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**LIQUID PHASE METHANOL LAPORTE PROCESS DEVELOPMENT UNIT:
MODIFICATION, OPERATION, AND SUPPORT STUDIES**

Topical Report

**Task 2.2: Alternate Catalyst Run E-6 and
Catalyst Activity Maintenance Run E-7**

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TABLE OF UNITS

%	Percent
Btu	British thermal unit
cc	Cubic centimeters
cm	Centimeters
°C	Degrees Celsius
°F	Degrees Fahrenheit
ft	Feet
gal	Gallons
gm	Grams
gmol/hr Kg	Productivity units: Gram moles of methanol per hour per kilograms of catalyst oxide.
gpm	Gallons per minute
hr	Hours
in	Inches
kg	Kilograms
l	Liters
lb	Pounds
m ²	Square meters
min	Minutes
mol%	Mole percent
ppb	Parts per billion by volume for gas by weight for liquid
psi	Pounds per square inch
psig	Pounds per square inch gauge
psia	Pounds per square inch absolute
scf	Standard cubic feet
SCFH	Standard cubic feet per hour
sec	Seconds
Sl/hr Kg	Space Velocity Units: Standard liters of feed gas per hour per kilograms of catalyst oxide
SV	Gas hourly space velocity Standard liters per hour per kilogram catalyst oxide
TPD	Tons per day
tons	Short tons (2000 lb)
wt%	Weight percent

ACRONYMS AND DEFINITIONS

CSI	Chem Systems Inc.
DOE	U.S. Department of Energy
EPRI	Electric Power Research Institute
LPMEOH	Liquid Phase Methanol, the technology to be demonstrated
MeOH	Methanol
NDG	Nuclear Density Gauge
PDU	Process Development Unit

Table of Contents

	<u>Page</u>
ABSTRACT	i
I. Executive Summary	1
II. Introduction and Background	3
A. Process Development Scale Experience	3
B. LPMEOH I and II Operations	7
C. LPMEOH III Operations	8
III. LaPorte LPMEOH PDU	9
A. Process Description	9
B. PDU Equipment Modifications	13
IV. Alternate Catalyst Evaluation Run (Run E-6)	14
A. Introduction	14
B. In-Situ Catalyst Activation	14
C. Methanol Synthesis Operation	14
D. Discussion of Results	18
1. Catalyst Evaluation	18
2. Reactor Internal Heat Exchanger	28
3. Methanol Composition	35
4. Conclusions	36
V. Catalyst Activity Maintenance Run (Run E-7)	38
A. Introduction	38
B. Methanol Synthesis Operation	38
C. Discussion of Results	58
1. Catalyst Activity Maintenance	58
2. Catalyst Analytical Results	71
3. Reactor Internal Heat Exchanger	71
4. Response to Process Upsets and Load Following	75
5. Online Catalyst Addition/Withdrawal	75
6. Methanol Composition	80
7. Conclusions	80
VI. Recommendations	84
VII. References	85

ABSTRACT

Liquid-entrained operations at the LaPorte LPMEOH Process Development Unit (PDU) continued from August 1988 through January 1989 under Task 2.2 of Contract No. DE-AC22-87PC90005 for the U. S. Department of Energy. The primary focus of this PDU operating program was to prepare for a confident move to the next scale of operation with a simplified and optimized process. The first operating objective was to evaluate the alternate catalyst identified and tested under Subtask 3.6 of this contract relative to the previously used baseline catalyst. The second objective was to evaluate the deactivation and performance of the preferred catalyst during a life run. Also to be examined during the life run were internal heat transfer, catalyst addition/withdrawal, and reactor load following.

Two equipment modifications were made prior to the PDU operations. The purpose of the changes was to: 1) improve the separation of oil from the product methanol by installing a new demister in the intermediate vapor/liquid separator, and 2) allow increased heat transfer within the reactor by equipping the reactor internal heat exchanger with an expansion loop to relieve the thermal stresses present during operation at high catalyst loadings and gas velocities. In addition, the reactor demister damaged during Run E-5 was replaced for a follow-up evaluation.

Run E-6 began in late August 1988 using the alternate commercial catalyst (F21/OE75-43) identified via the laboratory efforts of Subtask 3.6. The new catalyst slurry was reduced in-situ, but was not fully activated. Overall, however, the new catalyst was capable of producing 9% more methanol in a 35 wt% slurry than the previous catalyst in a 40 wt% slurry. Hence, the alternate catalyst became the preferred candidate, and operations continued from September 1988 through January 1989, as Run E-7, for a 120-day activity maintenance study. The nominal conditions were 10,000 SI/hr-kg cat, 462°F, 750 psig, and 35 wt% oxide slurry. The baseline catalyst deactivation rate was no more than 0.2%/day, half the rate of Run E-3 in 1985.

Heat transfer through the reactor internal heat exchanger was stable during the run. The measured values indicated that the Deckwer correlation was an effective method of prediction for the shell-side heat transfer coefficients.

Throughout the run, the LPMEOH process demonstrated its adaptability to process upsets. Startup was simple and productivity was unchanged after a 3-day shutdown for Hurricane Gilbert. Similarly, during load following cuts of up to 80% in flow, at rates as great as 16.0%/min, were easily accommodated with minimal temperature variance. Furthermore, downtime was less than one day when roughly half of the catalyst slurry was replaced during the catalyst changeout. Results indicated that both activated catalyst storage and catalyst changeout are viable process operations.

I. EXECUTIVE SUMMARY

The effort to prove the technical feasibility of the LPMEOH process at the PDU scale has been conducted since 1981 by Air Products and Chemicals, Inc. and the U.S. Department of Energy (DOE), as part of DOE's indirect coal liquefaction program. Chem Systems Inc. (CSI) has been the key subcontractor in the program. Air Products has been joined by the Electric Power Research Institute (EPRI) as a private cost sharing participant. This work has been funded under DOE Contracts DE-AC22-81PC30019, DE-AC22-85PC80007 and the current contract DE-AC22-87PC90005. Additional details of the development results are available in the previous contract reports.

The primary focus of this PDU operating program was to prepare for a confident move to the next scale of operation with a simplified and optimized process. The main purpose of these runs was the evaluation of the alternate commercial catalyst that had been identified in the laboratory under Subtask 3.6. If the catalyst proved superior to the previous catalyst, then the evaluation run would be continued into a 120-day life run.

Also, minor changes were made to the PDU system to improve operations and reliability. The damaged reactor demister from Run E-5 was replaced, and a new demister was installed in the intermediate V/L separator. The internal heat exchanger was equipped with an expansion loop to relieve thermal stresses so operation at higher catalyst loadings and gas velocities would be possible. These aggressive conditions are important for improving process economics.

Alternate Catalyst Evaluation

Run E-6 began in late August 1988 using the alternate commercial catalyst (F21/OE75-43) identified via the laboratory efforts of Subtask 3.6. Autoclave results indicated that the new catalyst activity was 10% higher than the old catalyst. The objective of Run E-6 was to evaluate the performance of the newly identified catalyst in the PDU.

The new catalyst slurry was reduced in-situ in Run ER-05 at 45 wt%. Unfortunately, the catalyst was not fully activated. Productivity appeared to increase with time on stream and dilution of the catalyst slurry. A variety of operating conditions were run, but the best productivity relative to the autoclave (100%) occurred at a space velocity of 9462 Sl/hr-kg cat and at a slurry concentration of 37 wt% oxide. Overall, the new catalyst produced 9% more methanol in 35 wt% slurry than the previous catalyst in 40 wt% slurry; furthermore, the new catalyst slurry had acceptable gas holdup and slurriability throughout the test cases.

Analysis of heat transfer within the reactor demonstrated that the overall heat transfer coefficients were predicted accurately and that, on average, the shell-side coefficients were predicted within 30%, supporting the use of the Deckwer correlation. The oil impurity in the product methanol was significantly reduced by the minor process changes. Methanol purity averaged 96 wt%.

