

CLEAN COAL TECHNOLOGY



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

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

A report on a project conducted jointly under
a cooperative agreement between:

The U.S. Department of Energy and
Air Products Liquid Phase Conversion Company, L.P.



AIR
PRODUCTS 

EASTMAN

**CLEAN
COAL
TECHNOLOGY**

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

Executive Summary	5
Background	6
Project Description	8
Operating History	13
Cost/Demonstration Schedule	15
Integration of LPMEOH™ with IGCC Power Production	16
Conclusion	19
Bibliography	20
Contacts for CCT Project and U.S. DOE CCT Program	23
List of Acronyms and Abbreviations	24

Cover image: Photo of LPMEOH™
Project at Kingsport,
Tennessee

Executive Summary

The Clean Coal Technology (CCT) Program is a government and industry co-funded effort to demonstrate a new generation of innovative coal-utilization processes in a series of "showcase" facilities built across the country. These projects are carried out on a sufficiently large scale to prove commercial worthiness and generate data for design, construction, operation, and technical/economic evaluation of full-scale commercial applications.

The goal of the CCT Program is to furnish the U.S. energy marketplace with a number of advanced, more efficient, and environmentally responsible coal-based technologies that can overcome the economic and environmental impediments that limit the full utilization of coal. To achieve this goal, beginning in 1985, a multiphased effort consisting of five separate solicitations was administered by the U.S. Department of Energy (DOE). Projects selected through these solicitations have demonstrated technology options with the potential to meet the needs of energy markets while satisfying relevant environmental requirements.

This report discusses the demonstration of Air Products and Chemicals, Inc.'s Liquid Phase Methanol (LPMEOH™) Process. The LPMEOH™ Process is designed to convert synthesis gas derived from the gasification of coal into methanol for use as a chemical intermediate or as a low-sulfur dioxide and low-nitrogen oxides emitting alternative fuel. Synthesis gas, frequently referred to as syngas, is basically a mixture of hydrogen and carbon monoxide; but, depending upon how it is produced, it may contain other gases, such as carbon dioxide. Since gasifiers can handle a wide range of coal types and produce a variety of syngas compositions, virtually any coal can be gasified to produce syngas as feedstock for the LPMEOH™ Process.

The LPMEOH™ Process differs from traditional methanol processes in that it uses a slurry

bubble column reactor (SBCR) instead of the usual fixed-bed reactor. In the SBCR, powdered catalyst is suspended in an inert oil rather than catalyst pellets being loaded into beds or tubes, as is the case in a gas-phase, fixed-bed reactor.

The SBCR has several advantages over a fixed-bed reactor. First, it has excellent temperature control, which is critical because the methanol production reactions are highly exothermic. Second, catalyst can be added to and removed from the reactor during operation, which permits high unit availability, maintenance of constant catalyst activity, and achievement of optimum catalyst activity level for a given set of operating conditions. In addition, higher syngas conversion levels are possible, and a wide range of gas compositions can be fed to the reactor.

The LPMEOH™ Process was developed during the 1980's with the financial support of DOE. The concept was proven in over 7,400 hours of operations in the DOE-owned Alternative Fuels Development Unit located in LaPorte, Texas. Although the LPMEOH™ Process can be utilized as a stand-alone unit, a major driving force behind its development was to enhance the performance of Integrated Gasification Combined Cycle (IGCC) power generation.

An important feature of the LPMEOH™ Process is its highly stable character. The slurry reactor is suitable for rapid ramping, idling, and even extreme start/stop operations. The thermal moderation provided by the liquid in the reactor acts to buffer short, transient operations such as changes in syngas composition that would not normally be tolerable in a gas-phase methanol synthesis reactor. This characteristic is especially advantageous in the environment of electricity demand load-following in IGCC facilities.

Another differentiating feature of the LPMEOH™ Process is that it can produce a high-quality methanol product directly from syngas rich in carbon oxides. Gas-phase methanol synthesis, which must rely on hydrogen-rich syngas, yields a crude methanol product with

4 to 20% water by weight. The product from the liquid phase process, when feeding carbon monoxide-rich syngas, typically contains only 1% water by weight. As a result, raw methanol, coproduced with electricity in an IGCC facility, is suitable for many uses at a substantial savings in purification costs.

Potential applications for the methanol are as a source of hydrogen or syngas for small fuel cells or industrial applications, as a feedstock for methyl tertiary butyl ether (MTBE) and other chemicals, as a clean-burning fuel, and as a source of peaking power for an IGCC plant.

The LPMEOH™ Demonstration Project is located at Eastman Chemical Company's chemicals-from-coal complex at Kingsport, Tennessee. There are a number of advantages to this site. In addition to producing syngas, the gasification complex at Kingsport also produces hydrogen-rich and carbon monoxide-rich gas streams. By mixing these gases in different proportions, a wide range of feed compositions were produced during the demonstration, thus simulating the feed gas from a variety of commercially available gasifiers. Another advantage is that Eastman is able to use the methanol produced as feedstock for downstream processes.

DOE selected the LPMEOH™ project in CCT Round III, and the cooperative agreement was awarded in 1992. Construction began in October 1995 and was completed in January 1997. The first production of methanol occurred on April 2, 1997, and nameplate capacity of 260 tons per day (TPD) was achieved on April 6, 1997. Production rates of over 300 TPD of methanol have been achieved, and availability for the demonstration unit has exceeded 96% since startup.

As part of the demonstration, as-produced methanol from the LPMEOH™ project is being tested at off-site locations for a variety of applications, including as fuel for buses, light vehicles, fuel cells, and stationary turbines.

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

Background

The Clean Coal Technology (CCT) Program, sponsored by the U.S. Department of Energy (DOE), is a government and industry co-funded technology development effort conducted since 1985 to demonstrate a new generation of innovative coal-utilization processes.

Although coal is our most abundant fossil energy resource, it has the reputation of being a dirty fuel. The CCT Program is dispelling that perception by demonstrating technologies that utilize coal in an environmentally responsible way.

The CCT Program involves a series of “showcase” projects, conducted on a sufficiently large scale to demonstrate commercial worthiness and to generate data for design, construction, operation, and technical/economic evaluation of full-scale commercial applications.

The goal of the CCT Program is to furnish the U.S. energy marketplace with advanced, more efficient coal-based technologies, technologies that are capable of mitigating some of the economic and environmental impediments that inhibit the use of coal as an energy source.

The CCT projects can be divided into four major categories: advanced electric power generation, environmental control devices, coal processing for clean fuels, and industrial applications. The Liquid Phase Methanol (LPMEOH™) Demonstration Project described in this report falls in the coal processing for clean fuels category.

The feed to the LPMEOH™ Process is synthesis gas (frequently referred to as syngas), a mixture of hydrogen and carbon monoxide. This mixture is called synthesis gas because it is the starting point for the manufacture of a wide variety of fuels and chemicals, ranging from hydrogen through methanol, ammonia, acetic anhydride, dimethyl ether (DME), methyl tertiary butyl ether (MTBE), liquid hydrocarbons, and



**Eastman Chemical Company's
chemicals-from-coal complex
at Kingsport, Tennessee.**

waxes. Syngas can also be burned directly as a fuel. An important way to make syngas is by partial oxidation of coal in a gasifier.

In addition to the versatility of the products that can be made from it, a major advantage of using syngas as a feedstock is that during its production, the sulfur and nitrogen in the coal are converted to hydrogen sulfide and ammonia, which are easily removed from the syngas by a variety of readily available processes. Furthermore, particulates are removed in the gasifier complex. Thus, the syngas which is produced is essentially free of contaminants. Consequently, the products made from the syngas are also free of contaminants. A final advantage is that almost any carbonaceous material can be converted to syngas, thus providing a great deal of gasifier feedstock flexibility.

In a stand-alone application, the as-produced methanol from the LPMEOH™ Process can be used directly in certain fuel and chemical applications; it can also be upgraded to chemical-grade methanol,

as required. The LPMEOH™ Process can enhance Integrated Gasification Combined Cycle (IGCC) power generation by converting part of the syngas from the gasifier to methanol, which can either be sold as a value-added product or used as a peak-shaving fuel.

