ALTERNATIVE FUELS FIELD TEST UNIT SUPPORT TO KINGSPORT LPMEOH™ DEMONSTRATION UNIT DECEMBER 1997 - JANUARY 1998

TOPICAL REPORT

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Abstract

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. (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™ Process Demonstration Unit was built at a site located at the Eastman chemicals-from-coal complex in Kingsport.

The Alternative Fuels Field Test Unit (AFFTU), which was designed and constructed under sponsorship of the DOE's Liquid Fuels Program (DE-FC22-95PC93052), was successfully deployed to Kingsport for the restart of the LPMEOH™ Demonstration Unit in December of 1997. The AFFTU autoclave reactor operated in parallel with the plant reactor, using a slipstream of the reactor feed gas. During 31 days onstream, the rate of catalyst deactivation in the autoclave was around the baseline deactivation rate of 1.2% per day. The concentrations of metal carbonyls and sulfur species in two process streams were monitored during the same period. These contaminants were found to be present at levels well below the process specifications (10 parts per billion by volume for each of the metal carbonyls, 60 parts per billion by volume total sulfur), with the exception of an occasional spike in carbonyl sulfide. The rapid rate of deactivation observed during the initial startup of the LPMEOH™ Demonstration Unit in April of 1997 was seen neither in the AFFTU autoclave nor in the LPMEOH™ Reactor.

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ACRONYMS AND DEFINITIONS

Air Products - Air Products and Chemicals, Inc.
AFDU - Alternative Fuels Development Unit - The “LaPorte PDU”
AFFTU - Alternative Fuels Field Trailer Unit
Balanced Gas - A syngas with a composition of hydrogen (H_2), carbon monoxide (CO), and carbon dioxide (CO_2) in stoichiometric balance for the production of methanol
Carbon Monoxide Gas - A syngas containing primarily carbon monoxide (CO); also called CO Gas
Catalyst Age (η -eta) - the ratio of the rate constant at any point in time to the rate constant for a freshly reduced catalyst (as determined in the laboratory autoclave)
Catalyst Concentration - Synonym for Slurry Concentration
Catalyst Loading - Synonym for Slurry Concentration
CSTR - continuous stirred tank reactor
DOE - United States Department of Energy
DOE-FETC - The DOE's Federal Energy Technology Center (Project Team)
DOE-HQ - The DOE's Headquarters - Coal Fuels and Industrial Systems (Project Team)
Eastman - Eastman Chemical Company
ECD - electron capture detector
FID - flame ionization detector
Fresh Feed - sum of Balanced Gas, H_2 Gas, and CO Gas
GC - gas chromatograph
Hydrogen Gas - A syngas containing an excess of hydrogen (H_2) over the stoichiometric balance for the production of methanol; also called H_2 Gas
IGCC - Integrated Gasification Combined Cycle, a type of electric power generation plant
LaPorte PDU - The DOE-owned experimental unit (PDU) located adjacent to Air Products’ industrial gas facility at LaPorte, Texas, where the LPMEOH™ process was successfully piloted
LPDME™ - Liquid Phase DME process, for the production of DME as a mixed coproduct with methanol
LPMEOH™ - Liquid Phase Methanol (the technology to be demonstrated)
MeOH - methanol
Methanol Productivity - the gram-moles of methanol produced per hour per kilogram catalyst (on an oxide basis)
ml - milliliter
MS - mass spectroscopy
Partnership - Air Products Liquid Phase Conversion Company, L.P.
PDU - Process Development Unit
PFD - Process Flow Diagram(s)
PLC - programmable logic controller
ppbv - parts per billion (volume basis)
ppmw - parts per million (weight basis)
Project - Production of Methanol/DME Using the LPMEOH™ Process at an Integrated Coal Gasification Facility
psi - Pounds per Square Inch
psia - Pounds per Square Inch (Absolute)
psig - Pounds per Square Inch (gauge)
Reactor Feed - sun of Fresh Feed and Recycle Gas
Recycle Gas - the portion of unreacted syngas effluent from the reactor “recycled” as a feed gas
rpm - revolutions per minute
sccm - standard cubic centimeters per minute
SCD - sulfur chemoluminescence detector
Slurry Concentration - percentage of weight of slurry (solid plus liquid) which is catalyst (on an oxide basis)
Sl/hr-kg - Standard Liter(s) per Hour per Kilogram of Catalyst
Syngas - Abbreviation for Synthesis Gas
Synthesis Gas - A gas containing primarily hydrogen (H_2) and carbon monoxide (CO), or mixtures of H_2 and 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)

ACRONYMS AND DEFINITIONS (cont'd)

TCD	-	thermal conductivity detector
Tie-in(s)	-	the interconnection(s) between the LPMEOH™ Process Demonstration Facility and the Eastman Facility
TPD	-	short Ton(s) per Day

Executive Summary

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. (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™ Process Demonstration Unit was designed, constructed, and is in operation at a site located at the Eastman chemicals-from-coal complex in Kingsport.

The technology being demonstrated is the product of a cooperative development effort by Air Products and DOE in a program that started in 1981. Developed to enhance electric power generation using integrated gasification combined cycle (IGCC) technology, the LPMEOH™ process is ideally suited for directly processing gases produced by modern day coal gasifiers. Originally tested at the Alternative Fuels Development Unit (AFDU), a small, DOE-owned experimental unit in LaPorte, Texas, the technology provides several improvements essential for the economic coproduction of methanol and electricity directly from gasified coal. This liquid phase process suspends fine catalyst particles in an inert liquid, forming a slurry. The slurry dissipates the heat of the chemical reaction away from the catalyst surface, protecting the catalyst and allowing the methanol synthesis reaction to proceed at higher rates.

The project involves the operation of an 80,000 gallons per day (260 short tons per day (TPD)) 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.

One of the long-term demonstration issues for the project is to determine the change in catalyst performance with time exposed to the trace poisons present in coal-derived syngas. A number of design and analytical steps were taken to characterize the presence of trace contaminants at the parts-per-billion level and to minimize their introduction to or generation within the LPMEOH™ Demonstration Unit. One of these actions was to test the syngas at the Eastman site prior to the initial operation of the LPMEOH™ Demonstration Unit. To accomplish this, a transportable laboratory, the Alternative Fuels Field Test Unit (AFFTU), was designed and constructed under sponsorship of the DOE's Liquid Fuels Program (DE-FC22-95PC93052). The AFFTU uses a continuous stirred-tank autoclave and an extensive analytical system to allow the testing of the long-term performance of methanol synthesis catalyst on the coal-derived syngas at a particular host site. Stable catalyst activity was demonstrated in the autoclave system during a 28-day test which was performed in May and June of 1996.

The AFFTU was again successfully deployed to the Eastman chemicals-from-coal complex in Kingsport for the restart of the LPMEOH™ Demonstration Unit in December of 1997. For 31 days, the AFFTU autoclave operated in parallel with the Kingsport reactor, using a slipstream of the reactor syngas feed. The concentrations of metal carbonyls and sulfur species were monitored in two process streams: the primary syngas feed to the LPMEOH™ Demonstration Unit (Balanced Gas), and the syngas feed to the LPMEOH™ Reactor.

Neither the Kingsport reactor catalyst nor the AFFTU autoclave catalyst deactivated at the high rates observed during the initial operation of the LPMEOH™ Demonstration Unit in April of 1997. The Kingsport reactor catalyst lost activity at about 1%/day, which compares favorably with the 3+%/day during the early days of the first run. However, it still deactivated more rapidly than the 4-month proof-of-concept run at the LaPorte AFDU in 1988/89, with a deactivation rate of 0.4%/day. The AFFTU autoclave catalyst deactivated at a rate of 1.1-1.3%/day. This figure may be overstated, due to the loss of catalyst to autoclave surfaces when a significant portion of the slurry oil had evaporated. An approximate calculation taking this effect into account results in an estimated activity loss of 0.6%/day, which is well below the historically observed baseline deactivation rate in laboratory autoclaves. Because the deactivation rates in the autoclaves and in the reactor are similar, no catalyst performance difference due to equipment or operating conditions in the demonstration unit relative to the AFFTU autoclave can be inferred.

The average copper crystallite size, which during the first Kingsport run had rapidly grown from 80 angstroms (Å) to 275 Å, grew at a much slower rate during this second run. After 31 days, the average crystallite sizes in catalyst samples from the AFFTU autoclave and Kingsport reactor were 149 Å and 132 Å, respectively. These are within the expected range for catalyst that has been online for several weeks.

Several species which are poisons to methanol synthesis catalyst were observed in the primary syngas feed to the LPMEOH™ Demonstration Unit (Balanced Gas) at levels well below the process specifications (10 parts per billion by volume (ppbv) for each of the metal carbonyls, 60 ppbv total sulfur). Hardly any hydrogen sulfide (H_2S) and nickel carbonyl ($Ni(CO)_4$) were detected in the Balanced Gas. The concentration of iron carbonyl ($Fe(CO)_5$) was usually less than 5 ppbv; no iron carbonyl was detected in the Kingsport reactor feed, which indicated that a carbon guard bed within the battery limits of the LPMEOH™ Demonstration Unit effectively removed iron carbonyl. Carbonyl sulfide (COS) was detected both in the Balanced Gas upstream of the carbon guard bed and in the Kingsport reactor feed. In the Balanced Gas, the COS concentration was usually around 20 ppbv, with occasional upswings and one spike to about 300 ppbv. In the Kingsport reactor feed, the typical concentration was about 4 ppbv, again with occasional upswings, and a spike to almost 40 ppbv. Sulfur loadings on catalyst samples from the AFFTU autoclave and Kingsport reactor remained low, at levels unlikely to affect catalyst performance.

