phase methanol reactor was forced to shut down. The test at the higher reactor temperature was completed on 31 August 1998 when accelerated changes in the calculated value for the catalyst age were observed. Catalyst samples were taken before and after this operating test to determine if the changes in calculated performance can be correlated to changes in either the concentrations of catalyst poisons or in other catalyst physical properties.

During the week of 07 September 1998, three batches of fresh catalyst were activated and added to the LPMEOH™ Reactor, which brought the catalyst loading to slightly above the

design value. For the remainder of the reporting period, the rate of change of catalyst activity during this period was 1.3% per day.

Catalyst slurry samples from the LPMEOH™ Reactor have been taken on a regular basis to correlate any change in unit performance with changes in the physical properties of the catalyst. Samples have continued to show an increase in arsenic loading, with levels in excess of the concentrations measured on the initial charge of methanol synthesis catalyst from December of 1997. No correlation to date between the change in arsenic readings and unit performance has been identified. Sulfur has been measured at the analytical detection limit. Levels of iron and nickel have remained steady since the restart in December of 1997.

The performance of the alternative gas sparger, which was designed by Air Products and installed into the LPMEOH™ Reactor prior to the restart of the LPMEOH™ Demonstration Unit in December of 1997, was monitored. During the reporting period, the gas sparger has shown a slight increase in flow resistance with time. The magnitude of this change is an increase of about 1.0 psi in the pressure drop. One possible explanation is that the actual liquid head between the pressure taps is increasing with the higher catalyst loading. Once the steady-state slurry concentration in the reactor has been reached, the flow resistance will be monitored closely for any continuing changes.

During the reporting period, a total of 5,422,626 gallons of methanol was produced at the LPMEOH™ Demonstration Unit. Since startup, over 25.7 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. The LPMEOH™ Demonstration Unit operated at 100% availability throughout the quarter and continues to operate at greater than 99% availability since being brought back onstream on 19 December 1997.

A meeting was held with the off-site catalyst reclaimer (Agmet) to review the handling of the spent catalyst slurry which was drained from the LPMEOH™ Reactor in November of 1997. The processing of this material is ongoing; however, the reclaimer is having difficulty with the mineral oil phase. Several ideas to limit the total free liquid were discussed, and parallel testing has begun in Eastman's laboratories and at Agmet's facilities. It is anticipated that a solution to better optimize the materials handling issues will be developed at some minimal cost impact to the project; this will allow the reclaiming of the spent catalyst to continue.

During this quarter, planning, procurement, and test operations continued on the seven project sites which have been accepted for participation in the off-site, product-use test program. A flexible fuel vehicle has completed over 3,400 miles of operation on fuel-grade methanol from inventory at the LaPorte AFDU. In a stationary turbine test, emissions testing was completed, and the concentration of nitrogen oxides was reduced from 25 ppm on Jet A fuel to less than 5 ppm on methanol. As part of the ongoing fuel cell test project, a proposal was submitted to conduct a small-scale reformer test to compare the behavior of chemical-grade methanol with fuel-grade methanol from the LPMEOH™ Demonstration Project.

During the reporting period, planning for a design verification test run of the Liquid Phase Dimethyl Ether (LPDME™) Process at the LaPorte AFDU continued. Air Products has

been performing laboratory autoclave tests of samples of the 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 LaPorte AFDU design verification test. Once the catalyst scale-up issues are resolved, a new date for the start of the campaign at the LaPorte AFDU will be selected.

The final version of the Demonstration Technology Start-up Report was submitted to DOE.

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 30 September 1998. Twenty-eight percent (28%) of the \$158 million of funds for the Phase 3 tasks have been expended (as invoiced), as of 30 September 1998.

## **APPENDICES**

### **APPENDIX A - SIMPLIFIED PROCESS FLOW DIAGRAM**

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

**Appendix B-1 - Summary Table of Eight Candidates (one page)**

**Appendix B-2 - Agenda for 14 October 1998 Review Meeting (one page)**

**Quarterly Reports:**

**Appendix B-3 - ARCADIS Projects (three pages):**

- Acurex FFV
- Stationary Turbine for VOC Control
- Aircraft Ground Equipment Emulsion

**Appendix B-4 - West Virginia University Stationary Gas Turbine (three pages)**

**Appendix B-5 - University of Florida Fuel Cell (three pages)**

**Appendix B-6 - Florida Institute of Technology Bus & Light Vehicle (twenty-six pages)**

**APPENDIX C - PROCESS ECONOMIC STUDY**

**Process Economics Study - Outline  
(Draft - 3/31/97 - four pages)**

**and**

**LPMEOH™ Process Economics - for IGCC Coproduction  
(Memo - 31 March 1997 - two pages)**

## **APPENDIX D - DME DESIGN VERIFICATION TESTING**



**APPENDIX E - SAMPLES OF DETAILED MATERIAL BALANCE REPORTS**

## **APPENDIX F - RESULTS OF DEMONSTRATION PLANT OPERATION**

**Table 1 - Summary of LPMEOH™ Demonstration Unit Outages -  
July/September 1998**

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

**Figure 1 - Catalyst Age ( $\eta$ ) vs. Days Onstream - Second Catalyst Batch**

**Figure 2 - Sparger Resistance Coefficient vs. Days Onstream  
(Post-19 December 1997 Restart)**

**Table 1 - Summary of LPMEOH™ Demonstration Unit Outages -  
July/September 1998**

Operation Start	Operation End	Operating Hours	Shutdown Hours	Reason for Shutdown
7/1/98 00:01	7/14/98 12:45	324.7	258.5	Syngas Outage
7/25/98 07:12	9/30/98 23:59	1624.8		End of Reporting Period
Total Operating Hours			1949.5	
Syngas Available Hours			1949.5	
Plant Availability, %			100.00	