The LPMEOH™ technology was developed by Air Products and Chemicals, Inc. during the 1980's with financial support from the DOE. The concept was proven in over 7,400 hours of test operations in the DOE-owned, 10-ton-per-day Alternative Fuels Development Unit (AFDU) located at LaPorte, Texas.

In 1989, the LPMEOH™ Process was selected under DOE's CCT Program for commercial-scale demonstration. The project is being carried out under a cooperative agreement between DOE and the Air Products Liquid Phase Conversion Company, L.P. (a partnership between Air Products and Chemicals, Inc. and Eastman Chemical Company), which was formed to conduct the demonstration.



View of LPMEOH™ Demonstration Unit with building housing catalyst facilities in foreground.

Project Description

The demonstration unit, which occupies 0.6 acres, is integrated into the existing 4,000-acre Eastman chemicals-from-coal complex located in Kingsport, Tennessee. The Eastman complex employs approximately 12,000 people. In 1983, Eastman constructed a coal gasification facility utilizing Texaco technology.

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, carbon monoxide, and 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.

Technology Description

There are many characteristics that distinguish the LPMEOH™ Process from conventional methanol-production technology, the most important being:

- Carrying out the synthesis in a slurry bubble column reactor (SBCR) employing a powdered catalyst suspended in an inert mineral oil.
- The stable nature of the LPMEOH™ Process, which accommodates rapid changes in feed rate and composition without operational problems or catalyst damage.
- The ability to operate on a syngas rich in carbon oxides and produce

a product that does not require further purification before being used as a fuel.

- Excellent temperature control and heat removal capabilities.
- The ability to add and withdraw catalyst while on-stream.

Methanol synthesis in a liquid medium is the main feature that differentiates the LPMEOH™ Process from conventional methanol-production technology. Conventional methanol reactors use fixed beds of catalyst pellets and operate in the gas phase, but the heart of the LPMEOH™ Process is the SBCR. In a SBCR, powdered catalyst is suspended in an inert liquid to form a slurry, and feed gas is introduced into the bottom of the reactor through a distributor. The upward flowing gas bubbles provide the energy to keep the slurry highly mixed.

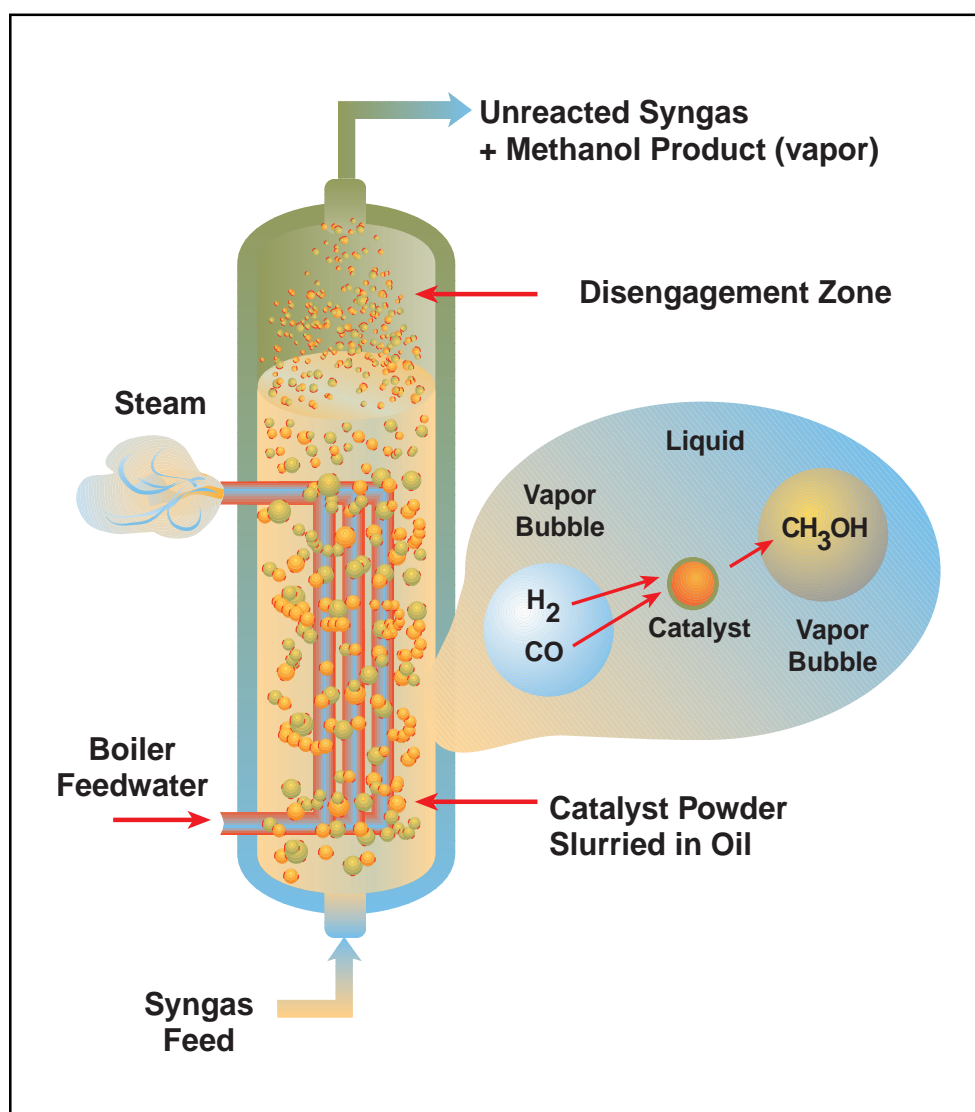
In the LPMEOH™ Process, the slurry medium is an inert mineral oil. The mineral oil acts as a temperature moderator and facilitates heat removal by transferring the heat of reaction from the catalyst surface to boiling water in an internal tubular heat exchanger. The heat transfer coefficient on the slurry side of the heat exchanger is relatively large. Thus, a relatively small heat transfer area is required, and the heat exchanger occupies only a small fraction of the cross-sectional area of the reactor.

This ability to efficiently remove heat and maintain a constant, highly uniform temperature throughout the entire length of the reactor allows the SBCR to achieve high syngas conversion.

The LPMEOH™ reactor's excellent temperature control capability allows the direct processing of syngas rich in carbon oxides (carbon monoxide and carbon dioxide). Gas-phase methanol technology, which uses fixed-bed reactors, requires such a feedstock to undergo stoichiometry adjustment by the water gas shift reaction (to increase the hydrogen content)

followed by carbon dioxide removal (to reduce the excess carbon oxides).

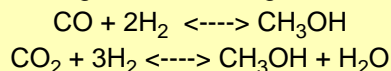
In conventional gas-phase reactors, either cool, unreacted gas is injected between catalyst beds, or the catalyst is loaded into tubes, and a cooling medium is circulated on the outside of the tubes to control temperature. With these schemes, conversion per pass is limited because of the limited heat removal capabilities of conventional reactor designs.



LPMEOH™ Slurry Bubble Column Reactor Schematic. In a SBCR, reactants from the gas phase dissolve in the liquid and diffuse to the catalyst surface, where they react. Products then diffuse through the liquid back to the gas phase. Heat is removed by generating steam in an internal tubular heat exchanger.

Chemistry of Methanol Production

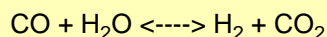
Methanol is produced by the hydrogenation of carbon oxides over a suitable catalyst, according to the following reactions:



Typical reaction conditions are a temperature of 225-270°C and a pressure of 725-1,450 psia. Because the volume of the products is less than the volume of the reactants, higher pressures favor higher conversion.

Both these reactions are highly exothermic; the first reaction liberates 21.7 kcal of heat per gram mole of carbon monoxide converted, and the second reaction gives off 12.8 kcal per gram mole of carbon dioxide reacted. One of the most difficult design problems of methanol synthesis is removing the heat of reaction while maintaining precise temperature control to achieve optimum catalyst life and reaction rate. Catalyst life is seriously reduced by excessive temperatures.

