AIR PRODUCTS LIQUID PHASE CONVERSION COMPANY

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

PROJECT PERFORMANCE SUMMARY
CLEAN COAL TECHNOLOGY DEMONSTRATION PROGRAM

JUNE 2004

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COAL PROCESSING FOR CLEAN FUELS

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

The LPMEOH™ process enhances the economics and performance of coal-based IGCC power systems and the coproduced methanol affords a low-cost source of clean fuels and chemicals.

OVERVIEW

This project is part of the U.S. Department of Energy's (DOE) Clean Coal Technology Demonstration Program (CCTDP) established to address energy and environmental concerns related to coal use. The project presented here was one of 13 selected from 48 proposals submitted in response to the CCTDP's third solicitation.

Air Products and Chemicals, Inc. (Air Products) in partnership with Eastman Chemical Company (Eastman) successfully demonstrated the Liquid-Phase Methanol LPMEOH™ process. The LPMEOH™ process represents a significant advancement in conversion of synthesis gas to methanol relative to conventional gas-phase processes, particularly for coal-derived synthesis gas. Methanol is a highly sought alcohol widely used in the chemical industry, and is currently used to a lesser extent as a clean fuel for transportation and stationary power applications, primarily due to cost. By enabling efficient cost-effective production of methanol from coal-derived synthesis gas, the LPMEOH™ process enhances the economics and performance of coal-based integrated gasification combined-cycle (IGCC) power systems — one of the cleanest and most efficient of the 21st century power generating options. And, the coproduced methanol affords a low-cost source of clean fuels and chemicals.

The LPMEOH™ process demonstrated at commercial scale (260 short tons/day) the advantages over conventional gas-phase methanol processes that were indicated from 10 short tons/day LPMEOH™ development tests. By carrying out the highly temperature-sensitive catalytic methanol conversion process in a liquid medium using a slurry bubble column reactor (SBCR), the LPMEOH™ process permitted effective control of heat generated from the highly exothermic process. This approach achieved much higher synthesis gas conversion per pass than its gas-phase counterpart and allowed swings in feedstock composition and quantity not tolerated in gas-phase systems. Also, the LPMEOH™ process is particularly well suited to coal-derived synthesis gas, which is rich in carbon monoxide.

Parallel design verification testing at DOE's Alternative Fuels Development Unit (AFDU) in LaPorte, Texas, proved the SBCR capable of producing dimethyl ether (a valued fuel/chemical product) through process modification. Fuel-use testing proved the LPMEOH™ product to be an extremely low-emissions fuel in automotive and stationary power applications.

All project objectives were met, including confirmation of the commercial economics for the LPMEOH™ process applied to IGCC in the coproduction of methanol and electricity. Overall plant availability over the 69-month operating phase of the demonstration was 97.5%, proving its commercial operating performance.

THE PROJECT

The LPMEOH™ project stemmed from DOE research efforts to develop a more efficient and economic means of converting coal-derived synthesis gas into methanol. Conventional gas-phase processes use either fixed beds of pelletized catalyst cooled by unreacted synthesis gas injected between the beds, or pelletized catalysts placed in tubes cooled by water passing over the outside of the tubes. Cooling limits the efficiencies of the fixed-bed reactors. The highly exothermic reactions of the synthesis gas, primarily hydrogen (H_2) and carbon monoxide (CO), in the presence of the catalysts generate massive amounts of heat that must be carried away from very temperature-sensitive catalysts. Catalyst life is seriously reduced by excessive temperatures. Because of this temperature sensitivity, gas-phase systems require diluted synthesis gas, which yields low conversion per pass, and they are not able to handle the high heat of reaction resulting from low H_2/CO molar ratio (high CO and CO_2 content) synthesis gas produced by coal gasifiers.

Testing of the LPMEOH™ process at the 10 short tons/day DOE AFDU LaPorte facility in the 1980s showed potential for superior performance relative to gas-phase processes, including the ability to handle low H_2/CO molar ratio synthesis gas produced by coal gasifiers. The challenge was to prove that the process could be scaled to commercial size ($\geq$260 short tons/day), outperform gas-phase processes at commercial scale, and confirm commercial economics for the LPMEOH™ process in IGCC coproduction applications producing methanol and electricity. The CCTDP project was designed to address these issues as well as to: (1) conduct fuel-use testing to determine suitability of the LPMEOH™ methanol product as a low-emissions alternative fuel for automotive and stationary power applications; (2) prove LPMEOH™ process adaptability to produce dimethyl ether (DME) as a mixed coproduct with methanol, and (3) use all methanol produced, except the 12,000 gallons set aside for fuel-use testing, for on-site production of methyl acetate, cellulose acetate, and acetic acid.

The Eastman Chemical Company facility in Kingsport, Tennessee, provided the ideal demonstration site by virtue of having Texaco gasifiers with proven reliability producing large volumes of coal-derived synthesis gas and separate CO and H_2 streams. These factors enabled variation of the synthesis gas H_2/CO molar ratio and simulation of LPMEOH™ operating in a coproduction mode with a range of gasifier types.

Project Sponsor
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 funding participant
Eastman Chemical Company — host, operator, synthesis gas and services provider
ARCADIS Geraghty & Miller — fuel methanol tester and funding participant

