### PROJECT DATA ON EASTMAN CHEMICAL COMPANY'S CHEMICALS-FROM-COAL COMPLEX IN KINGSPORT, TN

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### <u>Abstract</u>

The Liquid Phase Methanol (LPMEOH<sup>™</sup>) 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. (the Partnership) to produce methanol from coal-derived synthesis gas (syngas). Air Products and Chemicals, Inc. (Air Products) and Eastman Chemical Company (Eastman) formed the Partnership to execute the Demonstration Project.

The LPMEOH<sup>™</sup> Demonstration Unit was built at a site located at the Eastman chemicals-fromcoal complex in Kingsport, TN. This Topical Report provides publicly available technical data on this complex and specific data on the operation of the Eastman catalyst guard bed and the wastewater treatment system. The chemicals-from-coal complex began operation in 1983 using various purchased technologies such as Texaco gasification, Linde AG Rectisol gas clean-up, and Lurgi fixed-bed methanol production as well as Eastman developed technologies for chemicals production. Initially, the plant was designed to produce approximately 500 million pounds per year of acetic anhydride and acetic acid to supply half of Eastman's acetyl raw material needs. The facility was expanded in 1991 and additional process improvement work brought the capacity to the current level (in excess of 1 billion pounds per year). Two gasifiers (one plus a spare) are campaigned to give gasifier system uptimes in excess of 98 percent with a maximum rate of approximately 1,350 tons per day of coal. This feed rate corresponds to 150 percent of the original design basis. The facility is operationally and economically a proven means of producing acetyl chemicals from coal.

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### ACRONYMS AND DEFINITIONS

<u>Term:</u>	Definition:
Ac <sub>2</sub> O	Acetic Anhydride
Air Products	Air Products and Chemicals, Inc.
AFDU	Alternative Fuels Development Unit - The "LaPorte PDU"
AFFTU	Alternative Fuels Field Test Unit
Balanced Gas	A synthesis gas with a composition of hydrogen $(H_2)$ , carbon monoxide
	(CO) and carbon dioxide (CO <sub>2</sub> ) in stoichiometric balance for the production
	of methanol (approximately 2:1)
Btu	British Thermal Unit
Carbon Monoxide Gas	A syngas containing primarily carbon monoxide (CO); also called CO Gas
Crude Methanol	Underflow from rectifier column, defined as 80 wt% minimum purity;
5.66	requires further distillation in existing Eastman equipment prior to use
DCS	Distributed Control System
DOE	United States Department of Energy
Eastman	Eastman Chemical Company
Gpm	Gallon(s) per minute
HUAC	A cette acid
Hydrogen Gas	A syngas containing an excess of hydrogen $(H_2)$ over the stoicniometric
1000	balance for the production of methanol, also called $H_2$ das
IGCC	Integrated Gasification Combined Cycle, a type of electric power generation plant
Ib	Pound
	Liquid Phase Methanol (the technology to be demonstrated)
MeOAc	Methyl acetate
MeOH	Methanol
MPC	Model Predictive Control
OSHA	Occupational Safety and Health Administration
Partnership	Air Products Liquid Phase Conversion Company, L.P.
PLC	Programmable logic controller
ppbv	Parts per billion (volume basis)
psig	Pounds per square inch (gauge)
SCF	Standard cubic feet
Syngas	Abbreviation for Synthesis Gas
Synthesis Gas	A gas containing primarily hydrogen (H <sub>2</sub> ), carbon monoxide (CO), or
	mixtures of H <sub>2</sub> and CO; intended for "synthesis" in a reactor to form
	methanol and/or other hydrocarbon products (Synthesis gas may also
	contain carbon dioxide (CO <sub>2</sub> ), water, and other gases)
TOC	Total organic compounds
TPD	Short ton(s) per day
Vol%	Volume percent
Wt%	Weight percent

### **Executive Summary**

The Liquid Phase Methanol (LPMEOH<sup>™</sup>) 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. (the Partnership) to produce methanol from coal-derived synthesis gas (syngas). Air Products and Chemicals, Inc. (Air Products) and Eastman Chemical Company (Eastman) formed the Partnership to execute the Demonstration Project. The LPMEOH<sup>™</sup> Demonstration Unit was designed, constructed, and is in operation at a site located at the Eastman chemicals-from-coal complex in Kingsport.

The project involves the operation of a 260 short tons per day (TPD), or 80,000 gallons per day, methanol unit utilizing coal-derived syngas from Eastman's integrated coal gasification facility. The new equipment consists of syngas feed preparation and compression facilities, the liquid phase reactor and auxiliaries, product distillation facilities, and utilities.

