

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

**TECHNICAL PROGRESS REPORT NO. 31**

**For The Period**

**1 January – 31 March 2002**

**Prepared by**

**Air Products and Chemicals, Inc.  
Allentown, Pennsylvania**

**and**

**Eastman Chemical Company  
Kingsport, Tennessee**

**for the**

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

**Prepared for the United States Department of Energy  
National Energy Technology Laboratory  
Under Cooperative Agreement No. DE-FC22-92PC90543**

**Patents cleared by Chicago on 30 May 2002.**

## **DISCLAIMER**

This report was prepared by Air Products & Chemicals, Inc. and Eastman Chemical Company for the Air Products Liquid Phase Conversion Company, L.P., pursuant to a Cooperative Agreement partially funded by the U.S. Department of Energy, and neither Air Products & Chemicals, Inc., Eastman Chemical Company, the Air Products Liquid Phase Conversion Company, L.P., nor any of their subcontractors nor the U.S. Department of Energy, nor any person acting on behalf of either:

(A) Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

(B) Assumes any liabilities with respect to the use of, or for damages resulting from the use of, any information, apparatus, method, or process disclosed in this report.

Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute its endorsement, recommendation, or favoring by the U.S. Department of Energy. The views and opinions of authors expressed herein does not necessarily state or reflect those of the U.S. Department of Energy.

## 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 95.48% availability during this quarter. A 54-hour forced outage was taken from 24 February 2002 to 27 February 2002 so that the reduction of a fresh charge of adsorbent for the 29C-40 catalyst guard bed could be completed. A 4.5-hour forced outage on 14 March 2002 was caused by an automatic plant shutdown that was initiated by a high level trip on the 29C-02 steam drum. A third forced outage (38.7 hours duration) began on 27 March 2002, during the process to remove spent catalyst slurry from the LPMEOH™ Reactor prior to the addition of freshly activated catalyst. Due to the low level of activity of the remaining inventory of catalyst, the LPMEOH™ Reactor was unable to sustain operation; the unit was able to be restarted after the first fresh batch of catalyst was activated and added. There was also a short syngas interruption that was experienced on 18 January 2002 (7.2 hours).

As part of the operating protocol following the completion of the in-situ activation of methanol synthesis catalyst in the LPMEOH™ Reactor, temperature programming continued during the quarter; this involved the increase of reactor temperature as necessary to control the reactor purge flowrate and maintain reactor productivity. Over the reporting period, the reactor temperature was increased from 226°C to the final temperature of 250°C (250°C is the design temperature for the LPMEOH™ Demonstration Unit). The reactor pressure was maintained at 700 psig during the reporting period. The flowrate of the primary syngas feed (Balanced Gas) to the LPMEOH™ Demonstration Unit was controlled at an average value of 540 KSCFH during this time.

Sufficient quantities of the syngas stream that contains primarily carbon monoxide (Carbon Monoxide Gas, or CO Gas) became available during the quarter, which allowed for CO-rich test cases to be performed. Cases at a ratio of hydrogen (H<sub>2</sub>) to CO in the reactor feed gas of approximately 0.7 were tested between 07 February 2002 and 19 February 2002. During these test dates, heat and material balances were generated for periods of at least 12 hours of steady operation.

A catalyst deactivation rate of 0.72% per day was calculated for the period 04 January 2002 to 14 January 2002 (11 days). A catalyst deactivation rate of 0.71% per day was calculated for the period 08 February 2002 to 18 February 2002 (11 days), during which the reactor inlet gas with a H<sub>2</sub>/CO ratio of 0.7:1 was fed to the LPMEOH™ Reactor. These are similar to the results that have been generally calculated over the past 2 years (averaging between 0.6% and 0.7% per day). As a basis of comparison, the calculated deactivation rate from the 4-month proof-of-

concept run at the LaPorte AFDU in 1988/89 was 0.4% per day (this run was performed on CO-rich syngas derived from natural gas at a reactor temperature of 250°C).

The first operating test using methanol synthesis catalyst activated in-situ (within the LPMEOH™ Reactor as opposed to the 29C-30 catalyst preparation vessel) was completed on 25 March 2002 when a catalyst withdrawal and addition campaign was undertaken to increase catalyst activity. A series of three withdrawals was conducted on 25 and 26 March 2002. Four batches of fresh catalyst were activated and added to the reactor between 27 March 2002 and 01 April 2002. After the fourth batch of freshly activated catalyst was transferred into the reactor, the catalyst inventory was calculated to be 40,904 pounds.

An assessment of the performance of the methanol synthesis catalyst following the completion of the in-situ activation procedure in August of 2001 was completed. Based on laboratory studies, it was found that storage of the fresh catalyst in the presence of mineral oil at elevated temperatures (the experiments were performed at approximately 200°C) prior to reduction was the cause of the lower than expected catalyst activity. During the August of 2001 in-situ activation at the LPMEOH™ Demonstration Unit, these conditions were present in the 29D-02 slurry tank, where batches of fresh catalyst slurry were stored during the catalyst loading procedure. Future modifications of the in-situ activation procedure will include eliminating the storage of the catalyst slurry at elevated temperature.

Analytical testing around the 29C-40 catalyst guard bed continued following the thermal regeneration procedure that was completed in the December of 2001. During the period of 20 December 2001 to 18 January 2002 (18 January 2002 represents 42 days of on-stream time since the regeneration), gas sampling was performed to assess the performance of the adsorbent (activated carbon impregnated with copper oxide). The analytical techniques involved analyzing the catalyst guard bed inlet and outlet streams for arsine (reported as arsine) using standard techniques. Initial performance was acceptable, as the average concentration of arsine across the guard bed was reduced from an inlet value of approximately 60 parts per billion by volume (ppbv) to a range of 5 to 6 ppbv. However, towards the end of the sampling period, the average concentration of arsine at the outlet of the catalyst guard bed was determined to be 14 ppbv, which indicated that the performance of the adsorbent was beginning to degrade.

A second thermal treatment of the adsorbent was completed between 04 February 2002 and 07 February 2002 to provide increased capacity for arsine removal. Analytical results from gas sampling indicated that this treatment was again successful in recovering arsine removal performance of the adsorbent; following the treatment, the average concentration of arsine was determined to be approximately 3 to 4 ppbv following the treatment.

As noted in Technical Progress Report No. 30, initial breakthrough of arsine from the adsorbent in the catalyst guard bed occurred after approximately two months of service. Based upon the decrease in the effective onstream time of the current charge of adsorbent, it was decided to replace the adsorbent in the catalyst guard bed with fresh material. The spent adsorbent was removed on 20 February 2002. The fresh copper impregnated activated carbon adsorbent was added to the catalyst guard bed on 21 February 2002. The material was successfully chemically reduced from 25 February 2002 to 27 February 2002 using

dilute syngas in nitrogen. (In this case, reduction refers to the reaction of the copper oxide with a reductant such as CO or H<sub>2</sub> to copper metal and either carbon dioxide [CO<sub>2</sub>] or water [H<sub>2</sub>O]). After reduction, the catalyst guard bed was pressurized with syngas to full header pressure (approximately 770 psig) without incident. The catalyst guard bed was not placed in service until 08 March 2002 until a damaged manual valve around the vessel could be repaired. Initial performance following the replacement of the adsorbent was acceptable, as the average concentration of arsine was reduced from an inlet value of approximately 55 ppbv to 3 ppbv.

Analyses of catalyst samples to determine changes in physical characteristics and levels of poisons have continued. Chemical analysis of catalyst samples has indicated the presence of all expected crystal phases. This analysis has indicated a significant increase in iron on the catalyst since the start of this current catalyst campaign. Efforts have been initiated to confirm whether the iron is present in the Balanced Gas feed to the unit or if the iron is being generated within the piping and equipment of the LPMEOH™ Demonstration Unit.

The performance of the gas sparger, which was designed by Air Products and first installed into the LPMEOH™ Reactor prior to the restart of the LPMEOH™ Demonstration Unit in March of 1999, was monitored. The device had been inspected and cleaned during the biennial outage in March of 2001. The sparger resistance continues to show no significant increase over time, which is consistent with the operating history with this device. The performance of the sparger will continue to be monitored closely for any changes.

During the reporting period, a total of 4,013,169 gallons of methanol was produced at the LPMEOH™ Demonstration Unit. Since startup, about 91.9 million gallons of methanol have 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.

A Topical Report entitled “Off-Site Testing of Stabilized Methanol from the Liquid Phase Methanol (LPMEOH™) Process” was issued during the reporting period. This report provides the results from the seven test sites.