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

Technology
Air Products' liquid phase methanol (LPMEOH™) process

Plant Capacity/Production
260 short tons/day

Coal
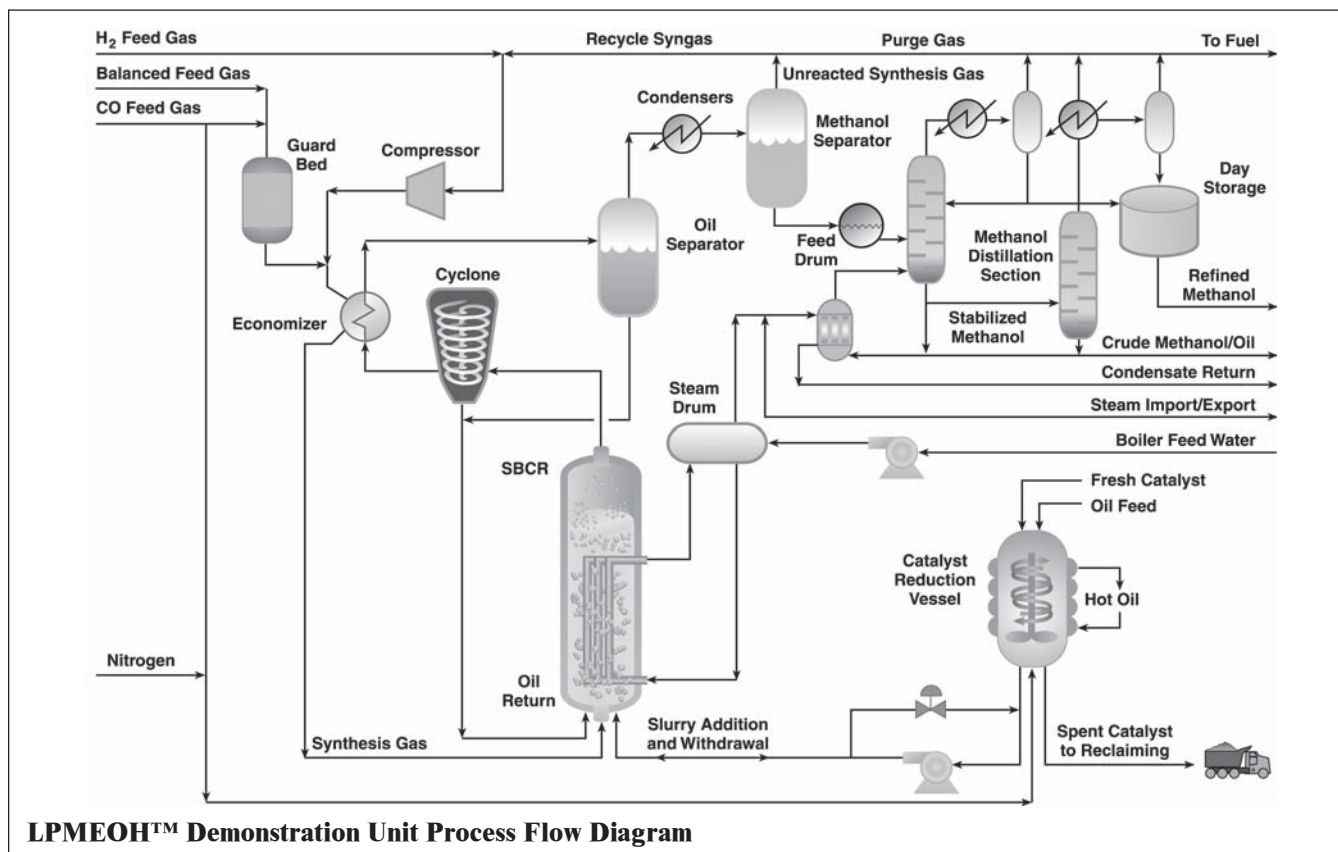Eastern high-sulfur bituminous, 3–5% sulfur

Demonstration Duration
April 1997–December 2002

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

THE TECHNOLOGY

LPMEOH™ Demonstration Unit Process Flow Diagram

System

In the LPMEOH™ demonstration, approximately half of the synthesis gas from the gasification facility is diverted from the existing methanol unit to the LPMEOH™ Unit. This is a "balanced gas" stream from a molar ratio stand-point, which is required by the existing gas-phase methanol units. Two other feed streams are supplied to the demonstration unit: a high-purity CO stream from the gasification facility, and a hydrogen-rich stream from the existing gas-phase methanol unit. Since the hydrogen-rich stream is at a lower pressure than the other two streams, it is combined with the LPMEOH™ recycle gas, and the combined stream is compressed in the recycle compressor.

The CO and balanced gas streams are combined and passed through a catalyst guard bed, packed with a metal impregnated activated carbon and designed to remove any trace levels of iron and nickel carbonyl and arsenic from the feed gas. The total feed stream is heated to approximately 400 °F in the feed/product economizer and sparged into the SBCR, typically operating at 725 pounds per square inch absolute (psia) and 440–520 °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 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 to 250 °F in the feed/product economizer, and any condensed process oil is collected in the high pressure oil separator and returned to the reactor along with the entrained slurry from the cyclone separator. Fresh mineral oil is added to the reactor to replace losses. The product gas is further cooled to 105 °F in air-cooled and water-cooled condensers and the methanol is collected in the methanol separator.

The condensed methanol is sent to a distillation section where the methanol is first flashed to about 70 pounds per square inch gauge (psig) in a feed drum prior to entering a two-column distillation train. Feed drum vapors are combined with the distillation column overheads. The first column removes low boiling point components and

stabilizes the product. In the second column, refined 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. The methanol produced from the first distillation column is the fuel-grade "stabilized methanol" used in off-site fuel-use testing.

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 a slurry containing 30% catalyst by weight. 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 distributer. The carbon monoxide reacts with the oxide form of the catalyst to convert it to the active metallic form. During activation, temperature is carefully increased while the consumption of carbon monoxide is monitored to determine when complete reduction has occurred. After activation, the catalyst is pumped to the LPMEOH™ reactor. Before fresh slurry is activated, an equivalent amount of spent slurry is removed and sent to metals recovery or safe disposal.

SBCR

The key feature enabling the LPMEOH™ process to outperform conventional gas-phase methanol conversion systems resides in carrying out the methanol synthesis in an liquid medium (mineral oil) using powdered catalyst in a SBCR in lieu of pellets in a fixed-bed reactor. The mineral oil/powdered catalyst slurry acts as a temperature moderator and facilitates rapid heat removal from the catalyst surface to water circulated in an internal heat exchanger. The heat exchanger occupies only a small fraction of the cross-sectional area of the SBCR because of the high heat transfer coefficient on the slurry side. In essence, heat transfers more efficiently in liquid/solid contact than in gas/solid contact, and the liquid media provides a heat sink.

