OFF-SITE TESTING OF STABILIZED METHANOL FROM THE LIQUID PHASE METHANOL (LPMEOH™) PROCESS

TOPICAL REPORT

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Prepared by

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Abstract

The Liquid Phase Methanol (LPMEOH™) Process uses a slurry bubble column reactor to convert synthesis (syngas) gas to methanol. Because of its superior heat management, the process can directly utilize the carbon monoxide (CO)-rich syngas characteristic of the gasification of coal, petroleum coke, residual oil, wastes, or other hydrocarbon feedstocks. When added to an integrated gasification combined cycle (IGCC) power plant for peak shaving, the LPMEOH™ Process converts a portion of the CO-rich syngas produced by the gasifier to methanol, and the unconverted gas is used to fuel the gas turbine combined-cycle power plant.

The LPMEOH™ Demonstration Project at Kingsport, Tennessee, is a $213.7 million cooperative agreement between the U.S. Department of Energy (DOE) and Air Products Liquid Phase Conversion Company, L.P., a partnership between Air Products and Chemicals, Inc. (Air Products) and Eastman Chemical Company (Eastman), to produce methanol from coal-derived syngas. A 260- short tons per day (TPD) LPMEOH™ Process Demonstration Facility has been in operation at Eastman's chemicals-from-coal complex in Kingsport, Tennessee since 02 April 1997. Nameplate capacity was achieved on 06 April 1997, and production rates have exceeded 300 TPD of methanol during test periods. Since startup, overall availability has exceeded 98.5%. Eastman has accepted all of the greater than 80 million gallons of methanol produced to date at the LPMEOH™ Demonstration Facility for use in downstream chemical processes.

One of the advantages of the LPMEOH™ Process for coproduction of electric power and methanol from coal-derived syngas is that the as-produced, stabilized (degassed) methanol product is of unusually high quality (e.g. less than 1 wt% water). This stabilized methanol product may be suitable for direct use premium fuel applications. When compared to conventional methanol synthesis processes, cost savings of $0.04 to $0.11 per gallon of methanol (including conversion and distillation costs) can be achieved in coproduction facilities. However, the suitability of the stabilized product methanol as a fuel must be demonstrated. A product-use test program was developed to enhance the early commercial acceptance of central clean coal technology processing facilities, coproducing electricity and methanol. The objective of this program was to demonstrate commercial market applications for the "as produced" or stabilized methanol as a replacement fuel and as a fuel supplement. The applications (for example, as a hydrogen source for fuel cells, and as a clean, transportable, and storable fuel for dispersed power) required testing of the stabilized methanol to confirm its suitability. Stabilized methanol produced at the LPMEOH™ Process Demonstration Facility in Kingsport was made available to seven applications selected to participate in this study. The results of the test program are presented in this report. Based upon these results, stabilized methanol from the LPMEOH™ Process can be substituted for chemical-grade methanol in most of the applications without loss of the environmental benefits or degradation in performance. Additional testing would be required to qualify the use of stabilized methanol as the source of hydrogen to a phosphoric acid fuel cell; methanol from the LPMEOH™ Process that is purified to chemical-grade specifications should be suitable for use in this application.

Table of Contents

Acronyms and Definitions

Air Products	-	Air Products and Chemicals, Inc.
AFB	-	Air Force Base
AFDU	-	Alternative Fuels Development Unit, the DOE-owned experimental unit located adjacent to Air Products' industrial gas facility at LaPorte, Texas, where the LPMEOH™ Process was successfully piloted
AGSE	-	Aircraft Ground Support Equipment
CEC	-	California Energy Commission
CO	-	Carbon Monoxide
CO_2	-	Carbon Dioxide
DOE	-	United States Department of Energy
Eastman	-	Eastman Chemical Company
EPA	-	United States Environmental Protection Agency
FFV	-	Flexible Fuel Vehicle
H_2	-	Hydrogen
IGCC	-	Integrated Gasification Combined Cycle, a type of electric power generation plant
ISO	-	International Organization for Standardization
KW	-	Kilowatt
LPMEOH™	-	Liquid Phase Methanol (the technology to be demonstrated)
NO_x	-	Nitrogen Oxides
M-85	-	A fuel blend of 85 volume percent methanol and 15 volume percent unleaded gasoline.
M-100	-	A fuel of 100 volume percent methanol.
mpg	-	Miles per Gallon
NETL	-	National Energy Technology Laboratory
O_2	-	Oxygen
Stabilized Methanol	-	Methanol which has been degassed to remove volatile components; this material may be used directly in certain chemical and power systems
Syngas	-	abbreviation for synthesis gas
Synthesis Gas	-	A gas containing primarily hydrogen (H_2) and carbon monoxide (CO); intended for "synthesis" in a reactor to form methanol and/or other hydrocarbons (synthesis gas may also contain CO_2, water, and other gases).
TPD	-	(short) tons per day
UHC	-	Unburned Hydrocarbons
VOC	-	Volatile Organic Compounds
WIF	-	water-in-fuel
wt%	-	weight percent
WVU	-	West Virginia University

Executive Summary

The Liquid Phase Methanol (LPMEOH™) Process uses a slurry bubble column reactor to convert synthesis gas (syngas), primarily a mixture of carbon monoxide and hydrogen, to methanol. Because of its superior heat management, the process can utilize *directly* the carbon monoxide (CO)-rich syngas characteristic of the gasification of coal, petroleum coke, residual oil, wastes, or other hydrocarbon feedstocks. When added to an integrated gasification combined cycle (IGCC) power plant, the LPMEOH™ Process converts a portion of the CO-rich syngas produced by the gasifier to methanol, and the unconverted gas is used to fuel the gas turbine combined-cycle power plant. In addition, the LPMEOH™ Process has the flexibility to operate in a daily load-following pattern, coproducing methanol during periods of low electricity demand, and idling during peak times. Coproduction of power and methanol via IGCC and the LPMEOH™ Process provides opportunities for energy storage for electrical demand peak shaving, clean fuel for export, and/or chemical methanol sales.

The LPMEOH™ Demonstration Project at Kingsport, Tennessee, is a $213.7 million cooperative agreement between the U.S. Department of Energy (DOE) and Air Products Liquid Phase Conversion Company, L.P., a partnership between Air Products and Chemicals, Inc. (Air Products) and Eastman Chemical Company (Eastman), to produce methanol from coal-derived syngas. Construction of the LPMEOH™ Process Demonstration Facility at Eastman's chemicals-from-coal complex in Kingsport was completed in January 1997. Following commissioning and shakedown activities, the first production of methanol from the facility occurred on 02 April 1997. Nameplate capacity of 260 short tons per day (TPD) was achieved on 06 April 1997, and production rates have exceeded 300 TPD of methanol during test periods. Since startup, overall availability has exceeded 98.5%. Eastman has accepted all of the greater than 80 million gallons of methanol produced to date at the LPMEOH™ Demonstration Facility for use in downstream chemical processes.