Activities associated with Design Verification Testing (DVT) of the Liquid Phase Dimethyl Ether (LPDME) Process have been completed. An initial draft of a Topical Report (January 2002) on the status of the current market for DME and an outlook on potential market developments through 2006 was submitted to DOE for review and comment. Following receipt of comments, a revision (March 2002) was also issued during the reporting period.

A letter was sent to DOE (dated 01 February 2002) requesting an in-scope technical redirection of funds from tasks that have been completed. This funding would be used for continued operation of the LPMEOH™ Demonstration Facility so that the tests described in the April of 2000 no-cost time extension to the Cooperative Agreement can be completed, and that a potential second attempt to perform the in-situ catalyst activation procedure can be performed. DOE approved the request in a letter to Air Products dated 08 March 2002. Based upon the results of the laboratory assessment of the results of the ongoing catalyst

performance, changes to the operating procedure are being prepared so that a second in-situ activation of methanol synthesis catalyst can be performed.

A draft report on publicly available technical data on the Eastman chemicals-from-coal complex in Kingsport was submitted to DOE for review and comment. This report provides operational performance of the chemical-from-coal complex in Kingsport as well as specific data on the major feed and effluent streams for the coal gasification and syngas cleanup systems.

One hundred percent (100%) 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 March 2002. Ninety percent (90%) of the \$158 million of funds for the Phase 3 tasks have been expended (as invoiced), as of 31 March 2002.

## Table of Contents

Abstract .....	2
Acronyms and Definitions.....	7
Executive Summary .....	9
A. Introduction.....	14
B. Project Description.....	14
C. Process Description.....	15
D. Results and Discussion.....	16
D.1 Off-Site Testing (Product-Use Demonstration) .....	16
D.2 DME Design Verification Testing.....	16
D.3 LPMEOH™ Process Demonstration Unit - Methanol Operation.....	17
D.4 Planning and Administration .....	22
E. Planned Activities for the Next Quarter .....	23
F. Conclusion .....	23
APPENDICES .....	27
APPENDIX A - SIMPLIFIED PROCESS FLOW DIAGRAM.....	27
APPENDIX B - SAMPLES OF DETAILED MATERIAL BALANCE REPORTS .....	28
APPENDIX C - RESULTS OF DEMONSTRATION UNIT OPERATION .....	29
APPENDIX D - MILESTONE SCHEDULE STATUS AND COST MANAGEMENT REPORTS .....	34

## ACRONYMS AND DEFINITIONS

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
Btu	-	British Thermal Unit
Carbon Monoxide Gas	-	A syngas containing primarily carbon monoxide (CO); also called CO Gas
Catalyst Activity	-	the rate at which the catalyst promotes the desired chemical reaction to proceed within the limitations of chemical equilibrium
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 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)
MW	-	molecular weight, pound per pound mole



## ACRONYMS AND DEFINITIONS (cont'd)

NEPA	-	National Environmental Policy Act
OSHA	-	Occupational Safety and Health Administration
$\rho$	-	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
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 <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 Unit and the Eastman Facility
TPD	-	Ton(s) per Day
V	-	volumetric flowrate, thousand standard cubic feet per hour
VOC	-	volatile organic compound
vol%	-	volume %
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 was 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 operating test phase and the completed off-site product-use test program have been developed to 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 has also completed design verification testing (DVT), including laboratory- and pilot-scale research and market verification studies, to evaluate whether to include a demonstration of the production of dimethyl ether (DME) as a mixed coproduct with methanol. 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 95.48% availability during this quarter. A 54-hour forced outage was taken from 24 February 2002 to 27 February 2002 so that the reduction of a fresh charge of adsorbent for the 29C-40 catalyst guard bed could be completed. A 4.5-hour forced outage on 14 March 2002 was caused by an upset in the Balanced Gas flow; this resulted in an automatic plant shutdown that was initiated by a high level trip on the 29C-02 steam drum. A third forced outage (38.7 hours duration) began on 27 March 2002, during the process to remove spent catalyst slurry from the LPMEOH™ Reactor prior to the addition of freshly activated catalyst. Due to the low level of activity of the remaining inventory of catalyst, the LPMEOH™ Reactor was unable to sustain operation; the unit was able to be restarted after the first fresh batch of catalyst was activated

and added. There was also a short syngas interruption that was experienced on 18 January 2002 (7.2 hours).

As part of the operating protocol following the completion of the in-situ activation of methanol synthesis catalyst in the LPMEOH™ Reactor, temperature programming continued during the quarter; this involved the increase of reactor temperature as necessary to control the reactor purge flowrate and maintain reactor productivity. On 15 January 2002, the reactor temperature was increased from 226°C to 228°C; on 21 January 2002, the reactor temperature was increased to 230°C; on 02 February 2002, the reactor temperature was increased to 235°C; on 21 February 2002, the reactor temperature was increased to 238°C; on 27 February 2002, the reactor temperature was increased to 240°C; on 04 March 2002, the reactor temperature was increased to 245°C; and, on 11 March 2002, the reactor temperature was increased to the final temperature of 250°C (250°C is the design temperature for the LPMEOH™ Demonstration Unit). The reactor pressure was maintained at 700 psig during the reporting period. The flowrate of the primary syngas feed (Balanced Gas) to the LPMEOH™ Demonstration Unit was controlled at an average value of 540 KSCFH during this time.

Sufficient quantities of the syngas stream that contains primarily carbon monoxide (Carbon Monoxide Gas, or CO Gas) became available during the quarter, which allowed for CO-rich test cases to be performed. Cases at a ratio of hydrogen (H<sub>2</sub>) to CO in the reactor feed gas of approximately 0.7 were tested between 07 February 2002 and 19 February 2002. During these test dates, heat and material balances were generated for periods of at least 12 hours of steady operation.

A catalyst deactivation rate of 0.72% per day was calculated for the period 04 January 2002 to 14 January 2002 (11 days). A catalyst deactivation rate of 0.71% per day was calculated for the period 08 February 2002 to 18 February 2002 (11 days), during which the reactor inlet gas with a H<sub>2</sub>/CO ratio of 0.7:1 was fed to the LPMEOH™ Reactor. These are similar to the results that have been generally calculated over the past 2 years (averaging between 0.6% and 0.7% per day). As a basis of comparison, the calculated deactivation rate from the 4-month proof-of-concept run at the LaPorte AFDU in 1988/89 was 0.4% per day (this run was performed on CO-rich syngas derived from natural gas at a reactor temperature of 250°C).

The first operating test using methanol synthesis catalyst activated in-situ (within the LPMEOH™ Reactor as opposed to the 29C-30 catalyst preparation vessel) was completed on 25 March 2002 when a catalyst withdrawal and addition campaign was undertaken to increase catalyst activity. A series of three withdrawals was conducted on 25 and 26 March 2002. Four batches of fresh catalyst were activated and added to the reactor between 27 March 2002 and 01 April 2002. After the fourth batch of freshly activated catalyst was transferred into the reactor, the catalyst inventory was calculated to be 40,904 pounds.

An assessment of the performance of the methanol synthesis catalyst following the completion of the in-situ activation procedure in August of 2001 was completed. Based on laboratory studies, it was found that storage of the fresh catalyst in the presence of mineral oil at elevated temperatures (the experiments were performed at approximately 200°C) prior to reduction was the cause of the lower than expected catalyst activity. During the August of

2001 in-situ activation at the LPMEOH™ Demonstration Unit, these conditions were present in the 29D-02 slurry tank, where batches of fresh catalyst slurry were stored during the catalyst loading procedure. In the laboratory experiments, the copper oxide component of the methanol synthesis catalyst reacted with the mineral oil to produce carbon dioxide (CO<sub>2</sub>). Upon activation of the catalyst, the resultant methanol synthesis activity was about half of its expected value, which was similar to results from the LPMEOH™ Demonstration Unit. Analysis of the resulting slurry has indicated that the lower activity of the catalyst is most likely due to sintering. Future modifications of the in-situ activation procedure will include eliminating the storage of the catalyst slurry at elevated temperature.

Analytical testing around the 29C-40 catalyst guard bed continued following the thermal regeneration procedure that was completed in the December of 2001. During the period of 20 December 2001 to 18 January 2002 (18 January 2002 represents 42 days of on-stream time since the regeneration), gas sampling was performed to assess the performance of the adsorbent (activated carbon impregnated with copper oxide). The analytical techniques involved analyzing the catalyst guard bed outlet stream for arsenic (reported as arsine) using standard techniques. Initial performance was acceptable, as the average concentration of arsine across the guard bed was reduced from an inlet value of approximately 60 parts per billion by volume (ppbv) to a range of 5 to 6 ppbv. However, towards the end of the sampling period, the average concentration of arsine at the outlet of the catalyst guard bed was determined to be 14 ppbv, which indicated that the performance of the adsorbent was beginning to degrade.