The LPMEOH™ technology is particularly well suited to coal-derived, carbon monoxide-rich syngas. In general, for syngas with a high carbon monoxide content, conversion is limited by hydrogen availability. If a higher conversion is desired than the hydrogen content of the syngas permits, one option is to utilize the inherent shift conversion activity of the methanol catalyst. This is done by adding steam to the reactor feed. The steam reacts with some of the carbon monoxide to form additional hydrogen as shown below:



The hydrogen thus produced reacts with carbon monoxide to form additional methanol. The extent of this reaction is equilibrium limited, and if syngas conversion in excess of 50% is required, then a carbon dioxide removal unit can be used in conjunction with steam addition.

Typically, a gas-phase reactor is limited to about 16% carbon monoxide in the reactor inlet gas. In contrast, for the LPMEOH™ Process, carbon monoxide concentrations in excess of 50% have been routinely processed in the laboratory and at the AFDU in LaPorte without any adverse effect on catalyst activity.

The features just discussed make the LPMEOH™ Process very stable and, thus, suitable for rapid ramping, idling, and even extreme start/stop operations. The thermal moderation provided by the liquid inventory in the reactor acts to buffer rapid transients that could not normally be tolerated in a gas-phase methanol synthesis reactor.

Another important characteristic of the LPMEOH™ Process is its ability to produce a high quality methanol product directly from a syngas rich in carbon oxides. Gas-phase methanol synthesis, which relies on hydrogen-rich syngas, results in a crude methanol product with 4 to 20% water by weight. The fuel-grade product from the LPMEOH™ Process typically contains only 1% water.

This fuel-grade methanol is suitable for many applications without purification at a substantial cost savings. However, if chemical-grade methanol is desired, sufficient steam is available from the reactor heat exchanger to achieve the required purity by distillation.

The ability of the LPMEOH™ Process to withdraw spent catalyst slurry and add fresh catalyst while on-stream facilitates uninterrupted operation while simultaneously maintaining a high productivity level in the reactor. The catalyst replacement rate can be set to optimize reactor productivity. Typically, catalyst replacement should be set to maintain the activity in the reactor at about half the fresh value, but the choice is ultimately an economic optimization of catalyst usage versus reactor productivity.



The Alternative Fuels Field Test Unit, containing state-of-the-art equipment, is used to determine the effect of poisons on catalyst performance and life.

Although there are many potential applications for the LPMEOH™ Process, a major driving force for its development was to enhance IGCC power generation. LPMEOH™ combined with IGCC allows power and methanol to be coproduced.

The Project Site

The LPMEOH™ Demonstration Project is located at Eastman's Kingsport, Tennessee, chemicals-from-coal complex.

Eastman began coal gasification operations at Kingsport in 1983. Texaco gasifiers are used to convert about 1,000 tons per day (TPD) of high-sulfur, eastern bituminous coal into syngas for the manufacture of methanol, acetic anhydride, and associated products. Oxygen for gasification is supplied by pipeline from an Air Products air separation unit. The crude syngas is quenched, sent to a shift converter to convert part of the carbon monoxide into hydrogen, and then subjected to acid gas (carbon dioxide and hydrogen sulfide) removal.

Part of the syngas is processed in a cryogenic separation unit to produce separate hydrogen-rich and carbon monoxide-rich streams. The hydrogen-rich stream is combined with clean syngas that bypasses the cryogenic unit to produce a stoichiometrically balanced feed for a conventional gas-phase methanol synthesis unit. Methanol from this unit is reacted with acetic acid to produce methyl acetate. Finally, the methyl acetate is reacted with the carbon monoxide stream to produce acetic anhydride.

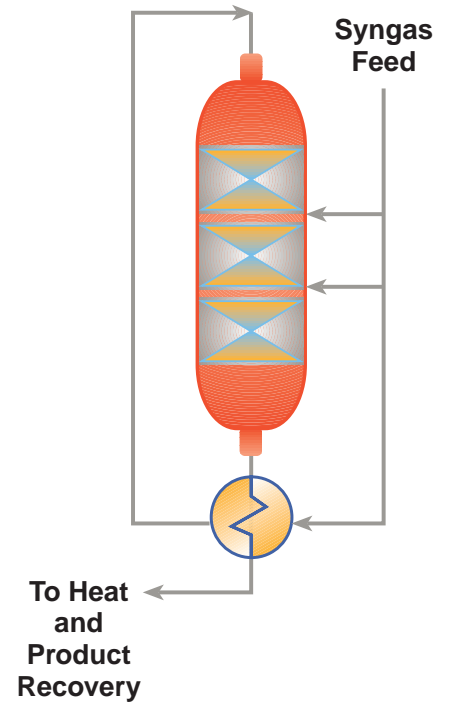
Because clean, balanced syngas, carbon monoxide-rich, and hydrogen-rich streams are individually available, the LPMEOH™ Demonstration Unit was designed with the capability to blend these streams and mimic the gas compositions of a range of gasifiers.

Off-site Testing and Product-Use Demonstration

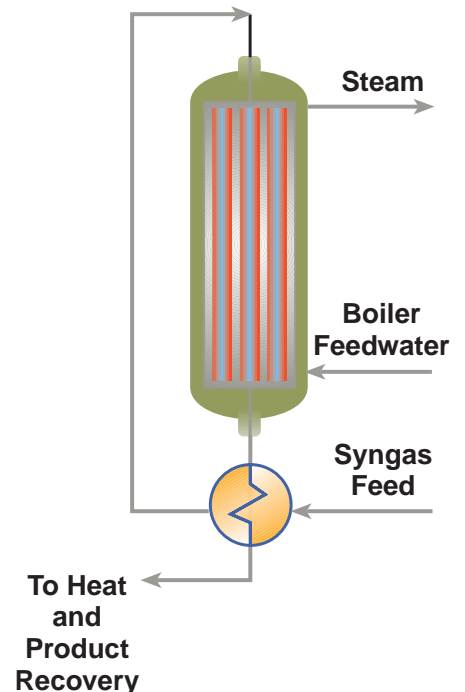
Although most of the methanol produced by the LPMEOH™ Demonstration Project is being used on-site by Eastman, some as-produced product, that is, product with only the light gases removed, is being shipped to a number of off-site locations for testing in a variety of applications.

The objective of this fuel-use testing is to demonstrate commercial market applications for the as-produced methanol as a replacement fuel and as a fuel supplement. Economics will be determined for the as-produced methanol for use as a fuel in municipal, industrial, and utility applications, and as a supplement for gasoline, diesel, and natural gas. A wide range of uses are being evaluated, including fuel for a flexible fuel vehicle, stationary turbines, buses, light-duty vehicles, and a fuel cell.

Gas Phase Reactor Catalyst in Beds



Gas Phase Reactor Catalyst in Tubes



Fixed-Bed Reactor Schematics. In gas-phase reactors, the catalyst is either placed in beds in the reactor shell or else placed in tubes. If the catalyst is in beds, then temperature is controlled by injecting cold syngas between the beds. If the catalyst is in tubes, then water is circulated outside the tubes, and heat is removed as steam.