Efficient heat transfer and the ability to maintain uniform temperature throughout the SBCR: (1) enables high synthesis gas conversion; (2) accommodates rapid changes in feed rate and composition (buffers transients); (3) allows synthesis gas rich in carbon oxides to be efficiently processed; and (4) produces fuel-grade methanol without the purification step required by gas-phase systems.

Coproduction

Coupling LPMEOH™ with coal-based IGCC offers synergies to enhance the overall economics and performance of such a coproduction plant, relative to IGCC and LPMEOH™ plants operating separately. In such a coproduction configuration, clean synthesis gas produced by the coal gasifier and associated gas cleanup systems is sent to the LPMEOH™ unit in varying quantities dictated by electricity demands. (Once-through methanol production reduces operating costs.) LPMEOH™ performance characteristics enable the varying feed and allow the gasifier to operate in a steady-state mode critical to efficient, economic gasifier performance. Stored methanol can be used as back-up fuel for the combined-cycle power block used for peaking power in on-site or off-site gas turbines or diesels, or sold on the market as a fuel/chemical feedstock.
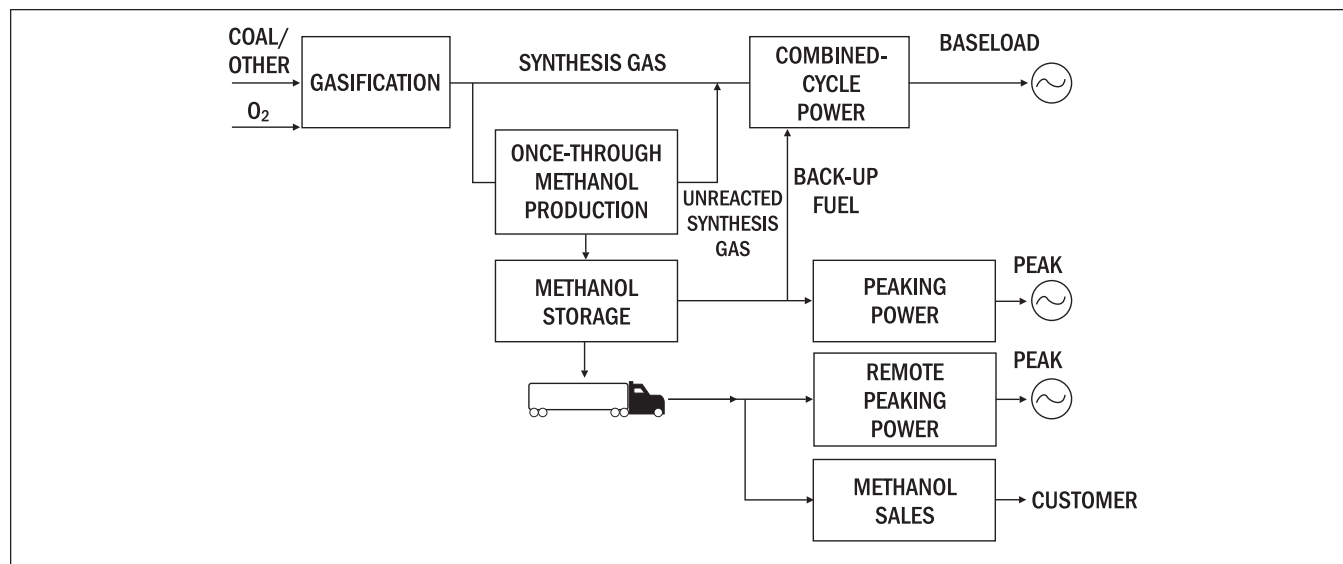
Integration of Methanol Production with an IGCC Facility

RESULTS SUMMARY

OPERATIONAL PERFORMANCE

- The LPMEOH™ demonstration unit achieved nameplate production capacity of 80,000 gallons per day (260 short tons/day) within four days of start-up, and 115% of design capacity four days later.

- Over the nearly 69-month test program, the LPMEOH™ unit averaged 97.5% availability, produced approximately 103.9 gallons of chemical grade methanol for production of methyl acetate (all of which was used at the Eastman facility), produced 12,000 gallons of stabilized methanol for off-site fuel-use testing, and achieved a maximum one-month production of 2.5 million gallons and a longest uninterrupted operating run of 94 days.

- The SBCR was successfully scaled from the 10 short tons/day (22-inch diameter) LaPorte AFDU to the 260 short tons/day (7.5 foot diameter) demonstration unit, exhibiting good temperature stability and achieving catalyst loadings up to 151% of the 40,000 pound design loading (slurry concentration of nearly 50%).

- Improvements made to the entrained slurry and condensed process oil recycle circuits reduced capital and operating costs. These included elimination of two slurry/process oil pumps through gravity drainage and simplification of the process oil make-up pump.

LPMEOH™ Demonstration Unit with catalyst facilities in foreground

- The gas sparger experienced a plugging problem that was resolved by replacement with a modified device (using the same design principles) and incorporation of a continuous flush of recycled process oil.

- Catalyst deactivation rates improved over the demonstration period. Initial rates exceeding 1%/day versus the design rate of 0.4%/day resulted from the presence of residual construction debris in the SBCR. Subsequent rates of 0.6–0.7%/day were attributed primarily to arsenic and sulfur trace poisons. Introduction of new adsorbents to the catalyst guard bed along with modified operating procedures brought deactivation rates down to 0.17%/day in the last six months of operation.

- The LPMEOH™ unit demonstrated the capability to operate in a coal-based IGCC environment, effectively handling a range of H_2/CO ratios and on/off ramping modes required in load following.

- A 25-day test of the Liquid Phase Dimethyl Ether (LPDME™) process carried out at the LaPorte AFDU showed promise for coproduction of dimethyl ether and methanol.

ENVIRONMENTAL PERFORMANCE

- Stabilized methanol produced for fuel-use testing was sulfur-free and contained less than 1% water by weight. In bus and fuel-flexible-vehicle (FFV) testing, stabilized methanol provided the same environmental benefits as chemical-grade methanol, with no penalty on performance or fuel economy. Stabilized methanol and methanol emulsions substituted for conventional oil fuels in gas turbine and diesel generator operations significantly reduced nitrogen oxide (NO_x) emissions.