A second thermal treatment of the adsorbent was completed between 04 February 2002 to 07 February 2002 to provide increased capacity for arsine removal. Analytical results from gas sampling of the outlet stream from the catalyst guard bed indicated that this treatment was again successful in recovering arsine removal performance of the adsorbent; the average concentration of arsine was determined to be approximately 3 to 4 ppbv following the treatment.

As noted in Technical Progress Report No. 30, initial breakthrough of arsine from the adsorbent in the catalyst guard bed occurred after approximately two months of service. Based upon the decrease in the effective onstream time of the current charge of adsorbent, it was decided to replace the adsorbent in the catalyst guard bed with fresh material. The spent adsorbent was removed on 20 February 2002. The fresh copper impregnated activated carbon adsorbent was added to the catalyst guard bed on 21 February 2002. The material was successfully chemically reduced from 25 February 2002 to 27 February 2002 using dilute syngas in nitrogen. (In this case, reduction refers to the reaction of the copper oxide with a reductant such as CO or H<sub>2</sub> to copper metal and either CO<sub>2</sub> or water [H<sub>2</sub>O]). After reduction, the catalyst guard bed was pressurized with syngas to full header pressure (approximately 770 psig) without incident. The catalyst guard bed was not placed in service until 08 March 2002 until a damaged manual valve around the vessel could be repaired. Initial performance following the replacement of the adsorbent was acceptable, as the average concentration of arsine was reduced from an inlet value of approximately 55 ppbv to 3 ppbv.

Analyses of catalyst samples to determine changes in physical characteristics and levels of poisons have continued. Chemical analysis of catalyst samples has indicated the presence of all expected crystal phases. This analysis has indicated a significant increase in iron on the catalyst since the start of this current catalyst campaign. Efforts have been initiated to confirm whether the iron is present in the Balanced Gas feed to the unit or if the iron is being generated within the piping and equipment of the LPMEOH™ Demonstration Unit.

The performance of the gas sparger, which was designed by Air Products and first installed into the LPMEOH™ Reactor prior to the restart of the LPMEOH™ Demonstration Unit in March of 1999, was monitored. The device had been inspected and cleaned during the biennial outage in March of 2001. The sparger resistance continues to show no significant increase over time, which is consistent with the operating history with this device. The performance of the sparger will continue to be monitored closely for any changes.

During the reporting period, a total of 4,013,169 gallons of methanol was produced at the LPMEOH™ Demonstration Unit. Since startup, about 91.9 million gallons of methanol have 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.

A Topical Report entitled “Off-Site Testing of Stabilized Methanol from the Liquid Phase Methanol (LPMEOH™) Process” was issued during the reporting period. This report provides the results from the seven test sites.

Activities associated with Design Verification Testing (DVT) of the Liquid Phase Dimethyl Ether (LPDME) Process have been completed. An initial draft of a Topical Report (January 2002) on the status of the current market for DME and an outlook on potential market developments through 2006 was submitted to DOE for review and comment. Following receipt of comments, a revision (March 2002) was also issued during the reporting period.

A letter was sent to DOE (dated 01 February 2002) requesting an in-scope technical redirection of funds from tasks that have been completed. This funding would be used for continued operation of the LPMEOH™ Demonstration Facility so that the tests described in the April of 2000 no-cost time extension to the Cooperative Agreement can be completed, and that a potential second attempt to perform the in-situ catalyst activation procedure can be performed. DOE approved the request in a letter to Air Products dated 08 March 2002. Based upon the results of the laboratory assessment of the results of the ongoing catalyst performance, changes to the operating procedure are being prepared so that a second in-situ activation of methanol synthesis catalyst can be performed.

A draft report on publicly available technical data on the Eastman chemicals-from-coal complex in Kingsport was submitted to DOE for review and comment. This report provides operational performance of the chemical-from-coal complex in Kingsport as well as specific data on the major feed and effluent streams for the coal gasification and syngas cleanup systems.

One hundred percent (100%) 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 March 2002. Ninety percent (90%) of the \$158 million of funds for the Phase 3 tasks have been expended (as invoiced), as of 31 March 2002.

## **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 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 has been demonstrating 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 has also evaluated the demonstration of the production of dimethyl ether (DME) as a mixed coproduct with methanol.

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<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 has been used 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)***

The LPMEOH<sup>TM</sup> Demonstration Project has completed the testing of stabilized methanol from both the LaPorte AFDU and the Kingsport LPMEOH<sup>TM</sup> Demonstration Unit in various off-site mobile and stationary applications. The product-use test program was 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<sup>TM</sup> 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 can be demonstrated.

Product-use tests commenced during the first year of demonstration operations. An inventory of approximately 12,000 gallons of stabilized methanol was produced at LPMEOH<sup>TM</sup> Demonstration Unit in February 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 produced and held at the LaPorte AFDU. The stabilized methanol from the February 1998 production campaign has been stored in an offsite facility; during the reporting period, the unused stabilized methanol was returned to Eastman for further distillation prior to use within the chemicals-from-coal complex.

A Topical Report entitled "Off-Site Testing of Stabilized Methanol from the Liquid Phase Methanol (LPMEOH<sup>TM</sup>) Process" was issued during the reporting period. This report provides the results from the seven test sites.

### ***D.2 DME Design Verification Testing***

The LPMEOH<sup>TM</sup> Demonstration Project has completed Design Verification Testing (DVT) to coproduce dimethyl ether (DME) with methanol via the Liquid Phase Dimethyl Ether (LPDME) Process. DVT was required to provide additional data for engineering design and evaluation of the potential for demonstration at the LPMEOH<sup>TM</sup> Demonstration Unit. The essential steps required for decision-making were: 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.

Execution of the LPDME DVT at the LaPorte AFDU was completed during October and November of 1999, and preliminary results from the operation were presented in Technical Progress Report No. 22. Results from a cost estimate for a commercial-scale LPDME plant were presented in Technical Progress Report No. 23. After discussing the results from the LPDME DVT activities and the ongoing performance results from Kingsport, the project participants agreed that the available resources should be directed toward improving the catalyst performance for the LPMEOH™ Process during the remaining time within the operating program; any improvement in the catalyst performance for the methanol synthesis catalyst will also yield benefits for the LPDME catalyst system.

A Topical Report, which presents the results of the DVT at the LaPorte AFDU, has been issued (March 2001).

An initial draft of a Topical Report (January 2002) on the status of the current market for DME and an outlook on potential market developments through 2006 was submitted to DOE for review and comment. Following receipt of comments, a revision (March 2002) was also issued during the reporting period.

### ***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 B 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 4,013,169 gallons of methanol was produced at the LPMEOH™ Demonstration Unit. Eastman accepted this entire 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 95.48% availability during this quarter. Appendix C, Table 1 contains the summary of outages for the LPMEOH™ Demonstration Unit during this quarter. A 54-hour forced outage was taken from 24 February 2002 to 27 February 2002 so that the reduction of a fresh charge of adsorbent for the 29C-40 catalyst guard bed could be completed. A 4.5-hour forced outage on 14 March 2002 was caused by an upset in the Balanced Gas flow; this resulted in an automatic plant shutdown that was initiated by a high level trip on the 29C-02 steam drum. A third forced outage (38.7 hours duration) began on 27 March 2002, during the process to remove spent catalyst slurry from the LPMEOH™ Reactor prior to the addition of freshly activated catalyst. Due to the low level of activity of the remaining inventory of catalyst, the LPMEOH™ Reactor was unable to sustain operation; the unit was able to be restarted after the first fresh batch of catalyst was