The AFFTU provides a state-of-the-art environment for determining the concentration of trace contaminants in coal-derived syngas. Future use of the AFFTU in determining the effects of trace contaminants on catalyst performance will be limited to those circumstances where the deactivation rate in the autoclave is significantly lower than the results calculated for the slurry reactor.

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. (the Partnership). Air Products and Chemicals, Inc. (Air Products) and Eastman Chemical Company (Eastman) formed the Partnership to execute the Demonstration Project. A demonstration unit producing 80,000 gallons per day (260 short tons per day (TPD)) of methanol was designed, constructed, and is operating at a site located at the Eastman complex in Kingsport. The Partnership will own and operate the facility for the four-year demonstration period.

This project is sponsored under the DOE's Clean Coal Technology Program, and its primary objective is to "demonstrate the production of methanol using the LPMEOH™ Process in conjunction with an integrated coal gasification facility." The project will also demonstrate the suitability of the methanol produced for use as a chemical feedstock or as a low-sulfur dioxide, low-nitrogen oxides alternative fuel in stationary and transportation applications. The project may also demonstrate the production of dimethyl ether (DME) as a mixed coproduct with methanol, if laboratory- and pilot-scale research and market verification studies show promising results. If implemented, the DME would be produced during the last six months of the four-year demonstration period.

The LPMEOH™ process is the product of a cooperative development effort by Air Products and the DOE in a program that started in 1981. It was successfully piloted at a 10-TPD rate in the DOE-owned experimental unit at Air Products' LaPorte, Texas, site. This demonstration project is the culmination of that extensive cooperative development effort.

B. Project Description

The demonstration unit, which occupies an area of 0.6 acre, is integrated into the existing 4,000-acre Eastman complex located in Kingsport, Tennessee. The Eastman complex employs approximately 12,000 people. In 1983, Eastman constructed a coal gasification facility utilizing Texaco technology. The synthesis gas (syngas) generated by this gasification facility is used to produce carbon monoxide and methanol. Both of these products are used to produce methyl acetate and ultimately cellulose acetate and acetic acid. The availability of this highly reliable coal gasification facility was the major factor in selecting this location for the LPMEOH™ Process Demonstration. Three different feed gas streams (hydrogen gas or H_2 Gas, carbon monoxide gas or CO Gas, and the primary syngas feed known as Balanced Gas) are diverted from existing operations to the LPMEOH™ Demonstration Unit, thus providing the range of coal-derived syngas ratios (hydrogen to carbon monoxide) needed to meet the technical objectives of the demonstration project.

For descriptive purposes and for design and construction scheduling, the project has been divided into four major process areas with their associated equipment:

- *Reaction Area* - Syngas preparation and methanol synthesis reaction equipment.
- *Purification Area* - Product separation and purification equipment.
- *Catalyst Preparation Area* - Catalyst and slurry preparation and disposal equipment.

- *Storage/Utility Area* - Methanol product, slurry, and oil storage equipment.

The physical appearance of this facility closely resembles the adjacent Eastman process plants, including process equipment in steel structures.

- *Reaction Area*

The reaction area includes feed gas compressors, catalyst guard beds, the reactor, a steam drum, separators, heat exchangers, and pumps. The equipment is supported by a matrix of structural steel. The most salient feature is the reactor, since with supports, it is approximately 84-feet tall.

- *Purification Area*

The purification area features two distillation columns with supports; one is approximately 82-feet tall, and the other 97-feet tall. These vessels resemble the columns of the surrounding process areas. In addition to the columns, this area includes the associated reboilers, condensers, air coolers, separators, and pumps.

- *Catalyst Preparation Area*

The catalyst preparation area consists of a building with a roof and partial walls, in which the catalyst preparation vessels, slurry handling equipment, and spent slurry disposal equipment are housed. In addition, a hot oil utility system is included in the area.

- *Storage/Utility Area*

The storage/utility area includes two diked lot-tanks for methanol, two tanks for oil storage, a slurry holdup tank, a trailer loading/unloading area, and an underground oil/water separator. A vent stack for safety relief devices is located in this area.

C. Process Description

The LPMEOH™ Demonstration Unit is integrated with Eastman's coal gasification facility. A simplified process flow diagram is included in Appendix A. Syngas is introduced into the slurry reactor, which contains solid particles of catalyst suspended in liquid mineral oil. The syngas dissolves through the mineral oil, contacts the catalyst, and reacts to form methanol. The heat of reaction is absorbed by the slurry and is removed from the slurry by steam coils. The methanol vapor leaves the reactor, is condensed to a liquid, sent to the distillation columns for removal of higher alcohols, water, and other impurities, and is then stored in the day tanks for sampling before being sent to Eastman's methanol storage. Most of the unreacted syngas is recycled back to the reactor with the syngas recycle compressor, improving cycle efficiency. The methanol is used for downstream feedstocks and in off-site, product-use testing to determine its suitability as a transportation fuel and as a fuel for stationary applications in the power industry.

D. Results and Discussion

In April of 1997, the LPMEOH™ Demonstration Unit at Kingsport, TN was brought onstream. Following the start-up, the catalyst activity dropped precipitously in the first month, to about 50% of its original activity, then continued to decline at a somewhat lower rate in the following months. Throughout the run, the deactivation rate was much higher than previously observed at the LaPorte AFDU or in laboratory autoclaves. Although several hypotheses have been proposed to explain the fast deactivation, not enough evidence has been found to convincingly establish any one cause. In November of 1997, the first run of the LPMEOH™ Demonstration Unit was terminated. The reactor was charged with fresh catalyst slurry and restarted in December of 1997. This presented an opportunity to more closely monitor the process during and after the restart. To capitalize on this opportunity, the Alternative Fuels Field Test Unit (AFFTU) was again deployed to Kingsport in November of 1997. The AFFTU was designed and constructed under sponsorship of the DOE's Liquid Fuels Program (DE-FC22-95PC93052). The AFFTU had originally been used to monitor the coal-derived syngas composition at Kingsport prior to startup of the LPMEOH™ Demonstration Unit, and to demonstrate that methanol synthesis catalyst exhibited an acceptable deactivation rate in the autoclave while operating on coal-derived syngas[1].

In case of another sharp decline in catalyst activity, one of the primary questions would be whether the deactivation was due to the quality of the syngas feed or due to some other, equipment-related, aspect of the LPMEOH™ Process. To answer this question, the AFFTU autoclave was operated in parallel with the LPMEOH™ Reactor, using a small slipstream of the Kingsport reactor feed gas as the AFFTU autoclave feed. If the AFFTU autoclave performance paralleled the Kingsport reactor performance, this would suggest that the syngas is responsible for the deactivation. If, on the other hand, the reactor catalyst would underperform relative to the autoclave catalyst, this would be evidence for a different process problem.

In addition to the autoclave diagnostic test, the AFFTU was also set up to monitor the syngas at two other locations, in order to determine the concentrations of several species which are poisons to methanol synthesis catalyst. The Kingsport process gas chromatograph (GC) for iron carbonyl ($Fe(CO)_5$) and nickel carbonyl ($Ni(CO)_4$) was not yet in service at the time of the restart. Similarly, instrumentation to measure sulfur levels (hydrogen sulfide (H_2S) and carbonyl sulfide (COS)) in the syngas had not yet been installed. Instrumentation and methods to analyze these components exist in the AFFTU, which was secondarily used as an extension of analytical capabilities for the duration of the deployment.

The following sections provide a chronological account of events during the restart and AFFTU deployment, followed by a summary and analysis of the results obtained during the run.

D.1 AFFTU Deployment and Restart of LPMEOH™ Demonstration Unit - December 1997

D.1.1 Equipment and syngas feeds

Details of the AFFTU equipment are given by a separate topical report[1]. Since its original deployment to Kingsport, the AFFTU had returned to the Air Products' Iron Run research facility in Allentown, PA, where it served as a laboratory for ongoing LPMEOH™ and Liquid Phase Dimethyl Ether (LPDME™) research. Several minor modifications to the equipment had been made during that time; several more were made in preparation for this second deployment. The modifications relevant to the field test are summarized below. The flow diagrams for the AFFTU as used during this test are included as Appendix B.

- *Primary Feed System*

The primary feed system was used to process syngas from the feed to the LPMEOH™ Reactor, which will be designated *loop feed* and *Kingsport reactor feed* in this report. The loop feed is supplied from the process downstream of the point where the primary syngas feed stream (Balanced Gas) and recycle gas mix, and also downstream of the feed-to-effluent heat exchanger. It has the same composition and properties as the gas fed into the LPMEOH™ Reactor. Therefore, it was used as the feed gas to the AFFTU autoclave.

The recycle gas contains small concentrations of methanol and water, corresponding to the vapor pressures of these species at the temperature of a water-cooled heat exchanger within the LPMEOH™ Process. After mixing with the Balanced Gas stream from Eastman, the dew point of the loop feed gas is approximately 32°C (at 785 psi). At the sample point, the loop feed gas is well above its dew point (169°C), but its temperature rapidly drops in the 100 ft of ¼" tubing leading to the AFFTU. When it reaches the AFFTU, the gas temperature has dropped to close to the outside temperature, which ranged between approximately -4°C and 17°C over the duration of the run. This means that at most times liquids condensed in the sample line.

The AFFTU is not equipped to handle a wet feed; in particular, the mass flow controllers cannot perform properly in the presence of liquid droplets. Therefore, a knockout system was installed in the primary feed line, just outside of the AFFTU. The system consisted of a 1,000 milliliter (ml) pressure vessel as the knockout pot, connected to a 300-ml vessel to allow safe draining of the knockout pot. Although piping and valves were installed to allow for bypassing the knockout system, the system was in service for the entire length of the run.

Once inside the heated trailer, the primary feed rapidly attained a temperature above that of the knockout pot outside, which ensured that the feed gas was free of liquid droplets. A thermocouple installed in the primary feed line just upstream of the mass flow controller for the feed to the AFFTU autoclave indicated temperatures just slightly below the trailer temperature (17-19°C) at all times.