Demonstration Unit Process Flow Description

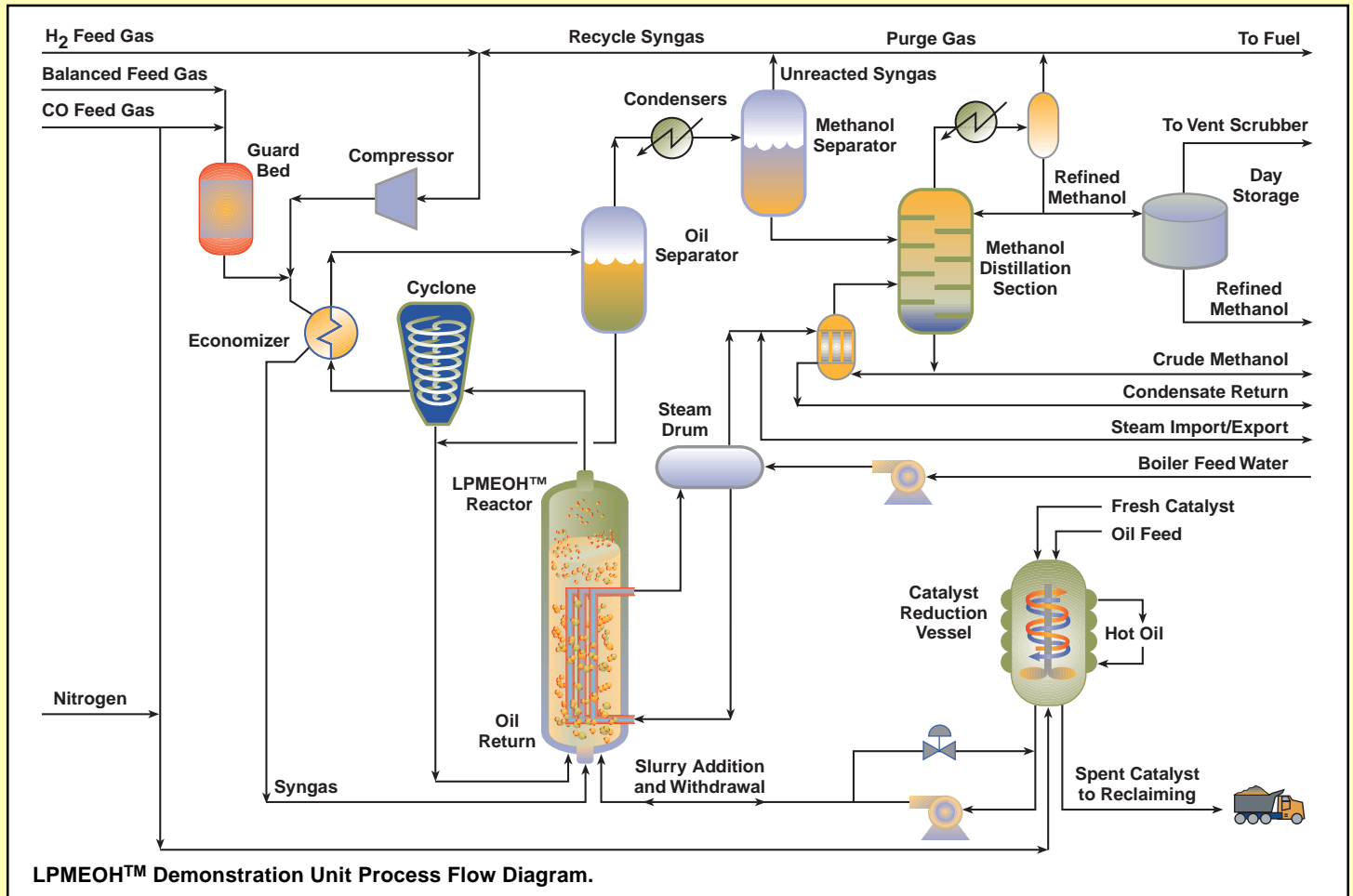
In the LPMEOH™ Demonstration, approximately half of the syngas from the gasification facility is diverted from the existing methanol unit to the LPMEOH™ Unit. Two other feed streams are supplied to the demonstration unit, a high-purity carbon monoxide stream from the gasification facility and a hydrogen-rich stream from the existing methanol unit. Since the hydrogen-rich gas stream is at a lower pressure than the other two feed streams, it is combined with the LPMEOH™ recycle gas, and the combined stream is compressed in the recycle compressor.

The carbon monoxide and fresh balanced syngas are combined and passed through the carbonyl guard bed, which is packed with activated carbon to remove possible contaminants in the feed gas. The combined fresh feed and recycle are preheated in the feed/product exchanger. The preheated feed gas is introduced into the LPMEOH™ reactor, where it mixes with the catalyst slurry and is partially converted to methanol vapor. The heat of reaction is absorbed by the slurry and transferred to the internal heat exchanger, where steam is generated. The slurry temperature of about 250°C is controlled by varying the steam pressure in the heat exchanger tubes.

The disengagement of the product gas from the catalyst/oil slurry occurs in the vapor space above the slurry in the upper part of the reactor. Any entrained slurry droplets in the gas leaving the top of the reactor are collected in a cyclone separator. The product gas from the cyclone is cooled in the feed/product exchanger, and any condensed oil is collected in the high pressure oil separator and returned to the reactor along with the entrained slurry from the cyclone separator.

The product gas is further cooled to condense the methanol product, which collects in the methanol separator. Inerts are purged from the system,

and the methanol is sent to the methanol separator. The methanol is then sent to the methanol distillation section for further purification. The refined methanol is stored in day storage tanks. The spent catalyst is sent to reclaiming.



and the remainder of the unreacted syngas is recycled.

The condensed methanol is sent to a two-column distillation train. In the first column, light impurities are removed. In the second column, chemical-grade methanol is recovered, along with a crude methanol bottoms stream containing higher alcohols, water, and traces of process oil. This bottoms stream is sent to the distillation system in Eastman's existing gas-phase methanol plant for recovery of the methanol it contains. As-produced, fuel-grade methanol for off-site product-use testing is produced at limited times by using only the first distillation column.

In addition to the equipment already discussed, the LPMEOH™ unit contains catalyst activation facilities, consisting of an agitated catalyst reduction vessel, where powdered catalyst in oxide form is combined with mineral oil to produce by weight containing 30% catalyst slurry. After the agitator is stopped, reducing gas, consisting of a blend of nitrogen and carbon monoxide, is introduced into the reduction vessel via a gas distributor. The carbon monoxide reacts with the oxide form of the catalyst to convert it to the active metallic form.

During reduction, slurry temperature is carefully increased while the consumption of carbon monoxide is monitored to determine when complete reduction has occurred. After reduction, the catalyst is pumped to the LPMEOH™ reactor. Before fresh slurry is added to the reactor, an equivalent amount of spent slurry is removed and sent to metals recovery or safe disposal.

Operating History

After checkout during the first quarter of 1997, the LPMEOH™ reactor was charged with nine batches of catalyst activated in the catalyst reduction vessel. This corresponds to about 50% of the design catalyst loading in the reactor. The activation procedure went very well, with the carbon monoxide usage for each batch being within 5% of the stoichiometric value.

Syngas was first introduced into the unit on April 2, 1997, and by April 6, 1997, the design production rate of 260 TPD of methanol had been reached. Four days later, on April 10, 1997, a production rate of more than 300 TPD was achieved. Rapid progression from first introduction of syngas to operation at greater than design rate is an indication of the inherent stability of the LPMEOH™ Process.