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

Case	Date	Days On Stream	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		Raw		U			
																		O-T-M Conv. (%)	Syngas Util. (SCF/lb)	MeOH Prod. (TPD)	Catalyst MeOH Prod. (gmol/hr-kg)	Reactor Vol. Prod. (TPD/r3)	Overall (Btu hr ft2 F)	Sparger dP (psi)	Sparger Resist. ("K")
2000-8	1-Jan-02	130	Balanced	226	700	629	2,233	2.72	87.4	0.65	4006	38.6	26.5	53.0	41,580	0.332	24.7	17.4	43.0	175.8	11.02	0.079	127	6.88	6.83
2000-8	2-Jan-02	131	Balanced	226	700	600	2,280	2.67	61.8	0.66	4039	38.8	25.6	52.0	41,580	0.327	24.3	17.2	41.3	174.5	10.94	0.080	127	7.02	6.60
2000-8	3-Jan-02	132	Balanced	226	700	605	2,276	2.68	63.4	0.66	4023	39.4	27.2	52.0	41,580	0.332	24.5	17.4	41.2	176.1	11.04	0.081	134	7.00	6.75
2000-8	4-Jan-02	133	Balanced	226	700	575	2,309	2.65	61.6	0.66	4033	39.2	26.7	52.0	41,580	0.306	22.8	16.3	41.8	165.1	10.35	0.076	120	6.91	6.56
2000-8	5-Jan-02	134	Balanced	226	700	550	2,334	2.65	58.8	0.65	4011	37.4	24.2	54.0	41,580	0.291	21.9	15.6	41.8	157.7	9.89	0.069	106	6.61	6.32
2000-8	6-Jan-02	135	Balanced	226	700	550	2,290	2.79	62.8	0.65	3982	37.7	25.0	54.0	41,580	0.290	22.3	15.4	42.4	155.6	9.76	0.069	107	6.55	6.66
2000-8	7-Jan-02	136	Balanced	226	700	549	2,295	2.84	63.4	0.65	3975	38.7	28.1	54.0	41,580	0.293	22.8	15.6	42.0	156.8	9.83	0.069	111	6.62	6.83
2000-8	8-Jan-02	137	Balanced	226	700	555	2,339	2.56	63.9	0.65	4020	38.5	26.1	54.0	41,580	0.290	21.3	15.6	42.0	158.7	9.95	0.070	110	6.84	6.51
2000-8	9-Jan-02	138	Balanced	226	700	550	2,317	2.56	68.5	0.65	4011	38.8	25.6	52.0	41,580	0.283	20.8	15.2	42.6	155.1	9.73	0.071	108	7.30	6.93
2000-8	10-Jan-02	139	Balanced	226	700	545	2,315	2.54	71.0	0.65	4003	37.3	21.8	52.5	41,580	0.280	20.7	15.2	42.4	154.2	9.67	0.070	102	6.31	5.99
2000-8	12-Jan-02	141	Balanced	226	700	547	2,311	2.52	74.1	0.65	3985	36.6	23.0	55.0	41,580	0.278	20.4	15.1	43.0	152.9	9.59	0.066	100	6.84	6.60
2000-8	13-Jan-02	142	Balanced	226	700	550	2,290	2.56	75.2	0.65	3975	38.8	25.7	52.0	41,580	0.280	20.7	15.2	43.0	153.5	9.63	0.070	108	6.99	6.83
2000-8	14-Jan-02	143	Balanced	226	700	550	2,283	2.68	73.7	0.65	3957	38.9	25.9	52.0	41,580	0.282	21.6	15.3	42.8	154.0	9.66	0.071	114	6.37	6.41
2000-8	16-Jan-02	145	Balanced	228	700	550	2,273	2.80	61.2	0.65	3948	37.4	25.5	55.0	41,580	0.278	23.0	15.8	42.0	157.3	9.86	0.072	115	6.51	6.58
2000-8	17-Jan-02	146	Balanced	228	700	555	2,263	2.81	61.1	0.64	3932	37.5	24.4	54.0	41,580	0.282	23.5	16.1	41.6	160.0	10.03	0.070	114	6.14	6.23
2000-8	19-Jan-02	148	Balanced	228	700	575	2,287	2.70	71.4	0.65	3967	38.7	25.9	52.5	41,580	0.280	22.7	16.2	42.9	160.8	10.08	0.073	118	6.75	6.65
2000-8	24-Jan-02	153	Balanced	230	700	555	2,205	3.24	69.6	0.63	3849	38.6	30.0	56.0	41,580	0.267	25.9	16.1	42.8	155.7	9.76	0.066	115	6.32	7.21
2000-8	25-Jan-02	154	Balanced	230	700	565	2,227	3.10	73.6	0.64	3893	37.7	26.9	55.5	41,580	0.270	25.2	16.2	42.8	158.5	9.94	0.068	115	6.38	6.99
2000-8	26-Jan-02	155	Balanced	230	700	558	2,240	3.07	72.2	0.64	3910	37.6	25.2	54.5	41,580	0.267	24.4	15.8	42.9	155.9	9.78	0.068	111	6.32	6.63
2000-8	27-Jan-02	156	Balanced	230	700	559	2,261	2.89	70.1	0.65	3929	36.4	20.8	54.0	41,580	0.267	23.6	16.0	42.4	158.2	9.92	0.070	113	5.95	6.17
2000-8	28-Jan-02	157	Balanced	230	700	548	2,287	2.66	72.5	0.65	3963	36.9	21.6	53.5	41,580	0.254	21.5	15.3	42.9	153.3	9.62	0.068	105	6.52	6.36
2000-8	29-Jan-02	158	Balanced	230	700	543	2,292	2.59	71.9	0.65	3961	38.0	23.7	52.5	41,580	0.251	20.9	15.2	42.9	151.9	9.53	0.069	105	6.84	6.58
2000-8	30-Jan-02	159	Balanced	231	700	550	2,288	2.61	77.4	0.65	3961	37.6	22.4	52.5	41,580	0.249	20.9	15.1	43.6	151.4	9.50	0.069	102	6.86	6.64
2000-8	31-Jan-02	160	Balanced	231	700	550	2,254	2.92	85.0	0.65	3922	37.6	20.9	51.5	41,580	0.249	21.7	15.0	44.2	149.3	9.37	0.069	97	6.46	6.64
2000-8	1-Feb-02	161	Balanced	230	700	547	2,282	2.71	76.5	0.65	3948	39.7	28.6	52.5	41,580	0.249	21.2	15.0	43.7	150.3	9.43	0.068	108	7.11	7.24
2000-8	2-Feb-02	162	Balanced	230	700	550	2,263	2.98	82.7	0.65	3919	36.9	23.8	55.0	41,580	0.257	22.7	15.1	44.0	150.0	9.41	0.065	107	6.07	6.67
2000-8	3-Feb-02	163	Balanced	230	700	575	2,246	2.94	86.9	0.64	3916	37.8	24.6	53.5	41,580	0.258	22.5	15.1	45.9	150.2	9.42	0.067	110	6.06	6.66
2000-8	5-Feb-02	165	Balanced	235	700	548	2,171	3.32	64.7	0.64	3881	38.1	21.3	51.0	41,580	0.248	26.1	16.0	42.0	156.6	9.82	0.073	108	5.56	6.47
2000-5	8-Feb-02	168	H2:CO = 0.7	235	693	495	2,393	0.54	95.7	0.68	4043	39.7	27.5	52.0	41,580	0.263	8.0	12.1	45.7	130.2	8.17	0.060	98	10.89	5.93
2000-5	11-Feb-02	171	H2:CO = 0.7	235	695	501	2,425	0.66	101.7	0.68	4077	38.4	26.5	54.0	41,580	0.287	7.8	11.7	46.5	129.1	8.10	0.057	97	11.03	6.09
2000-5	12-Feb-02	172	H2:CO = 0.7	235	695	497	2,407	0.68	101.8	0.68	4056	39.2	23.8	50.5	41,580	0.281	7.7	11.4	47.7	125.0	7.85	0.057	88	10.73	6.01
2000-5	13-Feb-02	173	H2:CO = 0.7	235	699	494	2,406	0.69	105.4	0.67	4054	39.2	24.6	51.0	41,580	0.278	7.8	11.6	46.6	127.0	7.80	0.059	92	10.75	6.10
2000-5	15-Feb-02	175	H2:CO = 0.7	235	700	496	2,393	0.65	100.5	0.67	4037	38.1	21.3	51.0	41,580	0.270	8.3	12.1	46.2	128.8	8.09	0.060	97	10.64	5.94
2000-5	16-Feb-02	176	H2:CO = 0.7	236	700	495	2,377	0.70	99.4	0.67	4018	38.3	26.5	54.0	41,580	0.266	8.3	12.3	45.9	129.2	8.11	0.057	98	11.09	6.14
2000-5	17-Feb-02	177	H2:CO = 0.7	235	700	497	2,384	0.73	101.0	0.67	4025	39.0	22.6	50.0	41,580	0.258	8.4	12.2	46.5	128.2	8.05	0.061	96	10.70	6.05
2000-5	18-Feb-02	178	H2:CO = 0.7	235	700	485	2,371	0.71	99.8	0.67	4013	38.5	24.0	52.0	41,580	0.253	8.1	11.8	46.5	125.2	7.86	0.057	100	10.59	6.00
2000-8	19-Feb-02	179	Balanced	235	700	543	2,160	2.98	81.2	0.62	3755	39.0	22.5	50.0	41,580	0.229	24.0	15.8	43.8	149.0	9.34	0.071	112	6.67	7.34
2000-8	20-Feb-02	180	Balanced	235	700	547	2,139	2.88	88.9	0.62	3733	36.2	17.4	52.5	41,580	0.226	23.6	15.9	44.3	148.0	9.29	0.067	107	6.67	7.15
2000-8	21-Feb-02	181	Balanced	235	700	553	2,163	2.79	96.4	0.63	3768	37.0	17.8	51.0	41,580	0.221	22.5	15.5	45.2	146.7	9.21	0.069	112	6.82	7.27
2000-8	23-Feb-02	183	Balanced	238	700	550	2,202	2.91	87.4	0.63	3797	40.0	23.9	49.0	41,580	0.206	23.0	15.5	44.7	147.6	9.26	0.072	109	6.65	7.17
2000-8	2-Mar-02	190	Balanced	240	700	546	2,201	2.78	114.3	0.64	3811	40.0	27.5	51.5	41,580	0.181	21.2	14.7	46.9	139.7	8.77	0.065	117	7.29	7.39
2000-8	3-Mar-02	191	Balanced	240	700	544	2,219	2.72	115.8	0.65	3850	38.8	24.6	52.0	41,580	0.177	20.5	14.5	46.7	139.7	8.76	0.064	118	8.82	8.78
2000-8	4-Mar-02	192	Balanced	246	700	548	2,226	2.83	90.9	0.66	3880	39.4	26.0	52.0	41,580	0.166	21.8	15.0	45.2	145.3	9.11	0.067	110	6.76	6.76
2000-8	5-Mar-02	193	Balanced	246	700	545	2,221	2.76	97.8	0.66	3860	39.2	22.3	50.0	41,580	0.162	21.4	14.9	45.6	143.6	9.01	0.068	111	6.53	6.46
2000-8	6-Mar-02	194	Balanced	247	700	545	2,218	2.76	104.0	0.65	3841	36.6	23.8	56.5	41,580	0.157	21.2	14.8	46.2	141.5	8.88	0.060	95	6.70	6.59
2000-8	7-Mar-02	195	Balanced	247	700	547	2,200	2.80	110.3	0.65	3810	37.3	22.4	54.0	41,580	0.157	21.5	14.8	46.8	140.2	8.80	0.062	103	6.78	6.78
2000-8	8-Mar-02	196	Balanced	245	700	542	2,183	2.82	110.8	0.64	3773	36.6	18.6	53.0	41,580	0.159	21.3	14.6	47.4	137.0	8.61	0.062	110	6.31	6.39
2000-8	9-Mar-02	197	Balanced	245	700	543	2,198	2.66	113.3	0.65	3811	40.9	30.3	52.0	41,580	0.158	20.4	14.5	47.3	137.7	8.65	0.063	111	8.52	8.30
2000-8	10-Mar-02	198	Balanced	245	700	547	2,223	2.64	117.1	0.65	3855	39.5	25.0	51.0	41,580	0.154	19.7	14.2	47.9	137.2	8.61	0.064</			