This Topical Report provides publicly available technical data on the Eastman chemicals-fromcoal complex in Kingsport, including the removal of mercury within the gasification section. The chemicals-from-coal complex continues to be a commercially viable operation for the production of acetyl chemicals from coal. A testament to its reliability and cost efficiency is Eastman's reliance on this facility to supply raw materials for one of the largest product streams within the company. Needless to say, Eastman's success depends to a great degree on the success of the gasification complex.

The operation (particularly the gasification process) is maintenance intensive, but can be managed to provide the proper balance between cost and reliability. Eastman has, through years of work, greatly improved the reliability, production, and thus the success of this process.

Other specific data on the operation of the Eastman guard bed to protect methanol synthesis catalyst and the wastewater treatment system are provided. Species of arsenic and sulfur from the Rectisol syngas clean-up plant are present at parts-per-billion by volume (ppbv) concentrations, and a catalyst guard bed has been in service to further reduce these concentrations prior to the introduction of the primary syngas feed (Balanced Gas) to either the fixed-bed methanol plant or the LPMEOH<sup>TM</sup> Demonstration Unit. The operation of the LPMEOH<sup>TM</sup> Reactor and associated systems has had no significant impact on the performance of the existing wastewater treatment system at the chemicals-from-coal complex, as there have been no permit excursions since the startup of the LPMEOH<sup>TM</sup> Demonstration Unit in April 1997.

Eastman's experience and expertise in gasification and chemical synthesis technology have made the chemicals-from-coal complex a world-class operation.

### 1. Introduction

The Liquid Phase Methanol (LPMEOH<sup>™</sup>) 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<sup>™</sup> Demonstration Unit 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), or 80,000 gallons per day, was achieved on 06 April 1997, and production rates have exceeded 300 TPD of methanol during test periods. Over the 69-month operating period, overall availability has exceeded 97.5%. Eastman has accepted all of the greater than 103.9 million gallons of methanol produced to date at the LPMEOH<sup>™</sup> Demonstration Unit for use in downstream chemical processes.

Sponsored under the DOE's Clean Coal Technology Program, the LPMEOH<sup>™</sup> 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 integrated gasification combined cycle (IGCC) technology, the LPMEOH<sup>™</sup> 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<sup>TM</sup> Process from conventional technology. Conventional methanol reactors use fixed beds of catalyst pellets and operate in the gas phase. The LPMEOH<sup>TM</sup> 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<sup>TM</sup> reactor's unique temperature control capabilities, it can *directly* process syngas rich in carbon oxides (carbon monoxide (CO) and carbon dioxide (CO<sub>2</sub>)). 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<sub>2</sub> removal. In a gas-phase reactor, temperature moderation is achieved by recycling large quantities of hydrogen (H<sub>2</sub>)-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 percent (vol%) in the reactor feed, as a means of constraining the conversion per pass to avoid excess heating. In contrast, for the LPMEOH<sup>TM</sup> reactor, CO concentrations in excess of 50 vol% have been tested in the

laboratory, at the AFDU, and at Kingsport, without any adverse effect on catalyst activity. As a result, the LPMEOH<sup>TM</sup> 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<sup>TM</sup> 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<sup>TM</sup> 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<sub>2</sub>-rich syngas feedstocks, yields a crude methanol product with 4 weight percent (wt%) to 20 wt% water. The product from the LPMEOH<sup>TM</sup> Process, using CO-rich syngas, typically contains only 1 wt% water. 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<sup>TM</sup> 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<sup>TM</sup> Process is the ability to periodically withdraw spent catalyst slurry and add fresh catalyst on-line. This facilitates uninterrupted operation and also allows perpetuation of high production rates of methanol from the reactor. Furthermore, choice of catalyst replacement rate permits optimization of methanol production rate versus catalyst replacement cost.

Figure 1 provides a simplified process flow diagram of the LPMEOH<sup>TM</sup> Demonstration Facility in Kingsport. Three different feed gas streams (hydrogen gas or H<sub>2</sub> Gas, carbon monoxide gas or CO Gas, and the primary syngas feed known as Balanced Gas) are diverted from existing operations to the LPMEOH<sup>TM</sup> Demonstration Unit, thus providing the range of coal-derived syngas ratios (H<sub>2</sub> to CO) needed to meet the technical objectives of the demonstration project. 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.

This report provides publicly available data on the Eastman chemicals-from-coal complex at Kingsport.