Stabilized (degassed) methanol from the project has been made available to seven test locations to study its feasibility of its use in transportation and power generation applications. Successful demonstration of the use of stabilized methanol in these applications can enhance the flexibility of and revenue from IGCC plants. In bus and flexible fuel vehicle (FFV) trials, stabilized methanol provides the same environmental benefits as chemical-grade methanol with no penalty on performance or fuel economy. Tests in a gas turbine and a diesel generator have shown that levels of nitrogen oxides (NO_x) in the exhaust air can be lowered when stabilized methanol or methanol emulsions are used instead of conventional oil fuels. As with chemical-grade methanol, lubrication additives will likely be required when stabilized methanol is fed to a gas turbine. Testing of stabilized methanol as the source of hydrogen to a phosphoric acid fuel cell has shown that conventional steam reforming catalysts are not compatible with the trace mineral oil present in the stabilized methanol; when auto-thermal reforming or partial oxidation reforming are used, the stabilized methanol would possibly be acceptable as a fuel. Methanol from the LPMEOH™ Process that is purified to chemical-grade specifications should be suitable for use in this application.

Successful demonstration of the LPMEOH™ technology and the use of stabilized methanol in transportation and power systems will add significant flexibility and dispatch benefits to IGCC electric power plants, which traditionally have been viewed as strictly a baseload power generation technology. Now, central clean coal technology processing plants, making coproducts of electricity and methanol, can meet the needs of local communities for dispersed power and transportation fuel. The LPMEOH™ Process provides competitive methanol economics at small methanol plant sizes, and a freight and cost advantage in local markets vis-à-vis large offshore remote gas methanol. Methanol coproduction studies show that methanol can be produced at economically competitive levels from an abundant, non-inflationary local fuel source, such as coal. The coproduced methanol may be an economical hydrogen source for small fuel cells, as a transportation fuel, and an environmentally advantaged fuel for dispersed electric power.

A. Introduction

The Liquid Phase Methanol (LPMEOH™) Demonstration Project at Kingsport, Tennessee, is a $213.7 million cooperative agreement between the U.S. Department of Energy (DOE) and Air Products Liquid Phase Conversion Company, L.P., a partnership between Air Products and Chemicals, Inc. (Air Products) and Eastman Chemical Company (Eastman), to produce methanol from coal-derived synthesis gas (syngas). Construction of the LPMEOH™ Process Demonstration Facility at Eastman's chemicals-from-coal complex in Kingsport was completed in January 1997. Following commissioning and shakedown activities, the first production of methanol from the facility occurred on 02 April 1997. Nameplate capacity of 260 short tons per day (TPD) was achieved on 06 April 1997, and production rates have exceeded 300 TPD of methanol during test periods. Since startup, overall availability has exceeded 98.5%. Eastman has accepted all of the greater than 80 million gallons of methanol produced to date at the LPMEOH™ Demonstration Facility for use in downstream chemical processes.

Sponsored under the DOE's Clean Coal Technology Program, the LPMEOH™ Demonstration Project culminates an extensive cooperative development effort by Air Products and DOE in a program that began in 1981. By the late 1980s, the technology was proven in over 7,400 hours of test operation at a 10-TPD rate in the DOE-owned Alternative Fuels Development Unit (AFDU) in LaPorte, Texas. Developed to enhance electric power generation using IGCC technology, the LPMEOH™ Process exhibits several features essential for the economic coproduction of methanol and electricity in the IGCC scenario.

The slurry bubble column reactor differentiates the LPMEOH™ Process from conventional technology. Conventional methanol reactors use fixed beds of catalyst pellets and operate in the gas phase. The LPMEOH™ reactor uses catalyst in powder form, slurried in an inert mineral oil. The mineral oil acts as a temperature moderator and heat removal medium, transferring the heat of reaction away from the catalyst surface to boiling water in an internal tubular heat exchanger. Since the heat transfer coefficients on both sides of the exchanger are relatively large, the heat exchanger occupies only a small fraction of the cross-sectional area of the reactor. As a result of this capability to remove heat and maintain a constant, highly uniform temperature throughout

the entire length of the reactor, the slurry reactor can achieve much higher syngas conversion per pass than its gas-phase counterparts.

Furthermore, because of the LPMEOH™ reactor's unique temperature control capabilities, it can *directly* process syngas rich in carbon oxides (carbon monoxide (CO) and carbon dioxide (CO_2)). Gas-phase methanol technology would require that syngas feedstocks with similar compositions undergo stoichiometry adjustment by the water-gas shift reaction, to increase the hydrogen content, and subsequent CO_2 removal. In a gas-phase reactor, temperature moderation is achieved by recycling large quantities of hydrogen (H_2)-rich gas, utilizing the higher gas velocities around the catalyst particles and minimizing the conversion per pass. Typically, a gas-phase process is limited to CO concentrations of about 16 volume % in the reactor feed, as a means of constraining the conversion per pass to avoid excess heating. In contrast, for the LPMEOH™ reactor, CO concentrations in excess of 50% have been tested in the laboratory, at the AFDU in LaPorte, and at Kingsport, without any adverse effect on catalyst activity. As a result, the LPMEOH™ reactor can achieve approximately twice the conversion per pass of the gas-phase process, yielding lower recycle gas compression requirements and capital savings.

A second distinctive feature of the LPMEOH™ reactor is its robust character. The slurry reactor is suitable for rapid ramping, idling, and even extreme stop/start actions. The thermal moderation provided by the liquid inventory in the reactor acts to buffer sharp transient operations 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.

A third differentiating feature of the LPMEOH™ Process is that a high quality methanol product is produced directly from syngas rich in carbon oxides. Gas-phase methanol synthesis, which must rely on H_2-rich syngas feedstocks, yields a crude methanol product with 4% to 20% water by weight. The product from the LPMEOH™ Process, using CO-rich syngas, typically contains only 1% water by weight. As a result, raw methanol coproduced in an IGCC facility would be suitable for many applications at a substantial savings in purification costs. The steam generated in the LPMEOH™ reactor is suitable for purification of the methanol product to a higher quality or for use in the IGCC power generation cycle.

Another unique feature of the LPMEOH™ Process is the ability to withdraw spent catalyst slurry and add fresh catalyst on-line periodically. This facilitates uninterrupted operation and also allows perpetuation of high production rate of methanol from the reactor. Furthermore, choice of catalyst replacement rate permits optimization of methanol production rate versus catalyst replacement cost.

At the Eastman complex in Kingsport, Tennessee, the technology is integrated with the coal gasification facility that has operated commercially since 1983. Texaco gasification converts over 1,000 tons-per-day of high-sulfur, Eastern bituminous coal to syngas for the manufacture of methanol, acetic anhydride, and associated products. The LPMEOH™ Demonstration Facility occupies an area of 0.6 acre within the 4,000-acre Eastman complex.