**Table D.3-1. Data Summary for LPMEOH™ Demonstration Unit (continued)**

Case	Date	Days On Stream	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			Raw		U		
																		O-T-M Conv. (%)	Syngas Util. (SCF/lb)	MeOH Prod. (TPD)	Catalyst MeOH Prod. (gmol/hr-kg)	Reactor Vol. Prod. (TPD/r3)	Overall (Btu hr ft2 F)	Sparger dP (psi)	Sparger Resist. ("K")
2000-8	15-Mar-02	#REF!	Balanced	250	700	547	2,241	2.76	135.5	0.66	3849	39.8	18.1	46.5	41,580	0.137	19.8	13.7	50.6	129.9	8.17	0.067	117	6.68	6.09
2000-8	16-Mar-02	#REF!	Balanced	250	700	546	2,250	2.73	140.2	0.66	3863	42.2	25.3	46.5	41,580	0.137	19.0	13.3	50.5	129.7	8.15	0.067	109	7.47	7.26
2000-8	17-Mar-02	#REF!	Balanced	250	700	556	2,208	2.67	128.0	0.66	3834	39.8	24.0	50.0	41,580	0.144	19.9	14.2	49.0	136.2	8.56	0.065	115	7.21	7.01
2000-8	18-Mar-02	#REF!	Balanced	250	700	559	1,916	2.65	139.5	0.59	3426	38.9	17.8	48.0	41,580	0.145	21.7	15.5	50.1	134.0	8.42	0.067	108	5.68	6.91
2000-8	19-Mar-02	#REF!	Balanced	250	700	551	2,012	2.61	138.6	0.61	3558	40.3	18.7	46.0	41,580	0.142	20.6	14.8	50.0	132.2	8.31	0.069	109	5.95	6.56
2000-8	20-Mar-02	#REF!	Balanced	250	700	553	2,179	2.62	136.7	0.65	3788	44.5	29.4	45.0	41,580	0.139	19.5	14.0	49.9	132.9	8.35	0.070	118	7.65	7.49
2000-8	21-Mar-02	#REF!	Balanced	251	700	503	2,251	2.75	103.4	0.65	3816	48.3	38.8	45.0	41,580	0.130	19.2	13.4	47.1	128.1	8.04	0.068	111	8.74	8.79
2000-8	22-Mar-02	#REF!	Balanced	251	700	505	2,556	2.72	108.0	0.66	3869	40.5	17.7	45.0	41,580	0.126	18.5	13.1	48.1	126.2	7.92	0.067	107	6.42	6.48
2000-8	23-Mar-02	#REF!	Balanced	251	700	507	2,246	2.87	106.6	0.65	3814	40.2	19.2	44.5	41,580	0.128	18.4	13.3	47.8	127.2	7.98	0.068	112	6.33	6.24
2000-8	24-Mar-02	#REF!	Balanced	250	700	506	2,224	2.62	120.6	0.65	3780	41.4	17.7	43.5	41,580	0.126	18.0	13.0	49.6	122.4	7.69	0.067	115	6.79	6.66
2000-8	31-Mar-02	#REF!	Balanced	235	700	589	2,325	2.32	84.0	0.61	3926	39.1	20.9	45.5	38,704	0.269	22.3	17.5	43.4	162.8	10.97	0.085	129	6.22	6.68

activated and added. There was also a short syngas interruption that was experienced on 18 January 2002 (7.2 hours).

#### Catalyst Life ( $\eta$ ) – January - March 2002

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 C, Figure 1 plots  $\log \eta$  versus days onstream for the third catalyst campaign (following the in-situ activation of methanol synthesis catalyst in the LPMEOH™ Reactor). 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 reactor temperature is changed.

As part of the operating protocol following the completion of the in-situ activation of methanol synthesis catalyst in the LPMEOH™ Reactor, temperature programming continued during the quarter; this involved the increase of reactor temperature as necessary to control the reactor purge flowrate and maintain reactor productivity. On 15 January 2002, the reactor temperature was increased from 226°C to 228°C; on 21 January 2002, the reactor temperature was increased to 230°C; on 02 February 2002, the reactor temperature was increased to 235°C; on 21 February 2002, the reactor temperature was increased to 238°C; on 27 February 2002, the reactor temperature was increased to 240°C; on 04 March 2002, the reactor temperature was increased to 245°C; and, on 11 March 2002, the reactor temperature was increased to the final temperature of 250°C (250°C is the design temperature for the LPMEOH™ Demonstration Unit). The reactor pressure was maintained at 700 psig during the reporting period. The flowrate of Balanced Gas was controlled at an average value of 540 KSCFH during this time.

Sufficient CO Gas became available during the quarter, which allowed for CO-rich test cases to be performed. Cases at a ratio of H<sub>2</sub> to CO in the reactor feed gas of approximately 0.7 were tested between 07 February and 19 February 2002. During these test dates, heat and material balances were generated for periods of at least 12 hours of steady operation.

A catalyst deactivation rate of 0.72% per day was calculated for the period 04 January 2002 to 14 January 2002 (11 days). A catalyst deactivation rate of 0.71% per day was calculated for the period 08 February 2002 to 18 February 2002 (11 days), during which the reactor inlet gas with a H<sub>2</sub>/CO ratio of 0.7:1 was fed to the LPMEOH™ Reactor. These are similar to the results that have been generally calculated over the past 2 years (averaging between 0.6% and 0.7% per day). As a basis of comparison, the calculated deactivation rate from the 4-month proof-of-concept run at the LaPorte AFDU in 1988/89 was 0.4% per day (this run was performed on CO-rich syngas derived from natural gas at a reactor temperature of 250°C).