Catalyst Life Run

After the encouraging results of Run E-6, the alternate catalyst became the preferred candidate, and operations continued, as Run E-7, for a 120-day deactivation study at nominal conditions of 10,000 Sl/hr-kg, 482°F, 750 psig, and 35 wt% oxide catalyst. The major objectives of this run were evaluation of catalyst deactivation, catalyst addition/withdrawal, reactor load following, and internal heat transfer.

Over the 120-day period, the baseline catalyst deactivation rate was no more than 0.2%/day, half the rate of Run E-3 in 1985. This is attributed to the reported improved stability of the alternate catalyst and the further elimination of carbon steel from the process loop, since carbonyls, formed in the presence of carbon steel, are a significant cause of deactivation. An exponential decay function was developed to model the deactivation, indicating the catalyst was only 81% activated after the ER-5 reduction procedure. Catalyst slurry samples had slow crystallite size growth, indicating marginal loss of copper surface area and hence marginal loss in activity. The temperature approach to methanol equilibrium increased linearly until just prior to catalyst changeout, another sign of slow deactivation.

A fouling factor of 0.0015 hr-ft²-°F/Btu was estimated for Run E-7 based upon the difference between predicted and calculated shell-side heat transfer coefficients. Two-thirds of this fouling occurred during Run E-6 and the remainder during the first 20 days of Run E-7.

Throughout the run, the LPMEOH process demonstrated its resilience to upsets. Operations were suspended for 3 days due to Hurricane Gilbert, yet startup was simple and productivity was unchanged. Similarly, for load-following, flow reductions of up to 80% and feed flow rate changes of up to 16.0%/min were accommodated easily with reactor temperature variances of 5°F or less. Additionally, when 58.4% of the slurry was replaced during catalyst addition/withdrawal, downtime was minimal, and new production levels were within 5% of predicted, assuming the added catalyst had the same activity as fresh catalyst. This assumption was confirmed in laboratory testing. The results supported the viability of catalyst changeout and activated catalyst storage.

Finally, product methanol purity was very consistent throughout the 120 days of Run E-7. Methanol purity increased gradually from 97.00 wt% to 97.75 wt% prior to catalyst changeout. Water concentrations were below 1.0 wt%, and oil impurities were generally below 0.2 wt% total. Product compositions returned to near initial levels after the catalyst addition/withdrawal.

Overall, Run E-7 was tremendously successful. Over 1000 tons of methanol were produced at high purity and the unit responded superbly to the variations of normal everyday operation. Total lost time was 137 out of 3100 hours, of which 130 were the result of electrical or gas supply outages unrelated to the LPMEOH PDU.

II. INTRODUCTION AND BACKGROUND

The LPMEOH process was conceived and patented by Chem Systems Inc. in 1975. Initial research and studies on the process focused on two distinct modes of operation. The first was a liquid fluidized mode with relatively large catalyst pellets suspended in a fluidizing liquid, and the second was an entrained (slurry) mode with fine catalyst particles slurried in an inert liquid. The development of both operating modes progressed in parallel from bench scale reactors, through an intermediate scale lab PDU, and then to the LaPorte PDU in 1984. The slurry mode of operation was ultimately chosen as the operating mode of choice due to its superior performance.

Development efforts on the slurry reactor have continued through 1988 both at the LaPorte PDU and in the laboratory. The work done during this period has focused on optimizing all aspects of the LPMEOH process. The key milestones in the development and scale-up of the current LPMEOH process are listed below:

<u>Date</u>	<u>Development Scale and Key Results</u>
1975	LPMEOH concept patented by Chem Systems
1979 - 1981	2 Liter bench scale stirred autoclave Concept Verification Catalyst/Oil Screening Initiated Catalyst Activation Methods Demonstrated
1981-1988	300 cc/1 Liter laboratory scale stirred autoclave Method to Activate Conc. Slurries Developed Catalyst Poisons Studied Feed Gas Composition Effects Determined
1983	4.5 in. ID x 7 ft. tall Lab. PDU (up to 0.14 TPD MeOH) Reactor Productivity Defined Hydrodynamic Behavior Identified Reactor Modeling Begun
1984 - 1985	2 in. ID x 18 ft. tall LaPorte PDU (up to 8 TPD MeOH) Reactor Performance Demonstrated Catalyst Life Demonstrated Materials of Construction Defined Operating Experience Base

A. Process Development Scale Experience

The primary function of the LaPorte PDU is to acquire data using a small, representative engineering scale for testing the feasibility of the LPMEOH process. Thus, the PDU was designed to generate and collect plant data over a wide range of operating conditions. The range of operating variables chosen for the original design is shown in Table II.1. In fact, the PDU has operated at flow, space velocity, and catalyst loading conditions well in excess of design.

TABLE II.1

RANGE OF OPERATING VARIABLES FOR LAPORTE PDU

	<u>Minimum</u>	<u>"Typical"</u>	<u>Maximum</u>
Reactor Pressure, psig	500	750	900
Reactor Temperature, °C	220	250	270
°F	428	482	518
Liquid-Fluidized Space			
Velocity, liter/hr-kg cat	1,000	2,500	4,000
Liquid-Entrained Space			
Velocity, liter/hr-kg cat	2,000	6,000	10,000
Liquid-Fluidized Catalyst			
Loading, Settled Bed Height, ft	5	7	7
Liquid-Entrained Catalyst			
Loading, wt%	10	20	33

NOTE: Space velocity based on standard liters (0°C, 14.7 psia), kg of oxide catalyst, and zero gas holdup in reactor.

The principal reactor feed gas compositions considered during design were:

- CO-Rich Type, in which the hydrogen and carbon oxide concentrations are not stoichiometrically balanced, but are representative of synthesis gas directly from a modern Texaco coal gasifier. This gas is typical of that for once-through methanol synthesis in a CGCC plant configured to make electric power and coproduct methanol.
- Balanced Type, representative of CO-rich gas which has undergone shift and O₂ rejection so that the hydrogen and carbon oxide concentrations are approximately stoichiometrically balanced (2:1) in order to achieve an "all-methanol" product.
- H₂-Rich Type, in which the hydrogen and carbon oxide concentrations are not stoichiometrically balanced, but are representative of synthesis gas from a steam methane reformer.

The compositions of the various gas streams are given in Table II.2. The different reactor feed gas compositions are blended from H₂, CO, N₂, and CH₄ supplied by Air Products' adjacent syngas facility at LaPorte. Carbon dioxide is trucked into the plant as a liquid and stored on-site. Since only a portion of the reactor feed is converted per pass, the unconverted synthesis gas is recycled and mixed with fresh makeup gas. The makeup gas is blended so that the reactor feed (makeup plus recycle) simulates either the balanced or CO-rich gas type in once-through operation. Recycling the unconverted synthesis gas reduces gas consumption by 70% for cost-effective operation at LaPorte.

TABLE II.2
GAS TYPES TESTED AT THE LAPORTE PDU

<u>Component mol%</u>	<u>CO-Rich Gas</u>	<u>Balanced Gas</u>	<u>H₂-Rich Gas</u>
Hydrogen	35.0	55.0	71.0
Carbon Monoxide	51.0	19.0	18.0
Carbon Dioxide	13.0	5.0	7.0
Methane	0.1	0.1	0.1
Nitrogen/Inerts	0.9	20.9	3.9
H ₂ /CO Ratio	0.69	2.89	3.94
$\frac{(H_2 - CO_2)}{(CO + CO_2)}$	0.34	2.08	2.56

TABLE II.3

LAPORTE PDU OPERATIONS SUMMARY

<u>Run #</u>	<u>Date</u>	<u>Objective</u>	<u>Operation Mode</u>	<u>Catalyst Type</u>	<u>Hours On Syngas</u>
F-1	Mar 84	Shakedown	Hybrid Fluidized/Slurry	Extrudates	248
E-1	Apr/May 84	Activity Maintenance	Hybrid Fluidized/Slurry	Extrudates	964
E-2	Jun 84	High Slurry Conc., High Throughput	Slurry	Powder	145
E-3	May/Jun 85	Activity Maintenance	Slurry	Powder	948
E-4	Jul 85	High Slurry Conc., High Throughput	Slurry	Powder	<u>231</u> 2536

B. LPMEOH I and II Operations

A total of five major synthesis runs were conducted at the LaPorte PDU from March 1984 through July 1985. A summary of these campaigns is presented in Table II.3.