After entering the AFFTU, the primary feed was split into two streams, each having a separate flow controller. One stream (about 2,500 standard cubic centimeters per minute (sccm)) was directed to the AFFTU autoclave reactor. To ensure that plant pressure fluctuations did not interfere with consistent operation of the autoclave, the pressure was boosted using one of the AFFTU compressors. The other portion (about 5,000 sccm) was continuously vented, to reduce the residence time of the feed gas in the sample line and to ensure that the tubing surfaces quickly attained adsorption equilibrium with all components of the feed gas. Samples could be taken from this second stream and sent to the analytical system (described below).

The wet test meter used for measuring the exit flow rate through the reactor (and, during reactor bypass, the inlet flowrate) was recalibrated directly after the field test. At that time, the meter underreported flow by 0.5%. This is so small a deviation that the flows were not recalculated to reflect this offset.

- *Secondary Feed System*

To best measure the concentrations of poison species and their fate in the guard bed and bubble column reactor, it was useful to analyze the fresh feed to the plant as well as the loop feed. For this purpose, a sample line was drawn into the AFFTU secondary feed system from the Balanced Gas stream; this is downstream of Eastman's sulfur/arsenic guard bed but upstream of the carbonyl guard bed within the LPMEOH™ Demonstration Unit. The syngas at this point is at ambient temperature and contains only minute quantities of condensible species. It was therefore not necessary to install a knockout system in the secondary feed system.

The secondary feed was continuously vented through a mass flow controller, at approximately 4,000 sccm. Gas samples were sent to the analytical system.

- *Analytical System*

The analytical equipment was the same as described for the first AFFTU field test[1]. A gas chromatograph (GC) to measure water content had been added for laboratory experiments since the first test, but it could not be safely transported in the trailer. The bulk GC measured the gas composition for components such as hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), nitrogen (N_2), and methanol (CH_3OH). The poisons GC measured concentrations of certain compounds which are known to be or suspected of being poisons to methanol synthesis catalysts; these include nickel carbonyl ($Ni(CO)_4$), iron carbonyl ($Fe(CO)_5$), hydrogen sulfide (H_2S), and carbonyl sulfide (COS).

- *Vent System*

To avoid the backup of condensed methanol from the autoclave product stream in the vent lines, a vent knockout system was installed outside of the AFFTU.

D.1.2 AFFTU Setup and Startup

The AFFTU was prepared for travel and shipped to Kingsport in mid-November of 1997. Upon arrival, it was thoroughly leak-tested, and the primary and secondary feed lines were connected. The gas chromatographs were all recalibrated, and the ambient CO and vent alarms were calibrated and activated. Aside from a few leaks, all equipment appeared to have survived the travel in good condition.

The autoclave was loaded with 20.02 grams of methanol synthesis catalyst and 120.73 grams of Drakeol-10 mineral oil. After a final leak check, the catalyst was reduced with dilute H_2 in nitrogen (N_2), following the standard lab reduction procedure. The reduction proceeded routinely.

Due to problems within the LPMEOH™ Demonstration Unit, the restart was delayed for 3 weeks. During this time, the AFFTU was left unattended, at room temperature and low pressure (60 psig), with a slow nitrogen purge and a reduced stirrer speed. Upon returning to the AFFTU in mid-December, the unit was running as it had been left behind. To ensure that the catalyst was fully reduced before startup, a shortened version of the reduction procedure was followed; no significant amount of hydrogen was taken up during this procedure.

On 20 December 1997, shortly after midnight, the demonstration unit was successfully restarted. At that time, the AFFTU autoclave was also started up on primary feed, at a space velocity of about 6,000 standard liters per hour per kilogram catalyst oxide (Sl/hr-kg).

D.1.3 Routine Operation

After the demonstration unit came up to full operating rates, a few days after startup, the space velocity in the AFFTU autoclave was increased to about 8,500 Sl/hr-kg, and held there for the remainder of the run in the AFFTU. The other operating conditions were the standard conditions used in laboratory experiments — 250°C, 750 psig, stirring at 1,200 revolutions per minute (rpm). The heat tracing on reactor effluent lines was maintained at slightly higher than normal temperatures, because of the high methanol concentration in the outlet when operating on hydrogen-rich feed gas.

During the run, the AFFTU was usually operated by one or two people; for one three-day stretch, it ran unattended, without any complications. Routine operating procedures included draining the feed and reactor vent knockout pots, changing gas cylinders feeding the GCs, recording operating conditions and keeping the GCs and associated computers running.

During normal operation, two sets per day of reactor inlet and outlet measurements were taken by bulk GC. This allowed two mass balances per day to be completed, and two instantaneous methanol synthesis rate constants to be calculated. The fresh feed was also sampled by the bulk GC at regular intervals.

At 3 days onstream, the tubing carrying reactor effluent sample to the bulk GC plugged several times. After the replacement of an inline filter did not solve the problem, the entire line was disconnected and flushed with solvent. About 4 drops of oil were recovered from the flush, indicating that a significant amount of oil had accumulated in this length of tubing. After the flush no further blockage problems were encountered.

At 18 days (417 hours) onstream, after an upset in the carbonyl sulfide level in the feed had been observed, the reactor was taken offstream, for the purpose of taking a sample. About 10 ml of slurry was extracted from the reactor, and 15.65 gram Drakeol-10 was added to partially make up for the liquid lost with the sample as well as evaporative losses. After the sample was taken, and the reactor was purged and leak-checked, the system was brought back on-line. The downtime was about 7 hours.

After a few weeks onstream, it was apparent that the calculated methanol synthesis rate constant exhibited fluctuations, most likely due to fluctuations in the feed syngas composition. To allow the calculation of the deactivation rate by a method independent of these feed fluctuations, the reactor was subjected to more standardized feed conditions at three times during the run. At these instances, it was fed a synthetic syngas blend from a cylinder (nominally 21.5 vol% CO, 4.5 vol% CO_2, 5 vol% N_2, and 69 vol% H_2), at approximately 6,000 Sl/hr-kg space velocity. These conditions were maintained for the duration of several hours, long enough to establish steady-state conditions in the reactor and feed system. The standard data points were taken at 18, 26 and 31 days onstream. The results on standard gas are not included in the graphs and calculations.

Throughout the run, the poisons GC measured concentrations of iron and nickel carbonyl, hydrogen sulfide and carbonyl sulfide, in both the fresh feed and the loop feed. Another class of suspect poisons, arsenic compounds, cannot be detected by GC at low concentrations. Instead, several gas samples were taken by adsorption onto activated carbon, using a sampling station in the demonstration unit. Samples were taken at prescribed flowrates, for various durations. Besides the carbon tubes that have historically been used for these measurements, some thermal desorption tubes were also loaded with gas sample, for analysis by GC/Mass Spectroscopy (MS).

At 31 days (725 hours) onstream, sufficient data had been collected, and the AFFTU was taken offstream to be transported back to the Air Products' Iron Run laboratory. After the autoclave was opened, 67.8 grams of slurry was recovered as liquid from the bottom of the reactor. In addition, 3.8 grams of a thicker, pasty material was recovered from the reactor walls and internals above the liquid level.

D.2 Gas Chromatograph Calibration

All GC/detector combinations were recalibrated upon arrival in Kingsport. This ensured that any shifts in chromatographic conditions or detector response factors due to the disassembly, transport and reassembly of the analytical equipment would not affect the quality of the analytical results. Standard gas mixes having similar compositions as the actual gas to be analyzed were used when possible.

D.2.1 Bulk Gas GC/Thermal Conductivity Detector (TCD)

The TCD method was calibrated using a cylinder containing a synthetic gas blended by Air Products' Specialty Gases Department. The blend, intended to simulate the composition of the reactor feed in the demonstration unit (*i.e.* the primary feed gas), was analyzed at the blending facility to have the following composition: 68.01 vol% H_2 , 22.20 vol% CO, 4.72 vol% CO_2, and 5.07 vol% N_2. After a small modification to the GC method in the first half of the run, the GC/TCD method was recalibrated using the same standard.

When standard data points were taken subsequently, using the same cylinder for feed gas as had been used for calibration, the inlet gas composition did not match the nominal cylinder composition. After the standard points had been taken, the cylinder was again connected to the calibration port, and the calibration was repeated. The reported concentrations were indeed different than during the original calibration, suggesting that the GC sensitivity had shifted somewhat. It is impossible to determine when the shift occurred; therefore, all results are based on the original calibration. In reality, the hydrogen concentrations may have been up to 1.7% lower than reported, CO_2 levels up to 1% higher, and CO and N_2 levels up to 4% higher (percentages given as fraction of component concentration, not of total concentration).

D.2.2 Bulk Gas GC/Flame Ionization Detector (FID)

The FID method was calibrated using a cylinder containing 5.08 vol% methanol in argon. The dew point temperature for this composition at 20 psig is rather close to ambient temperature. Since the standard cylinder had been transported through winter weather, it is likely that some liquid condensed inside the cylinder. This would be expected to evaporate once ambient temperatures had once again been attained. The calibration was not done until several days after heat was restored to the AFFTU. The methanol concentration in the standard is by necessity much smaller than the concentration in the reactor outlet. The calibration at the lower level assumes that the GC/FID maintains a linear response up to the reactor outlet concentrations, up to 14 vol%.

D.2.3 Poisons GC/Sulfur Chemoluminescence Detector (SCD)

The SCD method was calibrated using a cylinder from Scott Gas containing approximately 250 ppbv each of H_2S and COS in nitrogen. The concentrations on Scott's certificate of analysis are 261 and 260 ppbv, respectively. The SCD should have essentially the same response factor for H_2S and COS. However, analysis of the standard gas resulted in a chromatogram having two very different-sized peaks, the H_2S peak being the smaller of the two.