The first operating test using methanol synthesis catalyst activated in-situ (within the LPMEOH™ Reactor as opposed to the 29C-30 catalyst preparation vessel) was completed on 25 March 2002 when a catalyst withdrawal and addition campaign was undertaken to increase catalyst activity. A series of three withdrawals was conducted on 25 and 26 March 2002. Four batches of fresh catalyst were activated and added to the reactor between 27

March 2002 and 01 April 2002. After the fourth batch of freshly activated catalyst was transferred into the reactor, the catalyst inventory was calculated to be 40,904 pounds.

An assessment of the performance of the methanol synthesis catalyst following the completion of the in-situ activation procedure in August of 2001 was completed. Based on laboratory studies, it was found that storage of the fresh catalyst in the presence of mineral oil at elevated temperatures (the experiments were performed at approximately 200°C) prior to reduction was the cause of the lower than expected catalyst activity. During the August of 2001 in-situ activation at the LPMEOH™ Demonstration Unit, these conditions were present in the 29D-02 slurry tank, where batches of fresh catalyst slurry were stored during the catalyst loading procedure. In the laboratory experiments, the copper oxide component of the methanol synthesis catalyst reacted with the mineral oil to produce CO<sub>2</sub>. Upon activation of the catalyst, the resultant methanol synthesis activity was about half of its expected value, which was similar to results from the LPMEOH™ Demonstration Unit. Analysis of the resulting slurry has indicated that the lower activity of the catalyst is most likely due to sintering. Future modifications of the in-situ activation procedure will include eliminating the storage of the catalyst slurry at elevated temperature.

Analyses of catalyst samples to determine changes in physical characteristics and levels of poisons have continued. Appendix C, Table 2 summarizes the results for the third catalyst campaign (following the completion of the in-situ catalyst activation procedure in August of 2001). Chemical analysis of catalyst samples has indicated the presence of all expected crystal phases. This analysis has indicated a significant increase in iron on the catalyst since the start of this current catalyst campaign. Efforts have been initiated to confirm whether the iron is present in the Balanced Gas feed to the unit or if the iron is being generated within the piping and equipment of the LPMEOH™ Demonstration Unit.

#### 29C-40 Catalyst Guard Bed Performance Monitoring and Assessment

Analytical testing around the 29C-40 catalyst guard bed continued following the thermal regeneration procedure that was completed in the December of 2001. During the period of 20 December 2001 to 18 January 2002 (18 January 2002 represents 42 days of on-stream time since the regeneration), gas sampling was performed to assess the performance of the adsorbent (activated carbon impregnated with copper oxide). The analytical techniques involved analyzing the catalyst guard bed outlet stream for arsine using standard techniques. Initial performance was acceptable, as the average concentration of arsine across the guard bed was reduced from an inlet value of approximately 60 parts per billion by volume (ppbv) to a range of 5 to 6 ppbv. However, towards the end of the sampling period, the average concentration of arsine at the outlet of the catalyst guard bed was determined to be 14 ppbv, which indicated that the performance of the adsorbent was beginning to degrade.

A second thermal treatment of the adsorbent was completed between 04 February 2002 to 07 February 2002 to provide increased capacity for arsine removal. Analytical results from gas sampling of the outlet stream from the catalyst guard bed indicated that this treatment was again successful in recovering arsine removal performance of the adsorbent; the average concentration of arsine was determined to be approximately 3 to 4 ppbv following the treatment.

As noted in Technical Progress Report No. 30, initial breakthrough of arsine from the adsorbent in the catalyst guard bed occurred after approximately two months of service. Based upon the decrease in the effective onstream time of the current charge of adsorbent, it was decided to replace the adsorbent in the catalyst guard bed with fresh material. The spent adsorbent was removed on 20 February 2002. The fresh copper impregnated activated carbon adsorbent was added to the catalyst guard bed on 21 February 2002. The material was successfully chemically reduced from 25 February 2002 to 27 February 2002 using dilute syngas in nitrogen. (In this case, reduction refers to the reaction of the copper oxide with a reductant such as CO or H<sub>2</sub> to copper metal and either CO<sub>2</sub> or H<sub>2</sub>O). After reduction, the catalyst guard bed was pressurized with syngas to full header pressure (approximately 770 psig) without incident. The catalyst guard bed was not placed in service until 08 March 2002 until a damaged manual valve around the vessel could be repaired. Initial performance following the replacement of the adsorbent was acceptable, as the average concentration of arsine was reduced from an inlet value of approximately 55 ppbv to 3 ppbv.

### Sparger Resistance

The performance of the gas sparger, which was designed by Air Products and first installed into the LPMEOH™ Reactor prior to the restart of the LPMEOH™ Demonstration Unit in March of 1999, was monitored. The device had been inspected and cleaned during the biennial outage in March of 2001. Appendix C, Figure 2 plots the average daily sparger resistance coefficient for the third catalyst campaign (which began with the completion of the in-situ catalyst activation procedure) until the end of the reporting period. The data for this plot, along with the corresponding average pressure drop, are also included in Table D.3-1. The sparger resistance continues to show no significant increase over time, which is consistent with the operating history with this device. The performance of the sparger will continue to be monitored closely for any changes.

### ***D.4 Planning and Administration***

A letter was sent to DOE (dated 01 February 2002) requesting an in-scope technical redirection of funds from tasks that have been completed. This funding would be used for continued operation of the LPMEOH™ Demonstration Facility so that the tests described in the April of 2000 no-cost time extension to the Cooperative Agreement can be completed, and that a potential second attempt to perform the in-situ catalyst activation procedure can be performed. DOE approved the request in a letter to Air Products dated 08 March 2002. Based upon the results of the laboratory assessment of the results of the ongoing catalyst performance, changes to the operating procedure are being prepared so that a second in-situ activation of methanol synthesis catalyst can be performed.

A draft report on publicly available technical data on the Eastman chemicals-from-coal complex in Kingsport was submitted to DOE for review and comment. This report provides operational performance of the chemical-from-coal complex in Kingsport as well as specific data on the major feed and effluent streams for the coal gasification and syngas cleanup systems.

The Milestone Schedule Status Report and the Cost Management Report, through the period ending 31 March 2002, are included in Appendix D. These two reports show the current schedule, the percentage completion and the latest cost forecast for each of the Work Breakdown Structure (WBS) tasks. One hundred percent (100%) 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 March 2002. Ninety percent (90%) of the \$158 million of funds for the Phase 3 tasks have been expended (as invoiced), as of 31 March 2002.

The monthly reports for January, February, and March were submitted. These reports include the Milestone Schedule Status Report, the Project Summary Report, and the Cost Management 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.
- Update operating procedures as necessary to the in-situ catalyst activation procedure and develop the schedule to complete this work by the end of June of 2002.
- Continue executing Phase 3, Task 2.1 Methanol Operation per the Demonstration Test Plan. Focus activities on monitoring catalyst activity, assessing the performance of the catalyst guard bed, and monitoring the performance of the gas sparger in the reactor.
- Schedule a Project Review Meeting with DOE.

#### **F. Conclusion**

The LPMEOH™ Demonstration Unit operated at 95.48% availability during this quarter. A 54-hour forced outage was taken from 24 February 2002 to 27 February 2002 so that the reduction of a fresh charge of adsorbent for the 29C-40 catalyst guard bed could be completed. A 4.5-hour forced outage on 14 March 2002 was caused by an upset in the Balanced Gas flow; this resulted in an automatic plant shutdown that was initiated by a high level trip on the 29C-02 steam drum. A third forced outage (38.7 hours duration) began on 27 March 2002, during the process to remove spent catalyst slurry from the LPMEOH™ Reactor prior to the addition of freshly activated catalyst. Due to the low level of activity of the remaining inventory of catalyst, the LPMEOH™ Reactor was unable to sustain operation; the unit was able to be restarted after the first fresh batch of catalyst was activated and added. There was also a short syngas interruption that was experienced on 18 January 2002 (7.2 hours).

As part of the operating protocol following the completion of the in-situ activation of methanol synthesis catalyst in the LPMEOH™ Reactor, temperature programming continued during the quarter; this involved the increase of reactor temperature as necessary



to control the reactor purge flowrate and maintain reactor productivity. On 15 January 2002, the reactor temperature was increased from 226°C to 228°C; on 21 January 2002, the reactor temperature was increased to 230°C; on 02 February 2002, the reactor temperature was increased to 235°C; on 21 February 2002, the reactor temperature was increased to 238°C; on 27 February 2002, the reactor temperature was increased to 240°C; on 04 March 2002, the reactor temperature was increased to 245°C; and, on 11 March 2002, the reactor temperature was increased to the final temperature of 250°C (250°C is the design temperature for the LPMEOH™ Demonstration Unit). The reactor pressure was maintained at 700 psig during the reporting period. The flowrate of Balanced Gas was controlled at an average value of 540 KSCFH during this time.