Figure 1 LPMEOH<sup>TM</sup> Demonstration Facility Process Flow Diagram



### 2. <u>Eastman Chemicals-from-Coal Complex</u>

### 2.1 Introduction

Eastman has nearly \$5 billion in annual sales and currently has approximately 15,000 people working to produce over 400 different chemicals, fibers, and plastics. The corporate headquarters are located in Kingsport, TN, also the site of Eastman's largest manufacturing unit, Tennessee Eastman Division.

The chemicals-from-coal complex is also located in Kingsport on a 55-acre site adjoining Eastman's existing chemical complex. The facility began operation in 1983 after four years of engineering and construction and more than eight years of work to identify, develop, and assemble the technologies necessary to make the operation viable.

The chemicals-from-coal complex was the first commercial use of a Texaco coal gasifier to provide feed gas for the production of acetyl chemicals. In addition to the first Texaco coal gasifier, the project was the first use of new technologies developed by Eastman to produce methyl acetate (MeOAc) and the final acetic anhydride (Ac<sub>2</sub>O) product.

For this significant advancement in acetyl chemicals production, Tennessee Eastman was awarded the prestigious Chemical Engineering Kirkpatrick Award in 1985.

In November 1995, the American Chemical Society recognized the chemicals-from-coal complex as a National Historic Chemical Landmark.

Acetyl chemicals are an important part of Eastman's overall portfolio of chemicals, fibers, and plastics, but they are particularly important to Tennessee Eastman Division. Five of the seven manufacturing divisions at the Kingsport site depend on acetyl raw materials. Over 3 million pounds per day of "new" acetic anhydride and acetic acid (HOAc) are produced in the chemicals-from-coal complex and are used in the production of cellulosic plastics and fibers that end up in consumer products like photographic film, tool handles, paints, and cigarette filters. Direct sales of acetic anhydride and acetic acid are used in a wide variety of industrial and pharmaceutical applications (Appendix, Figure 1).

### 2.2 History (1983-2000)

Prior to the installation of the chemicals-from-coal complex, all of Eastman's acetyl raw materials were derived from petroleum and natural gas. Ethane, propane, and naphtha were cracked to form propylene and ethylene. The ethylene was converted to acetaldehyde at Texas Eastman Division. The acetaldehyde was transported to Kingsport and further oxidized to acetic acid and then converted to acetic anhydride via natural gas-fired, ketene cracking furnaces.

The oil shortages of the 1970's and specifically the oil embargo of 1973 provided the incentive for Eastman to begin to explore the possibility of supplying the acetyl stream from coal mined in nearby Southwest Virginia and Eastern Kentucky, instead of oil.

Eastman engineers, along with Bechtel Corporation as the contractor, began to identify existing technologies as well as developing new ones to make the dream a reality. The first gasifier startup occurred on June 19, 1983 and by April of 1984, the entire complex was in full production. The original capacity of the plant supplied one half of Eastman's acetyl demand. After several years of successful operation, the decision was made to expand the facilities to meet the entire acetyl demand from coal (Appendix, Figure 2).

This expansion was completed in 1991; however, the gasification plant was not significantly expanded. In addition, the percentage of raw syngas used to produce methanol was reduced and diverted to the higher value acetic anhydride production. In this way, the acetic anhydride production was doubled without a two-fold increase in raw syngas produced. This mode of operation generally requires some internal methanol demand to be met via outside purchases.

After this expansion, the gasifiers operated at about 128% of the original design capacity of 900 tons per day of coal. Today, through years of continual process improvement work, the gasifiers operate at a maximum of 150% of the original design (approximately 1,350 tons per day of coal).

Appendix, Table 1 is a chronological listing of the historical milestones of the complex.

### 2.3 Description of Chemicals-from-Coal Complex

The chemicals-from-coal complex is divided into two major operating areas – syngas production and chemicals production.

The syngas production area contains the coal handling/slurry preparation plant, the gasification plants, the Rectisol gas clean-up plant, the  $CO/H_2$  separation plant, and the sulfur recovery plant. Air Products supplies oxygen from an air separation plant adjacent to the chemicals-from-coal complex.

Oxygen and coal are supplied to either of two Texaco quench gasifiers (Appendix, Figure 3). Raw gases produced are split into two process streams. About one third of the raw syngas is routed to the shift reactor to produce enough  $H_2$  to make the correct stoichiometric composition for methanol production. Both gas streams are cooled in the cooling trains and pass through beds of sulfur-impregnated activated carbon for mercury removal prior to being fed to the Rectisol plant. Steam, at a rate of approximately 200,000 pounds per hour, is produced in the cooling trains and utilized in downstream processes.