Upon return to Allentown, the calibration gas cylinder was reanalyzed by Air Products' Analytical Group. The micro-analytical lab reported an H_2S concentration of 253 ppbv. The infrared lab reported a COS concentration of approximately 300 ppbv. Given the larger margin of error of the latter measurement, these results support Scott's original analysis of the standard mixture.

The only explanation for the lower H_2S peak is that some of the H_2S is lost, perhaps to adsorption onto tubing walls or in the GC injection system, before it can be analyzed. Without additional standards, it is impossible to express this effect quantitatively. Before a further experiment involving H_2S can be carried out, this problem must be understood and addressed. For the purposes of this field test, H_2S was assigned the same calibration factor as COS. If the calibration factor was calculated based on the smaller area of the H_2S peak for the standard injection, higher levels of H_2S would have been reported during the field test. However, even then the level of COS would always have exceeded that of H_2S.

D.2.4 Poisons GC/Electron Capture Detector (ECD)

Two metal carbonyl standard mixtures were taken to Kingsport. The first, Standard A with 2,600 ppbv $Ni(CO)_4$ and 800 ppbv $Fe(CO)_5$, was ultimately intended for use as a standard at the plant analytical station; the second, Standard B with 559 ppbv $Ni(CO)_4$ and 241 ppbv $Fe(CO)_5$, was intended for use in the AFFTU. It was deemed to be a more appropriate standard for the purposes of this run, since its lower concentration is more likely to be in the linear range of the instrument, even though the concentration is still much higher than likely process concentrations.

Both standards were used in an attempt to calibrate the GC/ECD. It was found that the response factor calculated from calibrating on Standard A was considerably higher than when calibrating using Standard B. Most detector responses level off as concentrations increase, so this result was unexpected. Standard A was an older standard that had recently been reanalyzed. Standard B was a newly mixed standard, analyzed after the concentrations in the cylinder were thought to be uniform. Since it is possible that Standard B still lost some of its metal carbonyls to adsorption on cylinder walls or other processes, the calibration factors obtained using Standard A were used during the field test.

Upon return to Allentown, Standard B was reanalyzed by Air Products' Analytical Group. At the time of second analysis (19 February 1998), lower concentrations were found in the cylinder: 421 ppbv $Ni(CO)_4$ and 124 ppbv $Fe(CO)_5$. Apparently, some of the metal carbonyls had been lost, *e.g.* to cylinder walls, between the two analyses of Standard B. In the case of $Fe(CO)_5$, the calibration factors on Standard A and Standard B (after reanalysis) were fairly close. The same did not hold for $Ni(CO)_4$; however, since $Ni(CO)_4$ was not usually seen during the field test, its calibration is of minor importance in this context.

D.3 Catalyst Activity

D.3.1 Mass Balance Calculations

Twice daily during most of the run, the concentrations of the AFFTU autoclave inlet and outlet streams were measured by GC. To best deal with fluctuations in the feed gas composition, the sequence of GC injections was typically two inlets, followed by three outlets, followed by two inlets. The mass balance was based on the average of all four inlet injections, and the average of the three outlet injections. Trends of GC data are included in Appendix C, Figures C-2 through C-5.

When examining the GC/TCD chromatograms, it was noticed that a peak appeared that did not correspond to any calibrated species. From further experiments and a study of the GC valve switching methodology, it was found that this peak had two separate causes, in different instances. The first only appeared when the concentration of nitrogen in the sample was much higher than the ordinary amount (about 5%). This condition was encountered when analyzing the reactor exit gas during reduction, and does not pose any problem, since in this case it is not important that nitrogen be analyzed accurately. The second cause for the peak was the presence of a different species in the gas sample. According to data collected during original GC commissioning, either oxygen or argon, which are likely to be present in the syngas, could elute in the vicinity of the unknown peak. Since the area of the unknown peak was higher in the reactor exit chromatograms than in the inlet chromatograms, argon was deemed to be the more likely species; oxygen would likely be converted in the reactor, either reacting with the copper on the catalyst or being reduced by hydrogen or carbon monoxide on the catalyst surface.

The response factors for most of the constituents of syngas were similar on the GC/TCD. The same response factor was chosen for the “argon” constituent, and included in the calibration method. In the mass balances, the concentration of “argon” is lumped with nitrogen. Using this procedure, the internal GC mass balances (the total of the analyzed concentrations of *either* the inlet *or* the outlet samples) were usually accurate to within one or two percent, with a few exceptions.

Two other process variables are required to conduct an external mass balance around the autoclave: the inlet and outlet flowrates. The outlet flowrate is periodically measured and recorded by the process programmable logic controller (PLC). Its measurement is about as accurate as the wet test meter used for the measurement, generally within 1% error. The inlet flowrate is set by the control box for the Brooks mass flow controller, and should be constant once set. However, considerable fluctuations in the exit flowrate, shown in Figure 1, could only be explained by swings in the inlet flowrate. Unfortunately, the inlet flowrate is not continuously measured. The procedure for its measurement requires that at least two operators are present, for safety reasons. Therefore it was only measured sporadically (red points on Figure 1). According to Brooks, the sensitivity of the mass flow controllers to temperature and pressure is minor (0.03%/psi; 0.015%/°F; both as a fraction of full-scale flow). A plot of the trailer temperature *versus* time can be found in Appendix C, Figure C-1. The sensitivity to gas composition could be higher (due to the varying heat capacities of the constituent gases), but still could not explain the rather large fluctuations (up to 20%).

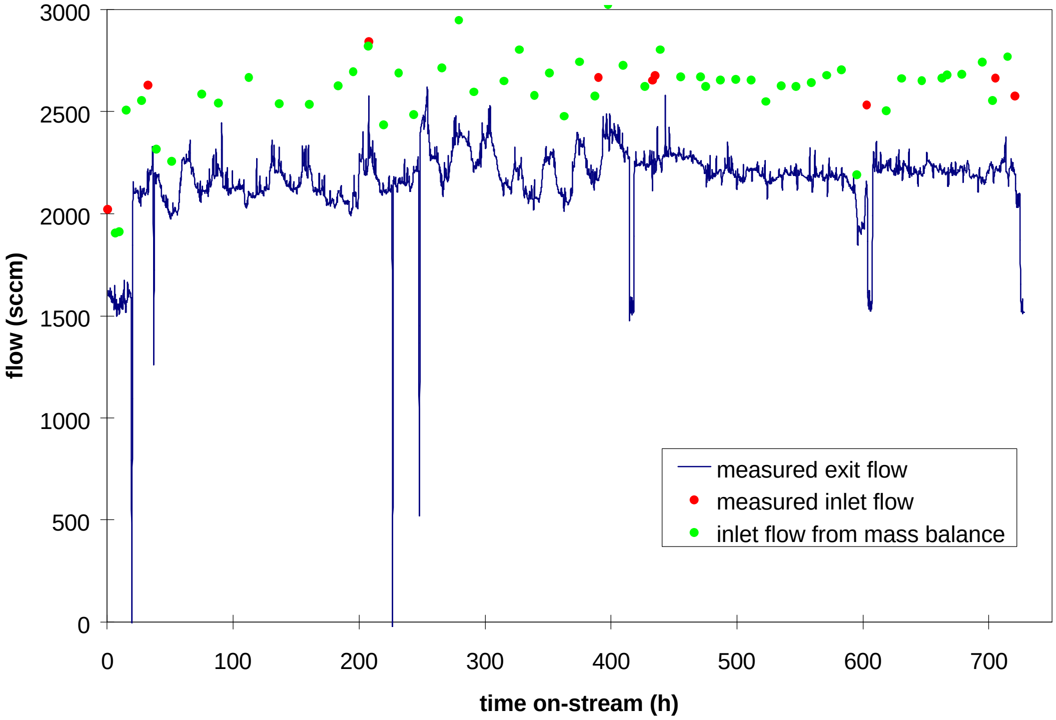

Figure 1. Measured and calculated flowrates in the autoclave system during the field test.

The fluctuations in the inlet flow, without a means to continuously monitor them, lead to deviations in the elemental mass balance around the reactor. If the exit flowrate measurement as well as the GC composition measurements are deemed to be relatively accurate, the inlet flow can be back-calculated to close the mass balance on any one element. Nitrogen is a good choice, since it appears only as an inert. The inlet flowrates calculated by this procedure are indicated by green points in Figure 1.

It is clear from Figure 1 that the fluctuations in exit flowrate were very pronounced up to about 420 hours on-stream. At that time, the catalyst sample was collected, and subsequently the exit flow trended much more smoothly. Possibly, a problem with the mass flow controller was cleared when the system depressurized for sampling.

D.3.2 Methanol Catalyst Rate Constant

From the data measured for each mass balance period, the methanol productivity may be calculated. For this calculation, the amount of catalyst in the AFFTU autoclave must be known. Here, the original amount of catalyst was used for calculations before the slurry sample was taken. For calculations after the sampling, the amount of catalyst removed in the slurry sample was subtracted. This amount was calculated assuming that the slurry in the AFFTU autoclave was uniform, with a volumetric composition identical to the initial composition, and found to be about 1.5 grams of catalyst.

