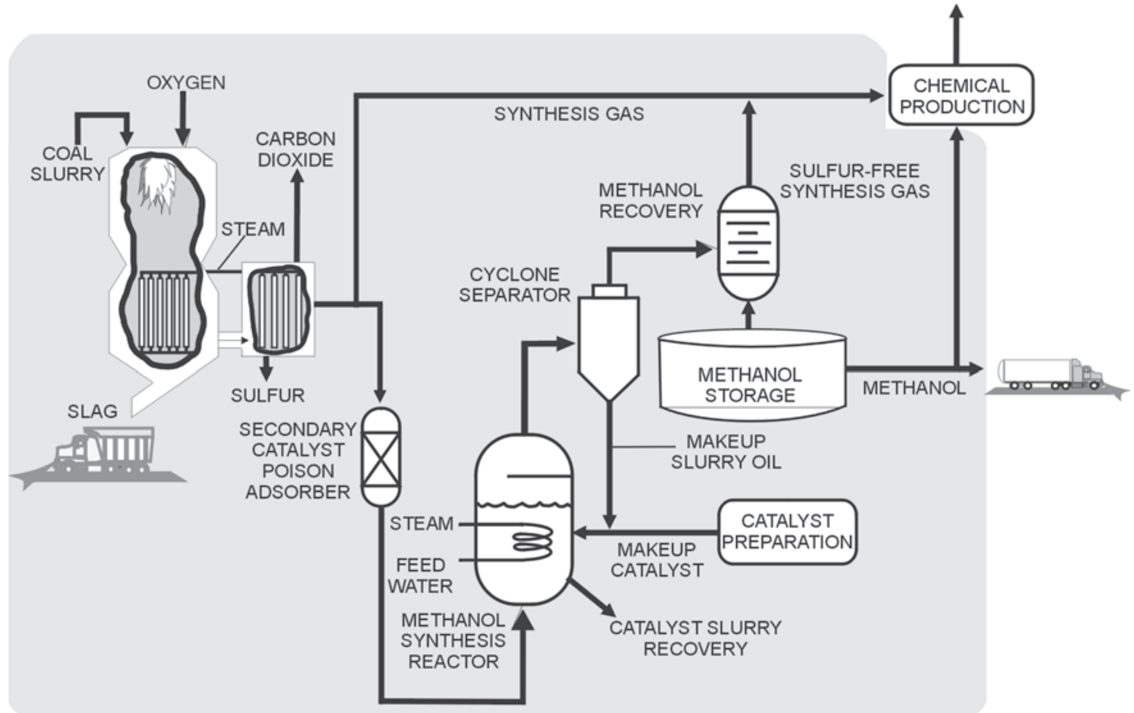
Commercial-Scale Demonstration of the Liquid Phase Methanol (LPMEOH™) Process



Participant

Air Products Liquid Phase Conversion Company, L.P. (a limited partnership between Air Products and Chemicals, Inc., the general partner, and Eastman Chemical Company)

Additional Team Members

Air Products and Chemicals, Inc.—technology supplier and cofunder

Eastman Chemical Company—host, operator, synthesis gas and services provider

ARCADIS Geraghty & Miller—fuel methanol tester and cofunder

Location

Kingsport, Sullivan County, TN (Eastman Chemical Company's Chemicals-from-Coal Complex)

Technology

Air Products and Chemicals, Inc.'s LPMEOH™ process

Plant Capacity/Production

80,000 gallons/day of methanol (nominal)