Sufficient CO Gas became available during the quarter, which allowed for CO-rich test cases to be performed. Cases at a ratio of H<sub>2</sub> to CO in the reactor feed gas of approximately 0.7 were tested between 07 February and 19 February 2002. During these test dates, heat and material balances were generated for periods of at least 12 hours of steady operation.

A catalyst deactivation rate of 0.72% per day was calculated for the period 04 January 2002 to 14 January 2002 (11 days). A catalyst deactivation rate of 0.71% per day was calculated for the period 08 February 2002 to 18 February 2002 (11 days), during which the reactor inlet gas with a H<sub>2</sub>/CO ratio of 0.7:1 was fed to the LPMEOH™ Reactor. These are similar to the results that have been generally calculated over the past 2 years (averaging between 0.6% and 0.7% per day). As a basis of comparison, the calculated deactivation rate from the 4-month proof-of-concept run at the LaPorte AFDU in 1988/89 was 0.4% per day (this run was performed on CO-rich syngas derived from natural gas at a reactor temperature of 250°C).

The first operating test using methanol synthesis catalyst activated in-situ (within the LPMEOH™ Reactor as opposed to the 29C-30 catalyst preparation vessel) was completed on 25 March 2002 when a catalyst withdrawal and addition campaign was undertaken to increase catalyst activity. A series of three withdrawals was conducted on 25 and 26 March 2002. Four batches of fresh catalyst were activated and added to the reactor between 27 March 2002 and 01 April 2002. After the fourth batch of freshly activated catalyst was transferred into the reactor, the catalyst inventory was calculated to be 40,904 pounds.

An assessment of the performance of the methanol synthesis catalyst following the completion of the in-situ activation procedure in August of 2001 was completed. Based on laboratory studies, it was found that storage of the fresh catalyst in the presence of mineral oil at elevated temperatures (the experiments were performed at approximately 200°C) prior to reduction was the cause of the lower than expected catalyst activity. During the August of 2001 in-situ activation at the LPMEOH™ Demonstration Unit, these conditions were present in the 29D-02 slurry tank, where batches of fresh catalyst slurry were stored during the catalyst loading procedure. In the laboratory experiments, the copper oxide component of the methanol synthesis catalyst reacted with the mineral oil to produce CO<sub>2</sub>. Upon activation of the catalyst, the resultant methanol synthesis activity was about half of its expected value, which was similar to results from the LPMEOH™ Demonstration Unit. Analysis of the resulting slurry has indicated that the lower activity of the catalyst is most likely due to sintering. Future modifications of the in-situ activation procedure will include eliminating the storage of the catalyst slurry at elevated temperature.

Analytical testing around the 29C-40 catalyst guard bed continued following the thermal regeneration procedure that was completed in the December of 2001. During the period of 20 December 2001 to 18 January 2002 (18 January 2002 represents 42 days of on-stream time since the regeneration), gas sampling was performed to assess the performance of the adsorbent (activated carbon impregnated with copper oxide). The analytical techniques involved analyzing the catalyst guard bed outlet stream for arsine using standard techniques. Initial performance was acceptable, as the average concentration of arsine across the guard bed was reduced from an inlet value of approximately 60 ppbv to a range of 5 to 6 ppbv. However, towards the end of the sampling period, the average concentration of arsine at the outlet of the catalyst guard bed was determined to be 14 ppbv, which indicated that the performance of the adsorbent was beginning to degrade.

A second thermal treatment of the adsorbent was completed between 04 February 2002 to 07 February 2002 to provide increased capacity for arsine removal. Analytical results from gas sampling of the outlet stream from the catalyst guard bed indicated that this treatment was again successful in recovering arsine removal performance of the adsorbent; the average concentration of arsine was determined to be approximately 3 to 4 ppbv following the treatment.

As noted in Technical Progress Report No. 30, initial breakthrough of arsine from the adsorbent in the catalyst guard bed occurred after approximately two months of service. Based upon the decrease in the effective onstream time of the current charge of adsorbent, it was decided to replace the adsorbent in the catalyst guard bed with fresh material. The spent adsorbent was removed on 20 February 2002. The fresh copper impregnated activated carbon adsorbent was added to the catalyst guard bed on 21 February 2002. The material was successfully chemically reduced from 25 February 2002 to 27 February 2002 using dilute syngas in nitrogen. After reduction, the catalyst guard bed was pressurized with syngas to full header pressure (approximately 770 psig) without incident. The catalyst guard bed was not placed in service until 08 March 2002 until a damaged manual valve around the vessel could be repaired. Initial performance following the replacement of the adsorbent was acceptable, as the average concentration of arsine was reduced from an inlet value of approximately 55 ppbv to 3 ppbv.

Analyses of catalyst samples to determine changes in physical characteristics and levels of poisons have continued. Chemical analysis of catalyst samples has indicated the presence of all expected crystal phases. This analysis has indicated a significant increase in iron on the catalyst since the start of this current catalyst campaign. Efforts have been initiated to confirm whether the iron is present in the Balanced Gas feed to the unit or if the iron is being generated within the piping and equipment of the LPMEOH™ Demonstration Unit.

The performance of the gas sparger, which was designed by Air Products and first installed into the LPMEOH™ Reactor prior to the restart of the LPMEOH™ Demonstration Unit in March of 1999, was monitored. The device had been inspected and cleaned during the biennial outage in March of 2001. The sparger resistance continues to show no significant increase over time, which is consistent with the operating history with this device. The performance of the sparger will continue to be monitored closely for any changes.

During the reporting period, a total of 4,013,169 gallons of methanol was produced at the LPMEOH™ Demonstration Unit. Since startup, about 91.9 million gallons of methanol have 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.

A Topical Report entitled “Off-Site Testing of Stabilized Methanol from the Liquid Phase Methanol (LPMEOH™) Process” was issued during the reporting period. This report provides the results from the seven test sites.

Activities associated with Design Verification Testing (DVT) of the LPDME Process have been completed. An initial draft of a Topical Report (January 2002) on the status of the current market for DME and an outlook on potential market developments through 2006 was submitted to DOE for review and comment. Following receipt of comments, a revision (March 2002) was also issued during the reporting period.

A letter was sent to DOE (dated 01 February 2002) requesting an in-scope technical redirection of funds from tasks that have been completed. This funding would be used for continued operation of the LPMEOH™ Demonstration Facility so that the tests described in the April of 2000 no-cost time extension to the Cooperative Agreement can be completed, and that a potential second attempt to perform the in-situ catalyst activation procedure can be performed. DOE approved the request in a letter to Air Products dated 08 March 2002. Based upon the results of the laboratory assessment of the results of the ongoing catalyst performance, changes to the operating procedure are being prepared so that a second in-situ activation of methanol synthesis catalyst can be performed.

A draft report on publicly available technical data on the Eastman chemicals-from-coal complex in Kingsport was submitted to DOE for review and comment. This report provides operational performance of the chemical-from-coal complex in Kingsport as well as specific data on the major feed and effluent streams for the coal gasification and syngas cleanup systems.

One hundred percent (100%) 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 March 2002. Ninety percent (90%) of the \$158 million of funds for the Phase 3 tasks have been expended (as invoiced), as of 31 March 2002.

## **APPENDICES**

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

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

## **APPENDIX C - RESULTS OF DEMONSTRATION UNIT OPERATION**

**Table 1 - Summary of LPMEOH™ Demonstration Unit Outages -  
January/March 2002**

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

**Figure 1 - Catalyst Age ( $\eta$ ): September 2001 - March 2002**

**Figure 2 - Sparger Resistance Coefficient vs. Days Onstream  
(September 2001 - March 2002)**

**Table 1**  
**Summary of LPMEOH™ Demonstration Unit Outages - January/March 2002**

Operation Start	Operation End	Operating Hours	Shutdown Hours	Reason for Shutdown
1/1/02 00:00	1/18/02 09:45	417.7	7.2	Syngas Outage
1/18/02 16:55	2/24/02 22:57	894.0	54.0	Guard Bed Adsorbent Reduction
2/27/02 05:00	3/14/02 01:30	356.5	4.5	Steam Drum High Level Trip
3/14/02 06:02	3/27/02 02:22	308.3	38.7	Catalyst Withdrawal / Low Activity
3/28/02 17:02	3/31/02 23:59	78.9		End of Reporting Period
Total Operating Hours			2055.6	
Syngas Available Hours			2152.8	
<b>Plant Availability, %</b>			<b>95.48</b>	

