

DOE/NETL-2004/1199

**Commercial-Scale Demonstration of the Liquid Phase
Methanol (LPMEOH™) Process**

A DOE Assessment

U.S. Department of Energy
Office of Fossil Energy
National Energy Technology Laboratory

October 2003



Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference therein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The view and opinions of authors expressed therein do not necessarily state or reflect those of the United States Government or any agency thereof.

Table of Contents

Executive Summary.....	5
I Introduction.....	9
II Project/Process Description	10
II.A Project Description.....	10
II.B Need for the Technology Demonstration.....	10
II.C Process Chemistry.....	12
II.D Technology Description.....	12
II.E Project Objective and Statement of Work	16
III Review of Technical and Environmental Performance	18
III.A Technical Performance	18
III.A.1 Sparger in the SBCR.....	18
III.A.2 Catalyst Deactivation.....	18
III.A.3 Catalyst Activation.....	18
III.B Demonstration Test Plan.....	19
III.C Operations.....	19
III.D Methanol Fuel-Use Testing.....	20
III.D.1 Transportation Systems.....	21
III.D.2 Power Generation Systems	22
III.E Liquid Phase Dimethyl Ether Design Verification Testing	22
III.F Environmental Performance	23
III.F.1 Spent Catalyst Slurry	23
III.F.2 Catalyst Guard Bed and Carbonyl Guard Bed Spent Adsorbents.....	23
III.F.3 Mineral Oil Waste Stream	23
III.F.4 Recovered Distillation Liquids	23
III.F.5 Waste Water Stream	24
IV Market Analysis.....	25
IV.A Market Size.....	25
IV.B Economics.....	26
IV.B.1 Capital Costs.....	26
IV.B.2 Operating Costs.....	26
IV.B.3 Economics.....	27

IV.C	Commercialization Plan.....	27
V	Conclusions.....	28
VI	Acronyms and Abbreviations	30
VII	References.....	31
VIII	Bibliography	32
Appendix A	33

List of Figures

Figure 1	Integration of Methanol Production with an IGCC Facility.....	11
Figure 2	Schematics of Gas-Phase Methanol Synthesis Reactors	13
Figure 3	Block Flow Diagram of LPMEOH™ Demonstration Unit.....	15

List of Tables

Table 1	Operating Periods	20
Table 2	Analysis of Stabilized Methanol.....	20
Table 3	Fuel-Use Test Program	21
Table 4	World Methanol Supply/Demand Forecast	25
Table 5	Operating Costs for a 500-Short Ton/Day LPMEOH™ Unit	26
Table 6	Economics for a LPMEOH™ Plant.....	27
Table A-1	Test Conditions for the LPMEOH™ Demonstration Program	33

Executive Summary

The U.S. Department of Energy (DOE) Clean Coal Technology (CCT) Program seeks to offer the energy marketplace more efficient and environmentally benign coal utilization technology options by demonstrating these technologies in industrial settings. This document is a DOE post-project assessment (PPA) of one of the projects selected in Round III of the CCT Program, the Commercial-Scale Demonstration of the Liquid Phase Methanol (LPMEOH™) Process.

Methanol is an important, large volume chemical with many uses. The desire to demonstrate a new process for the production of methanol from coal prompted Air Products and Chemicals, Inc. (Air Products) to submit a proposal to DOE. In October 1992, DOE awarded a cooperative agreement to Air Products to conduct this project. In March 1995, this cooperative agreement was transferred to Air Products Liquid Phase Conversion Company, L.P., a partnership between Air Products and Eastman Chemical Company (Eastman). Air Products, the technology supplier, provided the engineering design, procurement, construction, and commissioning of the 260-short tons/day LPMEOH™ Demonstration Unit. Eastman provided the host site, synthesis gas, and services to the unit, and served as the plant operator. Another team member, ARCADIS Geraghty & Miller, participated in the offsite fuel-use testing of stabilized methanol.

Operation of the LPMEOH™ Demonstration Unit began in April 1997. The demonstration unit is sited at Eastman's chemicals-from-coal complex in Kingsport, Tennessee, which also contains a preexisting gas-phase methanol unit. Synthesis gas, also called syngas, a mixture of hydrogen (H₂) and carbon monoxide (CO), was first introduced on April 2, and stable operation at design conditions was achieved on April 6. On April 10, a test run reached 115 percent of the design methanol production rate. Although the operating phase of the LPMEOH™ project was completed on December 31, 2002, Eastman continues to operate the LPMEOH™ Demonstration Unit for the production of methanol. DOE provided 43 percent of the total project funding of \$213.7 million.

The LPMEOH™ process represents a major departure from traditional gas-phase routes to methanol in the method of removing the heat of reaction. The formation of methanol from syngas is highly exothermic. Because catalyst life is seriously reduced by excessive temperatures, reactor temperature control is very important. One of the most difficult design problems is removing the heat of reaction while maintaining precise temperature control. In conventional designs for gas-phase methanol reactors, the catalyst is present in a series of fixed beds, with cold feed gas being injected between beds to control temperature, or a heat exchanger-type reactor is used with catalyst packed in the tubes and a coolant circulated on the shell side to remove heat.

In contrast, the LPMEOH™ process uses fine catalyst particles slurried in an inert mineral oil. The catalyst is kept in suspension by reactant gas, which bubbles up through the catalyst slurry. This type of reactor is typically referred to as a slurry bubble column reactor (SBCR). The mineral oil acts as a temperature moderator and a heat removal medium, transferring the heat of reaction from the catalyst surface to boiling water in an internal tubular heat exchanger. As a result of its capability to remove heat and maintain a constant uniform temperature throughout the reactor, the SBCR can achieve a much higher syngas conversion per pass, compared to a gas-phase reactor. Side reactions produce small amounts of higher alcohols and other oxygenated compounds. In addition, the produced methanol contains trace amounts of process mineral oil, as well as some water, generally less than 1 percent by weight for a CO-rich syngas.

The LPMEOH™ Demonstration Unit was designed to have three feed-gas streams: balanced gas (stoichiometric syngas with a H₂/CO ratio of about 2.0), which is diverted from the feed to a preexisting gas-phase methanol unit; a high pressure CO stream, available from the Kingsport facility; and a hydrogen stream from the exit of the gas-phase unit. The hydrogen stream was not available, and was not used during this project; however, this did not impact the execution of the Demonstration Test Program. The fresh feed is mixed with recycled gas and sparged into the bottom of the reactor. Upon contact with the catalyst, methanol synthesis occurs. Disengagement of the product gas (methanol vapor and unconverted syngas) from slurry occurs in the freeboard volume in the reactor above the slurry catalyst bed. The exit gas is cooled and condensed into liquid methanol, which is collected in a product separator. Part of the overhead stream from the separator is recycled to the reactor, and the rest is sent to the fuel gas header.

The raw methanol stream is sent to a two distillation column recovery section. In the first column, dissolved gases are removed and sent to the fuel header. The underflow from this column is sent to the second distillation column, where purified methanol is recovered overhead. The bottom stream, consisting of some methanol, higher alcohols, water, and mineral oil, is sent to the distillation system of the preexisting gas-phase unit for methanol recovery. The LPMEOH™ Demonstration Unit was designed to produce a refined-grade methanol product suitable for use in downstream applications at the Kingsport site.

The primary objective of this project was to demonstrate the production of methanol using the LPMEOH™ process, feeding syngas produced by an integrated coal gasification facility. Specific technical objectives were:

- To demonstrate the scale-up of the LPMEOH™ process slurry reactor from the 10-short tons/day scale at the DOE Alternative Fuels Development Unit (AFDU) in LaPorte, Texas, to a production rate of at least 260 short tons/day.
- To demonstrate that the LPMEOH™ process, operating on a coal-derived syngas, compared favorably to conventional gas-phase processes in operability and economics.
- To determine the suitability of methanol produced during this demonstration for use as a chemical feedstock, or as a low emission (sulfur dioxide (SO₂) and nitrogen oxides (NO_x)) alternative fuel in stationary power generation and transportation applications.
- To confirm commercial economics for the LPMEOH™ process for coproduction of once-through methanol, and integrated gasification combined cycle (IGCC) electric power.

A significant problem was a higher methanol synthesis catalyst deactivation rate than expected, based on a four-month proof-of-concept test run conducted at the LaPorte AFDU. The problem was caused by trace contaminants, particularly arsenic, sulfur, and iron entering the LPMEOH™ reactor. To counter this problem, the Eastman guard bed (upstream of both the preexisting gas-phase methanol plant and the LPMEOH™ Demonstration Unit) was filled with manganese dioxide, and the sorbent in the carbonyl guard bed in the LPMEOH™ Demonstration Unit was replaced with copper oxide-impregnated activated carbon. These changes appear to have improved long-term catalyst performance.