Figure A-1
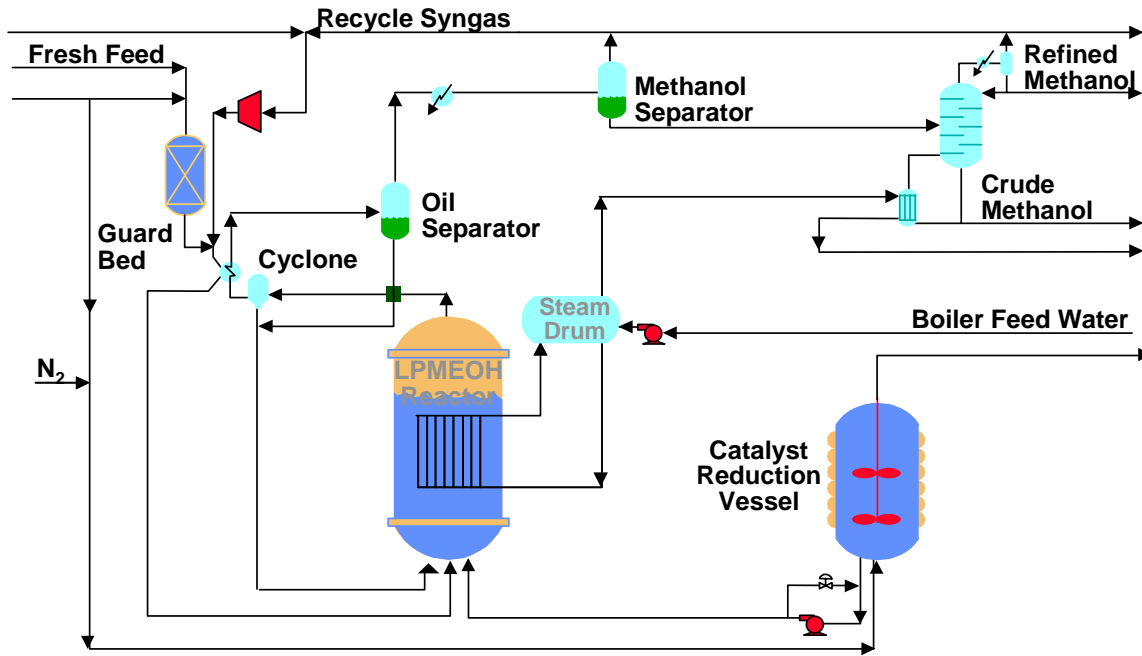**LPMEOH™ Demonstration Facility Process Flow Diagram**

Figure A-1 provides a simplified process flow diagram of the LPMEOH™ Demonstration Facility in Kingsport. Syngas enters the bottom of the slurry reactor, which contains solid particles of catalyst suspended in liquid mineral oil. The syngas dissolves through the mineral oil, contacts the catalyst surface, and reacts to form methanol. The highly exothermic heat of reaction is absorbed by the slurry and removed from the reactor by steam coils. The product methanol vapor diffuses from the catalyst surface through the mineral oil, and exits the reactor with unreacted syngas, is condensed to a liquid, and sent to distillation columns for removal of higher alcohols, water, and other impurities. Most of the unreacted syngas is returned to the reactor by the syngas recycle compressor, improving overall cycle efficiency.

A.1 IGCC Coproduction Options

The LPMEOH™ Process is a very effective technology for converting a portion of an IGCC electric power plant's coal-derived syngas to methanol, as depicted in Figure A-2. The process has the flexibility to handle wide variations in syngas composition. It can be designed to operate in a continuous, baseload manner, converting syngas from oversized gasifiers or from a spare gasifier. Alternatively, the process can be designed to operate only during periods of off-peak electric power demand, consuming a portion of the excess syngas and reducing the electricity output from the combined-cycle power unit. In this scenario, the gasification unit continues to operate at full baseload capacity, so that the IGCC facility's major capital asset is always fully utilized.

Figure A-2
Once-through Methanol Coproduction with IGCC Electric Power
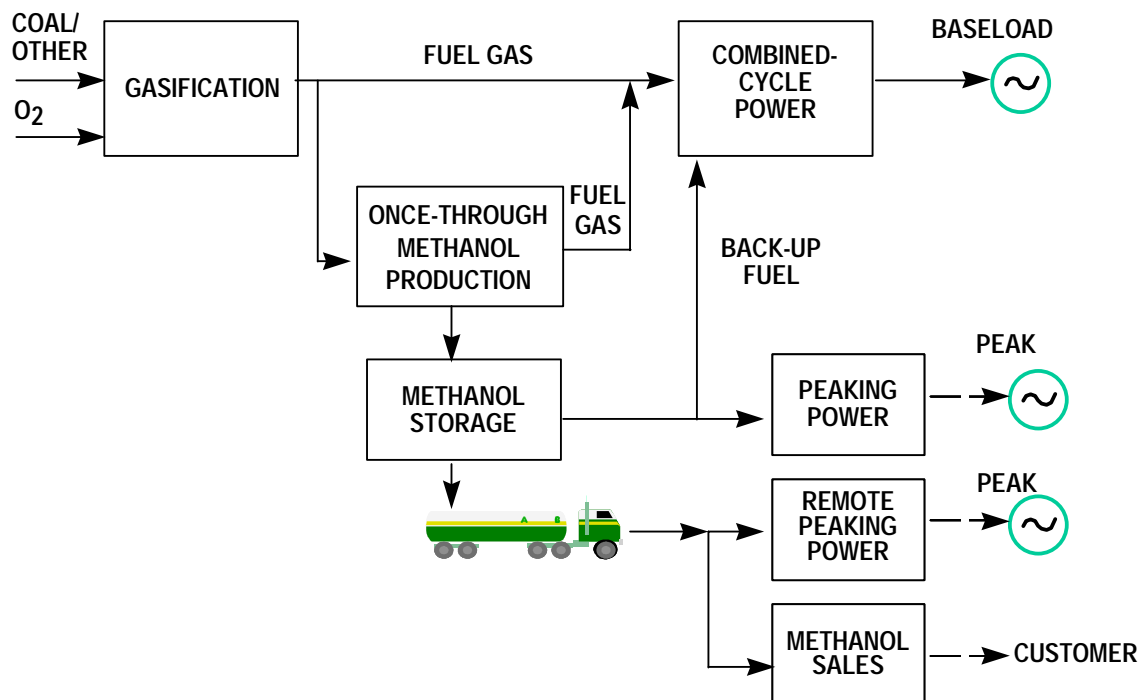
In either baseload or cycling operation, partial conversion of between 20% and 33% of the IGCC plant's syngas is optimal, and conversion of up to 50% is feasible. The required degree of conversion of syngas, or the quantity of methanol relative to the power plant size, determines the design configuration for the LPMEOH™ unit. In its simplest configuration, syngas at maximum available pressure from the IGCC power plant's gasifier system passes once-through the LPMEOH™ unit and is partially converted to methanol without recycle, water-gas shift, or CO_2 removal. The unreacted gas is returned to the IGCC power plant's combustion turbines. If greater syngas conversion is required, different design options are available.