Carbon dioxide (CO<sub>2</sub>) and hydrogen sulfide (H<sub>2</sub>S) are removed from the gas streams in chilled methanol absorbers (Appendix, Figure 4). The H<sub>2</sub>S is sent to a Claus/SCOT recovery unit for recovery of sulfur. The CO<sub>2</sub> is vented to the atmosphere. The process gas stream is sent to the CO/H<sub>2</sub> cryogenic separation plants to produce the carbon monoxide used in the acetic anhydride plant. The CO/H<sub>2</sub> gas mixtures received from the cryogenic separation units are mixed with the gas stream from the shifted gas train to provide syngas for the methanol plants.

The chemicals production area contains the methanol plants, methyl acetate plants, acetic anhydride plants, and catalyst recovery plants. Methanol is produced in a Lurgi unit (fixed bed reactor) as well as the LPMEOH<sup>TM</sup> Demonstration Unit. The methanol is reacted with acetic acid to produce methyl acetate in a proprietary Eastman process. Methyl acetate is reacted with carbon monoxide in a proprietary catalytic process to produce acetic anhydride with coproduction of acetic acid.

### 2.4 Key Operational Issues

Production rate, reliability, maintenance cost, and safety are of primary importance to the operation of the chemicals-from-coal complex. Of course there are many other important areas to consider, but the success in these four areas is key to the acetyl business.

### 2.4.1 Production Rate

Because the acetyl stream is such an important part of Eastman's overall business, the production rate of acetyl products is critically important. As with any capital-intensive investment, the incremental cost to make additional product is much lower than the fully allocated cost. By executing process improvement initiatives, the coal feed rate (and subsequent production rate) has been increased from 128% of original design to recent levels as high as 150% of the original design. Appendix, Figure 5 gives the total gas production for the last several years. The steady

trend upward indicates that the accomplishments that have been made by continuation of the process improvement programs.

### 2.4.2 Reliability

Perhaps more important than production rate is reliability. Outages of the gasification complex result in downtime in the chemicals production areas, and depending on the duration, can drastically affect production in the majority of the operating divisions at Tennessee Eastman. The primary measure of reliability is percent uptime (or gas availability to the chemical plants).

Since 1986, the gasifier uptime (not including planned complex shutdowns every two years) has consistently been above 98% (Appendix, Figure 6). (Note that a plant-wide power outage was a major contributing factor toward the performance results for 1998.) To achieve this high level of reliability, a two-gasifier design is key. In 2001, the average gasifier run length was in excess of 40 days. Each time a gasifier is taken off-line, it is "turned around" (i.e., made ready for the next run) typically within 7 to 14 days. Then, if a problem develops on the operating gasifier which doesn't cause immediate shutdown, the spare gasifier can be started and put online without interruption of the gas supply to the downstream plants.

There are a number of operating and maintenance problems that can cause a gasifier to shutdown. See Appendix, Figures 7 and 8 for historical and recent shutdown causes. In past years, the fuel injector (often referred to as "burner") has been the primary cause for shutdown. However, Eastman experts have had recent breakthroughs in feed injector design, which have effectively prolonged the life of a burner far beyond the run life of other system components.

It appears that the next run length limit will be due to plugging in the quench and black water systems, specifically the steam generators. Projects have been identified to alleviate this bottleneck.

Key to this continual improvement is a "run review" held after each shutdown. Essentially, experts perform an autopsy of the run, identify key problems, analyze critical data, and generate projects to improve the process performance.

### 2.4.3 Maintenance Cost

Of the operating cost factors, maintenance cost is the highest controllable cost. However, due to reliability, capacity, and safety demands, there has always been a struggle to find the right level of maintenance support. The chemicals-from-coal complex has historically been supported by around the clock maintenance including 10 to 12 mechanical, electrical, and instrumentation mechanics and an expanded day shift crew. However, Eastman has recently cut back on the level of off-hour support in an effort to reduce overall maintenance costs. Eastman has adopted a philosophy of performing a higher percentage of "planned maintenance" and continually assessing the maintenance need while working to identify and implement reliability projects to take work out of the system.

As a result, turnaround times have increased, but because of the lower number of failures (a product of reliability projects), 2000 has been the most productive year on record. Additionally, maintenance costs have been reduced by 10 to 15%.

One of the most expensive items in the annual maintenance budget is refractory replacement. Refractory wear is obviously related to temperature and slag properties, but our experience has shown that it is also proportional to gasifier rate. Even though the refractories have improved over the years, the increased coal throughput has reduced the operating time per liner. However, the amount of production per liner has remained relatively constant. Currently, the approximate operating time per liner is 7,000 hours. Cooler operating temperatures may improve refractory life in the future.