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

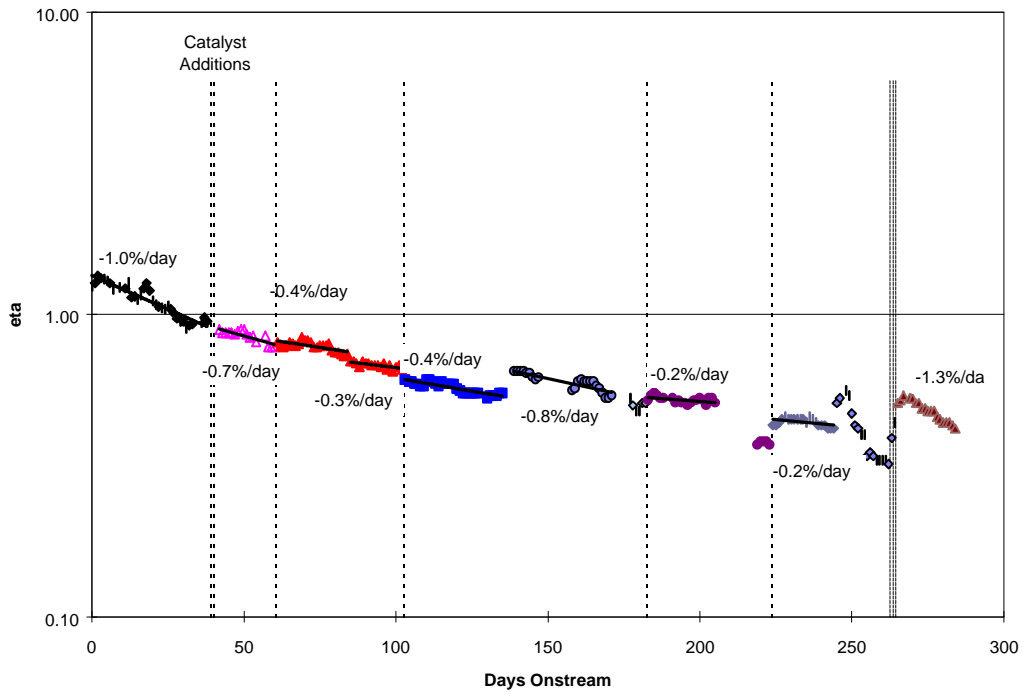
Sample	Identity	XRD		BET	Analytical (ppmw)				
		Cu	ZnO	m <sup>2</sup> /g	Fe	Ni	S	As	Cl
K9804-1	Reduction Sample 4/2/98 - Alternative Catalyst	72.5	84.9	105	23	11	<=110	<=12	
K9712-1	Transfer sample from 29D-02 to Reactor	95.3	74		362	47.2	66.7	10.2	nd
K9712-2	Reactor Sample Day 1	100	123.8	75	92.1	<=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						

**Notes:**

- 1) nd = none detected
- 2) \* - these XRD values represent re-analysis

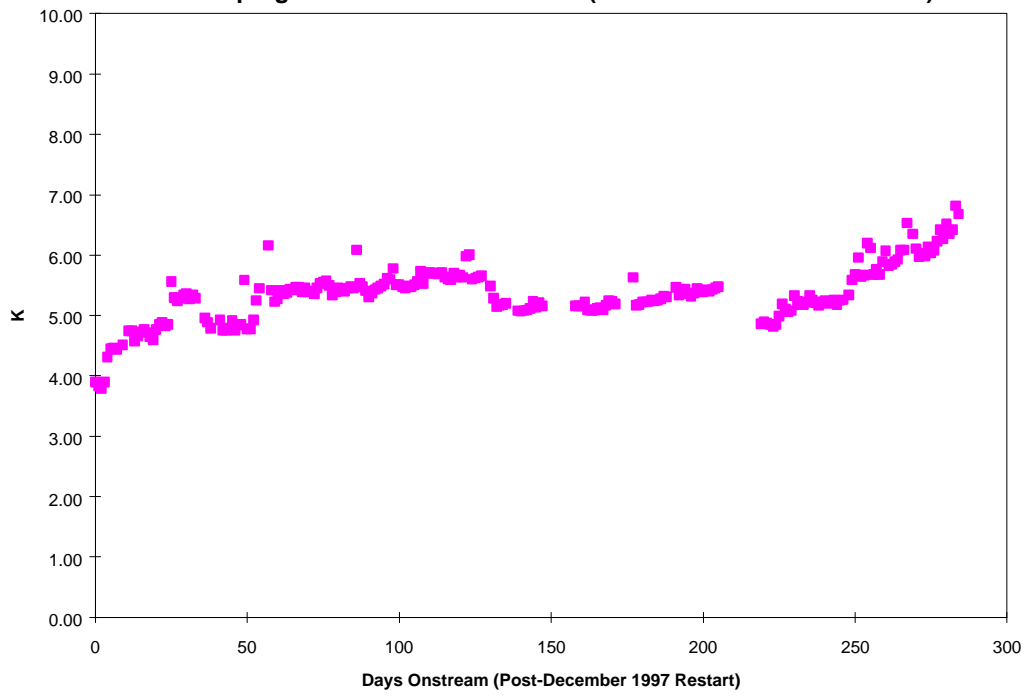
**Figure 1**

**Catalyst Age (eta)**



**Figure 2**

**Kingsport LPMEOH™  
Sparger Resistance Coefficient (Post December 1997 Restart)**



**APPENDIX G - PROJECT REVIEW MEETING (26-27 AUGUST 1998)**

**APPENDIX H - MILESTONE SCHEDULE STATUS AND COST MANAGEMENT  
REPORTS**