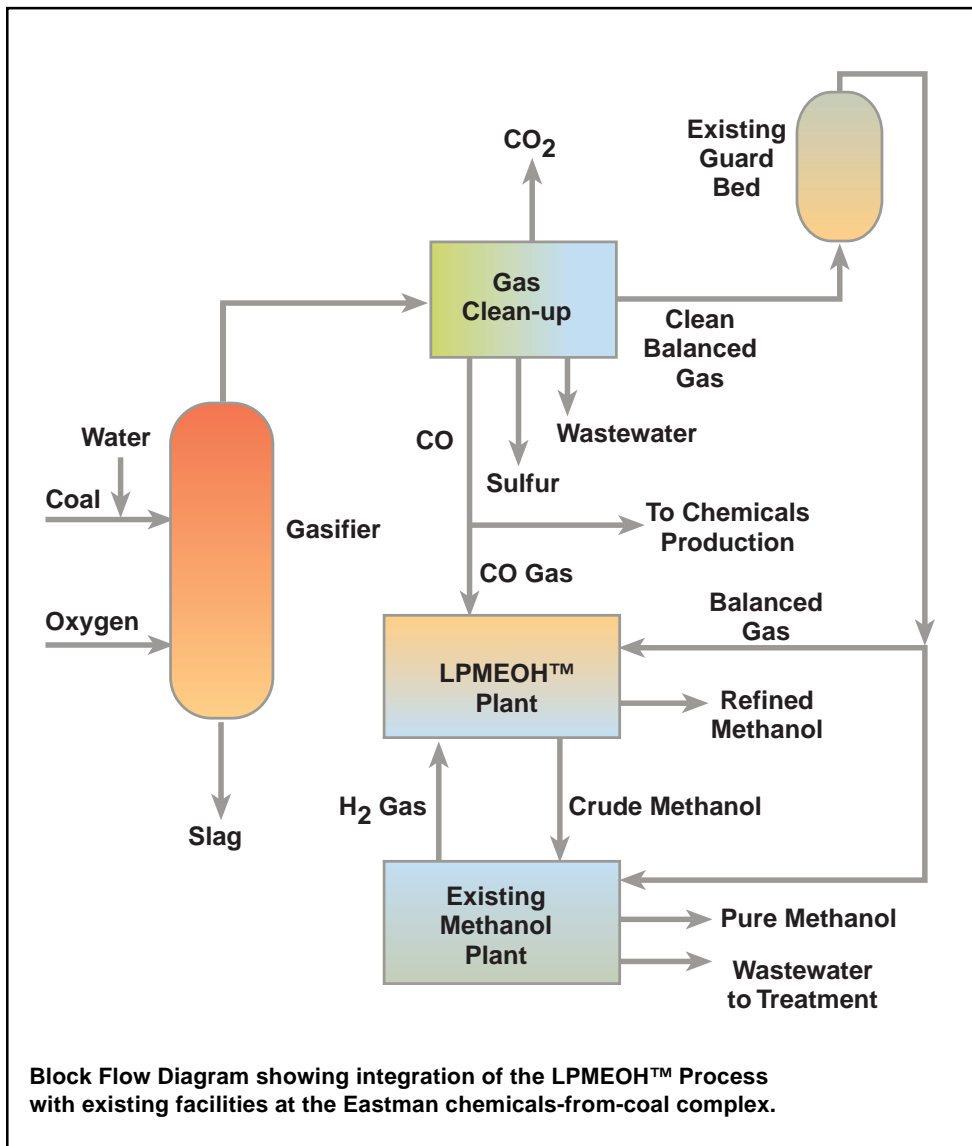
Much of the 1997 operating period was dedicated to confirming design and scale-up assumptions that had been based on laboratory and LaPorte AFDU data. Since startup, the heat removal performance of the LPMEOH™ reactor has been outstanding. The heat transfer coefficient for the internal heat exchanger has exceeded the design value, and there has been little indication of fouling.

Temperatures throughout the reactor have been quite uniform, with the difference between the maximum and minimum temperatures being only a few degrees. Measurements from pressure-differential transmitters located at regular intervals along the length of the reactor showed that hydrodynamics matched the predictions of correlations developed from LaPorte AFDU data.

Some initial operational problems related to slurry flows and solids accumulation within the demonstration unit were resolved with minor piping modifications and additional flush connections.



Erection of the reactor vessel at the LPMEOH™ Demonstration Unit.



These modifications are expected to result in significant benefits for future designs, including significant capital cost savings, increased operating flexibility, and lower maintenance costs.

Throughout its operation, overall performance of the LPMEOH™ Demonstration Unit has been monitored to determine the change in activity as the catalyst is exposed to the trace contaminants present in coal-derived syngas. Determining catalyst life is one of the major goals of the demonstration project.

Initial catalyst activity was excellent, confirming the validity of the activation procedure for the catalyst, but during the first month of operation the rate of deactivation was much higher than expected. However, from June through November 1997, the deactivation rate declined to a value more typical of laboratory results.

Analyses of catalyst samples from the LPMEOH™ reactor indicated that, for unexplained reasons, a large increase in the concentration of iron on the catalyst occurred during the initial six weeks of operation. Although arsenic levels were also higher than expected, arsenic poisoning does not appear to totally account for the deactivation observed.

Because the initial catalyst charge had experienced significant deactivation, the reactor was drained, and a new charge of fresh catalyst was activated during December 1997. At the same time, to determine if there was any unusual concentration of catalyst poisons in the Kingsport syngas, the Alternative Fuels Field Test Unit (AFFTU), containing state-of-the-art testing and analytical equipment, was installed on a slip stream of the feed to the LPMEOH™ Unit.

The initial performance of the fresh catalyst charge at a slightly reduced temperature of 235°C was excellent, with methanol production again exceeding nameplate capacity. No rapid decrease in activity occurred during the initial month

on-stream, as had happened in the first startup in April 1997. Furthermore, the rate of activity decline was slightly less than in the parallel AFFTU, although the deactivation rate was measurably greater than in the LaPorte AFDU.

This is thought to be the result of higher levels of catalyst poisons (iron, sulfur, arsenic, etc.) in the coal-derived syngas at Kingsport compared to the natural gas-derived syngas used at the LaPorte AFDU, which experienced a very slow loss of activity with time.

A very successful 24-day operating period ended on July 14, 1998. During this operation at 235°C, the catalyst deactivation rate was only 0.2% per day, which is less than half the target rate from the tests at the LaPorte AFDU.

In test runs using carbon monoxide-rich feed gas, the hydrogen-to-carbon monoxide molar ratio of the reactor feed was varied between 0.4 and 0.8. The methanol production rate was as expected, and the catalyst deactivation rate was equivalent to that with hydrogen-rich feed gas.

From April 1997, when initial operations began, to December 1998 the LPMEOH™ Demonstration Unit achieved an availability in excess of 96%. This includes a period of 94 days in which the unit was continuously available.

Since startup, the hydrogen-to-carbon monoxide ratio in the reactor feed stream has varied from 0.4 to 5.6 with no negative effect on performance. Important parameters, such as reactor inlet superficial gas velocity, expanded slurry-bed level, and the overall heat transfer coefficient of the internal heat exchanger, have been shown to be satisfactory at 115 to 120% of design feed rate. On-line catalyst addition has been performed successfully. Over 32 million gallons of methanol have been produced, and product purity has consistently met Eastman's requirements for downstream chemical processing.

Cost/Demonstration Schedule

The estimated total project cost is \$214 million, of which DOE's share is \$93 million or 43%.

A 40-month schedule was developed, which includes basic and detailed design, permitting, fabrication, construction, tie-ins, and program management. After receipt of the required permits, construction was started in October 1995 and was completed in January 1997. Startup operations began following completion of construction, and syngas was first introduced to the unit on April 2, 1997. Operation at design capacity of 260 TPD of methanol was reached on April 6, 1997.

The demonstration phase, which began in April 1997 and will extend into the first quarter of 2001, has a number of objectives, including:

- Determination of catalyst aging rate when feeding coal-derived syngas.
- Operation with syngas simulating various gasifiers, such as Texaco, Destec, BGL, and Shell, as well as syngas from natural gas reforming.
- Operation at high gas velocity and high syngas conversion.
- Gaining experience with the addition and withdrawal of catalyst while on-stream.
- Simulation of load-following operations (turndown, ramping, on/off tests).
- Production of fuel-grade methanol for off-site product-use tests.
- Determination of maximum allowable catalyst concentration and maximum reactor productivity.
- Operation with steam addition.
- Operation with an alternative catalyst.
- Identification of modifications to equipment and operations that will improve performance and decrease costs (some have already been implemented).
- Collection of a large body of operating data that will be available for the benefit of DOE, project participants, and others.