Initially, catalyst was activated in small (~2,000 lb) batches in the catalyst preparation system. However, it was much more efficient to activate the entire batch (>40,000 lb) at the same time in the slurry reactor. Temperature-programmed operation of the LPMEOH™ reactor was also adopted. Rather than periodically removing the spent catalyst and replacing it with fresh

material, temperature programming involves starting at the lowest temperature at which desired conversion is achieved and gradually increasing temperature as the catalyst ages to maintain a constant activity. The choice of batch-wise addition or in-situ activation can be made, based upon the requirements of the project, and can provide another way to optimize the economics of the LPMEOH™ process.

During the performance period, the unit produced almost 104 million gallons of methanol, all of which was accepted by Eastman for the production of methyl acetate, and ultimately cellulose acetate and acetic acid. Average availability of the unit from April 1997 through December 2002 was 97.5 percent. Availability is defined as the percentage of time the unit is available to operate, excluding scheduled outages.

The purpose of the fuel-use test program was to demonstrate commercial market applications for stabilized methanol as a replacement fuel and/or as a fuel supplement. Stabilized methanol is made by using only the first distillation column, which removes low boiling components and stabilizes the product for shipment. A limited supply (approximately 12,000 gallons) of stabilized methanol from the LPMEOH™ Demonstration Project was made available for fuel-use tests offsite.

Two potential applications of stabilized methanol were investigated: transportation systems and power generation systems. In vehicle trials, stabilized methanol provided the same environmental benefits as chemical-grade methanol with no penalty on performance or fuel economy. Tests in a gas turbine and a diesel generator showed that levels of NO_x in the exhaust were lowered when stabilized methanol or methanol emulsions were used; however, lubrication additives will probably be required when stabilized methanol is fed to a gas turbine. Testing of stabilized methanol as the source of hydrogen for a phosphoric acid fuel cell showed that conventional steam reforming catalysts are not compatible with the trace amount of mineral oil present in the stabilized methanol, methanol from the LPMEOH™ process (purified to chemical-grade specifications) should be suitable for use in this application.

A very interesting concept is to couple a methanol plant with a coal-based IGCC facility. In this concept, part of the syngas produced by the coal gasifier is sent to the methanol plant. If the methanol plant is flexible enough to accept a varying feed stream, this option would permit the gasifier—the largest capital cost item in the facility—to operate at a constant rate, regardless of electric power demand. Excess syngas could be sent to the methanol unit, whose production rate would vary inversely with electric power demand. If more power were required than could be satisfied by the gasifier, some of the stored methanol could be burned in gas turbines. Operation of the LPMEOH™ Demonstration Unit has generated data to assist in evaluating the technical and economic merits of this concept.

To be most efficient, the methanol plant in such a complex should be able to operate on low H₂/CO molar ratio syngas, typical of that produced by a coal gasifier. Gas-phase reactors are not well adapted to this type of syngas, because of the high heat of reaction. However, the LPMEOH™ process, which uses a slurry-phase reactor with an inherently high heat removal capability, is well suited to this application. Thus, this project was very important in establishing the commercial readiness of the LPMEOH™ process and its applicability to coproduction (production of both electric power and methanol) operations.

Economics tend to be site specific, since they depend upon a large number of factors. The Final Report (Volume 2) presents economics for a 500-short tons/stream day plant, built in conjunction

with an IGCC system. This means that capital equipment for much of the gas cleanup is included in the IGCC plant and, thus, not included in the capital for the LPMEOH™ plant, except for the equipment used to remove the last traces of contaminants from the feed gas.

Capital cost for a once-through, 500-short tons/day LPMEOH™ plant feeding syngas with a H₂/CO molar ratio of 0.68 is estimated to be \$31.1 million (2002 dollars). The syngas is assumed to be available at a pressure of 1,000 psig with a carbonyl sulfide (COS) content of 5 parts per million (ppm) by volume. This estimate is based largely on the costs incurred in the construction of the LPMEOH™ Demonstration Unit at Kingsport, including lessons learned during the project. Fixed operating costs are estimated to be \$1,358,000/yr, and variable operating costs are \$15,853,000/yr. The cost of methanol from a LPMEOH™ unit integrated into an IGCC system is estimated in the range of 50 to 60 cents/gal on a current dollar basis, or 40 to 50 cents/gal on a constant dollar basis. The market for conventional uses of methanol is predicted to be relatively flat over the next 5 to 6 years. Therefore, the major opportunity for using the LPMEOH™ process will be in conjunction with coproduction of electricity in coal-based IGCC systems.

This was a very successful project. The SBCR was successfully scaled from the 10-short tons/day LaPorte AFDU (22-inch reactor diameter) size to the 260-short tons/day (7.5 ft diameter) demonstration unit size. The scaled up reactor exhibited good temperature stability and was operable at a catalyst concentration of nearly 50 percent by weight. During the demonstration, a new technique for activating the catalyst was developed, and a procedure for maintaining catalyst activity through programming the reactor temperature was developed. This new approach obviated the need for catalyst withdrawal and addition during a test run, which can improve the economics for certain applications of the technology.

Tests made during the demonstration project confirmed that a LPMEOH™ process unit has the capability to operate satisfactorily in a coal-based IGCC environment, in that it has the capability to operate on a syngas with a range of H₂/CO ratios, on/off, and ramping modes. These capabilities are necessary to adjust the varying syngas feed rate that results from the power plant's following the electrical demand. As electrical demand varies, the amount of syngas available for conversion to methanol also varies. The unit was able to achieve at least a 5 percent change in feed rate per minute during ramping, showing that the process is very flexible and stable.

The success of this project can be attributed to the following reasons: unit design based on high quality data from test units; good cooperation among all parties involved; well thought out test plan; well qualified operating crew; and a highly competent engineering staff, able to solve problems as they arose.

I Introduction

The U.S. Department of Energy (DOE) Clean Coal Technology (CCT) Program seeks to offer the energy marketplace more efficient and environmentally benign coal utilization technology options by demonstrating them in industrial settings. This document is a DOE post-project assessment (PPA) of one of the projects selected in Round III of the CCT Program, the commercial-scale demonstration of the Liquid Phase Methanol (LPMEOH™) Process, initially described in a Report to Congress by DOE in 1992.

Methanol is an important, large-volume chemical with many uses. The desire to demonstrate a new process for the production of methanol from coal, prompted Air Products and Chemicals, Inc. (Air Products) to submit a proposal to DOE. In October 1992, DOE awarded a cooperative agreement to Air Products to conduct this project. In March 1995, this cooperative agreement was transferred to Air Products Liquid Phase Conversion Company, L.P. (the Partnership), a partnership between Air Products and Eastman Chemical Company (Eastman). DOE provided 43 percent of the total project funding of \$213.7 million.

Operation of the LPMEOH™ Demonstration Unit, which is sited at Eastman's chemicals-from-coal complex in Kingsport, Tennessee, commenced in April 1997. Although operation of the CCT project was completed in December 2002, Eastman continues to operate the LPMEOH™ Demonstration Unit for the production of methanol. The independent evaluation contained herein is based primarily on information from Volume 2 of the project's Final Report (Air Products Liquid Phase Conversion Co., L.P. 2003), as well as other references cited.

II Project/Process Description

II.A Project Description

A limited partnership between Air Products, and Eastman, was formed to carry out the CCT project. Air Products, the technology supplier, provided the engineering design, procurement, construction, and commissioning of the 260-short tons/day LPMEOH™ Demonstration Unit. Eastman provided the host site, synthesis gas, services to the unit, and served as plant operator. ARCADIS Geraghty & Miller, another team member, participated in the offsite fuel-use testing of stabilized methanol.

The demonstration unit, which occupies a 0.6 acre plot, is integrated into Eastman's 4,000 acre chemicals-from-coal complex in Kingsport, Tennessee. In 1983, Eastman constructed a coal gasification facility based on Texaco gasifiers. The synthesis gas, also called syngas, a mixture of hydrogen (H₂) and carbon monoxide (CO), is generated by the gasifiers and used to produce carbon monoxide and methanol, which in turn are used for the production of methyl acetate, and ultimately cellulose acetate and acetic acid. The high reliability of the chemicals-from-coal complex was a major factor in its selection as the site for the LPMEOH™ project.