- Testing of stabilized methanol in a phosphoric acid fuel cell showed that the catalysts used to reform the methanol are not compatible with trace amounts of mineral oil present.

ECONOMIC PERFORMANCE

- The estimated capital costs of a 500 short ton/day LPMEOH™ unit producing stabilized methanol in a coal-based IGCC plant is $31.1 million; economic studies show that the price of the coproduced methanol can be less than $0.50 per gallon.

OPERATIONAL PERFORMANCE

The LPMEOH™ unit achieved nameplate production capacity of 80,000 gallons/day (260 short tons/day) within four days of start-up and production rates exceeding 115% of nameplate capacity four days later. Over the course of the 69-month demonstration, the LPMEOH™ unit operated for 1,967 days and produced approximately 103.9 million gallons of refined methanol, all of which was used by Eastman to produce methyl acetate, and ultimately, cellulose acetate and acetic acid. Approximately 12,000 gallons of stabilized methanol was produced for off-site fuel-use testing in automotive and stationary power applications.

Availability

Table 1 summarizes LPMEOH™ unit availability during the 69-month demonstration program and identifies the primary causes of the unplanned outages. Overall availability was 97.5% (availability is the percentage of time the LPMEOH™ unit was available to operate, with the exclusion of scheduled outages).

In 1997, the only unplanned outage related to catalyst performance occurred. Iron from residual construction debris caused severe poisoning of the catalyst, requiring replacement of the full catalyst charge. Also, the condensed

process oil/slurry recycle pump circuit failed to perform adequately. Two twin-screw make-up oil pumps did not provide sufficient seal flush pressure to the two twin-screw process oil/slurry recycle pumps. Elevating the process oil/slurry collection equipment enough to permit gravity drainage permanently resolved the problem. The modification reduced capital and operating costs by eliminating the two recycle pumps and their ancillaries and allowing substitution of a single, simpler and more reliable oil make-up pump for the original two twin-screw units.

In 1998, the longest uninterrupted operating run of 94 days occurred in the July to October time frame. This was preceded by a continuous run of 65 days earlier in the year.

In 1999, leaks in the heat exchanger circuit accounted for the only unplanned outages.

In 2000, an accumulation of unrelated instrumentation and electrical control failures contributed to unscheduled downtime, along with failure of the LPMEOH™ cooling water rupture discs induced by an external electrical outage. Also, this year marked the beginning of downtime associated with change-out of adsorbent in the LPMEOH™ catalyst guard bed to enhance catalyst life (discussed under catalyst deactivation). No change-out of catalyst guard bed material was anticipated over the demonstration period, so no isolation valves were provided to prevent downtime (commercial designs will incorporate this feature).

In 2001, the unit had to be shut down for a short period during a catalyst withdrawal/addition operation; and catalyst guard bed related downtime continued.

In 2002, the catalyst guard bed issue was resolved and the LPMEOH™ unit set a monthly production record of 2.5 million gallons in October. For 23 days the LPMEOH™ unit exceeded nameplate capacity.

SBCR Sparger

Although the SBCR sparger did not contribute to unplanned outages, modifications were made to ensure consistent optimum performance. The original sparger experienced a gradual increase in pressure drop over time, which limited the flow of the synthe-

TABLE 1. LPMEOH™ UNIT AVAILABILITY & CAUSES OF UNPLANNED OUTAGES

Operating Year[a]	1997	1998	1999	2000	2001	2002[b]
Availability (%)	94.9	99.5	99.4	96.3	97.7	94.1
Unplanned Outage Causes & Hours						
Catalyst	149.3	0.0	0.0	0.0	38.7	0.0
Catalyst Guard Bed	0.0	0.0	0.0	118.9	120.6	198.9
Electrical	20.7	24.6	0.0	42.3	0.0	0.0
Instrumentation	12.8	1.3	0.0	4.7	7.0	0.0
Mechanical	142.8	19.2	52.8	145.5	0.0	0.0
Total	325.6	45.1	52.8	311.4	166.3	198.9

[a] Operating Year = April–March

[b] Through December 31, 2002

sis gas to the reactor. Adherence of catalyst particles to the sparger orifices was the apparent cause of the partial plugging. An initial attempt to correct the problem in 1997 showed only marginal improvement. However, a second attempt in 1999 succeeded. The correction entailed separating the condensed process oil recycle from the slurry recycle and using this process oil to continuously flush the sparger. Gravity drainage proved sufficient to effect the flushing. The sparger with process oil flush was installed in March 1999 and showed no increase in pressure drop with time.

Catalyst Deactivation

LPMEOH™ catalyst performance is critical to the cost and performance of the process. Catalyst performance is measured by the deactivation rate. The design catalyst deactivation rate is 0.4%/day based on proof-of-concept testing at the LaPorte AFDU. In carrying out the demonstration, testing was broken down into four catalyst campaigns, as shown in Table 2.

Campaigns 1 and 2 employed the catalyst activation system described previously (see The Technology, page 5), which activates the catalyst outside of the SBCR in small batches of approximately 2,000 pounds. These small batches are then injected after a like amount of spent catalyst is removed from the SBCR. In this scenario, the product output is controlled by the amount of catalyst and percentage of fresh catalyst.

Campaigns 3 and 4 used a modified approach whereby a full LPMEOH™ catalyst charge (40,000–50,000 pounds) is activated at once. This *in-situ* approach uses a dilute mixture of balanced synthesis gas in nitrogen as the reducing gas, which is sparged into the SBCR. Once positive gas flow from the recycle circuit is established, the nitrogen flow is stopped. The recycle gas and balanced synthesis gas complete catalyst reduction, and operation on normal synthesis gas feed follows. In operation, the in-situ approach uses temperature to control product output, rather than periodically replacing spent catalyst. Operation starts at the lowest temperature at which the desired conversion is achieved, and the temperature is increased as the catalyst ages to maintain a constant output. The *in-situ* procedure is estimated to reduce capital costs by 10% by eliminating separate processing equipment for the withdrawal/addition procedure. Temperature control is projected to increase catalyst life.