The first PDU run (F-1) was a 10-day shakedown run. The PDU operated smoothly, and the mechanical integrity and process flexibility of the unit were demonstrated. Up to 8 TPD of methanol were produced. The second PDU run (E-1) was a 40-day continuous run on CO-rich synthesis gas ($H_2/CO=0.7$). Stable operation was achieved, but a slow, continuous decline in catalyst activity was observed, in excess of that anticipated from isothermal laboratory autoclave experiments. The accumulation of trace poisons seen on the catalyst was the major cause of this loss of activity (1.1% per day). A third PDU run (E-2) was conducted for 6 days using a commercially available catalyst powder at very high slurry concentration (up to 45 wt%). In-situ activation was performed. The plant operated well mechanically, providing valuable experience for the operations and engineering staff in handling high-viscosity catalyst slurries. Methanol productivity, however, was below the values predicted from laboratory autoclave results. A supporting laboratory program funded by EPRI determined that inadequate catalyst activation at LaPorte was the reason for the off-performance at the high solids loading in Run E-2. Changes in the activation procedure were identified to remedy this problem.

Analysis of the results of the 1984 operating program indicated that selective upgrading of materials of construction of the PDU would lead to lower levels of trace contaminants. Process improvements which would increase the data gathering capability were also specified. As a result, modifications were made to the LaPorte PDU in early 1985. New equipment was installed to improve the measurement of slurry concentration and methanol product flow. Also, selected vessels and piping were replaced or modified in order to reduce the levels of trace catalyst poisons, primarily iron and nickel carbonyls formed by the reaction of CO with the carbon steel pipe walls. A chemical cleaning program was also undertaken to remove residual contaminants.

Upon completion of these activities, a second 40-day activity maintenance test (Run E-3) using CO-rich gas and 25 wt% catalyst slurry was conducted in May-June 1985. The reactor conditions matched the earlier extended operating campaign at the PDU (Run E-1). In Run E-3, however, the revised in-situ catalyst activation procedure was successfully applied and, combined with the new metallurgy, the reactor performance matched laboratory predictions for catalyst life and activity. High onstream reliability for the PDU was achieved.

A second operation of the LaPorte PDU at elevated slurry concentrations (again up to 45 wt%) was subsequently performed. A successful catalyst activation was achieved. High operability was again maintained during this 10 day test; the reactor performance exceeded the previous run at these conditions (Run E-2) but catalyst productivity was still less than laboratory predictions. The deficiency in productivity was attributed to a mass transfer limitation and/or inadequate gas/slurry mixing or distribution at these elevated slurry solid loadings.

TABLE II.4

LAPORTE PDU OPERATIONS SUMMARY

<u>Run #</u>	<u>Date</u>	<u>Objective</u>	<u>Operation Mode</u>	<u>Catalyst Type</u>	<u>Hours On Syngas</u>
GH-03	Jun 88	Evaluation of Reactor Hydrodynamics	Two Phase Gas Holdup Studies with N ₂ and Syngas	None	-
E-5	Jun/ Jul 88	Process Equipment Evaluation	Step by Step Elimination of Slurry Loop	Powder	259

C. LPMEOH III Operations

An additional major synthesis run, the first LP-III run, was conducted during June and July 1988.

The Two-Phase Gas Holdup tests (GH-03) studied the reactor hydrodynamics, measured carbonyl catalyst poison levels, and trained operating personnel on the new design. The new sparger provided constant holdup with external slurry circulation and improved holdup without external circulation. Gas holdup profiles were uniform over the height of the reactor. Initial levels of carbonyls were below 70 ppb, but dropped to 19 ppb of Fe(CO)₅ and 4 ppb of Ni(CO)₄ after 20 hours on stream.

The objective of Run E-5 was to systematically evaluate each new piece of equipment (sparger, internal heat exchanger, V/L disengagement zone, demister, and cyclone) which had been added to the process, and to attempt to run the reactor in an internal-only mode without the slurry pump. The new gas sparger improved both methanol productivity and gas holdup. The internal heat exchanger was not found to be a hindrance to reactor mixing. Trials without external slurry circulation proved that the new reactor design reduced mixing and mass transfer limitations, and that the completely internal design represented the state-of-the-art technology for this process. Hence, the maintenance-intensive slurry pump as well as the external slurry exchanger could be eliminated. In addition, a successful catalyst reduction with a concentrated (45 wt% oxide) slurry was accomplished.

LaPorte PDU operations successfully demonstrated LPMEOH process technology at a representative engineering scale. The PDU has accumulated over 2700 hours of methanol synthesis operation with an on-stream factor of 96-100%. Low catalyst deactivation while operating the liquid-entrained system with a 25 wt% catalyst slurry for an extended period of time on CO-rich synthesis gas was a notable achievement. The ability to activate methanol synthesis catalyst powders in an inert liquid at high concentrations was also noteworthy. Methanol production levels above 9 TPD were achieved; the purity of the methanol product from CO-rich gas was consistently higher than 96 wt%, a good fuel-grade quality. Finally, the elimination of the external slurry loop while simultaneously increasing productivity exhibited continuing optimization of the process.

III. LAPORTE LPMEOH PDU

A. Process Description

A simplified flowsheet for the process configuration used at the LaPorte PDU for Runs E-6 and E-7 is shown in Figure III.1. The makeup synthesis gas is compressed to the reactor pressure (500-900 psig) by the feed compressor. The compressed makeup and recycle gases are mixed and preheated in the feed/product exchanger before being fed into the methanol reactor. The gaseous reactor feed mixes with the inert hydrocarbon liquid/catalyst slurry forming a three-phase bubble column reaction zone. The slurry phase disengages from the unconverted synthesis gas and methanol product vapor in the upper freeboard region of the reactor. The heat of reaction from the exothermic methanol reaction is effectively absorbed by the presence of the oil phase resulting in an essentially isothermal reaction. The slurry is heated or cooled by an internal slurry heat exchanger to maintain the constant reactor temperature. A utility oil system provides the heating or cooling duty to the slurry exchanger.

The unconverted synthesis gas/product methanol stream leaving the reactor freeboard flows through an external axial cyclone to insure removal of any entrained slurry droplets from the exiting vapor stream. This gas stream is cooled against incoming feed gas and the condensed oil is separated in the secondary V/L separator. The uncondensed vapor is further cooled in the product cooler. Condensed methanol is then separated from the synthesis gas, degassed and piped to product storage. The bulk of the unconverted synthesis gas is compressed and returned to the front end of the PDU. A small purge stream is sent to flare to control the buildup of inert gases in the process. Additional systems are present to activate the catalyst and provide continuous oil flushing to the axial cyclone.

A schematic of the LaPorte reactor system is given in Figure III.2. The feed gas enters the reactor through a gas sparger providing the driving force for mixing and suspension of the catalyst particles. The system is equipped with two separate vapor/liquid disengagement devices, a reactor internal demister, and an external cyclone. It was anticipated that only one disengagement method would be required but both were included for test purposes. It is possible to bypass each device to individually evaluate their performance. The cyclone is continually flushed with condensed process oil to prevent fouling. The flush oil and any carry-over slurry is returned to the reactor through a small positive displacement pump. The actual configuration of the 27.10 reactor is shown in Figure III.3.