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

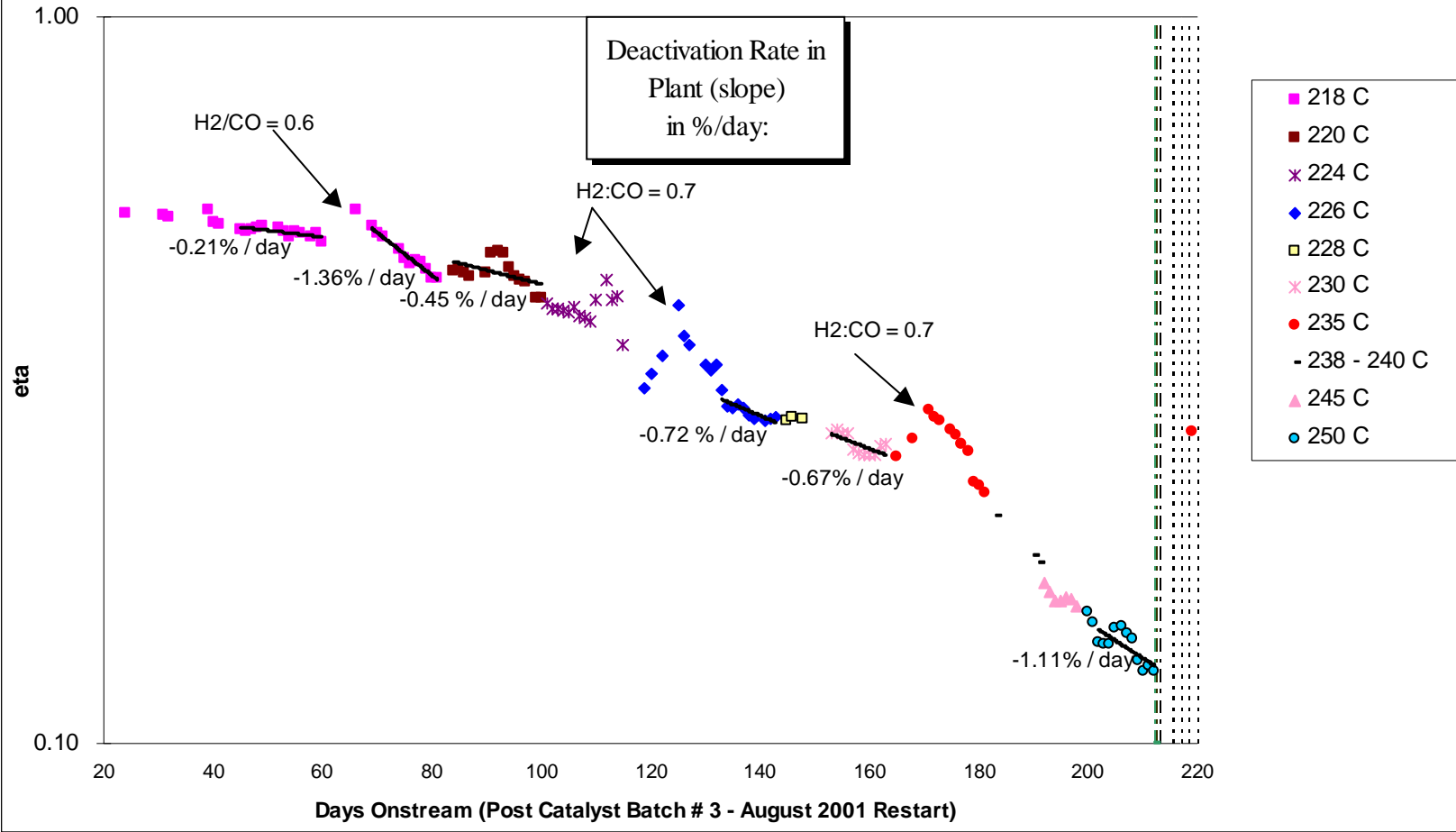
Sample	Identity	XRD		BET	Analytical (ppmw)				
		Cu	ZnO	m <sup>2</sup> /g	Fe	Ni	S	As	Cl
K0109-1	Reactor Sample 9/5/01	178	90	78	48	≤19	< 140	≤73	nd
K0109-2	Reactor Sample 9/12/01	188	88						
K0109-3	Reactor Sample 9/19/01	185	159	85	52	< 10	< 140	≤70	nd
K0110-1	Reactor Sample 10/3/01	181	78	82	71	< 10	≤85	65	nd
K0110-2	Reactor Sample 10/17/01	203	98	82	97	< 10	≤100	83	40
K0110-3	Reactor Sample 10/31/01	197	45	78	147	< 10	≤120	139	nd
K0111-1	Reactor Sample 11/14/01	200	80	80	191	< 10	≤130	138	50
K0111-3	Reactor Sample 11/30/01	204	79	82	241	< 10	≤140	150	30
K0112-1	Reactor Sample 12/12/01	256	77	74	293	≤20	≤80	260	nd
K0201-1	Reactor Sample 1/09/02	212	78	50	355	<10	≤95	192	30
K0201-2	Reactor Sample 1/23/02	207	121		363	≤10	≤57	152	nd
K0202-1	Reactor Sample 2/6/02	211	84		390	<10	≤91	138	nd
K0203-1	Reactor Sample 3/6/02	220	71		428	<10	<40	210	nd
K0203-2	Reactor Sample 3/14/02	216	102						
K0203-3	Reactor Sample 3/20/02	215	143						
K0203-4	Reactor Sample 3/25/02	218	101						
K0204-1	Reactor Sample 4/4/02	213	87						

**Notes:**

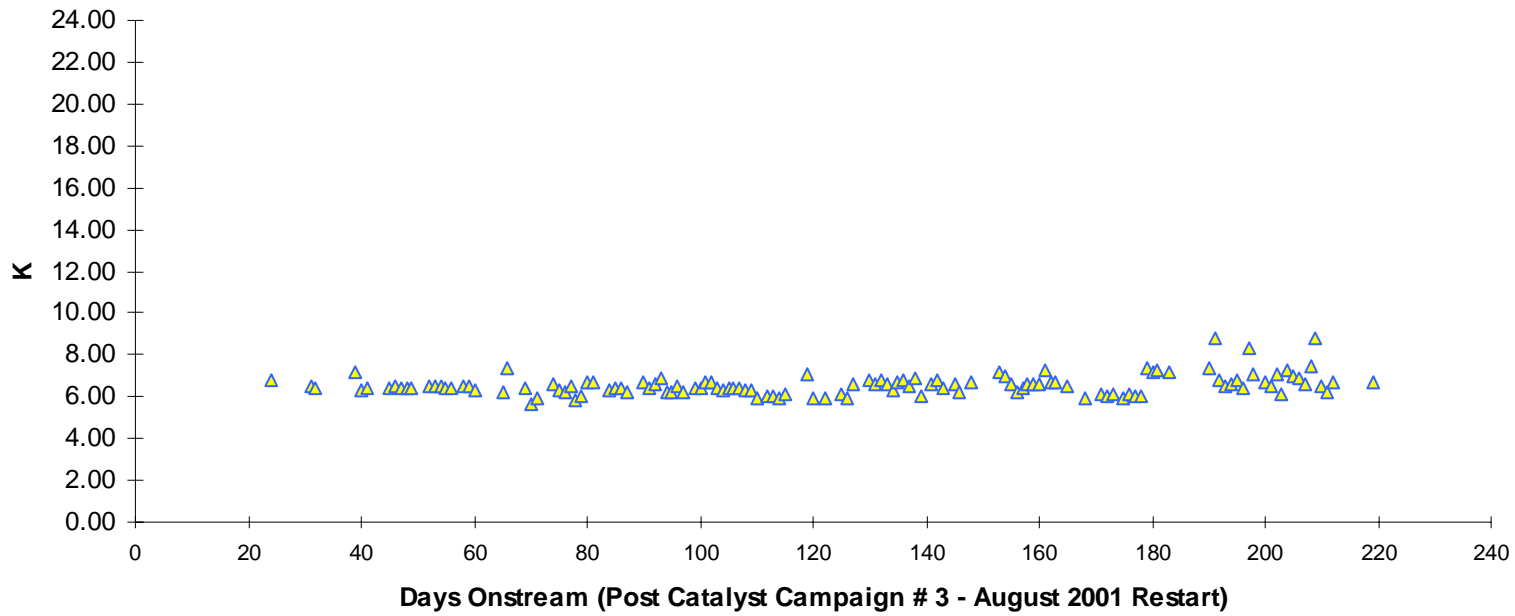
- 1) nd = none detected
- 3) na = data not available



Figure 1 - Kingsport LPMEOH™ Catalyst Age (eta): September 2001 - March 2002



**Figure 2 - Kingsport LPMEOH™ Sparger Resistance Coefficient  
September 2001 - March 2002**



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