Campaign 1 was significantly impacted by the presence of residual iron from post-construction debris. Despite attempts to correct the matter by adding six charges of fresh catalyst and raising the temperature to 260 °C for about a week, the decision was made to dump the contaminated charge and start over. The average catalyst deactivation rate for Campaign 1 was 1.3%/day.

Campaign 2 used a lower reactor temperature, predominately 235 °C in an attempt to extend catalyst life. Operation spanned more than three years, during which catalyst withdrawal and addition was demonstrated as an effective means of controlling the desired methanol production. The rate of catalyst deactivation improved to 0.6%/day.

Campaign 3 marked the first application of the in-situ activation procedure and temperature programming for methanol production control. The LPMEOH™ catalyst did not exhibit the expected initial activity following catalyst activation. This was attributed to elevated storage temperatures experienced by the fresh LPMEOH™ catalyst slurry prior to activation and a relatively high temperature ramp rate during activation. Also, levels of iron, arsenic, and sulfur increased during Campaign 3. The resulting Campaign 3 catalyst deactivation rate was 0.6%/day.

TABLE 2. CATALYST CAMPAIGNS					
Campaign	**Operating Period**	**Days**	**Activation**	**Control**	**Temperature (°C)**
1	4/6/97 – 11/3/97	171	Batch	Add Catalyst Only	250 – 260
2	12/20/97 – 8/6/01	1,325	Batch	Add/Withdraw Catalyst	235 Primarily
3	8/24/01 – 6/4/02	284	*In-situ*	Temperature	216 – 242
4	6/28/02 – 12/31/02	187	*In-situ*	Temperature	215

Campaign 4 again used the in-situ activation procedure and temperature programming for methanol production control. However, the activation procedure was modified by controlling pre-activation catalyst slurry temperature to no more than 100 °C and using a relatively slow temperature ramp rate during activation. The modified procedure produced the expected initial LPMEOH™ catalyst activity. During the six months of Campaign 4 operation, the SBCR was held at a constant low temperature of 215 °C. Also, the catalyst guard bed was controlling trace contaminates. The average catalyst deactivation rate was 0.17%/day.

The campaigns determined that trace amounts of arsenic (in the form of arsine), and to a lesser extent sulfur, had the greatest impact on catalyst deactivation. With the exception of accidental introduction of iron to the system, the catalyst guard bed adequately protected the LPMEOH™ catalyst from iron and nickel carbonyls. In-situ activation and temperature programming, enabling minimum operating temperature to be used, also contributed to reduced deactivation rates.

In parallel with the catalyst campaigns, an effort was undertaken to improve catalyst guard bed performance relative to arsenic and sulfur control. During Campaign 2, the catalyst guard bed was charged with a 50-50 mixture by volume of manganese dioxide and activated carbon.

The manganese dioxide allowed arsenic breakthrough, prompting trial of copper-oxide impregnated activated carbon (Cu/C) during the latter part of Campaign 3 and Campaign 4. The Cu/C adsorbent proved effective, but only had a 2-month service life. The Cu/C service life was extended through application of an innovative thermal treatment.

SBCR being installed

SLURRY BUBBLE COLUMN REACTOR

Unreacted Synthesis Gas + Methanol Product (vapor)

Disengagement Zone

Steam

Liquid

Vapor Bubble

H_2
CO
Catalyst
CH_3OH
Vapor Bubble

Boiler Feedwater

Catalyst Powder Slurried in Oil

Synthesis Gas Feed

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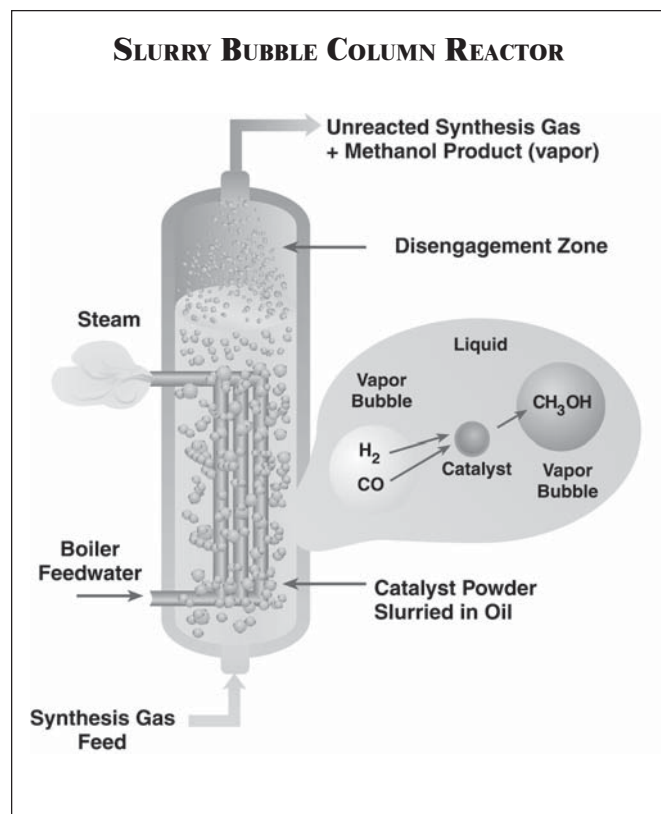
Simulated IGCC Coproduction

The LPMEOH™ unit was subjected to 13 separate campaigns to validate the processes' capability to handle a range of low H_2/CO synthesis gas ratios. The H_2/CO synthesis gas ratios ranged from 0.43 to 1.08. Reasonable methanol production levels were maintained and catalyst deactivation rates were calculated to be the same as those for balanced synthesis gas. It should be noted that H_2/CO synthesis gas ratios can be adjusted upward by increasing the catalyst slurry concentration. Increased slurry concentration increases CO conversion and increases the H_2/CO ratio of the recycle gas.