The internal heat exchanger consists of ten parallel 1-inch-diameter tubes manifolded at each end by a 16-inch-diameter heater ring. The heat exchanger occupies only 3.5% of the reactor cross-sectional area and did not interfere with reactor hydrodynamics in Run E-5. The success of the internal heat exchanger allowed the elimination of two large high-pressure vessels (the vapor/slurry separator and the heat exchanger shell) and the slurry circulation pump.

Figure III.1

SIMPLIFIED PROCESS FLOWSHEET FOR LAPORTE PDU

Figure III.2

Figure III.3

LPMEOH
REACTOR
AT LAPORTE
PDU

An external nuclear density gauge is used to monitor the catalyst bed height in the reactor. The gauge is mounted in a mechanical framework which allows it to traverse the reactor in a vertical direction. During the slurry operation, the gauge is used to directly measure three-phase density and subsequently determine hydrodynamic information about the reactor.

B. PDU Equipment Modifications

Although the PDU had been very reliable in the prior campaigns, two equipment modifications were made prior to the PDU operations in Run E-6. The purpose of the changes was to: 1) improve the separation of oil from the methanol by installing a new demister in the intermediate vapor/liquid separator, and 2) allow increased heat transfer within the reactor by equipping the reactor internal heat exchanger with an expansion loop to relieve the thermal stresses present during operation at high catalyst loadings and gas velocities. In addition, the reactor demister damaged during Run E-5 was replaced for a followup evaluation.

The remainder of the reactor design (diameter, liquid height, instrumentation, etc.) was unchanged from the Run E-5 PDU reactor design.

IV. ALTERNATE CATALYST EVALUATION RUN E-6

A. Introduction

Run E-6 was started in late August using an alternate commercial catalyst (Catalyst F21/OE75-43). The alternate commercial catalyst was identified through the laboratory efforts in February 1988 under Subtask 3.6: Testing of Alternate Commercial Catalysts. Laboratory autoclave results indicated that the new catalyst activity was about 10% higher than that of the old catalyst activity (Catalyst F21/OE75-44). The objective of Run E-6 was to evaluate the performance of the newly identified catalyst in the PDU scale reactor. If the alternate catalyst performed equivalent to or better than the catalyst used in previous runs, the alternate catalyst run would be continued for 120 days to evaluate baseline (thermal) deactivation.

B. In-Situ Catalyst Activation

A batch of 42 wt% (oxide base) slurry using the newly identified catalyst F21/OE75-43 and Drakeol-10 oil was mixed in the slurry prep tank and pressure-transferred to the reactor. The reducing gas was blended and the catalyst activation Run ER-5 procedure began at 1325 on 23 August 1988. The target condition for the reduction gas was 3 mol% hydrogen in nitrogen at a flow rate of 34,500 SCFH. An unusually high level of reactor vibration was observed during the reduction. The reactor vibration continued throughout the reduction period but was not observed during the methanol synthesis operations. One possible cause for the vibration is vapor phase slugging or channeling in the reactor at the high catalyst loading. This theory is supported by the observation of nonuniform gas holdup in the reactor during the reduction and the thick appearance of the slurry samples. No other work was done to identify the cause of this reactor behavior. Further details of the catalyst activation are presented in the Run Chronology (Table IV.1).

The hydrogen uptake during the catalyst activation was slower than expected but the activation initially appeared to have been executed successfully. The higher than theoretical hydrogen uptake by the catalyst and a recheck of the reduction gas flowmeter indicated, however, that the reduction gas flowrate measurement was overstated by 10%.

C. Methanol Synthesis Operation

After the completion of the catalyst activation, the CO-rich synthesis gas flow was brought on-line and the PDU began operating at the first conditions for Run E-6. The run consisted of a series of process variable scans (Table IV.2) to determine the performance of the catalyst slurry under various operating conditions. After approximately one week on synthesis gas, during Run E-6, the decision to go ahead with the catalyst life Run E-7 using the new alternate catalyst was made. The Run chronology in Table IV.3 gives the detailed account of the run.

TABLE IV.1

CATALYST REDUCTION RUN ER-05 CHRONOLOGY

<u>Date</u>	<u>Time</u>	<u>Cumulative Time On Reduction Gas (hours)</u>	<u>Notes and Observations</u>
22 Aug 88	1135		Charged 3,162 lb of Drakeol-10 oil to Slurry Prep Tank and began heating to 200°F.
	1700		Charged 2,545 lb of F21/OE75-43 catalyst to Slurry Prep Tank.
23 Aug 88	1200		Transferred slurry to Primary V/L Separator and began slurry circulation at 135 gpm.
	1205		Charged 347 lb of oil to Slurry Prep Tank, ran agitator for 1 minute, then blew over to Primary V/L Separator to flush the transfer line. Start at 42 wt% oxide.
	1213		Slurry flow increased to 225 gpm. Reactor temperature at 150°F.
	1315		Sending 3% H ₂ in N ₂ reducing gas to reactor and trying to stabilize flow at 34,500 SCFH.
	1325	0	Official start of ER-5. Using external slurry loop and heating with external heat exchanger only.
	1350	0.42	Demister bypass valve opened 1 turn to vent freeboard during reduction. Slurry level at 207.5" on tape (right at exit nozzle).
	1355	0.50	Good reactor temperature control.
	1450	1.42	Difficulty controlling H ₂ concentration due to fluctuating feed line pressure.
	1520	1.92	H ₂ concentration stabilizing.
	1940	6.25	Slurry sample taken from external loop.
	2200	8.58	Noticed reactor vibrating about 0.25 to 0.50".
	2300	9.58	Hydrogen composition in reactor effluent unchanged over last 1.5 hours.
	2350	10.42	Slurry samples taken from external loop.
24 Aug 88	0030	11.08	Slowed temperature ramp greatly to allow H ₂ concentration to catch up.
	0115	11.83	Hydrogen concentration starting to catch up.

TABLE IV.1

CATALYST REDUCTION RUN ER-05 CHRONOLOGY

<u>Date</u>	<u>Time</u>	Cumulative Time On Reduction <u>Gas (hours)</u>	<u>Notes and Observations</u>
24 Aug 88	0155	12.50	Hydrogen consumption improving.
	0245	13.33	Increasing reactor temperature.
	0615	16.83	Difficulty in controlling H ₂ feed due to fluctuating line pressure.
	0815	18.83	Beginning of hold period; still consuming H ₂ .
	0900	19.58	Slurry Prep Tank opened for inspection. Estimated 68 lb of oxide left behind. No slurry found in transfer line.
	1000	20.58	Cleaning the prep tank by hydroblasting.
	1030	21.08	Still consuming H ₂ . Solids estimate from NDG scan is 42 wt%. Starting to heat the slurry prep tank to drive off the water from hydroblasting.
	1100	21.58	Slurry prep tank temperature above 212°F; purging tank with N ₂ through top and bottom vents.
	2100	31.58	Reactor still vibrating about 0.25 to 0.50". Noticed slurry flow down to 150 gpm, returned it to 225 gpm. Solids estimate from NDG scan is 43.5 wt%; decreasing 10.50 seal flush to thicken to 45 wt%.
	2145	32.33	NDG scan results show reactor profile unstable; lighter on top than bottom, evidence of settling. Assuming 44 wt% catalyst with estimated gas holdup of 25 vol%. (Hindsight note: we believe NDG readings were artificially high, possibly due to vapor channeling, and that true values were closer to 40 wt% and 18 vol% gas holdup.) Increased the seal flush flow rate to 0.06 gpm to stop thickening process and dilute down.
	2250	33.42	Began final temperature ramp.
	2315	33.83	Reactor profile stable. Turned down seal flush flowrate to 0.014 gpm.
	2400	34.58	Slurry sample taken from external loop, looks very thick - comparable to a 50 wt% F21/0E75-44 slurry.