The LPMEOH™ Demonstration Project was conducted in three phases: design, construction, and operation. The design phase started in October 1993 and was completed in June 1996; construction started in October 1995, and the LPMEOH™ Demonstration Unit was commissioned in March 1997. Syngas was first introduced on April 2, 1997, and stable operation at design conditions was achieved on April 6. On April 10, a test run reached 115 percent of the design methanol production rate.

The original schedule for the project called for operations to end on March 31, 2001, with project closeout to occur by December 31, 2001. However, operational issues were encountered with the gas sparger in the slurry reactor, and with the impact of trace contaminants present in the coal-derived syngas on the long-term performance and life of the methanol synthesis catalyst. In addition, modes of operation that had not been contemplated during the development of the original Demonstration Test Plan were identified during the execution of the project. In order to complete all of the original project objectives, plus these newly identified tests, the project completion date was extended to June 30, 2003. The operating phase of the LPMEOH™ project was completed on December 31, 2002.

II.B Need for the Technology Demonstration

Methanol has a broad range of commercial uses. It can be substituted for, or blended with gasoline to fuel vehicles, and it is an excellent fuel for the rapid-start combustion turbines used by utilities to meet peak electricity demands. Methanol is sulfur free and is a low emitter of nitrogen oxides (NO_x) when burned. In addition to its use as a fuel, methanol serves as an intermediate in many chemical synthesis applications.

A very interesting concept is to couple a LPMEOH™ plant with a coal-based integrated gasification combined cycle (IGCC) facility to coproduce electric power and methanol. In this concept (see Figure 1), part of the syngas produced by the coal gasifier is sent to the methanol plant. If the methanol plant is flexible enough to accept a varying feed stream, this option would permit the gasifier—the largest capital cost item in the facility—to operate at a constant rate,

regardless of electric power demand. The excess syngas not needed for power production could be sent to the methanol unit, whose production rate would vary inversely with electric power demand. If more power were required than could be satisfied by the gasifier, some of the stored methanol (see Figure 1) could be burned in gas turbines. Operation of the LPMEOH™ Demonstration Unit has generated data to aid in evaluating the technical and economic merits of this concept.

To be most efficient, the methanol plant in such a complex should be able to operate on low H₂/CO molar ratio syngas, typical of that produced by a coal gasifier. Gas-phase reactors are not well adapted to this type of syngas because of the high heat of reaction. However, the LPMEOH™ process, which uses a slurry-phase reactor with an inherently high heat removal capability, is well suited to this application. Thus, this project was very important in establishing the commercial readiness of the LPMEOH™ process and its applicability to coproduction (production of both electric power and methanol) operations.

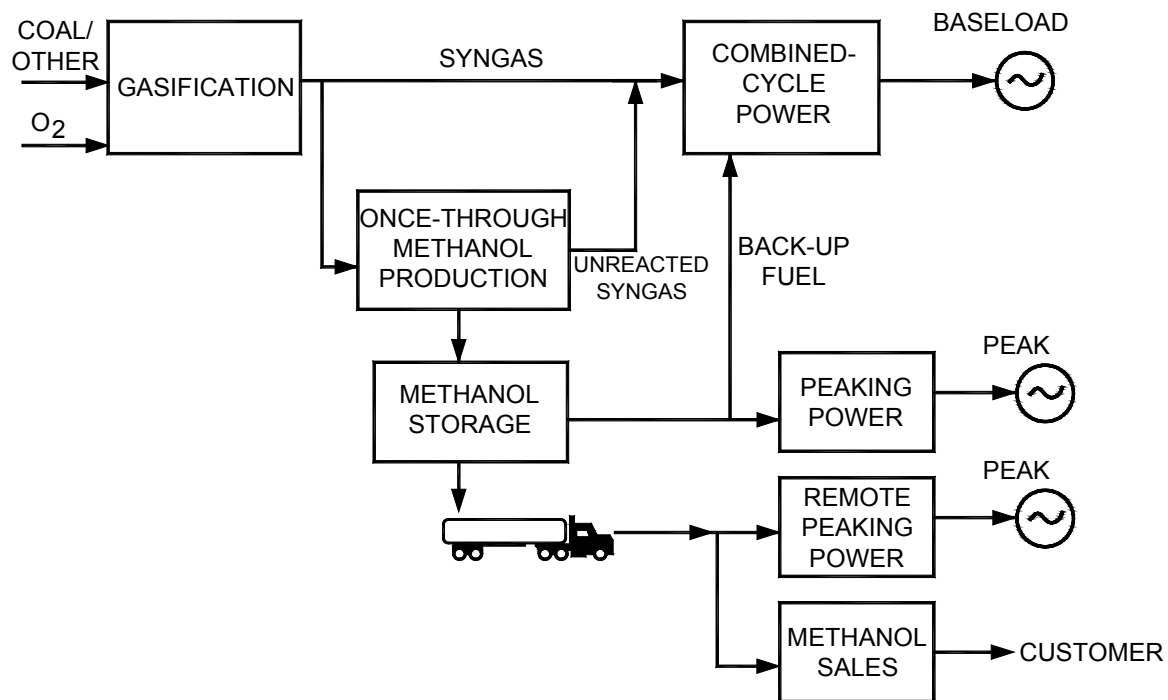


Figure 1 Integration of Methanol Production with an IGCC Facility

II.C Process Chemistry

The LPMEOH™ process represents a major departure from traditional gas-phase routes to produce methanol in the method of removing the heat of reaction. The formation of methanol from syngas is highly exothermic, as shown by the following equations.



In addition to these methanol synthesis reactions, the water-gas shift reaction also occurs.

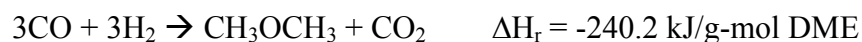


This reaction generates hydrogen and can impact the overall production of methanol, depending on the concentrations of H₂, CO, carbon dioxide (CO₂), and water (H₂O). Typical methanol synthesis reaction conditions are 710 psig and 440 to 520 °F. In addition to the above reactions, side reactions produce small amounts of higher alcohols and other oxygenated compounds. Also, the product methanol contains trace amounts of process mineral oil. Depending on the extent of the water-gas shift reaction, water is also present in the reactor effluent.

A secondary objective of this project was to demonstrate the production of dimethyl ether (DME) as a mixed coproduct with methanol. This can be achieved by adding a dehydration catalyst to the system to promote the following reaction:



For a CO-rich syngas, the overall reaction for the production of DME is:



Under this concept, the DME/methanol product blend would be used directly as a fuel. Alternatively, the product could be separated into DME and methanol streams.

II.D Technology Description

One of the most difficult design problems for a methanol synthesis unit is removing the heat of reaction while maintaining precise temperature control. This is important, because catalyst life is seriously reduced by excessive temperatures. Figure 2 shows conventional designs for gas-phase methanol reactors, with the catalyst in the form of pellets. Typically, the catalyst is present in a series of fixed beds with cold feed gas being injected between beds to control temperature. Another option uses a heat exchanger type reactor with catalyst in the tubes, and a coolant circulated on the shell side to remove heat. Such reactors are satisfactory only for stoichiometrically balanced syngas feed with low per pass conversion.