A.2 Economics for Baseload Coproduction of Methanol and Power

Design studies for the LPMEOH™ Process have focused principally on the aforementioned IGCC applications. A comparison of the cost of methanol as produced from the LPMEOH™ Process and from a conventional gas-phase process as applied to a generic 500 TPD methanol plant as part of an IGCC coproduction facility was performed. The cost of methanol is calculated as the sum of three terms: the methanol conversion cost (which includes the fixed and operating costs for the methanol unit), the distillation cost to produce fuel grade methanol, and the syngas cost from the IGCC facility. A proprietary cost estimation screening program was used to

calculate the methanol conversion cost and the distillation cost from the LPMEOH™ Process and the gas-phase process for various syngas supply pressures and on-stream factors. Based on this analysis, the methanol conversion cost from the LPMEOH™ Process in a coal-based IGCC facility is $0.02 to $0.07 per gallon lower than from the gas-phase methanol process depending on syngas supply pressure and composition and facility on-stream factor.

As noted above, the LPMEOH™ Process can directly convert coal-derived syngas which is rich in CO, to produce a crude methanol product with nominally about 1 wt% water. Whereas, gas-phase methanol synthesis results in a crude methanol product with 4-20 wt% water, depending on the amount of CO_2 in the syngas which is converted to methanol and water. This results in lower purification cost ($0.02 to $0.04 per gallon) for the LPMEOH™ Process for the applications where high purity distillation is not required.

Methanol coproduction, by IGCC and the once-through LPMEOH™ Process, does not require large methanol plant sizes to achieve good economies of scale. The gasification plant is necessarily at a large economical scale for power generation, so the syngas manufacturing economies are already achieved. Methanol storage and transport economies are also achieved by serving local markets, and realizing freight savings over competing methanol, which is usually shipped from the U. S. Gulf Coast.

B. Results and Discussion

As noted earlier, methanol which is produced directly from CO-rich syngas has only 1% water by weight in the condensed stream entering the first distillation column. Significant capital and operating costs (corresponding to a purification cost of $0.02 to $0.04 per gallon of methanol) can be avoided if stabilized methanol, which is produced via removal of dissolved gases such as CO_2 from the first column, can be directly used in some chemical and power systems. A study within the LPMEOH™ Demonstration Project was envisioned to demonstrate the suitability of stabilized methanol as a liquid transportation and stationary fuel.

The product-use test program attempted to develop broader market applications and commercial fuels comparisons by evaluating new utility dispersed electric power developments, and possibly new mobile transport engine developments. The objective of the product-use test program was to demonstrate commercial market applications for the stabilized methanol as a replacement fuel and as a fuel supplement. During the program definition phase, attempts were made to develop sites to test stabilized methanol in municipal, industrial, and utility applications and as fuel supplements for gasoline, diesel, and natural gas. These tests were envisioned based upon the U.S. energy market needs projected through the 2018 time period when the LPMEOH™ technology is expected to be commercialized.

Because the generation of electric power is not a feature of the demonstration project at Kingsport, the coproduction of methanol with electric power could not be demonstrated. However, the product-use test program was developed to provide data on potential applications of stabilized methanol in order to enhance the early commercial acceptance of central clean coal technology processing facilities, coproducing electricity and methanol to meet the needs of the local community. These applications required testing of the product to confirm its suitability.

A limited quantity of the stabilized methanol from the demonstration facility was made available for product-use tests. Product-use tests commenced during the first year of demonstration operations. An initial inventory of approximately 12,000 gallons of stabilized methanol was produced at LPMEOH™ Demonstration Facility to supply the needs of the product-use test program. Analysis of the stabilized methanol from tests conducted using a CO-rich feed gas is

Table B-1
Stabilized Methanol Composition - Texaco-Type Feed Gas

	Kingsport Sample #1 (wt%)	Kingsport Sample #2 (wt%)	LaPorte AFDU Sample (wt%)
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

shown in Table B-1. Results from two Kingsport tests are quite comparable with results from a test campaign at the LaPorte AFDU. The difference in the water and higher alcohol content of the two Kingsport samples is related to the age or activity of the catalyst and the amount of CO_2 in the reactor feed gas.

The status of the seven projects which have been defined within the product-use test program is reviewed. Two categories of potential applications of stabilized methanol were under investigation, transportation systems and power generation systems. Detailed reports from each of the test locations are provided in one of the following volumes:

B.1 Volume I - Transportation Systems

A total of five vehicles have been tested on fuel blends made from stabilized methanol from the LPMEOH™ Demonstration Project. These tests, which have been performed at three different locations, were designed to determine if there are any differences in fuel economy, maintenance, or exhaust emissions when compared to the performance with fuels made with chemical-grade methanol.

B.1.1 FLORIDA INSTITUTE OF TECHNOLOGY BUS & LIGHT VEHICLES

Three of the vehicles are located at the Florida Institute of Technology, and all were tested on stabilized methanol from the LPMEOH™ Demonstration Project. A 1988 Chevrolet Corsica flexible-fuel vehicle (FFV) was driven a total of 4,455 miles on M-85 (85 volume % methanol/ 15 volume % gasoline) and M-100 (100 volume % methanol) fuel blends. Repairs have been of a routine nature and independent of the type of methanol used or the fuel blend. A total of 32 refuelings have been performed under the sponsorship of the product-use program, with an average fuel economy of 10.88 miles per gallon (mpg). When compared with the U.S. Environmental Protection Agency (EPA) rated gasoline mileage of 19.0 mpg, the methanol blends are less efficient on an energy density basis (methanol has a lower energy content per gallon than gasoline). Additional data on the base gasoline performance is necessary in order to complete this analysis.

The second vehicle is a 1993 Ford Taurus FFV which was acquired during the project. During the project, a total of 7,648 miles have been accumulated on fuel blends with stabilized methanol content ranging from M-85 to M-15. Since the car was acquired in July of 1998, the car has operated well; the fuel pump was replaced due to routine wear not related to the use of either stabilized methanol or chemical-grade methanol fuel blends. The fuel economy has ranged from 14.68 mpg on M-85 to 19.81 mpg for M-15. This latter figure matches both the measured fuel economy with pure gasoline and the EPA rated gasoline mileage.

A bus which had been operated by the Jacksonville Transportation Authority was driven a total of 937 miles on M-100 during the project. Due to the costs associated with hiring a driver for this vehicle, no further tests beyond the initial shakedown of the bus were conducted.

B.1.2 ARCADIS GERAGHTY & MILLER FLEXIBLE FUEL VEHICLE

A second set of FFV trials was performed at ARCADIS Geraghty & Miller in a 1996 Ford Taurus FFV. During sponsorship by the product-use program, the FFV was driven a total of 3,206 miles on a M-85 fuel blended from chemical-grade methanol, and 3,479 miles were accumulated on M-85 produced from stabilized methanol. The fuel economy of about 16 mpg was the same for both fuel blends (Table B-2).