Coal

Eastern high-sulfur bituminous, 3–5% sulfur

Project Funding

Total	$213,700,000	100%
DOE	92,708,370	43
Participant	120,991,630	57

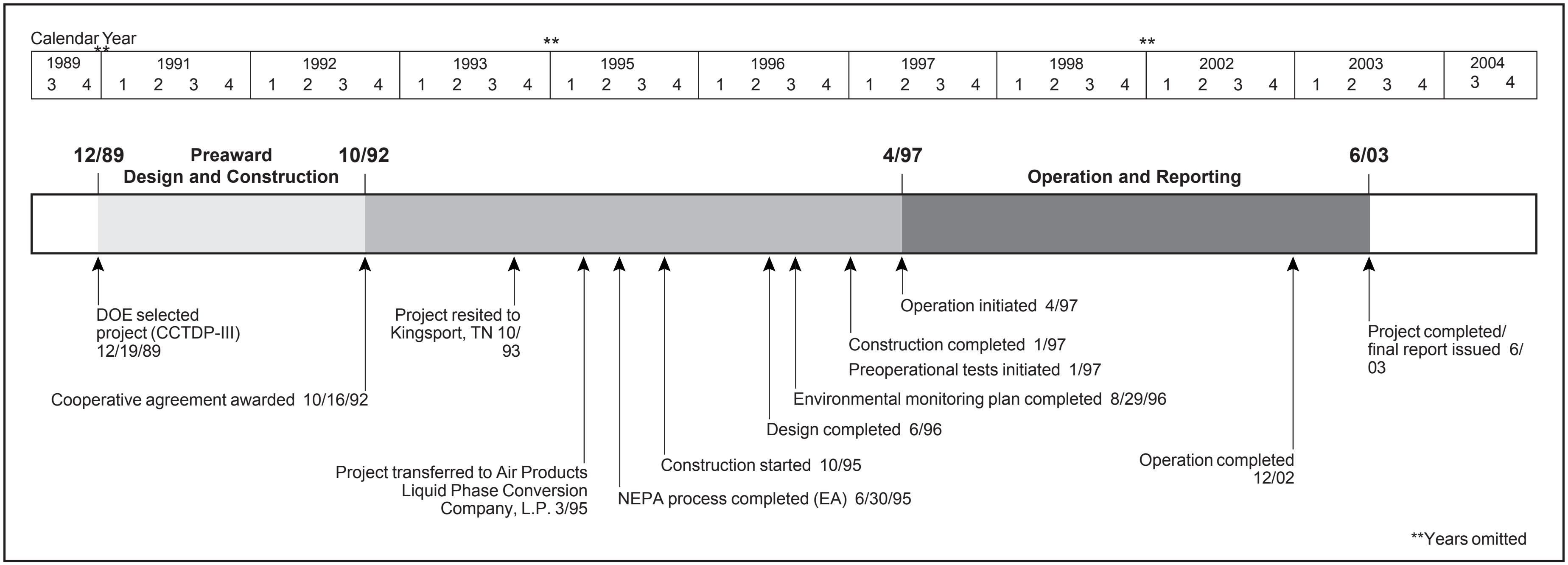
Project Objective

To demonstrate on a commercial scale the production of methanol from coal-derived synthesis gas using the LPMEOH™ process; to determine the suitability of methanol produced during this demonstration for use as a chemical feedstock or as a low-SO_x emitting, low-NO_x emitting alternative fuel in stationary and transportation applications; and to demonstrate, if practical, the production of dimethyl ether (DME) as a mixed co-product with methanol.

Technology/Project Description

This project has completed the demonstration, at commercial scale, of the LPMEOH™ process to produce methanol from coal-derived synthesis gas. The combined reactor and heat removal system is different from other commercial methanol processes. The liquid phase not only suspends the catalyst but functions as an efficient means to remove the heat of reaction away from the catalyst surface. This feature permits the direct use of synthesis gas streams as feed to the reactor without the need for water-gas shift conversion. Synthesis gas feed to the LPMEOH™ reactor is produced by the gasification of eastern high-sulfur bituminous coal (Mason seam) containing 3% sulfur (5% maximum) and 10% ash.

Methanol fuel testing was conducted in off-site stationary and mobile applications, such as fuel cells, buses, and distributed electric power generation. Stabilized methanol from the project was made available to several test locations to study the feasibility of using the product as a feedstock in transportation and power generation applications.



Results Summary

Environmental

- Stabilized methanol from the LPMEOH™ process has less than 1% of water by weight, is free of sulfur, and can potentially be used directly in transportation and power applications.
- Stabilized methanol produced from the LPMEOH™ demonstration unit has been tested in bus and flexible fuel vehicles. Results show that methanol produced from the process provides the same environmental benefits as chemical-grade methanol with no penalty on fuel economy or performance.
- Diesel generator and gas turbine tests show that levels of NO_x in exhaust air can be lowered when stabilized methanol or methanol-oil-water emulsions are used instead of conventional oil fuels.