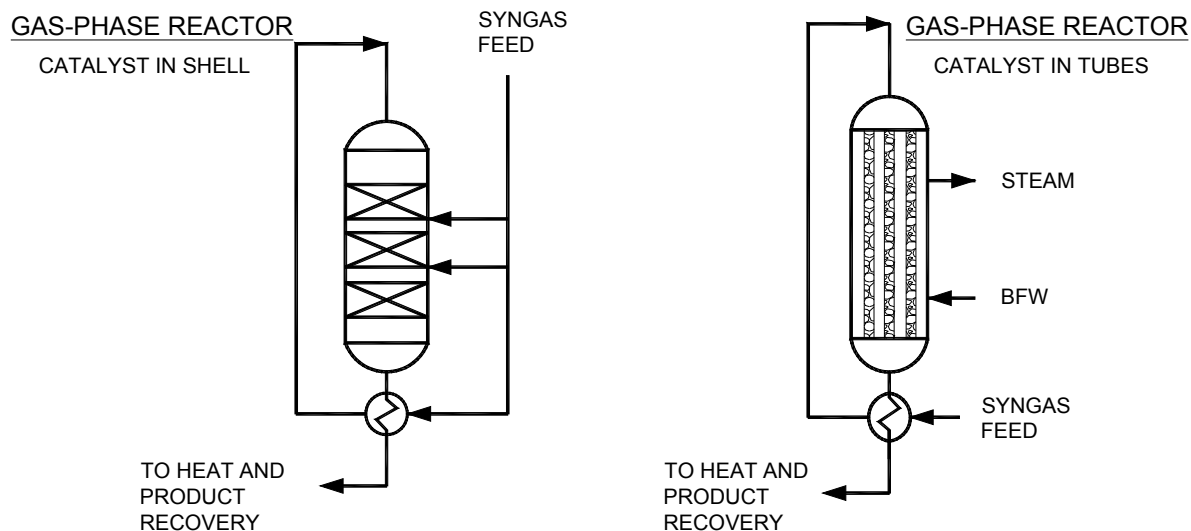


Figure 2 Schematics of Gas-Phase Methanol Synthesis Reactors

In contrast, the LPMEOH™ process uses fine catalyst particles supported in an inert mineral oil. The mineral oil acts as a temperature moderator and a heat removal medium, transferring the heat of reaction from the catalyst surface via the liquid slurry to boiling water in an internal tubular heat exchanger. As a result of this capability to remove heat and maintain a constant uniform temperature throughout the reactor, the slurry bubble column reactor (SBCR) can achieve a much higher syngas conversion per pass compared to a gas-phase reactor.

Figure 3 provides a simplified block diagram of the as-built LPMEOH™ Demonstration Unit. It does not include changes made after unit startup, as discussed later. The unit can be divided into three main sections: feed gas purification/compression, reactor loop/catalyst activation, and distillation. The LPMEOH™ Demonstration Unit was designed to have three feed gas streams, balanced gas (stoichiometric syngas), which is diverted from the feed to a preexisting gas-phase methanol unit; a high pressure CO stream, available from the Kingsport facility; and a hydrogen stream from the exit of the gas-phase methanol unit. The CO and balanced gas streams are combined and passed through a carbonyl guard bed, packed with activated carbon and designed to remove any trace levels of iron and nickel carbonyls from the feed gas. Since the hydrogen stream is available at a lower pressure, it is combined with the recycle gas, compressed in the recycle gas compressor, and mixed with the CO/balanced gas stream from the carbonyl guard bed. A typical analysis of the total feed stream is 60.9 mol % H₂, 25.1 mol % CO, 4.1 mol % nitrogen (N₂), and 9.0 mol % CO₂. This feed stream is heated to approximately 400 °F in the feed/product exchanger and sparged into the SBCR, typically operating at 725 psia and 440 to 520 °F. In the reactor, the feed mixes with the catalyst slurry and is partially converted to

methanol vapor. The heat of reaction is removed by the generation of steam in submerged heat exchange tubes in the reactor. Slurry temperature is controlled by adjusting the steam pressure.

Disengagement of the exit gas (methanol vapor and unreacted syngas) from slurry occurs in the freeboard volume above the slurry catalyst bed in the reactor. Entrained slurry droplets are recovered in a cyclone separator. The exit gas stream is cooled to 250 °F in a feed/effluent exchanger. Condensed mineral oil is collected in a high pressure separator and returned to the reactor, along with entrained catalyst and oil from the cyclone separator. Fresh mineral oil is added to the reactor to replace losses. The exit gas is further cooled to 105 °F in an air-cooled exchanger and a water cooled exchanger. Liquid methanol is collected in a product separator. Approximately 91 percent volume of the overhead stream from the separator, which contains 0.9 percent by volume methanol, and about 2 parts per million (ppm) by weight of mineral oil, is recycled to the reactor, and the rest is sent to the fuel gas header. This purge stream going to the fuel gas header prevents the buildup of inerts in the recycle stream.

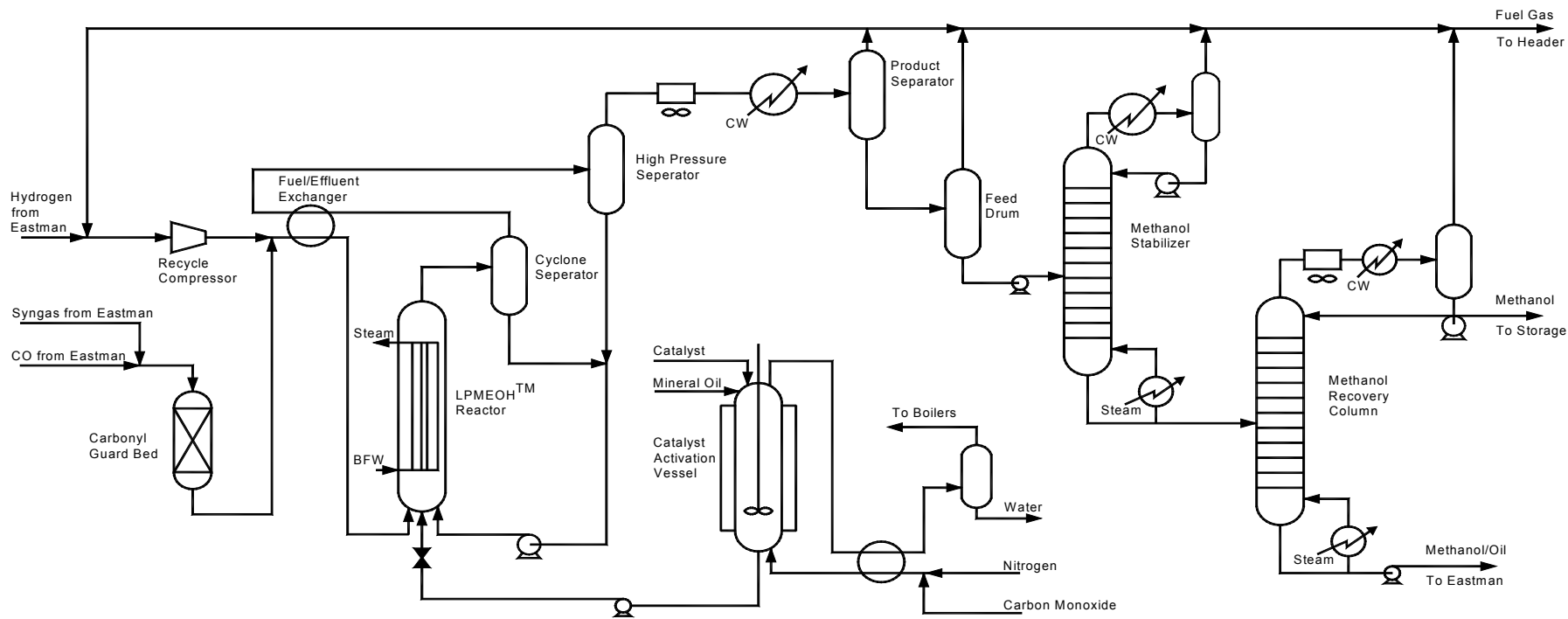


Figure 3 Block Flow Diagram of LPMEOH™ Demonstration Unit

Catalyst batches (~2,000 lb) can be activated (reduced) in the catalyst reduction vessel, which is an agitated, stainless steel vessel with a heating/cooling jacket. This vessel has three purposes: (1) fresh slurry mix tank, (2) catalyst reduction/activation vessel, and (3) spent slurry receiver. Catalyst is activated by adding mineral oil to this vessel, heating the mineral oil, and then adding catalyst in the oxide form. Reducing gas (96 mol % N₂, 4 mol % CO) is sparged into the vessel. The CO content of the exit gas is monitored to follow the extent of reaction. Once reduction is complete, the activated catalyst slurry is pumped to the LPMEOH™ reactor. During operation, before fresh catalyst is added to the reactor, spent slurry may be removed to maintain a fixed catalyst inventory in the reactor.

The condensed methanol from the separator contains about 6 percent by volume of dissolved gases, methyl formate, water, and higher alcohols. These impurities are removed in a two column distillation train. The raw product is first flashed in the methanol stabilizer feed drum at about 70 psig. The flashed gas is combined with the vapor overheads from the two columns and sent to the fuel header.

The first distillation column removes dissolved gases and lighter boiling impurities, such as methyl formate. The underflow from this column is fed to the second column, where purified methanol product is removed as a top liquid product. The bottoms from this column contains about 25 percent of the methanol, plus higher alcohols, water, and any mineral oil carried over from the reactor. This stream is sent to the preexisting gas-phase unit distillation system for production of additional refined methanol. After recovery of the methanol, the remainder of this stream is sent to Eastman's wastewater treatment system. The product, referred to as refined-grade methanol, is first stored in lot tanks on site until purity checks are complete. The methanol is then transferred to bulk storage at Eastman. The objective of the LPMEOH™ unit was to produce a refined-grade methanol product suitable for use in downstream applications at the Kingsport site.