Table B-2
ARCADIS Geraghty & Miller FFV
Fuel Economy Results

	Fuel Economy, mpg	
	Chemical-Grade M-85	LPMEOH™ M-85
In-use	16.2	16.4
Emission Test on Dynamometer	16.9	16.3

Results of emissions testing on a dynamometer are presented in Table B-3. The FFV exhibited higher emissions for total hydrocarbons, carbon monoxide, carbon dioxide, and methane for the stabilized methanol fuel blend; emissions of non-methane hydrocarbons and nitrogen oxides (NO_x) were higher for the M-85 fuel blended with chemical-grade methanol. For each of these parameters, emissions for both fuels were within the standards established by the state of

Table B-3
ARCADIS Geraghty & Miller FFV
Emissions Results

	Constituent Emission Rate, grams/mile		California Emission Standard, grams/mile
	Chem-Grade M-85	LPMEOH™ M-85	
Carbon Dioxide	334	346	No Standard
Carbon Monoxide	0.867	0.923	3.4
Nitrogen Oxides	0.138	0.121	0.4
Total Hydrocarbons	0.093	0.132	No Standard
Methane	<0.001	0.011	No Standard
Non-methane Hydrocarbons	0.120	0.118	0.25
Methanol	0.143	0.252	No Standard
Formaldehyde	0.0194	0.0337	0.015

California. Emissions of methanol and formaldehyde were greater for the stabilized methanol blend, and the readings for formaldehyde were above the California standard for both fuel blends (there is no standard for methanol emissions). It was concluded that further engine tuning would bring the formaldehyde emissions into compliance for both fuel blends.

Overall, the FFV operated by ARCADIS Geraghty & Miller exhibited similar performance characteristics for both fuel economy and emissions when the vehicle was operated on fuel blends from either stabilized methanol or chemical-grade methanol.

B.1.3 WEST VIRGINIA UNIVERSITY STUDY OF STABILIZED METHANOL IN TRANSIT
         BUS

West Virginia University (WVU) has developed a transportable laboratory facility which specializes in the measurement of emissions from heavy-duty vehicles. Figure B-1 is a photograph of the laboratory, and one of the pieces of test equipment.

Figure B-1
West Virginia University
Transportable Heavy Duty Emissions Testing Laboratory

WVU mobile emissions
laboratory

WVU mobile testing equipment

Under this project effort, three buses operated on M-100 by Tri-Boro Coach in New York were tested. The buses were manufactured in 1993 and 1994 by Transit Motor Corp. The Detroit Diesel 6V92 methanol engines in the buses are rated at 253 horsepower. All buses were operated on the Central Bus District Cycle, which is intended to simulate the use of a transit bus in city service and is also used to rate the performance of new buses. One bus was also tested using a 5-mile cycle, which uses five different segments of acceleration, cruise, and deceleration.

The results from the average vehicle emissions for this product-use test are presented in Table B-4. On average, emissions of hydrocarbons (primarily unburned methanol and aldehydes) and particulate matter were increased slightly when stabilized methanol is used as the fuel. Also shown for reference are recent test results as reported by the laboratory for a new diesel engine; methanol fuels offer substantial advantages in lower emissions of NO_x with minor changes in other components when compared with diesel fuel.

Table B-4
West Virginia University - Tri-Boro Coach
Emissions Results

	Constituent Emission Rate, grams/mile		
	Chemical-Grade M-85	LPMEOH™ M-85	New Diesel Engine with Diesel Fuel
Carbon Dioxide	2,773	2,811	2,611
Carbon Monoxide	10.41	9.60	4.9
Nitrogen Oxides	5.60	5.11	30.1
Total Hydrocarbons	5.39	6.88	0.13
Particulate Matter	0.21	0.24	0.24

B.2 Volume II - Power Generation Systems

As indicated in Figure B-1, one of the primary applications for stabilized methanol derived from syngas streams rich in carbon monoxide is in the generation of electric power. The more classical approach is to generate electricity in a methanol-fired gas turbine at the power plant during periods of peak power demand. In recent years, changes in the power generation and transmission industry and technological improvements in smaller turbine and fuel cell systems have spawned the concept of distributed power. A local power producing system will be able to provide the electricity for a small number of users (for example, the heating and air conditioning needs of an office complex or shopping center). Methanol, produced at a centrally located coal-fired IGCC plant, can be produced at prices which are competitive in these distributed power applications.

The product-use test program was designed to study the uses of stabilized methanol in a variety of power generation systems (turbines, fuel cells, generators).

B.2.1 WEST VIRGINIA UNIVERSITY STATIONARY GAS TURBINE

This program was designed to compare the emissions and operational aspects of gas turbine operation on stabilized methanol compared with conventional liquid fuel. At WVU, a research aircraft was built using a GTC-85-72 gas turbine as the power source. This unit, which is rated at 235 horsepower in the form of compressor bleed air, was used in this study. Several of the turbine subsystems (fuel tank and pumps, speed and fuel flow controller, ignition system, bleed air load controller) had to be modified to accommodate the stabilized methanol fuel.

Testing has shown that the present configuration of the gas turbine does not allow operation on methanol at startup. Conventional fuel (in the form of Jet A) was used for initial turbine firing, and a fuel emulsifier was added to assure a smooth transition from Jet A to stabilized methanol. At low power loads, flameout occurred during the transition to methanol; this appears to be the result of the higher heat of vaporization of methanol when compared with Jet A. Two glow plugs were added to overcome this problem. Initial testing was also performed without any additives in order to determine if the trace amounts of the inert oil from the LPMEOH™ Process were sufficient to provide the necessary lubrication for the fuel pump and controller. It was determined that the oil levels in the stabilized methanol did not adequately lubricate these systems.

Testing was performed by the WVU Transportable Heavy Duty Emissions Testing Laboratory in order to compare the emissions generated from Jet A and stabilized methanol fuels. The results are provided in Figure B-2, and demonstrate the capability of stabilized methanol to meet the same expected performance results as chemical-grade methanol for significantly reducing the levels of NO_x in gas turbine exhausts.

Following this work, a second set of performance tests and emissions measurements were performed with stabilized methanol and the selected lubricant to determine if any differences from the earlier testing could be determined. Figure B-3 contains a representative set of results for a 2% mixture of the lubricant in methanol; emissions of NO_x were again substantially lower than for a kerosene fuel, and levels of CO, hydrocarbons, and particulates were also reduced.

The investigators recommend that additional work could be focused on optimizing the selection and concentration of the lubricant and solving the problems with operation at low power load.