Integration of LPMEOH™ with IGCC Power Production

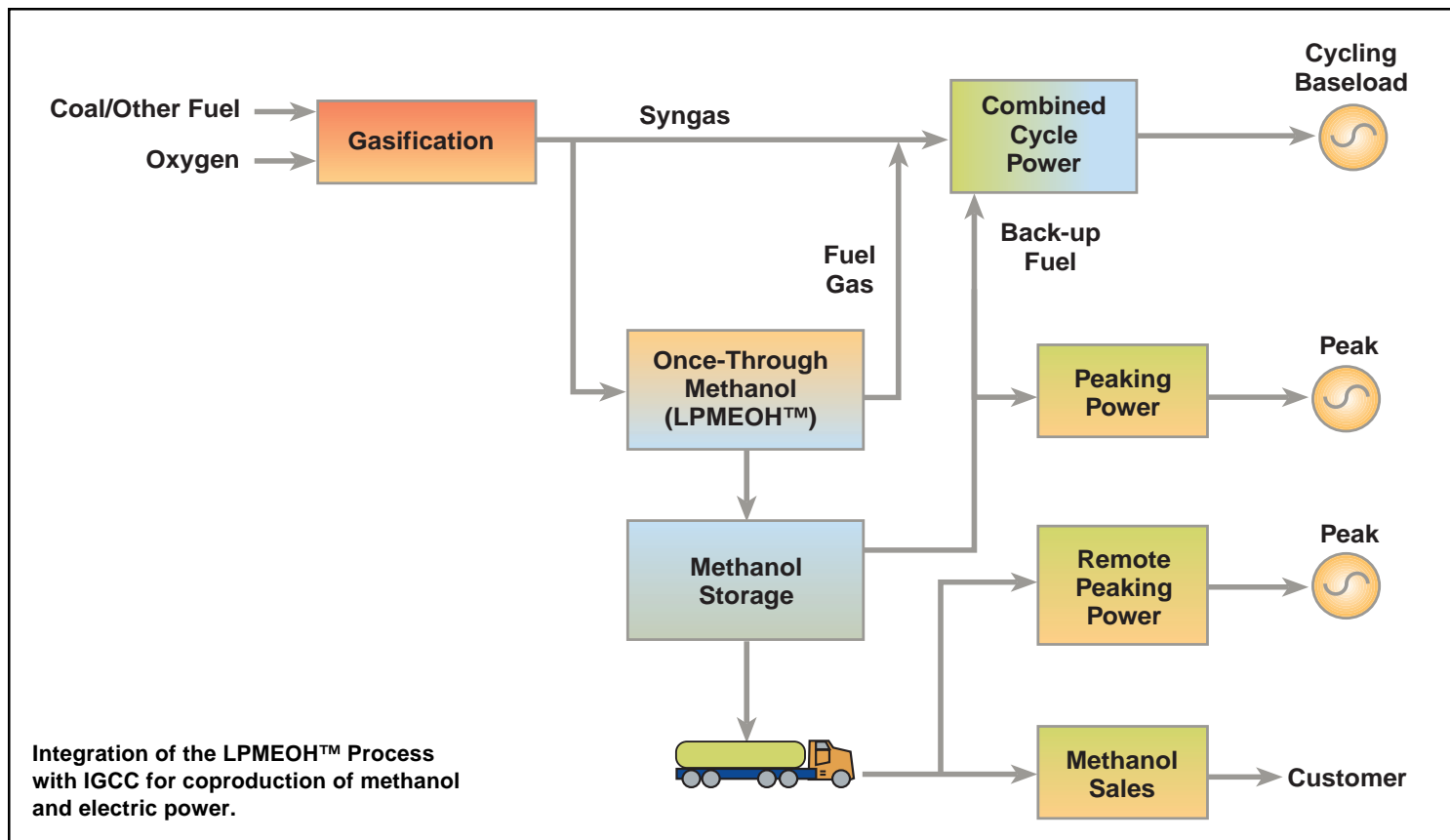
In IGCC power production, coal is first converted to syngas in a gasifier. After the syngas has been cleaned by removal of hydrogen sulfide, ammonia, and particulates, it is burned in a combustion turbine. The hot exhaust gas from the turbine is sent to a heat recovery steam generator, and the steam raised is sent to a steam turbine for additional power production.

IGCC offers great potential for high efficiency, environmentally responsible power generation from coal. The LPMEOH™ Process can be effectively coupled with IGCC

to further improve efficiency and flexibility. The advantages of the LPMEOH™ Process discussed previously, particularly its ability to operate over a wide range of carbon monoxide-rich feed gases and its ability to handle rapid fluctuations in feed rate, make it ideal for integration with IGCC.

Several options are available for integrating methanol production with IGCC. In one concept, clean syngas from the gasifier is first sent to the LPMEOH™ unit, which operates in a once-through mode, that is, without recycle of unconverted feed. Syngas that is not converted to methanol in the LPMEOH™ unit is sent to power production. Operating costs are reduced by operating methanol production in a once-through fashion.

As an alternative, instead of operating continuously, the methanol unit can be operated only during periods of off-peak



power demand to consume the syngas not required for power production. This allows the gasifier, which is the IGCC's major capital asset, to operate at full baseload capacity regardless of the power demand; thus, the gasifier is always fully utilized. In either baseload or cycling operation, partial conversion of between 20% and 33% of the IGCC plant's syngas is optimal, with conversions of up to 50% being feasible.

In the simplest configuration combining LPMEOH™ technology with IGCC, syngas at maximum available pressure from the gasifier in the IGCC facility is fed to the LPMEOH™ unit, operating in once-through mode. In the LPMEOH™ unit, the syngas is partially converted to methanol, and unreacted gas is fed to the IGCC power plant's combustion turbines. If requirements of a specific project make greater syngas conversion desirable, various design options are available to accomplish this.

One of these is feed gas compression. Since the reaction rate is increased at higher pressure, if the feed from the gasifier is not available at a sufficiently high pressure, a compressor can be added to boost feed gas pressure. Another option is to use partial recycle of the unconverted gas to increase conversion.

Still another option for improving reactor performance is to use staged reactors, that is, reactors in series rather than a single reactor. Potential advantages of staged reactors are the ability to optimize operating conditions for each reactor, being able to operate with only one reactor during low syngas availability (high power demand) situations, and the possibility of adding fresh catalyst to the second reactor and cascading the displaced catalyst to the first reactor, so that the first reactor acts as a partial guard bed, thus increasing catalyst life and productivity.

Market Potential

The encouraging results obtained from the LPMEOH™ Demonstration Project are expected to generate significant commercial interest in the technology. Because of its operational flexibility, the LPMEOH™ Process can be a very effective technology for converting a portion of an IGCC power plant's coal-derived syngas to methanol.

Because of its excellent fit with IGCC, design studies for the LPMEOH™ Process have focused principally on IGCC applications. For a given gasification plant size, the IGCC coproduction plant can be designed to accommodate a range of methanol to power output ratios. For example, a gasification plant with two gasifiers of 1,735 million Btu (HHV) per hour output each could be sized for baseload power output of 426 MWe of electricity and for methanol coproduction of 500 TPD.



View of LPMEOH™ Unit's 700-HP syngas recycle compressor.

If the baseload fuel gas value is taken to be \$4.00 per million Btu, then 500 TPD of methanol can be coproduced from coal for under \$0.50 per gallon. This compares with new methanol plants which, based on natural gas feed at \$0.50 to \$1.00 per million Btu, produce chemical-grade methanol delivered to the U.S. Gulf Coast at \$0.55 to \$0.60 per gallon.

Methanol coproduction, using the once-through LPMEOH™ Process in conjunction with IGCC, does not require a large methanol plant size to achieve good economies of scale. Since the gasification plant is necessarily at an economic scale for power generation, the syngas manufacturing economies of scale are already achieved. Also, methanol storage and transport economies can be realized by serving local markets, thus decreasing freight costs over methanol shipped from the U.S. Gulf Coast or other remote locations.



The DOE-Owned Alternative Fuels Development Unit (AFDU) at LaPorte, Texas, where the test operations for the LPMEOH™ Process were conducted.

Applications for the Coproduced Methanol

As discussed previously, economic evaluations have indicated that the LPMEOH™ Process can coproduce a clean, high-quality methanol product at less than \$0.50 per gallon from coal, an abundant local fuel source that is not likely to show rapid price increases. The methanol coproduced at an IGCC electric power plant could serve local markets for a variety of applications, such as:

- An economical hydrogen source for small fuel cells for transportation applications. Fuel cells are a new technology under rapid development and offer the potential of high efficiency and low emissions. Methanol is easily reformed to hydrogen and is much more easily stored and transported than hydrogen.
- As a feedstock for the manufacture of MTBE. MTBE is added to gasoline as an octane improver and as an oxygenate to meet clean air mandates.
- As a clean-burning fuel for a variety of applications, such as spark ignition engines, diesel engines, gas turbines, etc.
- Methanol can be reformed under mild conditions to provide a source of hydrogen, carbon monoxide, or syngas for small industrial applications.
- As a source of peaking power at the IGCC plant where the methanol is produced. Methanol produced during off-peak periods could be burned in combustion turbines to produce power during peak periods.