The above description is of the unit as originally built. After startup, some changes occurred to the original operation design. For example, a new in situ catalyst activation procedure was developed, which can eliminate the need to use the reduction vessel for catalyst activation in some applications. Also, the hydrogen stream from the preexisting gas-phase methanol unit was not available during the demonstration. Other changes also occurred, as discussed later in this report.

II.E Project Objective and Statement of Work

The primary objective of this project was to demonstrate the production of methanol using the LPMEOH™ process in conjunction with an integrated coal gasification facility. A secondary objective was to demonstrate, if practical, the production of DME as a mixed coproduct with methanol. Specific technical objectives were:

- To demonstrate the scale-up of the LPMEOH™ process slurry reactor from a 10-short tons/day size at the DOE Alternative Fuels Development Unit (AFDU) in LaPorte, Texas, to a production rate of at least 260-short tons/day.
- To demonstrate, subject to design verification testing (DVT), the SBCR's capability to produce DME as a mixed coproduct with methanol.

- To demonstrate that the LPMEOH™ process, based on a coal-derived syngas, compared favorably to conventional gas-phase processes.
- To determine the suitability of methanol produced during this demonstration for use as a chemical feedstock, or as a low emissions (sulfur dioxide and nitrogen oxides) alternative fuel in stationary power generation and transportation applications.
- To confirm commercial economics for the LPMEOH™ process for coproduction of methanol and IGCC electric power.

III Review of Technical and Environmental Performance

III.A Technical Performance

As the project proceeded, some modifications to the process were implemented to improve performance. The more important of these modifications are discussed briefly in the following sections.

III.A.1 Sparger in the SBCR

Since the performance of an SBCR depends heavily on mixing syngas with catalyst slurry, correct operation of the gas sparger is critical. During operation of the LPMEOH™ Demonstration Unit, three different gas sparger designs were used, all based upon the design principles for the device in the LaPorte AFDU. The original sparger, used from startup until November 1997, developed a problem of gradually increasing pressure drop, apparently due to plugging of catalyst particles. During this time, use of fresh mineral oil as a flush was successfully demonstrated, but success was limited since there was only a small loss of oil with the methanol product (about 0.1 gal/min). A continuous flush of the condensed mineral oil, collected from the process (about 1 gal/min), was effective in reducing the rate of increase of pressure drop. This mineral oil stream was returned by gravity, rather than a pump, which greatly simplified plant operation. A modified sparger was installed in December 1997, but the problem was not entirely solved until another modified sparger was installed in March 1999. The replacement sparger has shown no increase in pressure drop with time.

III.A.2 Catalyst Deactivation

Another problem was a higher methanol synthesis catalyst deactivation rate than expected, based on a four-month proof-of-concept test run at the LaPorte AFDU. The problem was caused by trace contaminants, such as arsenic, sulfur, and iron, entering the LPMEOH™ reactor. Laboratory studies have confirmed that arsenic (in the form of arsine) is a powerful catalyst poison. To counter this problem, the sorbent in the Eastman guard bed (upstream of both the gas-phase methanol plant and the LPMEOH™ Demonstration Unit) was replaced with manganese dioxide, and the sorbent in the carbonyl guard bed within the LPMEOH™ Demonstration Unit was replaced with copper oxide-impregnated activated carbon. To prevent high temperatures from causing sorbent damage, the copper oxide was chemically reduced with balanced gas, diluted with nitrogen before being put into service. These changes appear to have improved long-term catalyst performance.

III.A.3 Catalyst Activation

Initially, catalyst was activated in small (~2,000 lb) batches in the catalyst preparation system. It was found, however, to be much more efficient in certain applications to activate the entire batch (>40,000 lb) at the same time in the SBCR. Temperature-programmed operation of the LPMEOH™ reactor was also adopted. Rather than periodically replacing spent catalyst, temperature programmed operation begins at the lowest temperature at which desired conversion is achieved, gradually increasing temperature as the catalyst ages, to maintain a constant activity.

III.B Demonstration Test Plan

The original Demonstration Test Plan included 37 specific test runs. However, as the project progressed, it became clear that certain tests could not be run or were not necessary. Some of the reasons for this were:

- The hydrogen stream to the LPMEOH™ Demonstration Unit was not available. Therefore, tests involving this stream were deleted. This did not, however, impact the execution of the Demonstration Test Plan.
- Increasing the catalyst slurry concentration in the LPMEOH™ reactor increased CO conversion, resulting in an increased H₂/CO molar ratio in the recycle gas, and at the reactor inlet. This eliminated the need to run a separate test using a syngas typical of that produced by natural gas reforming.
- More time was needed to study reactor performance at temperatures below the original design operating temperature of 482 °F, thus decreasing the time available for other tests.
- During the demonstration program, desirable operating modes were identified that were not anticipated at the time the Demonstration Test Plan was developed, thus requiring updating of the Demonstration Test Plan.

The updated test plan (see Table A-1) included ramping tests and rapid startup tests. These tests were designed to show that the LPMEOH™ process was capable of rapidly starting up and shutting down, and that only a short time was required to change the feed rate. These load-following characteristics are necessary for the LPMEOH™ process to be suitable for incorporation into a coal-based IGCC system. Other tests were designed to show the advantages of the in-situ activation procedure. This procedure not only saves time by activating the entire batch of catalyst at the same time, but also eliminates the need for certain equipment in some applications, thus lowering capital costs.

III.C Operations

The demonstration program can be divided into four operating periods based on the four charges of catalyst that were used, as shown in Table 1. During the performance period, the unit produced almost 104 million gallons of methanol, all of which was accepted by Eastman for the production of methyl acetate, and ultimately cellulose acetate and acetic acid. Average availability of the unit from April 1997 through December 2002 was 97.5 percent. Availability is defined as the percentage of the time that the unit is available to operate, excluding scheduled outages.

Table 1 Operating Periods

Catalyst Campaign	How Activated	Period of Operation		Duration, Days
		Start	End	
1	In catalyst preparation facilities	April 1997	November 1997	171
2	In catalyst preparation facilities	December 1997	August 2001	1,325
3	In situ	August 2001	June 2002	284
4	In situ	June 2002	December 2002*	187

* End of project; catalyst still active.

III.D Methanol Fuel-Use Testing

The purpose of the fuel-use test program was to open a broader market for methanol by evaluating advanced utility dispersed electric power and mobile transport engine applications. The objective was to demonstrate commercial market uses for stabilized methanol as a replacement fuel and/or as a fuel supplement. Stabilized methanol is made by using only the first distillation column, which removes low boiling components and stabilizes the product. Producing stabilized methanol is less expensive than producing refined-grade or chemical-grade (high purity) methanol. A limited supply (approximately 12,000 gallons) of stabilized methanol from the LPMEOH™ Demonstration Project was made available for fuel-use tests. Analyses of this material (produced from a syngas having a H₂/CO mole ratio of 0.7) are shown in Table 2.

Table 2 Analysis of Stabilized Methanol*

	Kingsport LPMEOH™ Product		LaPorte AFDU Sample
	Sample 1	Sample 2	
Methanol	98.08	99.26	98.40
Ethanol	0.31	0.25	0.60
C ₃ +	0.40	0.18	0.46
Water	1.22	0.31	0.54

* Differences in analyses of the two Kingsport samples are due to differences in catalyst activity and/or CO₂ content of the feed gas.

Seven tests (see Table 3) were conducted. These tests involved two potential applications of stabilized methanol: transportation systems and power generation systems.