Figure B-2
West Virginia University Stationary Gas Turbine
Emissions Test Results – 1998 Testing

Emissions during fuel type change over from Jet-A to Methanol at t=5 minutes and back to Jet A at t=11 minutes at 45% power level, August 18, 1998
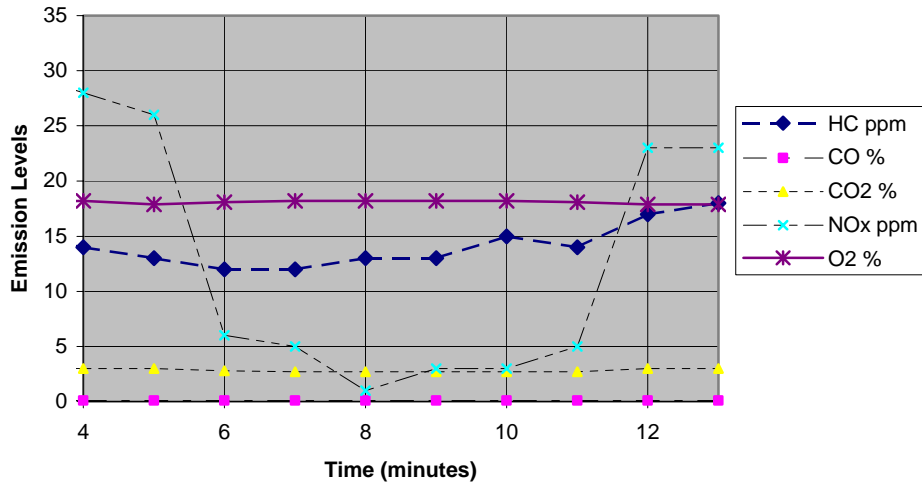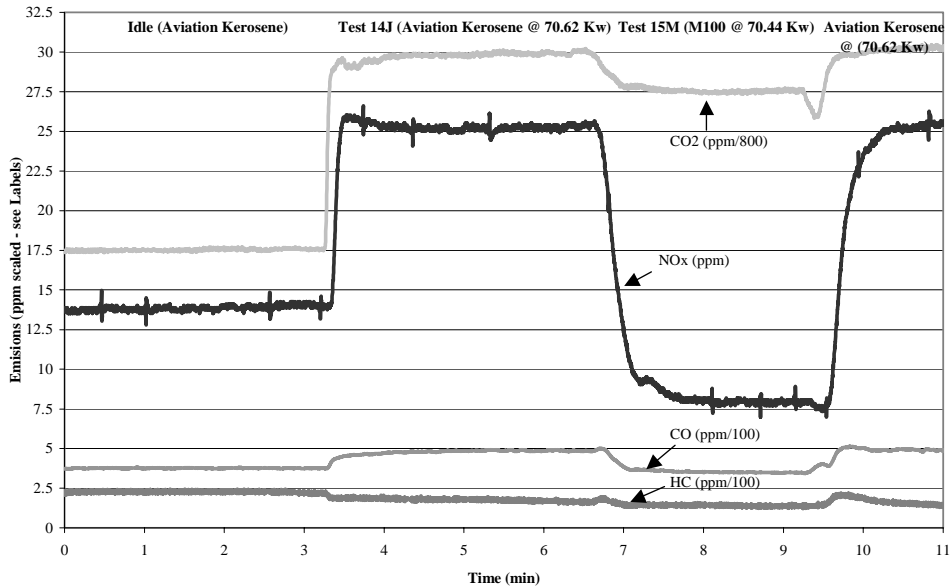

Figure B-3
West Virginia University Stationary Gas Turbine
Emissions Test Results – 2000 Testing

Emissions During Fuel Type Change Over From Aviation Kerosene To Methanol, 3/14/00 Tests - Idle, Test 14J (Aviation Kerosene @ 70.62 Kw), 15M (70.44 Kw) And Back To Aviation Kerosene @ 70.62 Kw

B.2.2 AIRCRAFT GROUND SUPPORT EQUIPMENT

In preparation for the possibility that combustion sources at U.S. Air Force bases may be required to reduce their emissions of NO_x, the Air Force had become interested in the evaluation of possible approaches to controlling NO_x emissions from aircraft ground support equipment (AGSE) diesel generators (part of a class of off-road power generation systems). These generators are very high NO_x emitters. It has been determined that the AGSE accounts for nearly 40 to 60 percent of a typical base's emissions of NO_x and the diesel generator accounts for 70 to 90 percent of the AGSE emissions. Replacement of these systems is expensive, and other alternative fuels (such as liquefied or compressed natural gas or liquefied petroleum gas) are not feasible. One NO_x control approach applicable to these engines is the use of a diesel/water emulsion fuel in place of standard diesel fuel.

The use of diesel/water emulsions containing nominally 5-percent methanol have been shown to be effective in achieving nominally 40-percent NO_x reductions from some engines. However, the diesel/water emulsion experience base is quite limited, and the long-term effects of such emulsions on engine performance were unknown. Thus, there was a need to evaluate the effectiveness and the long-term performance of this NO_x control approach when applied to AGSE.

ARCADIS Geraghty & Miller developed a project to perform an extended evaluation of the use of a diesel/water/methanol emulsion, prepared using stabilized methanol from the LPMEOH™ Demonstration Project as the methanol component. Testing was planned on an Air Force flight line generator at Tyndall Air Force Base (AFB), Florida. Previous work supported by the Air Force Green AGSE Program developed an additive package that is effective in both stabilizing a diesel/water emulsion and preventing engine part corrosion. Two of these generators at Tyndall AFB were made available to this project. Of these, one was to be operated on the emulsion fuel during the evaluation, and the other was to be run on a military jet fuel (specification JP-8). JP-8 jet fuel is used in the mobility applications of the generators, and the Air Force has standardized the use of JP-8 in diesel engines to reduce the need to manage and maintain two fuel types and fueling systems. Engine performance and emissions testing were planned to be conducted before the start and after the end of this 6-month period to quantify emission reductions and performance impacts. Engine inspections were also planned, to address durability and corrosion issues.

The water-in-fuel (WIF) emulsion containing the stabilized methanol and additives was the emulsion fuel that was evaluated in these tests. The WIF emulsion was prepared to contain nominally 30 percent water, 5 percent methanol, and 1 percent additives, with the balance being JP-8.

When this project was originally planned, substantial support of the effort was offered by several Air Force and contractor organizations at Tyndall AFB. As the project proceeded, however, mission priorities of all the Air Force organizations supporting the evaluation changed to the point that further support of the project was not possible. As a result of these changes, support for the project could no longer be offered after May 1999, and the project needed to be

concluded. Up to that point, a series of initial performance and emissions tests had been completed. The report summarizes the results of these tests.

In the initial performance and emissions tests that were completed, engine emissions of oxygen (O_2), CO, CO_2, NO_x, and unburned hydrocarbons (UHC) were measured from engines fueled with both WIF and JP-8. Particulate emissions measurements were also performed using a dilution tunnel measurement technique. However, the 30-minute sampling time at each test load was not long enough to allow collecting measurable quantities of particulate on the sampling train filters.

Results of the tests were as follows:

- As shown in Figure B-4, the use of the WIF emulsion reduced engine NO_x emissions by 21 to 57% over the engine load range, with the greater emission reductions achieved at lower engine loads. The International Organization for Standardization (ISO) cycle weighted average NO_x emissions were reduced 34% from 1,550 ppm at 15% O_2 with JP-8 fuel to 1,030 ppm at 15% O_2 with the emulsion.
- CO emissions from the engine did not vary significantly with load for the JP-8 fuel, and were nominally 500 ppm at 15% O_2. With the WIF emulsion, CO emissions were relatively constant at engine loads from full load to 50 percent load, but increased substantially at lower engine loads.