TABLE IV.1

CATALYST REDUCTION RUN ER-05 CHRONOLOGY

<u>Date</u>	<u>Time</u>	Cumulative Time On Reduction <u>Gas (hours)</u>	<u>Notes and Observations</u>
25 Aug 88	0020	34.92	Hydrogen feed line pressure low, backing off feed gas slightly to maintain composition.
25 Aug 88	0100	35.58	Bringing internal heat exchanger into service with external in order to lower the temperature difference between the utility oil and the slurry during the final ramp.
	0700	41.58	Final ramp complete - end of ER-5.

TABLE IV.2

LAPORTE LPMEOH PDU
RUN E-6 OPERATING CONDITIONS

$$V_1 = 0 \text{ ft/sec}$$

<u>Case</u>	<u>P</u> <u>psia</u>	<u>T</u> <u>°F</u>	<u>V_g</u> <u>ft/sec</u>	<u>Slurry</u> <u>Conc.</u> <u>wt% ox.</u>	<u>Hrs. at</u> <u>Condition</u>
E-6A	767	481	0.34	39.0	48
E-6B	767	483	0.56	40.2	12
E-6C	766	482	0.30	39.0	24
E-6D	767	481	0.34	37.7	4
E-6E	767	482	0.28	34.9	24
E-6F	766	482	0.50	36.7	24

D. Discussion of Results

1. Catalyst Evaluation

The cumulative hydrogen uptake for in-situ catalyst activation Run ER-5 is shown in Figure IV.1. The targeted hydrogen uptake value (2.58 SCF/lb cat) was obtained after 26 hours. As stated earlier, however, the reduction flow indication was in error by +10%. When the measured hydrogen consumption was corrected by this amount, the actual hydrogen uptake versus temperature ramp fell below the standard curve which was set in the laboratory. It has been established from earlier work that failing to maintain the hydrogen uptake above the standard curve results in less than full activation even when the target level of hydrogen uptake is achieved. This was confirmed by an autoclave performance test of a sample of the freshly activated catalyst indicated only 75% activation. This less than optimum level of catalyst activity was considered sufficient to continue the operation program.

Gas holdup results for the new alternate slurried catalyst are shown in Figure IV.2 and Table IV.4. The gas holdup with the new catalyst increased with increasing outlet gas velocity and with decreasing catalyst weight percent, as expected. However, the new catalyst had a lower gas holdup than the base catalyst slurry, as shown in Figure IV.2. This decrease in gas holdup was maintained over the entire range of catalyst weight fractions tested.

TABLE IV.3

RUN E-6 CHRONOLOGY

<u>Date</u>	<u>Time</u>	<u>Cumulative Time On Production Gas (hours)</u>	<u>Notes and Observations</u>
25 Aug 88	0700		Final temperature ramp complete for reduction - end of ER-5.
	0755		Cooling reactor to 450°F before introducing syngas.
	0805		Slurry bypass valve 342-S opened; slurry flow to reactor is 190 gpm.
	0825		Beginning reactor isolation - switched from reducing gas to high pressure nitrogen (note: no flow indication on this line).
	0840		Gassed slurry level appears to be at proper level, 193" on the tape. Slurry flow blocked out.
	0900		Stopping gas flow to get ungassed level, level at 171.25" on the tape. Gas holdup at unknown nitrogen flow is 11 vol%; ungassed slurry measurement gives 37 wt% slurry. Using 37 wt% with pre-isolation NDG readings gives 22 vol% gas holdup. (Hindsight note: it is believed that the NDG readings were artificially high, due to channeling and higher gas holdup in the center of the reactor)
	1030		Transferred excess slurry from external loop to slurry prep tank for storage.
	1100		Started syngas feed to reactor.
	1105		Stopped utility oil flow to external heat exchanger.
	1120		Started reactor loop recycle flow.
	1130	0	Reactor feed flowrate is 45,500 SCFH. GC sample of reactor effluent shows 0.1 mol% methanol. Beginning of Run E-6.
	1148	0.30	Began condensed oil return from intermediate oil separator to reactor.
	1200	0.50	Reactor feed flowrate is 90,000 SCFH with a nominal space velocity of 5,000 Sl/hr-kg cat.
	1405	2.58	Reactor effluent methanol concentration is 4 mol%. The expected concentration value at 5,000 Sl/hr-kg cat is 9 mol%.

TABLE IV.3

RUN E-6 CHRONOLOGY

<u>Date</u>	<u>Time</u>	Cumulative Time On Production <u>Gas (hours)</u>	<u>Notes and Observations</u>
25 Aug 88	1430	3.00	Condensed oil return was set too high, and 30 gallons of oil were accidentally added to the reactor. Reaction took off - 6 mol% methanol in effluent. Cut back on oil return rate.
	1900	7.50	Slurry level and oil return rate stabilized; decided to verify the weight percent catalyst and gas holdup numbers by performing a reactor isolation shutdown test.
	1943	8.22	Feed gas to the reactor stopped. NDG scans performed. Change in level was 35.5". Volume change implies 15.2 vol% holdup, versus 16.1 vol% calculated before shutdown. Ungassed slurry density profile gives 38.4 wt% catalyst in reactor with 527 kg catalyst inventory.
	2020	8.22	Restart syngas flow to reactor.
	2330	11.38	Day tank shows methanol level.
	2400	11.88	Calculated methanol production for initial starting period is 760 gallons.
26 Aug 88	0300	14.88	Plant lined out and official start of Case E-6A.
	0400	15.88	Attempted to take slurry sample from reactor, but slurry would not flow.
27 Aug 88	0530	41.38	Reactor temperature swings $\pm 2.5^{\circ}\text{F}$.
	0645	42.63	Methanol production falling off. TPD down to 7.1-7.4. Operators have to increase heat to utility oil flow to keep reaction going.
	2330	59.38	Methanol production dropping off still. A 15°F rise in utility oil temperature over the last 24 hours is needed to maintain reactor temperature.
28 Aug 88	0300	62.88	End of run E-6A. Start ramping up of reactor feed flow to 160,000 SCFH with slurry overflow line open to reduce catalyst inventory.
	0335	63.46	Feed flow at 134,000 SCFH, end of slurry spillover. (Note: shutdown test at 0005 on 31 Aug shows catalyst inventory was reduced to 486 kg.)

TABLE IV.3

RUN E-6 CHRONOLOGY

<u>Date</u>	<u>Time</u>	Cumulative Time On Production	<u>Notes and Observations</u>
		<u>Gas (hours)</u>	
	0350	63.72	Feed flow at 160,061 SCFH, and level at 208" on the tape.
	0500	64.88	Reaction appears to be improving. Gas holdup is 23 vol%. Attempting to take a slurry sample.
	0530	65.38	Sample bomb still cold after 0.50 hour - no flow. Closing up sample system.
	0800	67.88	Flows and temperature lined out. Start of E-6Bp.
	1030	70.38	Reactor temperature dropping.
	1100	70.88	GC analyses results show probable cause of reactor temperature drop was off-spec feed composition; found that hydrogen line pressure is fluctuating. Making moves to correct composition, reactor temperature recovering.
	1200	71.88	Reactor temperature lined out again.
	1600	75.88	<u>Very</u> preliminary production rate, based only on first 8 hours of case, is 8.7 TPD.
	2000	79.88	Reactor feed composition finally lined out to desired CO-Rich composition. End of Run E6-Bp and start of run E6-B.
29 Aug 88	0325	87.30	High MeOH production. 8.28 mol% MeOH in Reactor effluent. Running at 10+ TPD.
	0700	90.88	8.42 mol% MeOH in reactor effluent. There is a concern over running this high of a heat load on the utility oil fin fan cooler with little or no margin for control during potential upsets.
	0800	91.88	End of Run E-6B
	0810	92.05	Started ramping reactor feed down to 150,000 SCFH to help maintain temperature control.
	1135	95.47	Started ramping 27.10 Reactor feed down to 130,000 SCFH because reaction is still taking off.