### 2.4.4 Safety

Eastman is committed to providing a safe work environment for its employees. Considering the potential hazards that exist in the complex (high pressure, toxic gases, rotating equipment, high level of maintenance activity, and extreme high and low temperatures), this is a major challenge. However, safety is always of prime importance in everything Eastman does. The past safety record has been excellent. Currently, the Acid Division, the business unit within which the chemicals-from-coal complex is located, has an Occupational Safety and Health Administration (OSHA) recordable rate less than 1.0.

The gasifier system, as well as other critical downstream processes, is equipped with a wellinstrumented safety system that will automatically shut off the feed if any unsafe conditions are detected. In order to maintain the safety of the operation without having false shutdowns, redundant instrumentation is typically used.

Area on-line CO and  $H_2S$  monitors are located throughout the operating area to warn of leaks that could create hazardous conditions. In addition, personnel entering the plants wear portable personal CO and  $H_2S$  detectors equipped with alarms.

### 2.5 Major Process Improvements and Enhancements

Over the seventeen years that the chemicals-from-coal complex has been in operation, many company resources have been invested into efforts to improve the process. The improvements indicated by the previous charts do not tell the full story. Some of the major process improvements and enhancements are discussed briefly below.

### 2.5.1 Burner Design Improvements

The major cause of shutdown has historically been failure of the feed injector. High temperature sulfidation corrosion has been blamed for the failures. Recent breakthroughs in injector design combined with rigorous inspection and checkout of various feed system components have resulted in greatly improved fuel injector life. Eastman has received 6 patents dealing with fuel injector improvements and is continuing to develop know-how in this important area of process reliability.

### 2.5.2 Complex Shutdown Planning and Execution

The entire chemicals-from-coal complex is shutdown for maintenance once every two years. During the 1999 shutdown, approximately 560 tasks were completed in the gasification area alone. Through careful planning and execution, these outages have been minimized to approximately 9 days in duration. The industry standard for acetyl plants for such major turnarounds is usually 2 to 3 times this amount of time and typically does not include the complexity of a Chemicals-from-Coal process.

### 2.5.3 State of the Art Distributive Control Systems

The gasification complex has been retrofitted with a state-of-the-art Honeywell distributive control system. This system has allowed complex algorithms to be added to the feed controls system as well as other systems in the plant. Additionally, Eastman's Controls Technology group has developed and implemented Model Predictive Control (MPC) techniques to fully utilize the plant capacity and maximize gas production without operator intervention.

### 2.5.4 Switching Gasifiers

Appendix, Figure 9 shows the average length of operation with a single gasifier. When it is necessary to switch from one gasifier to another and a complete shutdown is not required, gas flow from the "new" gasifier is valved into the cooling train while the gas from the "old" gasifier is valved out. This has historically been a slow, careful process taking a few hours. A "quick switch" procedure has been developed which allows this transition in less than one hour. This improved process also minimizes the impact to downstream plants allowing production to continue and reduces the waste gas produced during switches. Appendix, Figure 10 shows the number of production interruptions (loss of gas supply to downstream plants) since startup. The typical duration of an interruption is 1 day or less. When compared to the number of gasifier shutdowns (Appendix, Figure 9), the benefit of skilled "switching" techniques is evident.

### 2.6 <u>Photograph of Eastman Chemicals-from-Coal Complex</u>

An aerial photograph of the Eastman Chemicals-from-Coal complex in Kingsport is provided in Appendix, Figure 11.

### 3. <u>Results and Discussion</u>

### 3.1 Information on Coal Gasification and Gas Clean-up Plants

The Intellectual Property Provisions to the Cooperative Agreement for the LPMEOH<sup>TM</sup> Demonstration Project calls for the release of publicly available information to provide a general understanding of the operation of the coal gasification and gas clean-up facility. The compositions, flow rates, and other information concerning the internal streams within the coal gasification and gas clean-up box of Appendix, Figure 1 are proprietary, except as hereinafter provided:

- (a) The average amount and composition of major streams entering the gasification facility, including:
- quantity of coal to the gasifier and its composition (proximate and ultimate analysis, heating value, sulfur and ash)
  - Coal (441,363 short tons per year)
  - Composition data expressed in weight %:
    - Ash: 4.83 10.35% (dry) (no representative analysis of the ash exists)
    - Heating Value: 13,556 14,597 Btu/lb (dry)
      - 15,077 15,484 Btu/lb (moisture and ash-free)
    - Sulfur: 1.83 2.71% (dry)
    - Carbon: 69.97 78.46% (dry)
    - Hydrogen: 4.35 7.93% (dry)
    - Nitrogen: 1.03 1.66% (dry)
    - Moisture: 3.09 7.82% as received
- quantity of oxygen to the gasifier
  - Oxygen (462,963 short tons per year)
- quantity of water to the gasifier
  - o 50 Million gallons per year (95 gpm)