Figure B-4
Aircraft Ground Support Equipment
Average NOx Emissions Reduction with WIF vs. JP-8
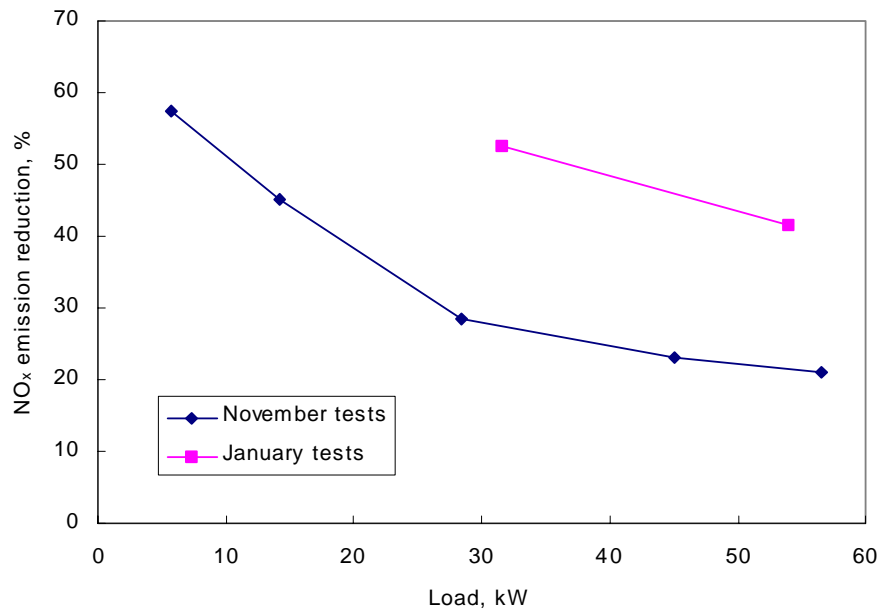
- Relative CO emissions for the two test fuels showed inconsistent behavior. For one series of tests, CO emissions with the WIF emulsion were lower than with JP-8 at engines loads of 50% or greater, but were higher at lower engine loads. ISO-cycle weighted average emissions for this test series were comparable for both fuels. For a second test series, CO emissions were substantially higher with the WIF emulsion than with JP-8 at all engine loads tested.

Stabilized methanol from the LPMEOH™ Demonstration Project was successfully used to produce the WIF emulsion which was used in this project. Although NO_x emissions reduction with the WIF were impressive, severe problems with cold starting and operation at low ambient temperatures were experienced. A few approaches to solve these problems were tried during this abbreviated project schedule without success. Until the cold start problem is solved, WIF use in Air Force applications was not recommended.

B.2.3 LOW-NO_X STATIONARY MICROTURBINE COMBUSTOR

As originally proposed by ARCADIS Geraghty & Miller, the objective of the subject project was to demonstrate cost-effective volatile organic compound (VOC) destruction by a small gas turbine operating in a distributed power generation application fired with stabilized methanol from the LPMEOH™ Demonstration Project. However, after an exhaustive search, no host site willing to participate in the project was identified during the project definition phase.

At this point it was decided to shift the environmental focus of the project. California, as well as the EPA, regulates NO_x as an ozone precursor. As a consequence, California continues to pursue very aggressive NO_x control strategies to facilitate bringing California ozone nonattainment regions into attainment. Moreover, such strategies will become more commonplace in the Midwestern and Northeastern states in response to EPA's decision to implement a NO_x cap and trade program in both the Northeastern states as well as the Midwestern states that contribute to the ozone nonattainment status of regions of the Northeast via transported ozone.

Given these mandates, it was clear that any new distributed generation capacity will need to be low NO_x emitting units. In response to this need, Alzeta Corporation, with support from the California Energy Commission (CEC), the National Energy Technology Laboratory (NETL), and a number of gas turbine manufacturers, has been developing an advanced low NO_x surface stabilized combustor technology for stationary microturbines in distributed generation applications. The opportunity arose for the LPMEOH™ Demonstration Project to participate in this program and extend demonstration testing to stabilized methanol. Accordingly, it was decided to redirect the project on VOC control to focus on completing a series of tests using stabilized methanol as a fuel for a low NO_x microturbine combustor targeted for use in a distributed generation application. In testing performed with natural gas fuel, it was possible to achieve combustor NO_x, CO, and UHC emissions approaching 2 ppm at 15 percent O_2. Parallel testing with stabilized methanol was performed in these tests to evaluate whether comparable performance could be achieved.

As shown in Figure B-5, NO_x emissions with stabilized methanol from the LPMEOH™ Demonstration Project were comparable to and, for several conditions, lower than those with natural gas fuel. Results of the tests showed that combustor NO_x emissions could be held below 6 ppm at 15 percent O_2 over the range of combustor firing rates corresponding to turbine idle to full load. Emissions as low as 1 ppm at 15 percent O_2 were achieved at a number of test conditions, and were 3 ppm at 15 percent O_2 or lower for all but the highest load tested. The low NO_x emissions were achieved with CO emissions at 20 ppm (at 15 percent O_2) or lower. CO emissions when stabilized methanol was used as fuel were also comparable to those with natural gas fuel. In fact, CO emissions were 4 ppm at 15 percent O_2 or lower at all but low load (firing rate) and high load.

In summary, stabilized methanol from the LPMEOH™ Process would seem to represent an acceptable liquid fuel for advanced low emission microturbines using the Alzeta combustor technology, offering emissions performance at or slightly better than the levels achieved with natural gas fuel.

Figure B-5
Low-NO$_x$ Microturbine
NOx Emissions with Stabilized Methanol vs. Natural Gas
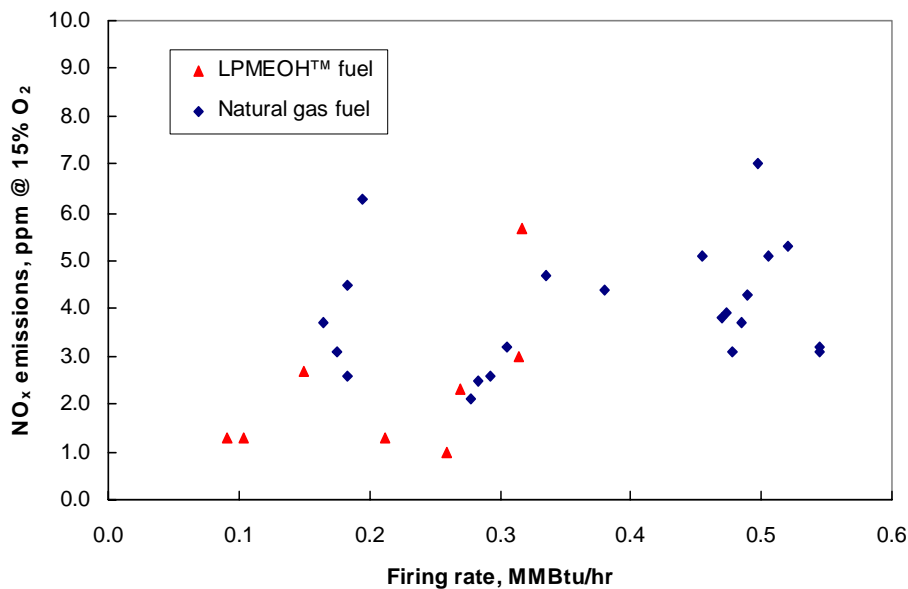
B.2.4 UNIVERSITY OF FLORIDA FUEL CELL

Over the past few years, progress has continued in the development of fuel cells, which can be used in either transportation or power applications.