TABLE IV.3

RUN E-6 CHRONOLOGY

<u>Date</u>	<u>Time</u>	<u>Cumulative Time On Production Gas (hours)</u>	<u>Notes and Observations</u>
29 Aug 88	1205	95.97	27.10 Reactor feed flow at 130,000 SCFH. 9.2 mol% MeOH in reactor effluent and 0.5 mol% MeOH in reactor feed. The PDU is running at a production rate of 10.4 TPD.
	1600	99.88	Decision is made to start decreasing space velocity to 5,600 Sl/hr-kg cat and maintain 38 wt% catalyst concentration for Run E-6C. Target reactor feed rate is 86,500 SCFH.
	1645	100.63	27.10 Reactor feed down to 86,500 SCFH.
	1800	101.88	Reactor temperature stabilizing but H ₂ concentration in feed is high (37 mol%). Making moves to obtain desired composition.
	2000	103.88	Start of Run E-6C. Nominal conditions of CO-Rich feed gas, space velocity of 5,600 Sl/hr-kg cat, 482°F, 750 psig with 38 wt% catalyst concentration. Slurry height is 13 inches below typical full height.
30 Aug 88	2030	104.38	NDG scans taken to estimate weight percent solids and gas holdup. Results show 38.6 wt% catalyst in reactor and 17.5 vol% gas holdup.
	0645	114.63	Calculation of space velocity in the 10 hour balance for Case E-6C shows that the PDU is at 4,672 Sl/hr-kg cat instead of 5,600 Sl/hr-kg cat. Reactor productivity currently running at 91% of autoclave.
	1735	125.47	Charged Intermediate Oil Separator with 45.2 gallons (319 lb) of oil in preparation for slurry dilution.
	2002	127.92	HIC-636 opened to 75%. Dilution started.
	2023	128.27	Reactor pressure drops off due to pressurizing of Primary V/L Separator. 10 gallons of oil charged to reactor so far. Plan to bring pressure back up then finish diluting.
	2030	128.38	Reactor pressure back up to 750 psig. The gas holdup did not change. Slurry level at 208" on tape.

TABLE IV.3

RUN E-6 CHRONOLOGY

<u>Date</u>	<u>Time</u>	<u>Cumulative Time On Production Gas (hours)</u>	<u>Notes and Observations</u>
	2100	128.88	Dilution completed. Beginning of Case E-6D. Three phase gas holdup equation results show dilution to be 37.2 wt% oxide (down from 38.5 wt%) and 17.9 vol% gas holdup.
	2330	131.38	27.10 Reactor effluent showing 9.5 mol% MeOH. This is up from 9.25 mol% MeOH before dilution.
	2400	131.88	End of case E-6D. Preparing for shutdown test.
31 Aug 88	0005	131.97	HV-150-2 closed, no flow to reactor. Shutdown NDG scans done to estimate weight percent solids and catalyst loading.
	0022	131.97	Shutdown test completed. Preparing for dilution down to 36.0 wt% catalyst. Putting 30,000 SCFH of CO-Rich gas once through reactor to maintain agitation during dilution.
	0030	132.10	Shutdown test results confirm 37.0 wt% (486 kg) solids in reactor. HIC-636 opened. Dilution started. Target to bring in 27 gal (191 lb) of oil into reactor.
	0100	132.60	Dilution to 36.0 wt% 1/2 complete with Reactor feed at reading 25,000 SCFH.
	0114	132.83	HIC-636 closed. Oil addition complete. Preparing for spillover of slurry from reactor to Primary V/L Separator.
	0118	132.90	Opening slurry transfer valve 1493-S. Reactor slurry level at 213 inches at start with a target level of 208". Feed gas flow to reactor reading 26,000 SCFH.
	0125	133.02	Slurry level down to 208". Preparing to close slurry transfer valve 1493-S. Feed gas flow to reactor ramped up to 50,000 SCFH.
	0129	133.08	Slurry transfer valve 1493-S will not close. Feed gas flowrate backed down to 40,000 SCFH while attempting to close valve. Reactor temperature at 470°F.

TABLE IV.3

RUN E-6 CHRONOLOGY

<u>Date</u>	<u>Time</u>	Cumulative Time On Production <u>Gas (hours)</u>	<u>Notes and Observations</u>
31 Aug 88	0150	133.43	Slurry transfer valve closed 50%, but still unable to close completely. Preparing to ramp reactor feed flowrate up to 60,000 SCFH and do reactor isolation shutdown test with valve open.
	0200	133.60	Reactor feed flowrate up to 60,000 SCFH. HV-150-2 closed, no flow to reactor. NDG shutdown scans being done.
	0226	133.60	27.10 Reactor shutdown test results show 34.3 wt% oxide in reactor with a catalyst loading of 439 kg oxide. Need 83,250 SCFH feed flow to reactor to obtain Case E6-E nominal space velocity of 5,000 Sl/hr-kg cat. Will continue to spill over with increasing rates.
	0240	133.83	Reactor feed flowrate up to 75,000 SCFH. Opened return oil valve from Intermediate Oil Separator 18" so as not to thicken up slurry while slurry is overflowing through valve 1493-S.
	0243	133.88	Slurry transfer valve 1493-S is closed. Continue ramping feed flowrates up to 83,250 SCFH. (Note: shutdown test at 0400 on 1 Sept shows catalyst inventory was reduced to 403 kg.)
	0400	135.17	Start of case E-6E with nominal conditions of CO-Rich feed gas, space velocity of 5,000 Sl/hr-kg cat, 482°F, and 750 psig. Slurry height is 13 inches below typical full height.
	0530	136.67	10+ mol% MeOH in 27.10 Reactor effluent.
	1515	146.42	Preparing to draw a slurry sample, but no flow.
	1525	146.58	Found methanol in the external slurry loop and 27.13 separator was warm. Checked slurry transfer valve 1493-S and found it was 0.25" open. Methanol may have been condensing in the external loop since 0243 today. Shut valve.
	1555	147.08	Slurry sample loop now flowing, sample drawn.
1 Sept 88	0240	157.84	Added 16 gallons of oil to Primary V/L Separator.

TABLE IV.3

RUN E-6 CHRONOLOGY

<u>Date</u>	<u>Time</u>	Cumulative Time On Production		<u>Notes and Observations</u>
		<u>Gas (hours)</u>		
	0250	158.00		Increase in plant pressure when pumping oil to 27.14 V/L Separator due to cold oil going to Reactor via the 10.52 pump. Slight initial quench in reaction. Purge flowrate went from 3700 SCFH to 5100 SCFH.
	0400	159.17		End of Case E-6E. HV-150-2 closed for reactor isolation shutdown test.
	0435	159.17		Reactor shutdown test results 33.1 wt% oxide in reactor with a catalyst loading of 403 kg oxide. Starting ramping reactor feed flowrate up to 146,000 SCFH to obtain nominal conditions for Case E-6F of 10,000 Sl/hr-kg cat, 33.1 wt% catalyst, 750 psig, and 482°F.
	0600	160.58		Start of Case E-6F.
	1000	164.58		Running smoothly except for change in H ₂ feed line pressure causing slight composition upset and temperature upset of $\pm 3^{\circ}\text{F}$.
2 Sept 88	0130	180.08		NDG scan taken. Results indicate 35 wt% oxide in reactor and 29.8 vol% gas holdup.
	0600	160.58		End of Case E-6F.
	1600	194.58		The partners teleconference results are that the start of Case E-6F be renamed as the start of the catalyst life run E-7. Thus, the nominal conditions for life run E-7 are 482°F, 750 psig, 10,000 Sl/hr-kg cat space velocity, and 35 wt% F21/0E75-43 oxide.