Conclusion

Design, construction, and startup of the LPMEOH™ Demonstration Project went quite satisfactorily, the only significant problem being a later-than-scheduled delivery of the reactor. Although there were some initial problems, which have been overcome with piping modifications, operations have also proceeded smoothly.

Within ten days of first introducing syngas to the LPMEOH™ reactor, the unit was exceeding the design methanol production rate. All the methanol produced has met Eastman's purity requirements for downstream processing. Unit availability has exceeded 96% since startup, and exceeded 99% during operation in 1998. Catalyst aging with coal-derived syngas was initially higher than with natural-gas-derived syngas, but due to operational improvements, the deactivation rate has now met or improved upon the target rate.

Successful demonstration of the LPMEOH™ technology will add significant flexibility and dispatch benefits to IGCC electric power plants, which have traditionally been viewed as strictly a baseload power generation technology.

The LPMEOH™ Process can provide commodity methanol from any carbonaceous feedstock, such as coal which is an abundant local fuel source that is not expected to increase significantly in price. Economic studies have shown that this methanol, even at small methanol plant sizes, is competitive with methanol from large remote gas projects and has a freight and cost advantage in local markets.



LPMEOH™ Demonstration Unit.

Bibliography

Bhatt, B.L., et al., "Adsorptive Removal of Catalyst Poisons from Coal Gas for Methanol Synthesis," *Separation Science and Technology* (Vol. 26, No. 12, pp 1559-1574), 1991.

Bhatt, B.L., et al., "Coal Gas Clean-Up for the Liquid Phase Methanol Process," *Twelfth North American Meeting of the Catalysis Society* (Lexington KY), May 1991.

Bhatt, B.L., et al., "Recent Developments in Slurry Reactor Technology at the LaPorte Alternative Fuels Development Unit," *Eighth International Technical Conference on Coal Utilization and Fuel Systems*, April 1993.

Bhatt, B.L., et al., "Recent Results from the LaPorte Alternative Fuels Development Unit," *First Annual DOE Joint Power and Fuel Systems Contractors Conference* (Pittsburgh PA), July 1996.

Brown, D.M., et al., "LPMEOH: Beyond LaPorte - Next Steps to Commercialization," *EPRI Fifteenth Annual Conference on Fuel Science and Conversion* (Palo Alto CA), June 1990.

Brown, D.M., et al., "A Novel Liquid Phase System for Methanol Synthesis," *First Tokyo Conference on Advanced Catalytic Science and Technology* (Tokyo, Japan), July 1990.

Brown, D.M., et al., "Clean Oxygenated Fuels from Coal," *ASME International Joint Power Generation Conference and Exposition* (San Diego CA), October 1991.

Brown, D.M., "Government and Industry Partnership in Developing New Technologies for Fuels and Chemicals," *1994 International Symposium on Gas Conversion and Utilization* (Florham Park NJ), May 1994.

Brown, W.R., et al., "Coproduction of Electricity and Methanol," *Eighth EPRI Coal Gasification Contractors Conference* (Palo Alto CA), October 1988.

Brown, W.R., and Frenduto, F.S., "Fuel and Power Coproduction: The Integrated Gasification/Liquid Phase Methanol (LPMEOH™) Demonstration Project," *First Annual Clean Coal Technology Conference* (Cleveland OH), September 1992.

Brown, W.R., and Moore, R.B., "Flexible Electric Power Generation: The Integrated Gasification/Liquid Phase Methanol (LPMEOH™) Demonstration Project," *Third Annual Clean Coal Technology Conference* (Chicago IL), September 1994.

Cook, S.L., "Commercial-Scale Demonstration of a Liquid-Phase Methanol Process," *209th ACS National Meeting* (Anaheim CA), April 1995.

Drown, D.P. et al., "Fuel and Power Coproduction - The Liquid Phase Methanol (LPMEOH™) Process Demonstration at Kingsport," *Fifth Annual DOE Clean Coal Technology Conference* (Tampa FL), January 1997.

Frank, M.E., "Methanol Production Scenarios," *Fourteenth Annual EPRI Fuel Science Conference* (Palo Alto CA), May 1989.

Frenduto, F.S., et al., "Liquid Phase Methanol Energy Storage with Gasification Combined-Cycle Power Generation," *Joint ASME/IEEE Power Generation Conference* (Kansas City KS), October 1993.

Frenduto, F.S., et al., "Cost-Effective Dispatchable Power from a Gasification Combined-Cycle System: Liquid Phase Methanol Energy Storage," *Power-Gen '93 Conference* (Dallas TX), November 1993.

Frey, J.H., et al., "Further Process Improvements at the LaPorte Liquid Phase Methanol Facility," *DOE Indirect Liquefaction Contractors Review Meeting* (Pittsburgh PA), November 1988.

Golden, T.C., et al., "Removal of Trace Iron and Nickel Carbonyls by Adsorption," *I&EC Research* (Vol. 29, pp 502-507), 1991.

Henderson, J.L., et al., "Operating Experience at the LaPorte LPMeOH PDU," *ASME Joint Conference on the Development and Introduction of Methanol as an Alternate Fuel* (Columbus OH), June 1986.

Heydorn, E.C., et al., "Liquid Phase Methanol Process Demonstration," *Industrial Catalyst News*, May 1998.

Heydorn, E.C., et al., "Liquid Phase Methanol (LPMEOH™) Initial Operating Experience," *The 15th Annual World Methanol Conference* (Tampa FL), December 1997.

Heydorn, E.C., et al., "Liquid Phase Methanol (LPMEOH™) Project Operational Experience," *EPRI Gasification Technologies Conference* (San Francisco CA), October 1998.

Heydorn, E.C., et al., "Liquid Phase Methanol (LPMEOH™) Project Start-Up," *EPRI Gasification Technologies Conference* (San Francisco CA), October 1997.

Hsiung, T.H., et al., "Recent Research Advances on the LPMeOH Process," *DOE Indirect Liquefaction Contractors Review Meeting* (Pittsburgh PA), November 1988.

Hsiung, T.H., et al., "Demonstration of a Slurry Phase Shift Process in the Alternative Fuels Development Unit," *DOE Contractors Conference* (Pittsburgh PA), September 1992.

Lewnard, J.J., and Hsiung, T.H., "Temperature Effects on Catalyst Activity in the Liquid Phase Methanol Process," *Tenth North American Catalysis Society Meeting* (San Diego CA), May 1987.

Mednick, R.L., and Klosek, J., "Progress in the LaPorte LPMeOH PDU Project," *AIChE Spring 1986 National Meeting* (New Orleans LA), April 1986.

Mednick, R.L., et al., "Design Issues for Once-Through Methanol Using the LPMeOH Process," *Eleventh Annual EPRI Clean Liquid and Solid Fuels Contractors Conference* (Palo Alto CA), May 1986.

Moore, R.B., et al., "Economies of the Integrated Production of Electricity and Clean Liquid Fuels," EPRI Conference on *Technologies for Generating Electricity in the Twenty-First Century* (San Francisco CA), November 1989.

Moore, R.B., "Coproduct of Power and Methanol Via IGCC and LPMeOH," *1989 World Methanol Conference* (Houston TX), December 1989.

Osterstock, E.R., "Dispatchable IGCC Facilities: Flexibility Through Coproduction," *Power-Gen Europe '97 Conference* (Madrid, Spain), June 1997.

Rao, P., et al., "Recent Laboratory Activities Towards Developing the Liquid Phase Methanol Process," *DOE Indirect Liquefaction Contractors Review Meeting* (Pittsburgh PA), December 1986.