While pure gaseous hydrogen is the ideal fuel for fuel cell power systems, it is also relatively expensive, difficult to transport, and difficult to store for onboard transportation systems. Consequently, there has been, and is, considerable interest in utilizing liquid hydrocarbon fuels for transportation fuel cell applications. For a liquid fuel to be a feasible alternative to hydrogen, it must be possible and practical to utilize a fuel processing system to transform the liquid fuel into a hydrogen-rich gas. More specifically, the hydrogen-rich gas must be compatible with long-term operation of the fuel cell system within which it would be utilized, with little or no degradation in performance. In earlier demonstrations with phosphoric acid fuel cells, chemical-grade methanol has been used successfully as the source of hydrogen.

Clearly, the implication is that a suitable fuel-fuel processor combination must maintain the ability to provide almost complete conversion of the liquid fuel feedstock into an acceptable hydrogen-rich gas over a long period of time and many cycles of operation. "Acceptable" hydrogen-rich gas in this case means a maximum concentration of hydrogen and virtually zero concentration of contaminants (primarily unreacted components from the liquid fuel) which would degrade the fuel cell stack life and/or performance. To meet this acceptability requirement, the fuel processor must also not undergo any significant decrease in its ability to convert the liquid fuel in a continuing and consistent manner. A prime mechanism for the fuel processor to experience a significant decrease in conversion ability would be through a deactivation of the catalyst in a catalyst-driven processor such as the steam reformer.

Catalyst deactivation can occur for many reasons including excess temperature, rapid temperature transients, or the introduction of oxygen. However, with the introduction of a new liquid fuel such as stabilized methanol, it is obvious that deactivation can occur as a result of one or more contaminants (such as higher alcohols or the trace quantity of mineral oil from the LPMEOH™ Process) contained in the liquid fuel. Given the cost of distillation ($0.02 to $0.04 per gallon) of stabilized methanol to chemical-grade purity, a fuel cell test site of this potential source of hydrogen was sought. The University of Florida had facilities and equipment in the Fuel Cell Research and Training Laboratory to perform this type of research, as well as two operational methanol-fueled fuel cell engines. As a result, an agreement was reached for the University of Florida to undertake the evaluation of the stabilized methanol as a suitable fuel for steam-reformed methanol/phosphoric acid fuel cell systems.

Since it was obviously important not to damage the operational fuel cell engines, the procedure was to fabricate small steam reformers using catalyst pellets of the type (copper oxide-zinc oxide) typically used for methanol steam reformation. The apparatus was designed so as to allow determination of areas of deactivation if they occurred as a result of the stabilized methanol fuel. A parallel reformer operating simultaneously with chemical-grade methanol was used as a control.

Initial results showed very rapid degradation of the catalyst exposed to the stabilized methanol. Analysis of the results indicated that a likely cause of the deactivation was the presence of high boiling point components in the methanol feedstock. A potential scenario for this deactivation was a probable coating of the catalyst with trace quantities of the mineral oil which is used as the liquid medium in the LPMEOH™ Reactor. Subsequent tests and modifications to the reformer unit were performed as well as the utilization of a higher temperature reformer catalyst to avoid rapid catalyst degradation. Higher temperatures did, as expected, result in less effect due to the mineral oil, but it also resulted in a more unfavorable balance among hydrogen, methane, carbon dioxide, and carbon monoxide in the reformate.

The results to date indicate that for the relatively low-temperature steam reforming of stabilized methanol, the trace mineral oil in the stabilized methanol would most likely have to be removed in order for it to be a suitable fuel. On the other hand, the limited higher temperature results indicate that possibly for auto-thermal reforming and probably for partial oxidation reforming, the stabilized methanol would be acceptable as a fuel. Methanol from the LPMEOH™ Process that is purified to chemical-grade specifications should be suitable for use in this application.

C. Conclusion

The LPMEOH™ Demonstration Project at Kingsport, Tennessee, is a $213.7 million cooperative agreement between the U.S. Department of Energy and Air Products Liquid Phase Conversion Company, L.P., a partnership between Air Products and Eastman, to produce methanol from coal-derived syngas. The LPMEOH™ Process is now being demonstrated at commercial scale under the DOE Clean Coal Technology Program. The demonstration facility, located at Eastman's chemicals-from-coal complex in Kingsport, Tennessee, has produced in excess of the 260 TPD of methanol nameplate capacity from coal-derived syngas. Since startup of the unit in April 1997, overall availability has exceeded 98.5%. Eastman has accepted all of the greater than 80 million gallons of methanol produced to date at the LPMEOH™ Demonstration Facility for use in downstream chemical processes.

Stabilized methanol from the project has been made available to seven test locations to study its feasibility as feedstock in transportation and power generation applications. Use in these applications is expected to enhance the flexibility of and revenue from IGCC electric power plants. In bus and FFV trials, stabilized methanol provides the same environmental benefits as chemical-grade methanol with no penalty on performance or fuel economy. Tests in a gas turbine and a diesel generator have shown that levels of NO_x in the exhaust air can be lowered when stabilized methanol or methanol emulsions are used instead of conventional oil fuels. As with the chemical-grade methanol, lubrication additives will likely be required when stabilized methanol is fed to a gas turbine. Testing of stabilized methanol as the source of hydrogen to a phosphoric acid fuel cell has shown that conventional steam reforming catalysts are not compatible with the trace mineral oil present in the stabilized methanol; when auto-thermal reforming or partial oxidation reforming are used, the stabilized methanol would possibly be acceptable as a fuel. Methanol from the LPMEOH™ Process that is purified to chemical-grade specifications should be suitable for use in this application.

Successful demonstration of the LPMEOH™ technology and the use of stabilized methanol in transportation and power systems will add significant flexibility and dispatch benefits to IGCC electric power plants, which traditionally have been viewed as strictly a baseload power generation technology. Now, central clean coal technology processing plants, making coproducts of electricity and methanol, can meet the needs of local communities for dispersed power and transportation fuel. The LPMEOH™ Process provides competitive methanol economics at small methanol plant sizes, and a freight and cost advantage in local markets vis-à-vis large offshore remote gas methanol. Methanol coproduction studies show that methanol can be produced at economically competitive levels from an abundant, non-inflationary local fuel source, such as coal. The coproduced methanol may be an economical hydrogen source for small fuel cells, as a transportation fuel, and an environmentally advantaged fuel for dispersed electric power.

D. References

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