The LPMEOH™ unit was also subjected to ramp up and rapid shutdown and on/off cycling to simulate load following in IGCC coproduction applications. The unit frequently had to shut down rapidly over the course of the demonstration and did so effectively. A ramp-up rate goal of 5% of design flow per minute, reflective of an IGCC coproduction application, was established for the demonstration and was met.

Dimethyl Ether Production

A secondary objective of the LPMEOH™ demonstration was design verification testing of Air Products' LPDME™ process. In the LPDME™ process, a dehydration catalyst is mixed with the LPMEOH™ catalyst in the mineral oil to promote the conversion of methanol to dimethyl ether (DME) within the same reactor. Conversion per pass with CO-rich synthesis gas can be higher for the LPDME™ process than for the LPMEOH™ process. Methanol can also be produced as a mixed coproduct with DME and can easily be separated and recovered.

The LPDME™ process successfully completed a 25-day design verification test at the LaPorte AFDU. The deactivation rate for both the methanol and dehydration catalysts was 0.7%/day, somewhat lower than obtained in autoclave tests. Methanol productivity remained relatively constant, while DME productivity showed a slight decline consistent with laboratory results.
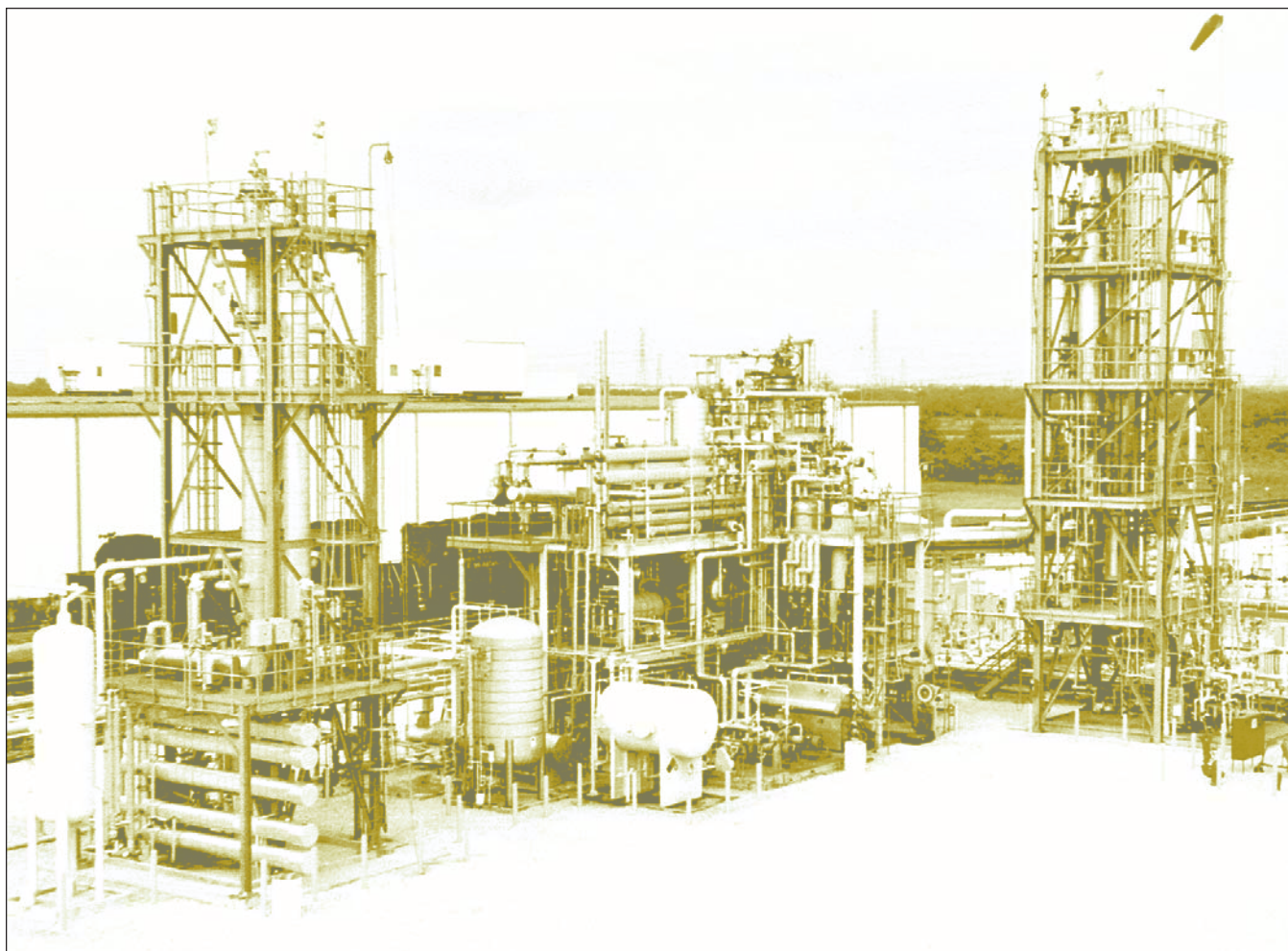
DOE's Alternative Fuels Development Unit in LaPorte, Texas

ENVIRONMENTAL PERFORMANCE

Waste Stream Disposition

The only LPMEOH™ unit waste streams included the spent catalyst slurry, catalyst guard bed spent adsorbents, waste process oil (mineral oil) from the oil-water separator, bottoms from the second distillation column (a crude-grade methanol), and wastewater separated from the refined methanol.

The spent catalyst slurry, comprised of copper and zinc oxides in mineral oil, was sent periodically to a company that reclaimed the metallic components for reuse. Some of the catalyst guard bed spent adsorbents exceeded the regulatory limit for arsenic, so all the material was classified as hazardous by Eastman, and was sent to a hazardous waste landfill where it was stabilized before landfilling. Waste process oil was sent for energy recovery to an on-site incinerator. Bottoms from the second distillation column, containing about 25% of the methanol produced in the LPMEOH™ unit, was sent to preexisting distillation equipment in the Eastman complex, and recovered mineral oil was used in LPMEOH™ catalyst slurry preparation.