Table 3 Fuel-Use Test Program

Program Participant	Application	Test Objective
Transportation Systems		
Florida Institute of Technology	1988 Chevrolet Corsica FFV 1993 Ford Taurus FFV Jacksonville Transit Authority bus	Fuel economy, maintenance, exhaust emissions as compared to chemical-grade methanol
ARCADIS Geraghty & Miller	1996 Ford Taurus FFV	Fuel economy and methane, non-methane hydrocarbons, and formaldehyde emissions as compared to chemical-grade methanol
West Virginia University Transportable laboratory facility	3 Transit Motor Corporation buses in New York	Hydrocarbon and particulate matter emissions as compared to diesel fuel and chemical-grade methanol
Power Generation Systems		
West Virginia University	GTC-85-72 gas turbine	Turbine emissions (CO, CO ₂ , NO _x , oxygen (O ₂)) and performance
ARCADIS Geraghty & Miller	Water-emulsion fuel for use in aircraft ground support equipment	Generator emissions (NO _x , CO) and performance
ARCADIS Geraghty & Miller	Distributed power generation	Generator emissions (in particular NO _x)
University of Florida	Hydrogen source for phosphoric acid fuel cells	Comparisons of reformation products, extent of conversion, and catalyst life between chemical grade methanol and stabilized methanol

III.D.1 Transportation Systems

Five vehicle types were tested on fuel blends made from stabilized methanol. These tests were designed to determine if there are any differences in fuel economy, maintenance requirements, or exhaust emissions, compared to performance with fuels made with chemical-grade methanol. In bus and fuel-flexible vehicle (FFV) trials, stabilized methanol provided the same environmental benefits as chemical-grade methanol with no associated penalty on performance or fuel economy.

FFVs tested at the Florida Institute of Technology experienced average fuel economies ranging from 10.88 miles per gallon (mpg) to 14.68 mpg for M-85 fuel blends (85 vol % methanol/15 vol % gasoline). The vehicles operated well on the fuel blends and required only routine repairs that were not related to fuel type.

The ARCADIS Geraghty & Miller FFV averaged approximately 16 mpg on M-85 for both stabilized methanol and chemical-grade methanol. The vehicle exhibited higher emissions for total hydrocarbons, CO, CO₂, and methane for the fuel blend made from stabilized methanol. Emissions of non-methane hydrocarbons and NO_x were higher for the M-85 fuel blends made

from chemical-grade methanol. However, emissions for both fuels were within the standards established by the state of California.

The West Virginia University transportable laboratory facility, which specializes in the measurement of emissions from heavy-duty vehicles, determined that emissions of hydrocarbons and particulate matter increased slightly when stabilized methanol was used to replace chemical-grade methanol as a bus engine fuel. However, stabilized methanol showed substantially (nearly 83 percent) lower NO_x emissions compared to diesel fuel.

III.D.2 Power Generation Systems

Four projects studied the use of stabilized methanol in either central power systems (as a supplement in peak power demand periods) or in distributed power generation systems. Tests in a gas turbine and a diesel generator showed lower NO_x levels in the exhaust when stabilized methanol or methanol emulsions were used in place of conventional hydrocarbon fuels. At one test site, a low-NO_x stationary gas turbine, fueled with stabilized methanol, exhibited NO_x emissions as low as 1 ppm by volume (corrected to 15 percent oxygen) at acceptable combustor CO emission levels. Lubrication additives will likely be required when methanol (either stabilizer or chemical-grade) is used to fuel a gas turbine. During gas turbine testing at West Virginia University, where potential lubrication additives were assessed, NO_x emissions were reduced by 75 percent, compared to liquid hydrocarbon fuel.

Although interest in fuel cells has increased considerably, fuel cells require H₂, which is difficult to transport and store for onboard transportation systems. One alternative is to use methanol, which can be converted into H₂. In tests with phosphoric acid fuel cells, chemical-grade methanol has been used successfully as the source of H₂. In tests at the University of Florida to reform stabilized methanol, the catalyst in the reformer (operating on stabilized methanol) deactivated rapidly, probably due to the presence of trace amounts of slurry mineral oil from the LPMEOH™ reactor. Acceptable results might be achieved using autothermal reforming or by distilling the stabilized methanol to chemical-grade specifications.

III.E Liquid Phase Dimethyl Ether Design Verification Testing

A secondary objective of the LPMEOH™ Demonstration Project was the DVT of Air Products' Liquid Phase Dimethyl Ether (LPDME™) process. In the LPDME™ process, a dehydration catalyst is mixed with the methanol synthesis catalyst in the mineral oil slurry to promote the conversion of methanol to dimethyl ether within the same reactor, as discussed in the section on process chemistry. Conversion per pass with CO-rich syngas can be higher for the LPDME™ process than for the LPMEOH™ process. Methanol may also be produced as a mixed coproduct with DME and can easily be separated and recovered.

Although DME is not now typically used as a fuel, it has properties similar to those of liquefied petroleum gas (LPG). Thus, there is potential to use DME in combustion turbines, in home heating, as a replacement for LPG in fueling automobiles, and as a diesel fuel substitute or combustion supplement. It is anticipated that this application will require lower than the 99 percent purity requirement for current uses, thus reducing the cost of product purification.

It was decided that the appropriate place to make a DVT run was in the LaPorte AFDU. In October and November 1999, a successful 25-day test run was made, jointly sponsored by the LPMEOH™ Demonstration Project and the DOE Liquid Fuels Program. The test run used

commercially produced catalysts. The deactivation rate for both the methanol synthesis and dehydration catalysts was 0.7 percent per day, somewhat lower than obtained in autoclave tests. Methanol productivity remained relatively constant throughout the run, while DME productivity showed a slight decline, consistent with laboratory results. No DME runs were made in the LPMEOH™ reactor at Kingsport.

III.F Environmental Performance

The LPMEOH™ Demonstration Project successfully confirmed a more efficient liquid-phase reaction process as a preferred alternative to gas-phase reactors for methanol production. During its operation, the facility achieved compliance with all federal and state regulatory requirements for air, water, and solid waste emissions. Based on the excellent environmental performance of the process, replication of the technology should cause no significant impacts on the environment.

Environmental impacts from the LPMEOH™ unit were minimal, since it was coupled with a preexisting coal gasification facility. Operation of the gasifier was not considered part of the LPMEOH™ Demonstration Project. The only waste streams of potential concern were the spent catalyst slurry, the catalyst guard bed and spent carbonyl guard bed spent adsorbents, waste oil (the mineral oil waste stream from the oil-water separator), recovered distillation liquids, and wastewater separated from the refined-grade methanol.

III.F.1 Spent Catalyst Slurry

The LPMEOH™ uses a catalyst comprised primarily of oxides of copper and zinc in powder form, slurried in mineral oil. During the demonstration period, a temperature programming procedure for reactor operation was developed, which increased catalyst life significantly, reducing the amount of spent catalyst generated. The spent catalyst slurry was sent periodically to a company that reclaimed the metallic components for reuse.

III.F.2 Catalyst Guard Bed and Carbonyl Guard Bed Spent Adsorbents

Spent materials from the catalyst guard bed and carbonyl guard bed were sent to a permitted hazardous waste landfill. These materials were stabilized prior to being landfilled.

III.F.3 Mineral Oil Waste Stream

Mineral oil waste, stemming from operation and maintenance of the LPMEOH™ facility during the demonstration period, was collected in an oil-water separator and sent for energy recovery to an incinerator within the Eastman complex.

III.F.4 Recovered Distillation Liquids

A crude-grade methanol stream, produced as a bottoms product from the second distillation column, and containing about 25 percent of the methanol that was produced in the LPMEOH™ unit, was sent to preexisting distillation equipment in the Eastman complex. This stream contains a small quantity of the mineral oil that is used in the preparation of the methanol catalyst slurry.

III.F.5 Waste Water Stream

The production of methanol from syngas yields water as a by-product. Water is separated from the refined-grade methanol in the methanol rectifier column and exits the demonstration unit as a crude-grade methanol stream. After further distillation in Eastman's facilities, water from the process is sent to a water treatment facility. Discharges from the water treatment system were in compliance with the National Pollutant Discharge Elimination System.

IV Market Analysis

IV.A Market Size

Table 4 presents the world supply and demand estimates for methanol through 2007 (Methanol Institute, 2002). Demand is predicted to remain fairly constant over this time period; the decreased demand for methanol (to produce methyl tertiarybutyl ether (MTBE)) will be offset by increases in other methanol-derived chemicals, such as formaldehyde and methyl methacrylate.

Table 4 World Methanol Supply/Demand Forecast

Supply, 10 ³ metric tons/yr	Year				
	2003	2004	2005	2006	2007
Capacity	35,680	38,617	40,692	39,944	40,910
Production	30,427	31,016	31,774	31,885	32,196
Excess Capacity	5,253	7,601	8,918	8,059	8,714
Operating Rate, %	85	80	78	80	79
Demand, 10 ³ metric tons/yr					
Formaldehyde	11,000	11,390	11,707	12,028	12,386
MTBE	7,506	7,428	7,197	6,598	6,207
Acetic Acid	3,339	3,374	3,649	3,735	3,826
Dimethyl Terephthalate	590	590	603	618	632
Methyl Methacrylate	892	923	979	1,004	1,030
Fuel Use	859	867	896	946	988
Solvent	1,285	1,313	1,342	1,379	1,411
Other	4,956	5,131	5,401	5,577	5,716
Total Demand	30,427	31,016	31,774	31,885	32,196

Adapted from the Methanol Institute fact sheet, "World Methanol Supply / Demand" Online: www.methanol.org.