Figure IV.1

ER-5 REDUCTION COMPARISON

Hydrogen Uptake vs Temperature

FIGURE IV.2

LaPORTE PDU THREE PHASE GAS HOLDUP COMPARISON

Run E-6 vs. Run E-5

TABLE IV.4
THREE-PHASE GAS HOLDUP COMPARISON

<u>Catalyst</u>	<u>Case</u>	<u>Inlet Gas Velocity (ft/sec)</u>	<u>Catalyst Weight % (as oxide)</u>	<u>Gas Holdup (vol %)</u>
F21/OE75-43	E-6A	0.34	39.0	17.5
	E-6B	0.56	40.2	28.9
	E-6C	0.30	39.0	17.6
	E-6D	0.34	37.7	18.0
	E-6E	0.28	34.9	19.0
	E-6F	0.50	36.7	30.0
F21/OE75-44	E-5D	0.41	45.0	27.6
	E-5E	0.51	34.1	34.0
	E-5F	0.51	33.9	33.8

For Run E-6, the initial condition of 5,633 sl/kg-hr space velocity at a catalyst loading of 39 wt% achieved only 79% of the predicted autoclave performance. The catalyst productivity improved, however, both with time and with dilution of the catalyst concentration in the slurry. During the seven days of Run E-6, the catalyst concentration was lowered from 39 to 35 wt% and the catalyst productivity increased from 80 to 100% of autoclave performance (Figure IV.3). The cause of the changing reactor performance during the initial stages of Run E-6 is somewhat uncertain, but is possibly due to slowly improving slurry hydrodynamic properties over the course of the run. The best productivity occurred at the end of the run at a high space velocity of 9462 Sl/hr-kg; the earlier, lower space velocity trials had productivities less than the autoclave predictions (Figure IV.4).

A comparison of the baseline and alternate catalysts at equal feed rates and reactor volumes showed that the alternate catalyst will produce 9% more methanol at 35 wt% than the previous catalyst had produced at 40 wt%. The complete run summary is provided in Table IV.5. The alternate catalyst was viewed as the preferred candidate and the run continued, as Run E-7, for a 120-day deactivation study at nominal conditions of 10,000 Sl/kg-hr, 482°F, 750 psig and 35 wt% oxide catalyst.

2. Reactor Internal Heat Exchanger

The overall heat transfer coefficient for the internal heat exchanger was calculated from the Run E-6 utility oil data. Hence, the measured overall heat transfer coefficient was based upon the actual utility oil flowrate, temperature rise, the predicted utility oil heat capacity, and the reactor temperature.

A quantitative comparison of the predicted and measured overall coefficients indicated that the average absolute error was 10.1% for the six cases of Run E-6 and no error was greater than 16% (see Table IV.6 and Figure IV.5). In all

Figure IV.3

RELATIVE PERFORMANCE vs. SLURRY CONCENTRATION

Run E-6, 750 psig, 250°C, CO-rich gas

Figure IV.4

MeOH PRODUCTIVITY vs. SPACE VELOCITY

Run E-6, 750 psig, 250°C, CO-rich gas

Table IV.5

LAPORTE LPMEOH PDU

DATA SUMMARY FOR RUN E-8

Case	Balance Period		Cumulative Hours on Syngas	Temp (deg C)	Pres. (psig)	Inlet Gas Velocity (ft/s)	Space Velocity (/hr-kg)	Slurry Conc. (wt% ox.)	Gas Holdup (vol %)	Catalyst Inventory (kg)	CO Conv. (%)	MeOH Productivity (gmol/hr-kg)	Pct. of Net MeOH Autocl. Production (%)	Net MeOH Production (TPD)
	Date & Time	Gas Type												
E-6A	08/26 0300 - 08/28 0300	CO-Rich	63.5	249.4	751.6	0.34	5633	39.0	17.5	526	12.2	15.3	79	7.10
E-6B	08/28 2000 - 08/29 0800	CO-Rich	92.5	250.4	751.3	0.56	8660	40.2	28.9	486	12.6	23.5	87	10.00
E-6C	08/29 2000 - 08/30 2000	CO-Rich	128.5	250.0	751.2	0.30	4672	39.0	17.6	486	14.4	15.2	91	6.40
E-6D	08/30 2100 - 08/31 0000	CO-Rich	133.5	249.4	751.6	0.34	4661	37.7	18.0	486	14.7	15.1	90	6.40
E-6E	08/31 0400 - 09/01 0400	CO-Rich	157.5	250.1	751.9	0.28	5327	34.9	19.0	403	15.0	17.7	95	6.20
E-6F	09/01 0600 - 09/02 0600	CO-Rich	181.5	250.1	751.2	0.50	9462	36.7	30.0	403	13.6	28.7	100	10.00

Figure IV.5

OVERALL COEFFICIENT vs. SUPERFICIAL GAS VELOCITY

Run E-6, 27.10B Internal Heat Exchanger

cases the uncertainty in the measured coefficients was low from a propagation of errors analysis, at approximately 11%. Hence, the predictions of the overall coefficients, using the Sieder-Tate and Deckwer correlations, were accurate within the range of uncertainty of the plant data.

TABLE IV.6

27.10B INTERNAL HEAT EXCHANGER COEFFICIENTS
(Btu/hr-ft²-°F)

Case Catalyst Conc. (wt%)	<u>E6A</u>	<u>E6B</u>	<u>E6C</u>	<u>E6D</u>	<u>E6E</u>	<u>E6F</u>
	39.0	40.2	39.0	37.7	34.9	36.7
<u>Overall Coefficient</u>						
Predicted	93.9	92.8	90.9	93.7	90.0	91.1
Measured	101.5	88.2	76.5	101.5	77.3	82.7
Percent Error	8.1	-4.9	-15.8	8.3	-14.2	-9.2
<u>Slurry Side Coefficients</u>						
Predicted	285.7	324.5	274.2	284.4	265.2	310.2
Measured	370.0	274.5	175.0	370.0	178.5	230.8
Percent Error	29.5	-15.4	-36.2	30.1	-32.7	-25.6

These uncertainties in the propagation of error analysis were based on generously assumed uncertainties in the physical readings and properties of 0.5% in the heat exchanger area, 5.0% in the utility oil heat capacity, 10.0% in the utility oil flowrate, 1.0% in both the utility oil temperature change and the log mean temperature across the heat exchanger, and 15.0% in the predicted internal tube-side heat transfer coefficient.

For the commercial scaleup of the LPMEOH process technology, a precise method of prediction for the shell-side coefficient of the reactor internal heat exchanger is needed. The measured shell-side coefficient was backed out from the measured overall coefficient and then compared to the values predicted by the Deckwer correlation. Although the reactor internal heat exchanger was originally designed as shell-side controlled, plant operating conditions resulted in tube-side controlled heat transfer. As a result, the calculated shell-side coefficient is considerably less accurate than the overall coefficient.

When the predicted shell-side heat transfer coefficients were plotted versus the superficial gas velocity, a band of curves was produced (Figure IV.6). These curves were based upon the average conditions of the six cases. Using slurries of 30 to 50 wt% oxide, the predicted coefficients ranged from 202 to 220 Btu/hr-ft²-°F at 0.10 ft/sec, to 340 to 370 Btu/hr-ft²-°F at 0.80 ft/sec. The average error between the calculated and predicted shell-side coefficients was 28.3%. Although the predicted values were confined to a thin band, the calculated coefficients were scattered on either side. The most accurate coefficients occurred in cases B and F. Significantly, both cases had high methanol production rates and consequently high heat transfer rates.