Fuel-Use Testing

Air Products designed and carried out a series of tests to assess the market potential for the LPMEOH™ stabilized methanol product as a replacement fuel or fuel supplement in automotive and stationary power applications. Production of stabilized methanol is less expensive than chemical-grade methanol, avoiding a distillation and purification step. Proving the effectiveness of this relatively low-cost clean fuel (free of sulfur and other impurities) in a broad market enhances the economic attractiveness of IGCC-based coproduction of electricity and methanol.

Table 3 summarizes the seven tests carried out in the fuel-use test program.

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, 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)
West Virginia University Transportable Laboratory Facility	Hydrogen source for phosphoric acid fuel cells	Comparisons of reformation products, extent of conversion, and catalyst life between chemical grade methanol and stabilized methanol

FFV: Fuel Flexible Vehicle

The approximately 12,000 gallons of stabilized methanol used in fuel-use testing were extracted from a lengthy run during which the Eastman synthesis gas shift reactor was off-line and the synthesis gas feed to the LPMEOH™ unit had an H_2/CO ratio of 0.7. During this run, the gas-phase methanol conversion unit was off-line, but Eastman was able to use the stabilized methanol in place of chemical-grade methanol in methyl acetate production. Table 4 provides results of stabilized methanol analysis, listing the concentrations of the constituents. Differences in analyses between the two Kingsport samples are due to differences in catalyst activity and/or CO_2 content of the feed gas.

Transportation Systems. In substituting stabilized methanol for chemical-grade methanol in bus and fuel-flexible vehicles (FFV) trials, results showed comparable fuel economy and maintenance requirements, with only slight changes in emissions.

FFVs tested at the Florida Institute of Technology experienced average fuel economies in miles per gallon (mpg) ranging from 10.88 mpg (1988 Corsica) to 14.68 mpg (1993 Taurus) for M-85 fuel blends (85 vol% methanol/ 15 vol% gasoline). M-15 fuel (15 vol% methanol/85 vol% gasoline) testing on the 1993 Taurus resulted in 19.81 mpg, which was comparable to the rated gasoline mileage (methanol is a lower energy density fuel than gasoline, so lower mileage ratings are expected).

The ARCADIS Geraghty & Miller FFV averaged approximately 16 mpg on M-85. Stabilized methanol use produced slightly higher total hydrocarbons, CO, CO_2, and methane emissions than chemical-grade methanol use, while non-methane hydrocarbons and NO_x emissions were slightly higher when using chemical-grade methanol. All of these emissions were below California emission standards.

The West Virginia University (WVU) transportable laboratory facility, specializing in heavy duty vehicle emissions measurements, determined that emissions of hydrocarbons and particulate matter increased slightly when stabilized methanol replaced chemical-grade methanol in bus engine tests (Detroit Diesel 6V92 methanol engines). However, stabilized methanol showed substantially (nearly 83%) lower NO_x emissions compared to diesel fuel.

Power Generation Systems. Testing of a GTC-85-72 gas turbine at the WVU Transportable Heavy Duty Emissions Testing Laboratory compared emissions generated from Jet A (kerosene) and stabilized methanol fuel. Re-

TABLE 4. CONCENTRATIONS OF STABILIZED METHANOL CONSTITUENTS (%)		
	Kingsport LPMEOH™ Product		LaPorte AFDU
	Sample 1	Sample 2	Sample
Methanol	98.08	99.26	98.40
Ethanol	0.31	0.25	0.60
C3+	0.40	0.18	0.46
Water	1.22	0.31	0.54

sults showed that stabilized methanol substantially lowered NO_x emissions, and also reduced CO, hydrocarbons, and particulate emissions. The residual mineral oil in the stabilized methanol failed to provide sufficient lubrication for the fuel pump and controller, requiring a 2% mixture of lubricant in the stabilized methanol. Also, flame-out occurred in transition from Jet A to stabilized methanol at low loads, requiring addition of a glow plug (other more effective methods are possible in future applications).

Only brief testing was possible on ARCADIS Geraghty & Miller water-emulsion fuel trials. Initial diesel engine performance testing comparing performance on JP-8 jet fuel versus an emulsion containing 30% water, 5% methanol, 1% additives, and 64% JP-8 jet fuel showed weighted average NO_x emissions reductions of 34%. However, military application would require resolution of problems with cold starting and operation at low ambient temperatures.

ARCADIS Geraghty & Miller testing on a microturbine incorporating low-NOx combustor technology showed that stabilized methanol operation produced comparable or lower NO_x and CO emissions than natural gas operation in a distributed generation application. The stabilized methanol-fueled microturbine achieved NO_x emissions levels of 1 part per million and CO levels of 4 parts per million.

University of Florida testing on a phosphoric acid fuel cell showed that the residual mineral oil in stabilized methanol compromised the steam reforming catalyst. This suggested that either a chemical-grade methanol be used or other more forgiving reforming approaches be applied, such as auto-thermal or partial oxidation reforming.

Economic Performance

Table 5 breaks down the capital costs for a once-through 500 short tons/day LPMEOH™ plant operated in conjunction with a coal-based IGCC. All synthesis gas cleanup except for removal of trace contamination is assumed to take place in the IGCC system. The total estimated capital cost of $31.1 million (2002 dollars) assumes the synthesis gas has a H_2/CO molar ratio of 0.68, is delivered at 1,000 psig, and has a carbonyl sulfide content of 5 parts per million 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.

Table 6 shows the operating costs for a once-through 500 short tons/day LPMEOH™ plant, assuming an on-stream factor of 0.9 and a LPMEOH™ catalyst deactivation rate of 0.4%/day. Fixed operating costs are estimated to be $1,358,000 per year, and corresponding variable operating costs would be about $15,853,000 per year.

Table 7 develops the economics of a typical once-through 500 short tons/day LPMEOH™ plant using the assumptions above plus a synthesis gas cost of $4.50/10^6$ Btu, 90% capacity factor, 15-year life, 303 gallons of methanol/short ton, and equity financing. Site-specific conditions significantly effect economics, so these figures should be treated as guidance only. Per the economic analysis, the cost of methanol from a LPMEOH™ unit integrated into an IGCC system is estimated 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. These prices include a return on investment of about 15%.