It is clear from this table that if the market for methanol is to grow, then it must occur through increased use of methanol as a fuel, including: use as a source of hydrogen for fuel cells, since methanol is readily reformed; use as a blending agent in motor fuels; however, the most promising is perhaps use as a coproduct with electricity in coal-based IGCC systems, with the produced methanol used as a turbine fuel for peak shaving. The potential for coal-based IGCC in the U.S. could be as high as 60 GW by 2020 (DOE 2002). If coproduction were able to capture 10 to 20 percent of this market, there would be considerable opportunity for installing the LPMEOH™ process. Methanol produced by coal-based IGCC operations should be lower cost than methanol produced by conventional methanol-only units, and could displace higher priced methanol from other sources.

When operating on a low H₂/CO molar ratio syngas, the methanol produced by the LPMEOH™ process has a water content of about 1 percent by weight, compared with 2 to 20 percent by

weight for methanol from gas-phase processes. Since fuel-grade methanol is allowed a water content as high as 1 percent by weight, directly producing a product with a water content in this range represents a savings in separation costs. Economic evaluations have indicated that the LPMEOH™ process has an advantage in any of the following circumstances: the syngas has a low H₂/CO molar ratio, syngas delivery pressure is high, only modest once-through conversion is required, the syngas has a low sulfur content, the inert content of the syngas is relatively high, and only fuel-grade methanol is required.

IV.B Economics

To a large extent, economics are site specific, since they depend upon the quality of syngas provided, and the required specifications for the methanol produced. Volume 2 of the Final Report by Air Products (2003) presents economics for a 500-short tons/stream day plant, built in conjunction with a coal-based IGCC system. This means that capital equipment for much of the gas cleanup is included in the IGCC plant, and these costs are not included in the capital for the LPMEOH™ unit, except for equipment for removal of the last traces of contaminants from the syngas feed.

IV.B.1 Capital Costs

Capital cost for a 500-short ton/day LPMEOH™ unit feeding syngas with a H₂/CO molar ratio of 0.68 is estimated to be \$31.1 million (2002 dollars). The syngas is assumed to be available at a pressure of 1,000 psig, with a carbonyl sulfide (COS) content of 5 ppm by volume. This estimate is based largely on the costs incurred in the construction of the LPMEOH™ Demonstration Unit at Kingsport, including lessons learned during the project.

IV.B.2 Operating Costs

Operating costs for the LPMEOH™ process, based on operation of the Kingsport unit, are shown in Table 5.

Table 5 Operating Costs for a 500-Short Ton/Day LPMEOH™ Unit*

Cost Parameter	Units	Quantity	\$/Unit	\$10 ³ /yr
Fixed O&M Costs				
Operating Labor	----	----	----	736
Maintenance Labor	----	----	----	249
Maintenance Material	----	----	----	373
Subtotal Fixed Costs				1,358
Variable Operating Costs				
Syngas	10 ⁶ Btu/hr	1,434	4.50	50,875
Unreacted Gas	10 ⁶ Btu/hr	(995)	4.50	(35,300)
Electric Power	kW	425	0.04	134
Low Pressure Steam (100 psig)	10 ³ lb/hr	3.515	3.00	83
Medium Pressure Steam (200 psig)	10 ³ lb/hr	(49.3)	4.00	(1,555)
Cooling Water (20 °F temp. rise)	10 ³ gal/min	0.652	0.12	37

Cost Parameter	Units	Quantity	\$/Unit	\$10 ³ /yr
Miscellaneous Utilities	----	----	----	240
Methanol Catalyst	----	----	----	989
Zinc Oxide	lb/yr	104,000	3.58	337
COS Hydrolysis Catalysis	lb/yr	6,000	3.63	13
Subtotal Variable Costs				15,853
Total O&M Costs				17,211

*Unit on-stream factor is 0.9.

IV.B.3 Economics

Estimated economics for the LPMEOH™ process are shown in Table 6. Since many factors, such as size, mode of operation (recycle or once-through), operating pressure, sulfur level in the syngas, on-stream factor, and syngas cost and delivery pressure affect economics, values in Table 6 should be considered as only for guidance purposes. The cost of methanol from an LPMEOH™ unit integrated into a coal-based IGCC system is estimated to be in the range of 50 to 60 cents per gallon on a current dollar basis, or 40 to 50 cents per gallon on a constant dollar basis.

Table 6 Economics for a LPMEOH™ Plant*

Cost Factor	Base, 10 ⁶ dollars	Basis			
		Current Dollars		Constant Dollars	
		Factor	Cents/Gal	Factor	Cents/Gal
Capital Charge	31.1	0.160	10.0	0.124	7.8
Fixed O&M Cost	1.358	1.314	3.6	1.000	2.7
Variable Operating Cost	15.853	1.314	41.9	1.000	31.8
Total Levelized Cost of Methanol		----	55.5	----	42.3

*Basis: 500 short tons/day, 90 % capacity factor; 15-yr life; 303-gal methanol/short ton; once-through operation; equity financing.

IV.C Commercialization Plan

During the development phase of the LPMEOH™ process, Air Products assembled a team to manage the various programs needed to achieve commercial readiness. With the conclusion of the demonstration project, the goal of commercial readiness was achieved. Future commercial activities will be managed from Air Products' Worldwide Hydrocarbon Equipment business unit. Future designs and economic analyses will incorporate the lessons learned from the LPMEOH™ Demonstration Project, including the in situ activation procedure and the ensuing improved catalyst life.

V Conclusions

This was a very successful project. The LPMEOH™ Demonstration Unit started up without any significant problems and reached design capacity within a week. Approximately 104 million gallons of methanol were produced during the operational phase, and all available methanol produced was accepted by Eastman for the production of methyl acetate and, ultimately, cellulose acetate and acetic acid. During its operation, the facility achieved compliance with all applicable environmental regulations. Based on the excellent performance of the process, replication of the technology should cause no significant negative impacts on the environment.

The SBCR was successfully scaled from the 10 short tons/day (22 inch diameter reactor) LaPorte AFDU scale to the 260-short tons/day (7.5 ft diameter reactor) demonstration unit size. The scaled-up reactor exhibited good temperature stability, and was operable at a catalyst concentration of nearly 50 percent by weight. The only significant problem occurred with the early performance of the gas sparger. The performance of the sparger proved to be unsatisfactory, but was successfully replaced with a modified device using the same design principles as the original. The use of condensed mineral oil from the LPMEOH™ process as a continuous flush to the sparger was demonstrated, and this stream was returned by gravity rather than a pump, which greatly simplified plant operation.

Initially, the catalyst deactivation rate was higher than expected. Most of this deactivation was due to the presence of trace poisons, particularly arsenic and sulfur, entering the LPMEOH™ reactor. The introduction of new adsorbents in the Eastman catalyst guard bed and the carbonyl guard bed improved long-term catalyst performance. During the demonstration test, a new technique for activating the catalyst was developed, and a procedure was demonstrated for maintaining catalyst activity by programming the reactor temperature. This new approach can eliminate the need for catalyst withdrawal and addition in certain applications.

Tests made during the demonstration period confirmed that a LPMEOH™ unit has the capability to operate satisfactorily in a coal-based IGCC environment; it is able to operate on a syngas having a range of H₂/CO ratios (see Table A-1) and in on/off and ramping modes to follow the electrical demand of the power plant. As electrical demand varies, the amount of syngas available for conversion to methanol also varies, requiring the LPMEOH™ unit to vary its feed rate over short time intervals. The unit was able to achieve at least a 5 percent change in feed rate per minute during ramping, showing that the process is very flexible and stable.

Offsite fuel-use tests of stabilized methanol were conducted. In bus and FFV trials, stabilized methanol provided the same environmental benefits as chemical-grade methanol with no penalty on performance or fuel economy. Tests in a gas turbine and a diesel generator showed that levels of NO_x in the exhaust were lowered when stabilized methanol or methanol emulsions were used. However, lubrication additives will probably be required when stabilized methanol is fed to a gas turbine. Testing stabilized methanol (as the source of hydrogen) in a phosphoric acid fuel cell has shown that conventional steam reforming catalysts are not compatible with the trace mineral oil present in the stabilized methanol; but methanol from the LPMEOH™ process that is purified to chemical-grade specifications should be suitable for use in this application.