Operational

- During the 69-month demonstration test program, the LPMEOH™ test unit had an overall availability of 97.5% with the longest operating run without interruption at 94 days.
- Over 103.9 million gallons of methanol were produced from the facility and accepted by Eastman Chemical Company for use in the production of methyl acetate. Methanol from the project was shipped to seven test locations to study the feasibility of its use in power and transportation applications.
- Nameplate production capacity of 80,000 gallons per day for the demonstration unit was achieved within four days of start-up, and production rates exceeding 115% of design capacity were achieved within six days.
- Investigations during the LPMEOH™ demonstration project were able to improve the long-term performance of the methanol synthesis catalyst. The average rate of catalyst deactivation during one six-month period was 0.17% per day, which is one-half of the original design basis, based on earlier proof-of-concept tests.
- In either baseload or cycling operation, partial conversion of between 20% and 33% of the syngas is economically optimal and conversion approaching 50% is feasible.
- Commercial viability of the Liquid Phase Dimethyl Ether (LPDME™) process was demonstrated on a 10 short ton per day scale using commercially produced catalysts.
- The deactivation rate for both the methanol synthesis and dehydration catalysts used in the LPDME™ process was 0.7% per day, which was lower than the 1.2% per day rate calculated during autoclave experiments.

Economic

- The capital cost of a 500 short ton per day LPMEOH™ plant that coproduces fuel-grade methanol in a coal-based IGCC plant was estimated to be $31.08 million.
- Economic studies show that the price of methanol co-produced in an IGCC power plant can be less than $0.50 per gallon.

Project Summary

The LPMEOH™ process accomplished the objectives set out in the cooperative agreement. The demonstration unit produced over 103.9 million gallons of methanol, operating at 97.5% availability. Originally developed to enhance electrical power generation using IGCC technology, the LPMEOH™ process is ideally suited for directly processing gases produced by modern coal gasifiers. The LPMEOH™ technology provides several improvements essential for the economic co-production of methanol and electricity directly from gasified coal. The 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.

Operational Performance

Operations began on April 2, 1997 and nameplate production capacity of 80,000 gallons per day was reached within four days. Production rates exceeding 115% of the design level were achieved within six days.

During the performance period, ideas to reduce the capital cost of future plants were implemented. The use of gravity to return entrained catalyst slurry and condensed process oil from downstream equipment back to the LPMEOH™ reactor was successfully demonstrated, and it eliminated the need for expensive slurry pumps within the synthesis loop. A new, *in situ* catalyst activation procedure was also developed. Previously, catalyst was activated in small quantities and transferred to the LPMEOH™ reactor. *In situ* activation involved charging the reactor with fresh catalyst and activating it at one time. The first *in situ* activation study began on August 24, 2001 and was completed on June 4, 2002. Additionally, "temperature programming" was used during this demonstration to improve catalyst performance. Temperature programming is the technique of initially operating at low temperatures and slowly increasing the temperature with time to maintain constant production of methanol and extend the life of the catalyst. The average catalyst deactivation rate for this demonstration was similar to earlier results.

A second, six-month, *in situ* activation study began on June 28, 2002. This study was similar to the first *in situ* activation study except that the procedure was revised to eliminate the storage of unreduced catalyst slurry at elevated temperatures. The average rate of catalyst deactivation during this study was 0.17% per day, which was about one-half of the design basis and lower than earlier results.

The LPMEOH™ demonstration project also focused on the impact of trace contaminants in coal-derived synthesis gas on catalyst performance and lifetime. The catalyst guard bed was changed to a new material that is expected to reduce catalyst poisons such as arsenic. This new adsorbent is an activated carbon impregnated with copper oxide. Typically, fresh adsorbent can be used for about two months before breakthrough of arsine at the LPMEOH™ demonstration unit. However, a thermal treatment was employed which extended the service life of the adsorbent by an additional two months.

The LPMEOH™ plant continues in commercial operation at Eastman Chemical Company.

Methanol product-use testing was conducted on-site and off-site. The on-site product-use testing involved constant monitoring of the refined-grade methanol according to a set of Eastman Chemical fitness-for-use criteria. Occasionally, a tank lot sample failed to meet the criteria, but the lot could be accepted on a case-by-case basis if there was no impact once the lot in question was mixed in the primary methanol storage tank. Through the end of December 1997, a total of 24 lots were accepted in this manner. Eastman Chemical accepted all of the available methanol for use in the production of methyl acetate, and ultimately cellulose acetate and acetic acid.