- (b) The corresponding amount and composition of major effluent streams:
- quantity of clean synthesis gas with its composition of hydrogen, carbon monoxide, hydrogen sulfide, and carbon dioxide
  - Synthesis Gas (18,486 million standard cubic feet per year):
    - H<sub>2</sub>: 67.7 vol%
    - CO: 29.3 vol%
    - H<sub>2</sub>S: 0.8 parts per million by volume
    - CO<sub>2</sub>: 2.57 vol%
- quantity of sulfur produced and its purity
  - 8,690 tons per year (>99.9 wt% purity)
- quantity of carbon dioxide produced and its purity
  - 8,962 million standard cubic feet per year (average 73.1% purity)
- quantity of slag generated
  - Dry Slag/Soot (42,439 tons per year) (wet 99,151 tons per year)
- wastewater generated
  - 841 million gallons per year (1,600 gpm)

- (c) Publicly available information concerning the operation of the coal gasification and gas clean-up facility, including nominal temperatures and pressures:
  - Gasifier operates at a nominal 1,400°C and 1,000 psig pressure.
  - Wet grinding reduces coal to fine sand-sized particles.
  - Slurry mixture is 60 to 70 wt% solids.
  - Two Texaco gasifiers used, each capable of supplying entire demand.
  - Slag removed through lock hopper system.
  - Soot removed through drum filtration system.
  - Mercury removed using sulfur-impregnated activated carbon at nominal 30°C and 1,000 psig pressure, 90-95% mercury removal at 5 minute contact time (based upon total packed volume) with an adsorbent life of 12 to 18 months.
  - Gas Clean Up is Linde AG Rectisol technology.
  - Cold methanol (-55°C) removes acid gases from syngas.
  - Carbon monoxide and hydrogen are separated cryogenically in two cold boxes.
  - 99.9% of the sulfur in the coal is recovered in Claus reactors for sale.
  - Shell Claus Offgas Treating used to remove sulfur in final vent gas to trace levels.

### 3.2 Trace Impurities Entering and Leaving 10C-30 Catalyst Guard Bed

In addition to the Rectisol gas clean-up plant, a catalyst guard bed (equipment number 10C-30) was installed by Eastman upstream of the fixed-bed methanol plant. Figure 2 shows the location of this vessel in relation to the syngas generation system and to both the fixed-bed methanol plant and the LPMEOH<sup>™</sup> Demonstration Unit. The Eastman catalyst guard bed was installed to remove trace contaminants which adversely impact the long-term performance of methanol synthesis catalysts. Prior to construction of the LPMEOH<sup>™</sup> Demonstration Unit, the Eastman catalyst guard bed was charged with both zinc oxide (for sulfur removal) and manganese oxide (for arsenic removal).

During the LPMEOH<sup>™</sup> Demonstration Project, several measurements and process calculations were performed in an attempt to quantify the concentrations of the sulfur and arsenic compounds that exited the Eastman catalyst guard bed. Analytical measurements were performed in the Alternative Fuels Field Test Unit (AFFTU), a portable laboratory designed to provide on-site testing of the quality of syngas feeds for conversion to methanol via the LPMEOH<sup>™</sup> Process. The AFFTU was shipped to Kingsport in May 1996 (prior to startup of the LPMEOH<sup>™</sup> Demonstration Unit) for six weeks of testing, and again in November 1997 for a one-month campaign.

A unique feature of the LPMEOH<sup>™</sup> Reactor is the ability to remove catalyst slurry from the process during normal operation in order to measure the change in the physical properties of the catalyst (including the concentration of species on the catalyst surface) with time. If the

Figure 2 Integration of Existing Eastman Facilities with LPMEOH<sup>™</sup> Demonstration Unit



cumulative syngas flow is known, an average concentration of components in the syngas stream can be estimated.

Table 1 provides a list of the trace components entering and exiting the Eastman catalyst guard bed that have been measured in syngas streams or calculated from uptake on the surface of catalyst samples during the execution of the LPMEOH<sup>TM</sup> Demonstration Project. Variations in the reported values are most likely attributed to either changes in the concentrations of species in the coal feed to the gasification plant, changes in operation of the Rectisol syngas clean-up plant, or changes in performance of the Eastman catalyst guard bed. Based upon the latter occurrence, the adsorbent material in the Eastman catalyst guard bed has been changed three times during the operation of the LPMEOH<sup>TM</sup> Demonstration Unit. During the first change (September 1997), the existing materials (zinc oxide and manganese oxide) were replaced with the same quantities of fresh adsorbent. In June 1999, this charge of adsorbent was removed and replaced only with manganese oxide. In October 2002, the manganese oxide was replaced with a fresh charge. It should be noted that, during sampling that was performed in 1995, mercury was not detected in any of the three syngas feed streams to the LPMEOH<sup>TM</sup> Demonstration Unit (Balanced Gas, CO Gas, H<sub>2</sub> Gas).