A 25-day test of the LPDME™ process was carried out in the LaPorte AFDU to evaluate the production of DME as a coproduct with methanol. This test showed promise, but no DME runs were made in the LPMEOH™ reactor at Kingsport.

The market for conventional uses of methanol is predicted to be relatively flat over the next 5 to 6 years. Therefore, the major opportunity for using the LPMEOH™ process is in conjunction with coproduction of electricity in coal-based IGCC systems.

The success of this project can be attributed to the unit design based on high quality data from test units; good cooperation among all parties involved; a well thought-out test plan; a well qualified operating crew; and a highly competent engineering staff, able to solve problems as they arose.

VI Acronyms and Abbreviations

AFDU	Alternative Fuels Development Unit
CCT	Clean Coal Technology
CO	carbon monoxide
COS	carbonyl sulfide
DME	dimethyl ether
DOE	U.S. Department of Energy
DVT	design verification testing
FFV	fuel-flexible vehicle
H ₂	hydrogen
IGCC	integrated gasification combined cycle
LPG	liquefied petroleum gas
LPMEOH™	Liquid Phase Methanol Process
MeOH	methanol
mol	mole
mpg	miles per gallon
MTBE	methl tertiarybutyl ether
NO _x	Nitrogen oxides
N ₂	nitrogen
PPA	post-project assessment
ppm	parts per million
psia	pounds per square inch absolute
SBCR	slurry bubble column reactor
SO ₂	sulfur dioxide

VII References

- Air Products Liquid Phase Conversion Co., L.P. *Commercial-Scale Demonstration of the Liquid Phase Methanol (LPMEOH™) Process*. Final Report, Volume 1: Public Design. Contract No. DE-FC22-92PC90543. January 2000.
- Air Products Liquid Phase Conversion Co., L.P. *Commercial-Scale Demonstration of the Liquid Phase Methanol (LPMEOH™) Process*. Final Report, Volume 2: Project Performance and Economics. Contract No. DE-FC22-92PC90543. June 2003.
- Methanol Institute. “World Methanol Supply / Demand” Online Fact Sheet:
<http://www.methanol.org/pdfFrame.cfm?pdf=methanolSupplyDemand02.pdf>. 2002.
- National Energy Technology Laboratory. *Forecasting the Benefits of DOE Programs for Advanced Fossil-Fuel Electricity Generating Technologies: The EIA High Fossil Electricity Technology Case*. October 2002. Online Report:
http://www.netl.doe.gov/coalpower/gasification/pubs/pdf/Forecast_of_FE_Program_Benefits_EIA_HFET_Case%2002-12-03.pdf
- U.S. Department of Energy. *Commercial-Scale Demonstration of the Liquid Phase Methanol (LPMEOH™) Process*. Comprehensive Report to Congress on the Clean Coal Technology Program. DOE/FE-0243P. August 1992.

VIII Bibliography

- Air Products Liquid Phase Conversion Co., L.P. *Commercial-Scale Demonstration of the Liquid Phase Methanol (LPMEOH™) Process Demonstration Technology Startup Report*. U.S. DOE Contract No. DE-FC22-92PC90543. September 1998.
- Air Products Liquid Phase Conversion Co., L.P. *Design and Fabrication of the First Commercial-Scale Liquid Phase Methanol (LPMEOH™) Reactor*. Topical Report U.S. DOE Contract No. DE-FC22-92PC90543. October 1998.
- Air Products Liquid Phase Conversion Co., L.P. *Economic Analysis of the LPMEOH™ Process as an Add-On to Integrated Gasification Combined Cycle (IGCC) for Coproduction*. Interim Report. U.S. DOE Contract No. DE-FC22-92PC90543. October 1998.
- Air Products Liquid Phase Conversion Co., L.P. *Liquid Phase Dimethyl Ether Demonstration in the LaPorte Alternative Fuels Development Unit*. U.S. DOE Contract No. Topical Report. DE-FC22-92PC90543. January 2001.
- Air Products Liquid Phase Conversion Co., L.P. *Off-Site Testing of Stabilized Methanol from the Liquid Phase Methanol (LPMEOH™) Process Volume I: Transportation Systems*. Topical Report. U.S. DOE Contract No. DE-FC22-92PC90543. February 2002.
- Air Products Liquid Phase Conversion Co., L.P. *Off-Site Testing of Stabilized Methanol from the Liquid Phase Methanol (LPMEOH™) Process Volume II: Power Generation Systems*. Topical Report. U.S. Doe Contract No. DE-FC22-92PC90543. February 2002
- Air Products Liquid Phase Conversion Co., L.P. *Market Outlook for Dimethyl Ether (DME)*. U.S. DOE Contract No. DE-FC22-92PC90543. April 2002.
- Air Products Liquid Phase Conversion Co., L.P. *Removal of Trace Contaminants from Coal-Derived Synthesis Gas*. U.S. DOE Contract No. DE-FC22-92PC90543. March 2003.
- Air Products Liquid Phase Conversion Co., L.P. *Project Data on Eastman Chemical Company's Chemicals-from-Coal Complex in Kingsport, TN*. U.S. DOE Contract No. DE-FC22-92PC90543. March 2003.
- Clean Coal Technology Compendium website:
<http://www.lanl.gov/projects/cctc/programs/program.html>
- Heydorn, E.C., V.E. Stein, P.J.A. Tijm, B.T. Street, and R.M. Kornosky. "Commercial-Scale Demonstration of the Liquid Phase Methanol (LPMEOH™) Process: Initial Operating Experience." *Proceedings of the Sixth Clean Coal Technology Conference*. (Reno NV), April 1998.
- U.S. Department of Energy. *Clean Coal Technology Commercial-Scale Demonstration of the Liquid Phase Methanol (LPMEOH™) Process*. Topical Report Number 11. U.S. DOE Contract No. DE-FC22-92PC90543. April 1999.

Appendix A

Table A-1 Test Conditions for the LPMEOH™ Demonstration Program

Run No.	Description	Typical Operating Conditions					Objective
		Temp., °C	Cat. Conc., wt%	H ₂ /CO at Inlet	Fresh Feed Rate, 10 ³ SCFH	MeOH Prod. Rate, ton/day	
1	Shakedown & design rate tests	250	31	3.5	833	248	Startup & shakedown
2	Measure gassed slurry level						Maximize reactor volumetric productivity
3	Test Texaco-type syngas feed	250	34	0.78	725	190	IGCC application; comparison to lab and LaPorte
5	Check @ Test 1 conditions	250	28	3.5	700	200	Catalyst life; comparison to lab and LaPorte
6	Catalyst addition & aging	235	36	4.1	750	225	Catalyst life
7	Test free drain of entrained/condensed oil to reactor						Enhance system flexibility and show economic benefit
8	Operation at design feed rate	235	43	4.0	850	256	Confirm operation at design conditions
9	Check for limitation on catalyst slurry concentration	235	49	3.7	750	207	Maximize reactor volumetric productivity
10	Catalyst addition to reach maximum productivity	235	44	3.5	700	196	Maximize reactor volumetric productivity
11	Catalyst withdrawal/addition test	235	44	3.2	670	190	Catalyst life
21	Test Destec-type syngas	235	45	1.0	700	200	IGCC application
2000-1	Catalyst withdrawal/addition test	235	43	3.2	725	210	Catalyst life
2000-2	Turndown & ramping tests						IGCC application
2000-3	Load following & on/off tests						IGCC application
2000-4	Study reactor feed H ₂ /CO ratio of 1.0	235	43	1.0	650	180	IGCC application

2000-5	Study reactor feed H ₂ /CO ratio of 0.7	235	39	0.67	500	130	IGCC application
2000-6	Reactor temperature ramp	235→250	47	2.6	580	165	Catalyst life
2000-7	Reactor inspection						Inspection of key system components
2000-8	In situ catalyst activation 1 & temperature programmed operation	216→250	40	3.0	500→650	150→200	Test of new commercial interest
2000-8	In situ catalyst activation 2 & temperature programmed operation	215	40	3.6	500→650	170→180	Test of new commercial interest
2000-9	Heat & material balance check; study reactor feed H ₂ /CO ratio of 0.5	220	42	0.5	575	160	IGCC application