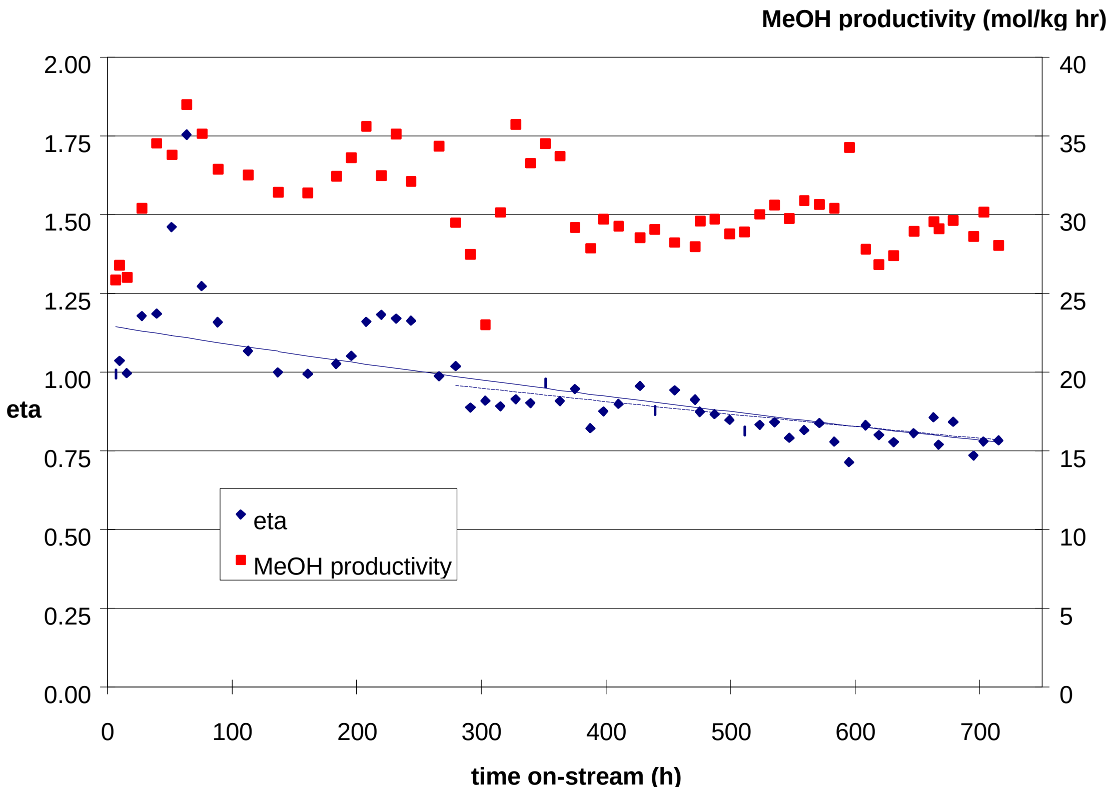

Figure 2. Methanol productivity and catalyst age η as a function of time on-stream during the field test. The solid curve represents an exponential fit to the entire range of data; the dashed curve is a fit to only the data from 270 h onward.

Using an Air Products proprietary kinetic model, the methanol synthesis rate constant is calculated from the methanol productivity and the component fugacities. The "age" of the methanol synthesis catalyst can then be expressed in terms of a dimensionless variable "eta" (η), which is defined as the ratio of the rate constant at any time to the rate constant for freshly reduced catalyst (as determined in the laboratory autoclave). Figure 2 shows the trends of methanol productivity and η over the length of the run. The cause for the unsteady behavior at the beginning of the run is unclear, but probably related to the plugging of the GC sample line. After the line was cleaned out, the calculated rate constant stabilized somewhat. Also, in the beginning of the run the gasifier exhibited several swings in the composition of Balanced Gas which strongly affected the reactor feed composition, and around 11 days on stream Eastman switched to a different gasifier to produce the fresh syngas, which may also have affected the reactor operation.

Due to imperfections in the engineering rate model, rates are not predicted correctly over the entire range of syngas compositions. Conversely, this means that the back-calculated rate constant varies with gas composition. Since the rate calculations are based on a continuous stirred tank reactor (CSTR) model, it is the exit gas composition that is used in these calculations. This means that both the incoming feed composition and the space velocity at which the reactor is run may affect the calculated rate constant.

The feed gas composition varied considerably over the length of the run. For instance, the hydrogen concentration varied between 59% and 82%. This explains some of the fluctuations in the calculated rate constant. As noted previously, the observed fluctuations in the composition of Balanced Gas smoothed considerably after about 420 hours. At about the same time, the calculated rate constant appeared to start following a steadier pattern. With the exception of one spike caused by a gasifier upset, the feed gas composition was also fairly steady over that time span.

Because of the unsteady behavior in the beginning of the run, it is impossible to establish the initial activity of the catalyst in the AFFTU autocalve. This complicates the determination of the catalyst deactivation rate that is obtained by fitting the activity data. The exponential decay curve fit to all of the data, with the exception of the two anomalously high points around 70 hours, can be expressed as:

$$\eta = 1.13e^{-1.3t} , 0 \leq t \leq 30 \text{ days} \tag{1}$$

If only the data from 260 hours onward, after the strongest fluctuations had passed, is used, the fit is:

$$\eta = 1.07e^{-1.1t} , 11 \leq t \leq 30 \text{ days} \tag{2}$$

So, depending on the span of data used, the deactivation rate in the AFFTU autoclave varied between 1.1 and 1.3%/day. In typical laboratory autoclave runs using clean gas, a deactivation rate of about 1.2%/day is observed. This is, for comparison purposes, the *baseline deactivation rate*, which will be discussed below. The deactivation rate calculated from the field test data is near this baseline rate. If significant poisoning had taken place, the expected deactivation rate would have been higher.

During the same time as the test in the AFFTU, the reactor catalyst deactivated at about 1.0%/day. The reactor was being operated at 230°C, which is significantly lower than the 250°C maintained over almost the entire length of the initial operation of the demonstration unit from April to November of 1997. The observed deactivation rate is much lower than this first campaign, although it is still higher than the deactivation rate of 0.4%/day from the LaPorte AFDU, which has been used in design calculations. The deactivation rates in the demonstration unit and in the AFFTU autoclave were similar over the length of the run, so that no difference in operation of the slurry reactor *versus* autoclave operation can be inferred.

Several mechanisms have been suggested to explain the loss of methanol synthesis activity with time in a liquid-phase methanol reactor. These mechanisms may be divided into three categories:

- Mechanical causes. The loss of activity is explained by the mechanical degradation and/or loss of catalyst in the process. The mobility of catalyst particles in the liquid-phase reactor is an important difference relative to gas-phase methanol processes. The particle motion can result in attrition, entrainment, and adherence to reactor surfaces. When these processes lead to loss of active catalyst from the slurry, this manifests itself as an apparent loss of catalyst activity, provided that the loss of catalyst is not accounted for in the calculations.

- Physical causes. The loss of activity is explained by the loss of active catalyst surface area by the process of sintering. Sintering is usually thought of as a thermally controlled process, but may be aided by the presence of a conducive external chemical environment. Trace contaminants may also promote sintering.

- Chemical causes. The loss of activity is attributed to the interaction of chemical species with the active catalyst surface. The interaction can be specific, with poison species binding strongly to the active sites on the catalyst, or less specific, *e.g.* when a coke layer blocks most of the surface, including the active sites. The deleterious species may be derived from the gas feed, or from chemical conversion (*e.g.* thermal cracking) of the mineral oil.

It is possible that the relative importance of these causes of deactivation are different in a laboratory autoclave than in a slurry reactor. Evidence for this exists in the fact that the *baseline deactivation rate* historically observed in each of the autoclaves operated at Air Products' Iron Run laboratories (about 1.2%/day) exceeds the deactivation rate determined from a trial at the La Porte AFDU (0.4%/day). The mechanism for the baseline deactivation is still being investigated; it is worth noting that in several isolated experiments, deactivation rates well below the baseline deactivation rate have been observed in the autoclaves.

Various differences exist between laboratory autoclaves and larger-scale facilities. The different means of agitation (stirring and gas sparging, respectively) can lead to different local and global levels of mechanical friction in the reactors. In addition, laboratory autoclaves are usually operated with a lower catalyst loading than full-scale reactors. Due to the higher surface-to-volume ratio of a small reactor, accumulation of catalyst on reactor surfaces is a more likely cause of activity loss in an autoclave. Also, the leaching of low levels of catalyst poisons such as iron and nickel from the reactor walls and internals is relatively more important in small reactors.

The higher baseline deactivation rate of the autoclaves relative to the LaPorte AFDU makes it impossible to discern conditions and catalysts at which the reaction system exhibits excellent stability (*e.g.*, 0.2-0.4%/day activity loss) from those at which the stability is on the high end of the acceptable range (0.4-0.6%/day). To discern between those ranges of deactivation rates, comparisons must be made between runs at the larger scale (La Porte AFDU or Kingsport). More severe deactivation, exceeding 1.2%/day, could be discerned even by the laboratory autoclaves.

At the conclusion of the run, the contents of the AFFTU autoclave were examined and collected. As previously stated, about 68 grams of slurry was recovered, along with 3.8 grams of a thicker paste from above the slurry level. During sample-taking, about 10 ml of slurry was taken from the reactor, and 15.65 grams oil was added to make up for oil losses. By simple mass balance, about 58% of the net oil input to the reactor was lost over the length of the run. This means that during most of the run the slurry was significantly more concentrated than the initial catalyst loading. The assumption that the composition of the slurry sample was representative of the overall initial slurry composition is therefore suspect; if loss of oil occurred linearly over time, and retaining the assumption that the slurry concentration was uniform, the amount of catalyst taken from the AFFTU autoclave with the sample would have been 2.4 grams rather than 1.5 grams.

While the nature of the liquid flow patterns inside the AFFTU autoclave during operation is unknown, it appears that a large fraction of the paste recovered from surfaces of the autoclave was not in the agitated slurry. Outside of the slurry, catalyst productivity would have been reduced to very low levels, due to the limited mass transfer of reactants and products to and from the catalyst surface. The caking of catalyst paste was first observed during sample-taking (18 days on-stream), indicating that this was an ongoing process throughout the run.