Date	Syngas <u>Stream(s)</u>	<u>Species</u>	Steady-State Concentration (ppbv)	Sample <u>Material</u>
May 1996 (AFFTU) after Eastman catalyst guard bed	Balanced Gas, CO Gas	Arsenic Arsenic COS H <sub>2</sub> S	27 40 7-15 1-6	Spent Catalyst Spent Adsorbent Syngas Syngas
June 1997 (Plant) after LPMEOH catalyst guard bed	Balanced Gas	Arsenic	87	Spent Catalyst
December 1997 - January 1998 (AFFTU) <i>after LPMEOH</i> catalyst guard bed	Balanced Gas	Arsenic COS H₂S Total S	> 31 10-20 < 2 37	Spent Adsorbent Syngas Syngas Spent Catalyst
January 1998 (Plant) after LPMEOH catalyst guard bed	Balanced Gas	Arsenic	8	Spent Catalyst
June 1999 (Plant) before Eastman catalyst guard bed	Balanced Gas	Arsenic	39	Syngas
September 1999 (Plant) before Eastman catalyst guard bed	Balanced Gas	Arsenic	53	Syngas
July 2000 (Plant) before Eastman catalyst guard bed	Balanced Gas	Arsenic	64	Syngas

### Table 1Summary of Trace Impurities Entering and Leaving Eastman Catalyst Guard Bed

### 3.3 Impact of Wastewater and Alcohols on Wastewater Treatment System

As shown in Figure 1, a stream of crude methanol is sent from the LPMEOH<sup>™</sup> Demonstration Unit to the existing Eastman methanol plant for further distillation. The crude methanol typically contains about 90 wt% methanol, 0.05 wt% ethanol, 0.02 wt% heavier components (such as C<sub>3</sub>+ alcohols and trace quantities of the mineral oil from the LPMEOH<sup>TM</sup> Reactor), 0.02 wt% light components (such as CO<sub>2</sub>), with the balance being water. This stream is distilled within the Eastman chemicals-from-coal complex to recover the methanol and vent the light components to the Eastman boiler system; water, ethanol, and the heavier components are sent to the existing Eastman wastewater treatment system. In Table 2, Eastman has provided data on the total organic compounds (TOC) and the flowrate to the wastewater treatment system (the LPMEOH<sup>TM</sup> Demonstration Unit was brought onstream on 02 April 1997). It should be noted that the sample location for the wastewater stream includes feeds from the LPMEOH<sup>™</sup> Demonstration Unit, the existing methanol plant, the methyl acetate production plants, and other facilities which operate on a campaign basis. This data indicates that the variations in the quantity of wastewater and the TOC of the stream are both within the range of operating results within this area of the Eastman chemicals-from-coal complex. It is also noteworthy that there have been no permit excursions during the 4+ years of operation of the LPMEOH<sup>™</sup> Demonstration Unit

### Table 2TOC Data for Composite Wastewater Stream(including streams associated with LPMEOH™ Demonstration Unit)

<u>Date</u>	TOC, lb/day	<u>Wastewater Flow, gpm</u>
Before LI	PMEOH <sup>TM</sup> Operation:	
1/97	2,318	248
2/97	3,354	330
3/97	3,412	416
After LPN	<b>IEOH<sup>TM</sup> Operation:</b>	
1/98	2,492	532
2/98	2,779	547
3/98	2,476	449

### 4. Conclusions

This Topical Report provides publicly available technical data on the Eastman chemicals-fromcoal complex in Kingsport, Tennessee. The chemicals-from-coal complex continues to be a commercially viable operation for the production of acetyl chemicals from coal. A testament to its reliability and cost efficiency is Eastman's reliance on this facility as the source of raw materials for one of the largest streams within the company. Needless to say, Eastman's success depends to a great degree on the success of the gasification complex. The operation (particularly the gasification process) is maintenance intensive, but can be managed to provide the proper balance between cost and reliability. Eastman has, through years of work, greatly improved the reliability, production, and thus the success of this process.