Sensitivity studies performed as part of the demonstration analysis indicate that the magnitude of the advantage in the methanol conversion cost for the LPMEOH™ process when compared with the conventional gas-phase

TABLE 5. BREAKDOWN OF CAPITAL COSTS FOR ONCE-THROUGH 500 SHORT TONS/DAY LPMEOH™ PLANT

Item	Cost (million 2002 $)
Compression	0.00
LPMEOH™ Equipment	5.09
Valves & Instruments	3.35
Construction	10.40
Freight & Miscellaneous	0.37
Air Products Process Studies	0.22
Air Products Technical Package	0.97
Project Engineering	1.63
Design Engineering	3.88
Field Engineering	1.15
Travel & Living	0.29
Reserve	0.00
License	Not Included
Sub-total Turnkey Plant	**27.35**
Owners Cost - 25% of Equipment	1.27
Methanol Storage	2.46
(30 Days-5.0 x 10⁶ Gallons)	
CO_2 Removal	0.00
Total Capital	**31.08**

TABLE 6. OPERATING COSTS FOR A 500-SHORT TONS/DAY LPMEOH™ UNIT*

Cost Parameter	Units	Quantity	$/Unit	$10³/yr
Fixed O&M Costs				
Operating Labor	—	—	—	736
Maintenance Labor	—	—	—	249
Maintenance Material	—	—	—	373
Subtotal Fixed Costs				**1,358**
Variable Operating Costs				
Synthesis gas	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
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.

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

process is increased when: (1) the synthesis gas is rich in CO, (2) synthesis gas is available at higher pressures, (3) only modest synthesis gas conversion to methanol is required, (4) synthesis gas is available with low H_2 and carbonyl sulfide content, (5) inert gases such as N_2 and O_2 are relatively high, and (6) fuel-grade methanol is required.

Comparative cost analyses were conducted between a 500 short tons per day LPMEOH™ plant and a comparably sized gas-phase methanol facility, both in IGCC coproduction mode producing fuel-grade methanol. The analyses assumed synthesis gas is normally available 90% of the time and synthesis gas is charged at $4.50/$10^6$ Btu. The results indicated that cost advantages of $0.04 to $0.11 per gallon of methanol could be realized by utilizing the LPMEOH™ process. The lower savings assumed 500 psig synthesis gas feed pressure and a 1:1 recycle ratio. The higher savings assumed 1,000 psig synthesis gas feed pressure and once-through processing.

Cost Factor	Base, 10^6 dollars	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**

Table heading: **TABLE 7. ECONOMICS FOR A LPMEOH™ PLANT** — Basis

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

COMMERCIAL APPLICATIONS

The Methanol Institute forecasts that the world's supply and demand for methanol will remain fairly constant through 2007, as shown in Table 8 (adapted from a 2002 Methanol Institute fact sheet). The table reflects the historical markets for methanol. Reduced demand for the fuel additive methyl tertiary-butyl ether (MTBE), currently being banned in many states, will be offset by increases in demand for methanol-derived chemicals. Fuel use shows only moderate growth from a relatively small demand base. The data suggests that growth in methanol demand will be dependent on increased use of methanol as a fuel in non-traditional markets.

Because low-cost production of fuel-grade methanol from LPMEOH™ is tied to coproduction from an IGCC plant, commercial application of LPMEOH™ is linked to commercialization of IGCC. In certain market scenarios, LPMEOH™ can enhance the economics of IGCC. For example, the most promising IGCC-LPMEOH™ coproduction application, at least initially, is use of the methanol on-site, or locally, as turbine fuel for peak shaving. Both products are marketable and the flexibility allows the gasifier to operate in a steady-state mode essential to IGCC efficiency. In the IGCC-LPMEOH™ coproduction mode, analyses have shown that economics are optimal when the LPMEOH™ unit uses between 20% and 40% by volume of the gasifier synthesis gas output.

LPMEOH™ produced fuel-grade methanol has the potential to compete economically with methanol derived from low-cost natural gas produced overseas when transportation costs are considered. As IGCC technology continues to improve, synthesis gas costs will go down, which will greatly impact LPMEOH™ derived methanol costs. Methanol conversion costs for LPMEOH™ in a once-through configuration are $0.15; the $4.50/$10^6$ Btu synthesis gas cost brings the production cost up to $0.50/gallon.

TABLE 8. 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.

The potential for coal-based IGCC in the United States could be as high as 60 GW by 2020, according to an October 2002 study conducted by DOE related to outcomes from the Fossil Energy research and development program. If coproduction were able to capture 10–20% of this market, there would be considerable opportunity for installing the LPMEOH™ process. Beyond the peak shaving application, methanol, as a clean fuel devoid of sulfur and having excellent low-NO_x emission characteristics, is likely to see increased use in an expanding distributed generation market. Distributed generation is the application of power at or near customer sites and is a major strategic measure to address growing energy security and reliability concerns. Gas turbines and diesel generators will play a role in distributed generation, and fuel cells will be the ultimate winner.

As discussed, LPMEOH™-derived methanol performed well in turbine and diesel engine testing. In addition to fueling distributed generation, methanol used as an alternative to fuel oil could also help solve problems of inadequate capacity reserves caused in part by restricted participation of oil-fired backup generators due to environmental restrictions. With further upgrading or application of more robust reforming measures, LPMEOH™-derived methanol should be an excellent fuel for stationary fuel cells. Moreover, fuel cell powered vehicles are another major potential market. The greatest challenge to automotive fuel cell applications is on-board hydrogen storage, which methanol solves by chemically bonding hydrogen but freeing it readily when needed.

In general, the LPMEOH™ process is a promising mechanism for supplementing national liquid fuel supplies with methanol made from indigenous coal reserves. This makes the LPMEOH™ process a valuable energy security asset not only to the United States, but to other coal-rich nations. China has expressed interest in the LPMEOH™ process because of the abundance of their coal reserves and an historic dependence on domestic chemical production.

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