Making the assumption that the paste does not contribute to the reaction at all, it is possible to attribute some of the apparent activity loss observed during the test to the physical loss of catalyst from the slurry. The paste is assumed to consist of 90 wt% catalyst. Further assumptions are that the initial value of η for the catalyst is 1.13 (from Equation (1) above), and the apparent value of η at the conclusion of the experiment is 0.76 (corresponding to a 1.3%/day deactivation rate). While the activity calculations are performed assuming 18.5 grams active catalyst in the reactor, the loss of 3.4 grams from the slurry would mean only 15.1 grams was contributing to the reaction. The intrinsic value of η would therefore be 0.93, which corresponds to a intrinsic decay rate of 0.62%/day. This is significantly below the accepted baseline deactivation rate. This compares with the deactivation rate in the LPMEOH™ Demonstration Unit over the same time (1.0%/day), and it is also slightly below the deactivation rate observed during the first AFFTU Test at Kingsport[1], when the catalyst deactivated at 0.9%/day.

D.4 Catalyst Analyses

D.4.1 Crystallite Size

The average sizes of the copper and zinc oxide crystallites for several catalyst samples were measured by x-ray diffraction. From past experience, this measurement technique has been more dependable/reproducible for copper than for zinc oxide. Table 1 summarizes the average crystallite sizes measured in the two catalyst samples from the AFFTU autoclave, as well as in several samples taken from the Kingsport reactor during the same time period.

Table 1. Average crystallite sizes in catalyst samples

AFFTU autoclave samples			**Kingsport reactor samples**		
Days on-stream	Cu (Å)	ZnO (Å)	Days on-stream	Cu (Å)	ZnO (Å)
18	140.4	74.3	0	95.3	142.3
31	149.1	88.7	1	100.0	123.8
			4	130.9	64.0
			10	126.8	73.3
			37	132.1	98.3

The copper crystallite size growth evident from both sets of samples Table 1 is in line with observations of samples from other experiments in the laboratory. The growth is certainly much less pronounced than during the initial operation of the LPMEOH™ Demonstration Unit in 1997, when the copper crystallites grew to 274 Å within 26 days. Apparently, the cause of the copper crystallite size growth during the first run was not present during the second run.

D.4.2 Poisons Analysis

- *Hydrogen Sulfide and Carbonyl Sulfide*

The GC/SCD monitored both syngas feeds (Balanced Gas and loop feed) throughout the AFFTU run. The only sulfur-containing components observed in these streams were hydrogen sulfide and carbonyl sulfide. From previous experience, including the first AFFTU field test, it was known that sulfur compounds, especially H_2S, have a tendency to be underreported in the analysis due to adsorption onto tubing and other surfaces in the sample system. The adsorption is apparently a reversible process, which reaches an equilibrium at any given gas-phase concentration. At equilibrium, the lines are saturated, and no further sulfide is lost. To minimize the loss of sulfur during this test, the sample lines for both feeds were continuously flushed through, the excess amount being vented. It was assumed that the lines were rapidly saturated by this process.

As discussed in Section D.2 of this report, hydrogen sulfide was apparently lost in a similar fashion during the calibration of the GC/SCD. Since the SCD responds linearly to the molar concentration of sulfur atoms, the response factor for COS was used for calibration of both species. The calibration results for H_2S and COS provide some evidence for the continued

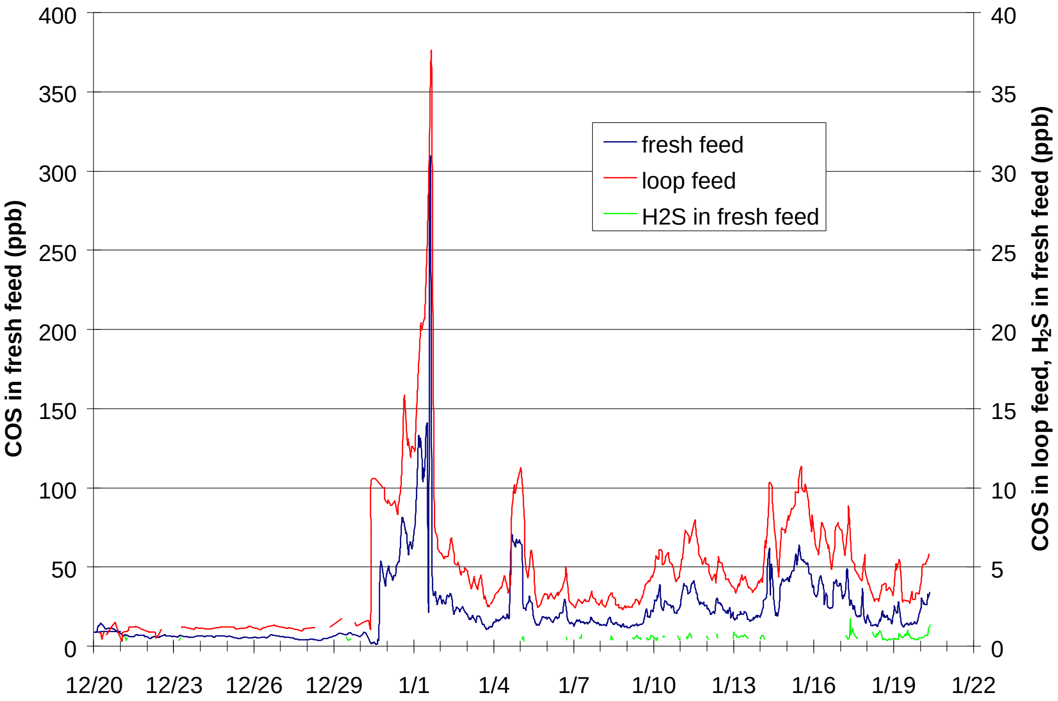

Figure 3. Trends of carbonyl sulfide in the fresh feed and the loop feed, and of hydrogen sulfide in the fresh feed.

loss of H_2S over a long timescale. This does cast a doubt on the validity of the H_2S data. On the other hand, COS appears to be measured without much lag, leading to a higher level of confidence in this data.

The trends of H_2S and COS through the field test are shown in Figure 3. The COS concentration is consistently much higher than the H_2S concentration (as measured). In fact, the H_2S concentration in the GC feed is close to the detection limit at most times; only where the measured concentration exceeded 0.5 ppbv is the data plotted. The highest measured H_2S concentration was below 2 ppbv. These results show that the Eastman sulfur guard bed effectively removes H_2S. Judging from the significantly higher COS concentrations, the guard bed is much less effective at removing COS. This is in line with expectations for the guard bed material operated at ambient temperature.

The gasifier providing the syngas feed was switched on 01 January 1998. Immediately after the switch, COS spikes of 300 ppbv in the Balanced Gas and 38 ppbv in the loop feed were measured. Before the gasifier change, the level of COS in the fresh feed had been remarkably stable below 10 ppbv; afterwards, the level fluctuated around 20 ppbv, with somewhat frequent minor upswings. The process specification for total sulfur in the fresh syngas stream is 60 ppbv, which is arbitrarily split between H_2S and COS[1]. Other than the transient on 01

January 1998, the concentration of sulfur species in the Balanced Gas were within the catalyst process specification.

Table 2 summarizes the analysis results for sulfur of catalyst samples taken from the AFFTU autoclave and from the Kingsport reactor. The measured sulfur levels are close to the detection limit for sulfur, so that the quantitation suffers from a poor signal-to-noise ratio. The loadings quoted here represent the average of two separate analyses using different techniques.

Table 2. Sulfur analyses of catalyst samples

AFFTU autoclave samples		**Kingsport reactor samples**	
Days on-stream	S (ppmw)	Days on-stream	S (ppmw)
18	45	0	<20
31	51	37	43

The sulfur accumulation on the catalyst, assuming quantitative uptake of COS by the catalyst, may also be calculated by integration of the loop feed COS curve in Figure 3. The outcome of this procedure is a loading of 37 ppmw sulfur on the catalyst. Given the measurement error of the analytical results, the measured and predicted loadings are not inconsistent. More importantly, by both methods the sulfur accumulation is less than 106 ppmw, the loading achieved during an autoclave experiment to determine the joint effects of arsenic and hydrogen sulfide on methanol synthesis catalyst. In that experiment, the sulfur loading did not affect the catalyst activity relative to the baseline deactivation rate in the autoclave.

- *Nickel Carbonyl and Iron Carbonyl*

The GC/ECD monitored both syngas feeds (fresh feed and loop feed) throughout the run. $Ni(CO)_4$, which has a higher detection limit (about 20 ppbv), was only detected in the fresh feed on a few isolated occasions. The concentration of $Fe(CO)_5$ in the fresh feed was usually around 2 ppbv, with fluctuations between 0.3 and 5 ppbv. On two occasions, the concentration briefly rose to about 15 ppbv. Most of the time, $Fe(CO)_5$ could not be detected in the loop feed. On the few occasions that it was detected, the concentration was below 1 ppbv.

These results indicate that metal carbonyls are effectively captured by the carbonyl guard bed within the battery limits of the LPMEOH™ Demonstration Unit. The catalyst in the LPMEOH™ Reactor is exposed to only minute quantities of metal carbonyls from the syngas feed. Even before the carbonyl guard bed, the $Fe(CO)_5$ and $Ni(CO)_4$ concentrations are nearly always below the catalyst process specification of 10 ppbv. These findings are consistent with gas pretesting work as well as the first AFFTU field test at Kingsport[1].

Table 3 summarizes the analysis results for iron and nickel of catalyst samples taken from the autoclave and from the Kingsport reactor. In the case of nickel, most concentrations were too low to be quantified. The iron concentrations in the autoclave samples are within the range that is detected in fresh catalyst. Clearly, very little iron or nickel accumulated on the catalyst, which is consistent with the GC/ECD results. The iron concentrations in the plant reactor samples appear to vary erratically. This may be due to the incorporation of non-catalyst material in some of the samples. For instance, the catalyst sample taken upon transfer to the bubble column just before restart (number in parentheses), showed an alarmingly high concentration of iron, but no evidence of such a high concentration was seen in subsequent samples. The scattered data provide no evidence for a steady accumulation of iron, although they may suggest that some iron was present from the beginning at a level somewhat higher than the one seen in fresh catalyst.