Other specific data on the wastewater treatment system and the operation of the Eastman catalyst guard bed have been provided. Species of arsenic and sulfur from the Rectisol syngas clean-up plant are present at ppbv concentrations, and a catalyst guard bed has been in service to further reduce these concentrations prior to the introduction of Balanced Gas to either the fixed-bed methanol plant or the LPMEOH<sup>TM</sup> Demonstration Unit. The operation of the LPMEOH<sup>TM</sup> Reactor and associated systems has had no significant impact on the performance of the existing wastewater treatment system at the chemicals-from-coal complex, as there have been no permit excursions since the startup of the LPMEOH<sup>TM</sup> Demonstration Unit in April 1997.

Eastman's experience and expertise in gasification and chemical synthesis technology have made the chemicals-from-coal complex a world-class operation.

### 5. <u>References</u>

- 1. L. T. Arms, "Eastman Chemical Company Gasification Plant Expansion and Operation Summary," Paper presented at the Eleventh Worldwide Texaco Licensee Symposium, New York, NY (October 1994).
- 2. T. L. Mitchell, W. L. Trapp, "Eastman Chemical Kingsport Plant Chemicals from Coal Operations 1983-1997," (October 1997).
- "Design and Construction of the Alternative Fuels Field Test Unit and Liquid Phase Methanol Feedstock and Catalyst Life Testing at Eastman Chemical Company (Kingsport, TN)," DOE Topical Report, Cooperative Agreement No. DE-FC22-95PC93052, March 1997.
- 4. "Alternative Fuels Field Test Unit Support to Kingsport LPMEOH<sup>™</sup> Demonstration Unit - December 1997 - January 1998," DOE Topical Report, Cooperative Agreement No. DE-FC22-92PC90543.

### APPENDIX - BACKGROUND ON EASTMAN CHEMICALS-FROM-COAL COMPLEX





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Figure 2: Chemicals-from-Coal Complex – **Block Flow Diagram** 



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# History of the Chemicals-from-Coal Complex

- Eastman scientists conducted a prescient planning study for chemical feedstocks. 1970
- Oil embargo: Oil prices increase (acetic anhydride produced from oil-based chemicals). 1973
- Eastman started R&D on the use of coal-based anhydride process. 1975
- First small pilot plants began operation. 1977
- Bechtel Corporation awarded contract for the design and construction of the chemicals-from-coal complex. 1978
- **Construction Complete** 1983
- Coal grinding and slurry operation Methyl Acetate plant startup March May
  - Startup of Gasifier #1 June 19
- Methanol Production started July 19 Aug 12 Oct 6
  - Startup of Gasifier #2
- First production of acetyl from coal
- Gasifiers onstream 85% of the time and acetic anhydride operated 75% of the time. Oct 83 – July 84
- July December Gasification plant on stream 97% while acetic anhydride plant on stream 95.5%. July – 2 week shutdown to install improvements necessary for full capacity. 1984
- Bechtel started the engineering and design work to double the acetic anhydride production. 1988
- Construction of the Phase II expansion completed (128% of original design; 1,200 TPD coal). 1991
- Gasifier coal feed rates reach 150% of original design; Gasifier run lengths exceed 75 days (1,350 TPD coal -> chemicals) 2000



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# Figure 5: Yearly Gasifier Production Rate



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(w/o Planned Biennial Shutdown or Power Failures) Figure 6: % Uptime



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### Figure 7: Top 10 Shutdown Causes 1983 – 2000

Rank	Shutdown Cause	% of total
<b>~</b>	Feed Injector Failure	18.7%
2	Slurry Feed Pump	15.2%
ო	Planned Switch	10.9%
4	Low Quench Water Flow	6.6%
Ŋ	Low Slurry Flow	5.8%
9	Low level in Gasifier	4.8%
7	Oxygen Leak	4.1%
∞	Relief Valve Failure	2.3%
ດ	Dip/Draft Tube	1.8%
10	<b>Distributed Control System -</b>	
	Programmable Logic	
	Controller Failure	1.8%

## Figure 8: Shutdown Causes 1999 – 2000

### 1999

# DescriptionCountPlanned switch3Planned switch3Seal water supply pump2Slag drag failure1Slag drag failure1Relief valve failure1Plugged quench ring1Lockhopper valve problems1High temp on injector jacket1Feed Injector Failure1

### 2000

Description	Count
Feed injector failure	2
Low quench flow (pump failure; hole in valve)	2
Plant wide power failure	~
Dip tube failure (coal contamination)	~
Black water exchanger fouling	~
Oxygen plant shutdown (lightning)	~
Pressure relief valve opened prematurely	~
Programmable logic controller	~

Figure 9: Average Single Gasifier Run Length (Days)



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## Hgure 10: Production Interruptions 1983 to Present



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### Figure 11

### Aerial Photograph of Eastman Chemicals-from-Coal Complex