Roberts, G.W., et al., "Catalyst Poisoning During the Synthesis of Methanol in a Slurry Reactor," *Chemical Engineering Science* (Vol. 45, No. 8, pp 2713-2720), July 1990.

Roberts, G.W., et al., "Catalyst Deactivation During the Synthesis of Methanol in a Slurry Reactor," *Eleventh International Symposium on Chemical Reaction Engineering* (Toronto, Canada), July 1990.

Schaub, E.S., et al., "An Update on Liquid Phase Methanol (LPMeOHTM) Technology and the Kingsport Demonstration Project," *Fourth Annual DOE Clean Coal Technology Conference* (Denver CO), September 1995.

Stein, V.E., et al., "Commercial Scale Demonstration of the Liquid Phase Methanol (LPMeOHTM) Process: Initial Operating Experience," *Sixth Clean Coal Technology Conference* (Reno NV), April-May 1998.

Studer, D.W., et al., "An Update of the LaPorte Liquid Phase Methanol Program," *DOE Indirect Liquefaction Contractors Review Meeting* (Pittsburgh PA), December 1987.

Studer, D.W., et al., "Status of the Development of Methanol Synthesis by the LPMeOH Process," *DOE Indirect Liquefaction Contractors Review Meeting* (Pittsburgh PA), November 1989.

Studer, D.W., et al., "Status Report on the Liquid Phase Methanol Process," *Fourteenth Annual EPRI Fuel Science Conference* (Palo Alto CA), May 1989.

Studer, D.W., and Brown, D.M., "Current Development and Future Commercial Demonstration of the LPMeOH Process," *Sixteenth International Conference on Coal and Slurry Technology* (Clearwater FL), April 1991.

Tijm, P.J.A., et al., "Overview of the Liquid Phase Methanol (LPMeOHTM) Process Demonstration at Kingsport," *AIChE Spring 1997 Meeting* (Houston TX), March 1997.

Tijm, P.J.A., et al., "Advances in Liquid Phase Technology," *ACS 1997 Spring Meeting* (San Francisco CA), April 1997.

Toseland, B.A., et al., "Flow Patterns in a High Pressure Slurry-Bubble-Column Reactor Under Reaction Conditions," *Second International Conference on Gas-Liquid-Solid Reaction Engineering*, March 1995.

Tsao, T.R., and Heydorn, E.C., "LPMeOH PDU Results," *DOE/FE Indirect Liquefaction Contractors Review Meeting*, December 1985.

Tsao, T.R., and Rao, P., "Development of LPMeOH Process: An Update," *Eleventh Annual EPRI Clean Liquid and Solid Fuels Contractors Conference* (Palo Alto CA), May 1986.

Underwood, R.P., and Hsiung, T.H., "Syngas Conversion to Mixed Alcohols in a Slurry Reactor," *AIChE Summer National Meeting* (Pittsburgh PA), August 1991.

Waller, F.J., et al., "Development of Alternative Fuels from Coal-Derived Syngas," *DOE Contractors Conference* (Pittsburgh PA), September 1991.

Waller, F.J., "Conversion of Syngas to Chemicals," *ACS 1996 Spring Meeting* (New Orleans LA), March 1996.

Weimer, R.F., et al., "Laboratory Kinetics and Mass Transfer in the LPMeOH Process," *AIChE National Meeting*, November 1987.

Weimer, R.F., et al., "Recent Research and Field Modifications for the LaPorte LPMeOH Program," *Thirteenth Annual EPRI Conference on Fuel Science and Conversion* (Palo Alto CA), May 1988.

The Clean Coal Technology Program

The Clean Coal Technology (CCT) Program is a unique partnership between the federal government and industry that has as its primary goal the successful introduction of new clean coal utilization technologies into the energy marketplace. With its roots in the acid rain debate of the 1980s, the program is on the verge of meeting its early objective of broadening the range of technological solutions available to eliminate acid rain concerns associated with coal use. Moreover, the program has evolved and has been expanded to address the need for new, high-efficiency power-generating technologies that will allow coal to continue to be a fuel option well into the 21st century.

Begun in 1985 and expanded in 1987 consistent with the recommendation of the U.S. and Canadian Special

Envoys on Acid Rain, the program has been implemented through a series of five nationwide competitive solicitations. Each solicitation has been associated with specific government funding and program objectives. After five solicitations, the CCT Program comprises a total of 40 projects located in 18 states with a capital investment value of nearly \$6 billion. DOE's share of the total project costs is about \$2 billion, or approximately 34% of the total. The projects' industrial participants (i.e., the non-DOE participants) are providing the remainder—nearly \$4 billion.

Clean coal technologies being demonstrated under the CCT Program are establishing a technology base that will enable the nation to meet more stringent energy and environmental goals. Most of the demonstrations are

being conducted at commercial scale, in actual user environments, and under circumstances typical of commercial operations. These features allow the potential of the technologies to be evaluated in their intended commercial applications. Each application addresses one of the following four market sectors:

- Advanced electric power generation
- Environmental control devices
- Coal processing for clean fuels
- Industrial applications

Given its programmatic success, the CCT Program serves as a model for other cooperative government/industry programs aimed at introducing new technologies into the commercial marketplace.

Contacts for CCT Project and U.S. DOE CCT Program

Air Products and Chemicals, Inc.

Contact

Edward C. Heydorn
Air Products and Chemicals, Inc.
7201 Hamilton Blvd.
Allentown PA 18195-1501
(610) 481-7099
(610) 706-7299 *fax*
heydorec@apci.com

Eastman Chemical Company

Contact

Barry T. Street
Eastman Chemical Company
P.O. Box 511
Kingsport TN 37662
(423) 229-6062
(423) 229-7268 *fax*
btstreet@eastman.com

U.S. Department of Energy

Contacts

Thomas A. Sarkus
Director
Major Projects & Agreements Division
U.S. Department of Energy
Federal Energy Technology Center
P.O. Box 10940
Pittsburgh PA 15236-0940
(412) 892-5981
(412) 892-4775 *fax*
sarkus@fetc.doe.gov

Robert M. Kornosky
Project Manager
U.S. Department of Energy
Federal Energy Technology Center
P.O. Box 10940
Pittsburgh PA 15236-0940
(412) 892-4521
(412) 892-4775 *fax*
kornosky@fetc.doe.gov

C. Lowell Miller
Director
Coal Fuels & Industrial Systems
U.S. Department of Energy
FE-24 Germantown Bldg.
Germantown MD 20874-1290
(301) 903-9451
(301) 903-2238 *fax*
lowell.miller@hq.doe.gov


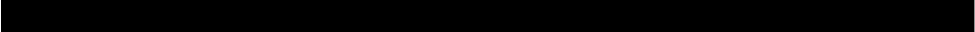
To Receive Additional Information

To be placed on the Department of Energy's distribution list for future information on the Clean Coal Technology Program, the demonstration projects it is financing, or other Fossil Energy Programs, contact:

Robert C. Porter, Director
Office of Communication
U.S. Department of Energy
FE-5
1000 Independence Ave SW
Washington DC 20585
(202) 586-6503
(202) 586-5146 *fax*
robert.porter@hq.doe.gov

Otis Mills
Public Information Office
U.S. Department of Energy
Federal Energy Technology Center
P.O. Box 10940
Pittsburgh PA 15236-0940
(412) 892-5890
(412) 892-6195 *fax*
mills@fetc.doe.gov

This report is available on the Internet
at U.S. DOE, Office of Fossil Energy's home page: www.fe.doe.gov

List of Acronyms and Abbreviations

AFDU	Alternative Fuels Development Unit
AFFTU	Alternative Fuels Field Test Unit
CCT	Clean Coal Technology
DME	Dimethyl Ether
DOE	Department of Energy
HHV	Higher heating value
IGCC.....	Integrated Gasification Combined Cycle
LPMEOH™	Liquid Phase Methanol Process
MTBE	Methyl tertiary butyl ether
SBCR	Slurry Bubble Column Reactor
TPD.....	Tons per day