Table 3. Iron and nickel analyses of catalyst samples

AFFTU autoclave samples			**Kingsport reactor samples**		
Days on-stream	Fe (ppmw)	Ni (ppmw)	Days on-stream	Fe (ppmw)	Ni (ppmw)
18	44	<50	0	40 (362)	31 (47)
31	39	<50	4	92	<=18
			10	126	<=22
			37	64	39

- *Arsenic*

Arsenic cannot be detected (at ppbv levels) by any of the gas chromatographs in the AFFTU. Because a detectable loading of arsenic was observed on the catalyst from the 1997 operation of the LPMEOH™ Demonstration Unit, gas samples were collected to measure the concentration of arsenic in the fresh feed. Due to sampling complications arising from interference by methanol, no samples of loop gas were taken. The samples, collected in tubes containing activated carbon, were analyzed by the micro-analytical lab. The analysis found evidence of breakthrough of arsenic across the carbon adsorbent bed, so that an accurate quantitation was not possible. At least 31 ppbv of arsenic was present in the gas at time of sampling. The breakthrough was unexpected, because when arsine from a mixture with CO and H_2 is captured into the carbon-containing tube, much higher arsenic loadings result. The adsorption of the arsenic-containing species is probably hindered by competitive adsorption of other components in the feed gas stream, most notably trace methanol.

Table 4 summarizes the analysis results for arsenic of catalyst samples taken from the autoclave and from the Kingsport reactor. It is not immediately clear why more arsenic accumulated on the autoclave catalyst than on the catalyst from the LPMEOH™ Reactor; the higher temperature in the autoclave may have affected the extent to which arsenic was taken up by the catalyst. Assuming quantitative uptake onto the catalyst in the AFFTU autoclave over 31 days, the average concentration of arsenic-containing species in the loop gas is about 5 ppbv. The analogous calculation based on the 37-day sample from the demonstration unit results in an average concentration of about 1.5 ppbv. With a ratio of fresh feed to reactor recycle of 1:3, the concentration of arsenic in the reactor feed gas (based on the concentration measured upstream of the carbon guard bed) would be 8 ppbv. This suggests that a substantial fraction of the arsenic introduced with the fresh feed is sorbed onto the carbonyl guard bed. The apparent acceleration in arsenic uptake onto the catalyst between

18 and 31 days may be indicative of break-through of arsine (which is assumed to be the form in which arsenic is present in the Balanced Gas) through the guard bed.

On catalyst samples from both autoclave and the demonstration unit, the final arsenic loading was much less than the value measured during the 1997 operation of the LPMEOH™ Demonstration Unit after one month (446 ppm).

Table 4. Arsenic analyses of catalyst samples

AFFTU autoclave samples		**Kingsport reactor samples**	
Days on-stream	As (ppmw)	Days on-stream	As (ppmw)
18	38	0	<10
31	104	37	29

- *Other Species*

No species besides those already mentioned were observed using the poisons GC. A sample of fresh feed gas collected onto a thermal desorption tube was analyzed by GC/MS. A multitude of organic compounds was detected at low concentrations. Several of these were identified by GC/MS, and the more prominent ones analyzed semi-quantitatively. Besides methanol, ethanol, and dimethyl ether, a variety of hydrocarbons were identified. In addition, 2-butylamine, 1,3-dithiolane, and acetonitrile were observed.

E. Conclusions

The AFFTU was successfully deployed to the Eastman chemicals-from-coal complex in Kingsport for the restart of the LPMEOH™ Demonstration Unit in December of 1997. For 31 days, the AFFTU autoclave operated in parallel with the Kingsport reactor, using a slipstream of the reactor syngas feed. The concentrations of metal carbonyls and sulfur species were monitored in two process streams: the primary syngas feed to the LPMEOH™ Demonstration Unit, and the syngas feed to the LPMEOH™ Reactor.

Neither the Kingsport reactor catalyst nor the AFFTU autoclave catalyst deactivated at the high rates observed during the initial operation of the LPMEOH™ Demonstration Unit in April of 1997. The catalyst in the demonstration unit lost activity at about 1%/day, which compares favorably with the 3+%/day during the early days of the first run. However, it still deactivated more rapidly than the 4-month proof-of-concept run at the LaPorte AFDU in 1988/89, with a deactivation rate of 0.4%/day. The AFFTU autoclave catalyst deactivated at a rate of 1.1-1.3%/day. This figure may be overstated, due to the loss of catalyst to autoclave surfaces when a significant portion of the slurry oil had evaporated. An approximate calculation taking this effect into account results in an estimated activity loss of 0.6%/day, which is well below the historically observed baseline deactivation rate in laboratory autoclaves. Because the deactivation rates in the autoclaves and in the reactor are similar, no catalyst performance difference due to plant equipment or operating conditions relative to the AFFTU autoclave can be inferred.

The average copper crystallite size, which during the first Kingsport run had rapidly grown from 80 Å to 275 Å, grew at a much slower rate during this second run. After 31 days, the average crystallite sizes in catalyst samples from the AFFTU autoclave and Kingsport reactor were 149 Å and 132 Å, respectively. These are within the expected range for catalyst that has been online for several weeks.

Several species which are poisons to methanol synthesis catalyst observed in the Balanced Gas at levels well below the process specifications (10 ppbv for each of the metal carbonyls, 60 ppbv total sulfur). Hardly any hydrogen sulfide and nickel carbonyl were detected in the Balanced Gas. The concentration of iron carbonyl was usually less than 5 ppbv; no iron carbonyl was detected in the reactor feed, which indicated that a carbon guard bed within the battery limits of the LPMEOH™ Demonstration Unit effectively removed iron carbonyl. Carbonyl sulfide was detected both in the Balanced Gas upstream of the carbon guard bed and in the Kingsport reactor feed. In the Balanced Gas, the COS concentration was usually around 20 ppbv, with occasional upswings and one spike to about 300 ppbv. In the Kingsport reactor feed, the typical concentration was about 4 ppbv, again with occasional upswings, and a spike to almost 40 ppbv. Sulfur loadings on catalyst samples from the AFFTU autoclave and Kingsport plant catalyst remained low, at levels unlikely to affect catalyst performance.

The AFFTU provides a state-of-the-art environment for determining the concentration of trace contaminants in coal-derived syngas. Future use of the AFFTU in determining the effects of trace contaminants on catalyst performance will be limited to those circumstances where the deactivation rate in the autoclave is significantly lower than the results calculated for the slurry reactor.

F. References

1. Andrew W. Wang. "Design and Construction of the Alternative Fuels Field Test Unit and Liquid Phase Methanol Feedstock and Catalyst Life Ttesting at Eastman Chemical Company (Kingsport, TN)". DOE Draft Topical Report, Contract No. DE-FC22-95PC93052, March 1997.

APPENDICES

APPENDIX A - SIMPLIFIED PROCESS FLOW DIAGRAM - LPMEOH™ DEMONSTRATION UNIT

APPENDIX B - AFFTU FLOW DIAGRAMS

APPENDIX C - MISCELLANEOUS TRENDS

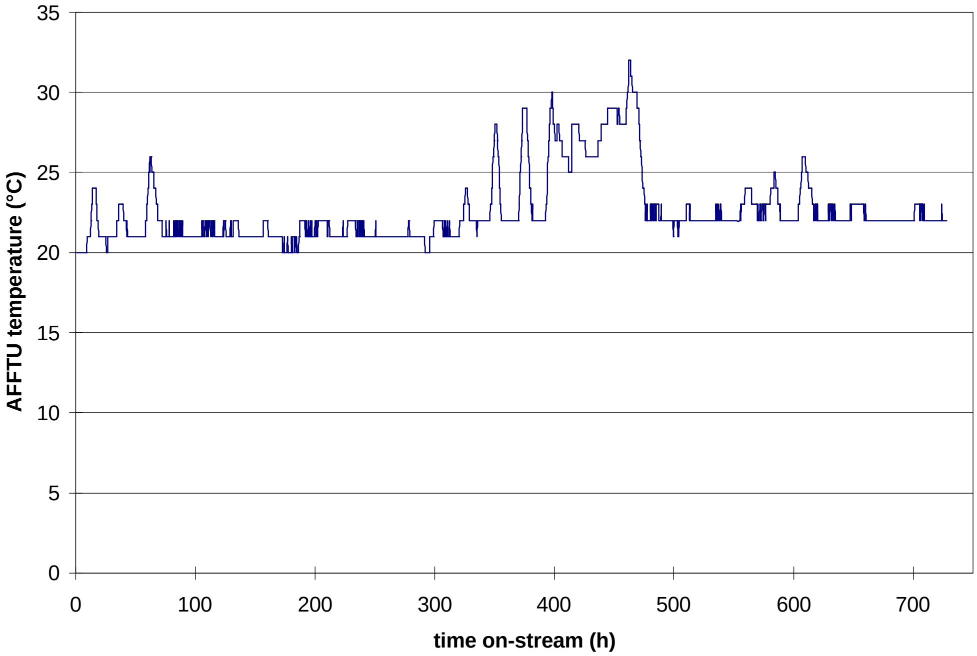

Figure C-1. Temperature in the laboratory side of the AFFTU. The temperature of the next-door office side is controlled by thermostat at a constant setpoint. The higher temperatures around 400 h are indicative of warm weather.