Off-site product testing consisted of transportation systems and power generation systems. Three vehicles at the Florida Institute of Technology were used to test methanol and methanol blends for bus and light-duty vehicles. Testing was limited, but no major problems were reported. Another set of tests at ARCADIS Geraghty & Miller showed methanol blends from the LPMEOH™ process exhibited similar performance for both fuel economy and emissions as when operated on fuel blends either stabilized methanol or chemical-grade methanol. West Virginia University (WVU) also tested three buses operation on methanol. On average, hydrocarbon (primarily unburned methanol and aldehydes) and particulate matter emissions were slightly higher than when chemical-grade methanol was used.

Power generation testing using stabilized methanol was conducted by WVU on an aircraft gas turbine, by ARCADIS on a U.S. Air Force aircraft ground support diesel generator, by ARCADIS on a low-NO_x stationary microturbine combustor, and by the University of Florida on a fuel cell. All of the test results were promising.

The LPMEOH™ project team performed a process design verification test run of the LPDME™ process to produce DME. The test was conducted at a pilot scale of 10 short tons per day at the LaPorte, Texas, Alternative Fuels Development Unit (AFDU). The plant was operated for 25 days using commercially produced catalysts to obtain scale-up information and to compare catalyst aging compared to laboratory results. The deactivation rate for both LPDME™ catalysts during the pilot scale test was 0.7%, which was an improvement over the 1.2% rate calculated during laboratory experiments.

Environmental Performance

Methanol produced from the LPMEOH™ process offers several advantages. It is a stabilized product that contains less than one percent of water by weight and is sulfur free, and could potentially be used as a replacement fuel for petroleum in transportation, a peaking fuel in power applications, a chemical feedstock, or as a source of hydrogen for fuel cells. Transportation tests were performed at three different locations on a variety of vehicles and methanol fuel blends. Methanol produced from the LPMEOH™ process showed little difference in vehicle performance when compared to fuels made with chemical-grade methanol. The LPMEOH™ methanol typically formed less NO_x than the chemical-grade methanol blends. Power application tests showed that stabilized methanol and methanol-oil-water emulsions could lower NO_x levels in the exhaust air from gas turbines and diesel engines that operate on conventional oil fuels.

Economic Performance

The economic base case for this project is a 500 short ton per day, LPMEOH™ plant that co-produces fuel-grade methanol in a coal-based IGCC power plant. The estimated capital cost for the LPMEOH™ facility in an IGCC power plant is $31.08 million. Improvements in catalyst performance, such as *in situ* activation, and temperature programming could provide an additional capital cost reduction of 10%.

Economic analyses show that methanol from the PMEOH™ process has a cost of less than $0.50 per gallon when co-produced in an IGCC power plant. As the economics of IGCC technology improve, so will the economics for coproduction of methanol. If the catalyst performance and lifetime improvements over the last six months can be maintained, variable costs for the LPMEOH™ process can be reduced by 25%. When combined with IGCC technology, the LPMEOH™ process can provide a pathway for local communities to meet their electric power, transportation, and chemical product needs.

Commercial Applications

In commercial U.S. applications, methanol is typically used as a feedstock to produce chemicals such as formaldehyde, methyl tertiary butyl ether (MTBE—a gasoline additive), acetic acid, dimethyl terephthalate, methyl methacrylate, and fuels and solvents. Future markets for methanol could include fuel cell applications. Currently, over 50% of the demand for DME is for use as a projectile agent. However, it is also used as a methylating agent, a laboratory system cleaning material, and in electronics. Future markets could include large-scale power production, substitution for diesel fuel, or as a replacement transportation fuel for liquefied petroleum gas.

Development of the LPMEOH™ process in the United States will depend on several factors, including development and timing of the IGCC industry, improvements in IGCC economics, new environmental regulations affecting coal-based power generation, and other incentives. Outside of the United States, most of the current interest in the LPMEOH™ technology has come from China. China has an abundance of coal and an historical dependence on domestic chemical production, making it a long-term option for use of the LPMEOH™ process.

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