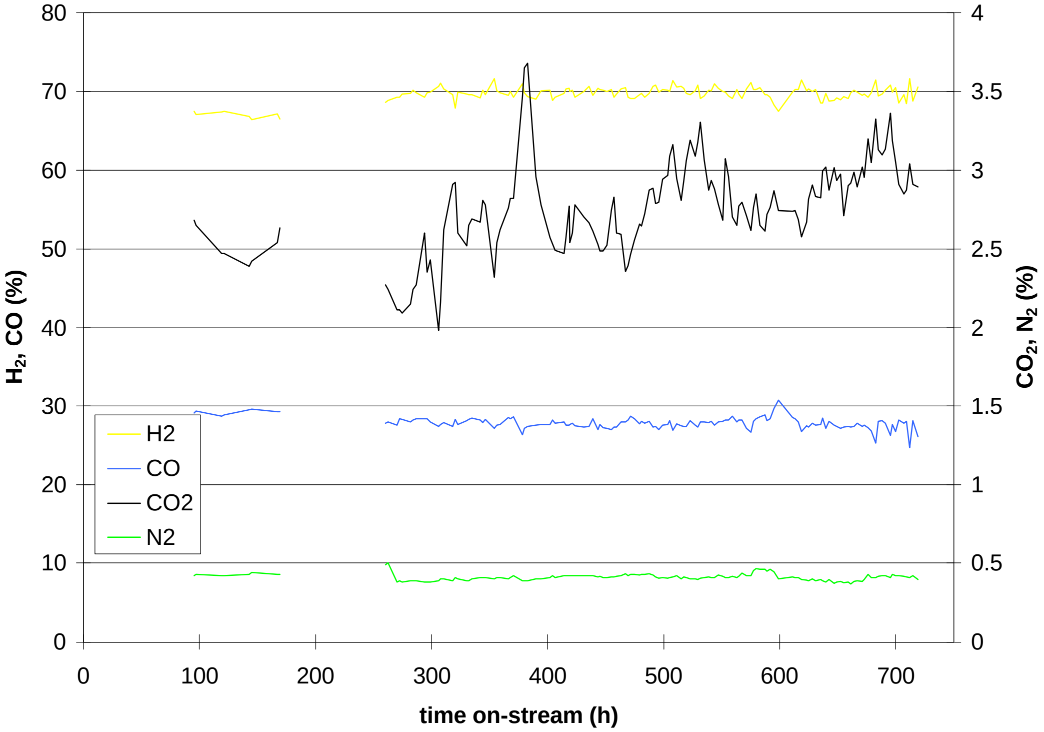

Figure C-2. Trends of bulk component concentrations in the fresh feed.

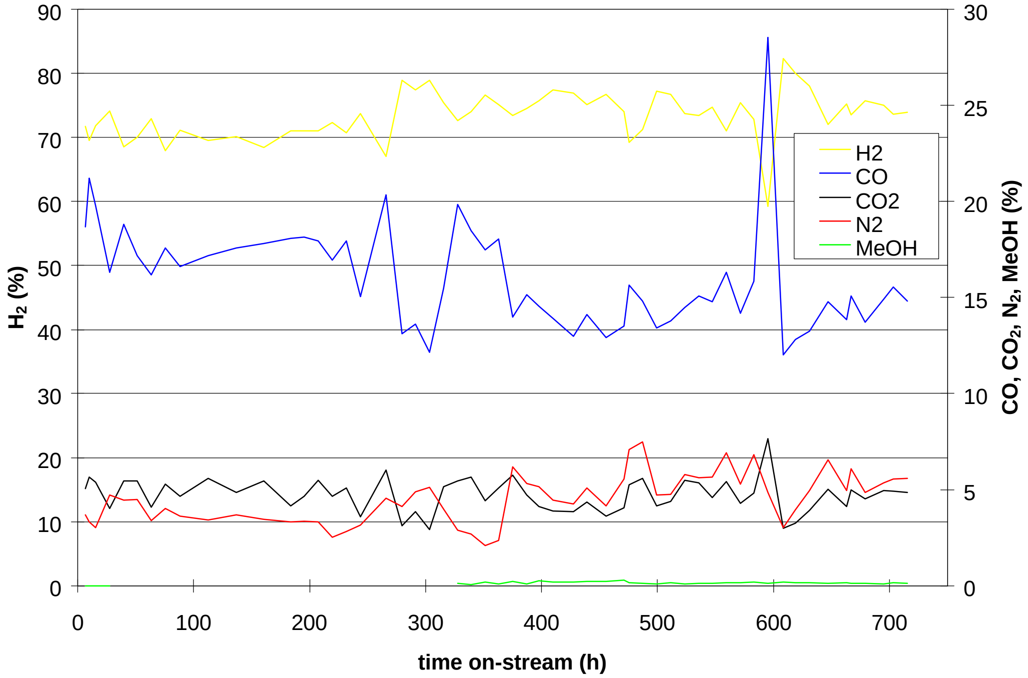

Figure C-3. Trends of bulk component concentrations in the autoclave feed.

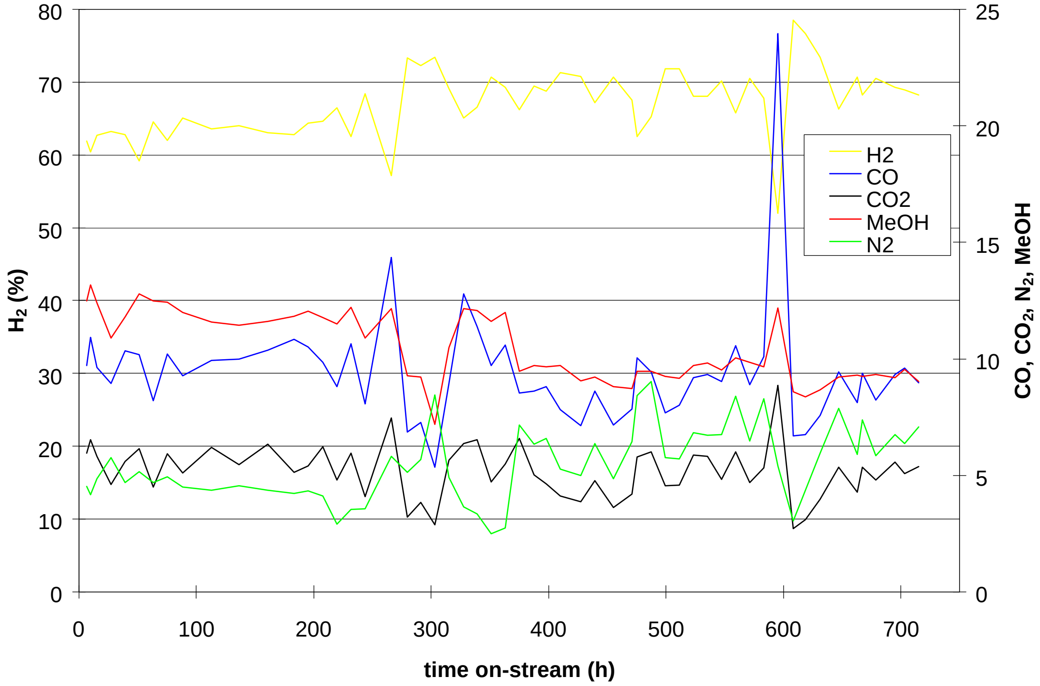

Figure C-4. Trends of bulk component concentrations in the autoclave product.

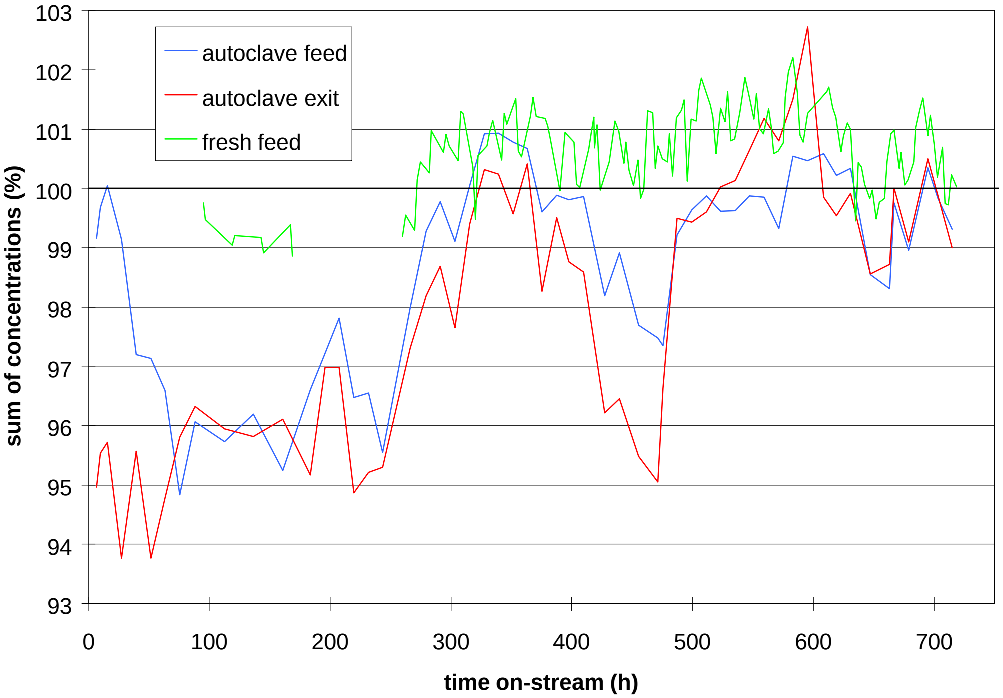

Figure C-5. GC mass balances on individual streams. The deviations from 100% arise from inaccuracies in GC measurement, either due to calibration problems or sampling problems.

APPENDIX D - PHOTOGRAPH OF ALTERNATIVE FUELD FIELD TRAILER UNIT (AFFTU)


Alternative Fuels
Field Test Unit
Air Products and Chemicals, Inc.
U.S. Department of Energy
Clean Fuels From Coal