Figure IV.6

SHELL-SIDE COEFFICIENT vs. SUPERFICIAL GAS VELOCITY

Run E-6, 27.10B Internal Heat Exchanger

The shell-side (slurry-side) heat transfer coefficient was backed out from the overall coefficient using the predicted tube-side heat transfer coefficient, which was calculated from the Sieder-Tate equation. The predicted shell-side heat transfer coefficients were calculated using the Deckwer correlation for heat transfer in slurries (Deckwer 1980).

$$St = \beta * (ReFrPr^2)^{-0.25}$$

where $St = h_o / (\rho * c_p * u_g)$
 $\beta = 0.10$

Methanol Composition

Typical methanol composition for Run E-6 is shown in Table IV.7. The methanol purity averaged 96 wt%, and the water impurity remained below 0.7 wt%. The balance was primarily higher alcohols. The additional demister, installed in the intermediate V/L separator prior to run E-6, was responsible for reducing the oil impurity in the methanol product from 0.6 wt% in Run E-5 to 0.2 wt% in Run E-6. There was no secondary oil phase observed during any part of the operating campaign.

TABLE IV.7

LAPORTE LPMEOH PDU

TYPICAL METHANOL COMPOSITIONS FOR RUN E-6

CASE:	<u>E-6A</u>	<u>E-6B</u>	<u>E-6C</u>	<u>E-6D</u>	<u>E-6E</u>	<u>E-6F</u>
GAS TYPE	CO-Rich	CO-Rich	CO-Rich	CO-Rich	CO-Rich	CO-Rich
Slurry Conc. (wt% ox.)	39.0	40.2	39.0	37.7	34.9	36.7
Space Velocity (SI/hr-kg)	5,633	8,660	4,672	4,661	5,327	9,462

METHANOL COMPOSITION (wt%):

Methanol	95.18	95.61	96.64	95.19	96.01	96.70
Water	0.58	0.50	0.69	0.58	0.43	0.53
Dimethyl ether	0.10	0.08	0.06	0.10	0.08	0.05
Methyl formate	0.96	1.00	0.78	0.96	0.88	0.80
Methyl acetate	0.41	0.37	0.20	0.41	0.34	0.22
Ethanol	1.22	1.11	0.75	1.22	1.04	0.79
Iso-propanol	0.02	0.02	0.00	0.02	0.01	0.00
N-propanol	0.52	0.46	0.29	0.52	0.43	0.31
Sec-butanol	0.05	0.04	0.03	0.05	0.04	0.03
Isobutanol	0.10	0.08	0.05	0.10	0.08	0.05
N-butanol	0.25	0.22	0.16	0.25	0.22	0.16
2&3-Pentanol	0.05	0.04	0.00	0.05	0.02	0.00
Isopentanol	0.08	0.07	0.05	0.08	0.07	0.05
1-Pentanol	0.14	0.13	0.09	0.14	0.12	0.09
Oil	0.34	0.27	0.21	0.34	0.23	0.22
Mol wt of product	32.56	32.52	32.28	32.56	32.48	32.34

4. Conclusions

During catalyst reduction, the actual hydrogen uptake ramp was below the standard curve due to 10% high gas flowrate measurements; as a result, the catalyst was only 75% activated.

During Run E-6, the catalyst productivity improved with time and dilution of the slurry. The best productivity (100%) relative to the autoclave occurred at a space velocity of 9462 SI/hr-kg cat. The new catalyst produced 9% more methanol in 35 wt% slurry than the previous catalyst in 40 wt% slurry. Hence, the new catalyst became the preferred choice for the subsequent activity maintenance run.

On average, the overall heat transfer coefficients for the reactor internal heat exchanger were predicted within 10.1%, but the shell-side coefficients were accurate only within 28.3%. The best accuracy was found in cases B and F at high heat transfer rates.

The oil impurity in the product methanol was reduced from 0.6 to 0.2 wt% due to the installation of the new demister. Methanol concentration in the product averaged 96 wt%.

V. CATALYST ACTIVITY MAINTENANCE RUN E-7

A. Introduction

The alternate catalyst was viewed as the preferred candidate and the run was continued, as E-7, for a 120-day deactivation study at nominal conditions of 10,000 sl/kg-hr, 482°F, 750 psig and 35 wt% oxide catalyst. The main objective of this run was to measure and evaluate catalyst deactivation under extended operations. Other goals included evaluation of on-stream catalyst addition and withdrawal, reactor load following, and internal heat exchanger performance.

B. Methanol Synthesis Operation

The PDU accumulated over 3100 hours of methanol synthesis operation during this catalyst life run E-7. Table V.1 lists the Run Chronology for the operating period of Run E-7.

The gradual increase in gas holdup observed in Run E-6 continued during the first 20 days of Run E-7. This elevation in gas holdup from 30 to 34 vol% resulted in a corresponding increase in the catalyst slurry concentration from 36.7 to 37.8 wt% (see Figure V.1). The performance of the PDU during this period was excellent and the catalyst productivity was maintained at 100% of autoclave predictions.

The initial methanol production rate in Run E-7 was slightly in excess of 10 TPD. As shown in Figure V.2, this was twice the initial production rate of previous catalyst life runs at equivalent conditions. There were primarily two reasons for the doubling in the methanol production rate. The first was the reported higher activity of the alternate catalyst. The second, and more significant reason, was the ability of the new reactor to operate with a more concentrated slurry. After 120 days of operation, the methanol production rate was still in excess of 8 TPD.

The PDU operated at the nominal steady run conditions for 109 of the 126 days of the run. The reactor was shut down between 15 and 18 September due to Hurricane Gilbert, and production was scaled down between 23 and 28 October due to reduced feed gas availability from the adjacent Air Products synthesis gas plant. Shutdown, startup, and ramping were all performed simply and without loss of product quality on these two occasions and during other short-term interruptions of service.

Load-following tests occurred from 19 to 22 December with rapid ramping of feed gas flow. Up to 80% decreases in gas flow were accomplished with temperature variances of 5°F or less in the reactor. Ramping rates as great as 16%/min were accomplished without incident. On 29 December, 54.2% of the catalyst slurry was withdrawn from the reactor and fresh catalyst slurry was added back to the reactor. The catalyst changeout was accomplished smoothly and the PDU returned to steady run conditions within 25 hours. The run continued smoothly after the changeout.

TABLE V.1

RUN E-7 CHRONOLOGY

<u>Date</u>	<u>Time</u>	Cumulative Time On Production <u>Gas (hours)</u>	<u>Notes and Observations</u>
1 Sept 88	0600	160.6	Start of Case E-6F.
	1000	164.6	Running smoothly except for change in H ₂ feed line pressure causing slight composition upset and temperature upset of $\pm 3^{\circ}\text{F}$.
2 Sept 88	0130	180.1	NDG scan taken. Results indicate 35 wt% oxide in reactor and 29.8 vol% gas holdup.
	0500	183.6	Reactor gas holdup is increasing slowly.
	1600	194.6	The partners teleconference decided that the start of Case E-6F be renamed as the start of the catalyst life run E-7. Thus, the nominal conditions for life run E-7 are 482°F, 750 psig, 10,000 Sl/hr-kg cat space velocity, and 35 wt% F21/OE75-43 oxide.
3 Sept 88	0900	211.6	NDG Scan shows that gas holdup is still increasing. The 2 Sept 88 average was 30.5 vol% with the weight percent solids of 35.6 wt%. This scan shows a 31.7 vol% gas holdup and a weight percent solids of 36.1 wt%.
	1030	213.1	Analyses of the slurry prep tank atmosphere showed 7 mol% H ₂ , 20 mol% CO, and the remainder N ₂ . Identified three valves which will be blocked off with blinds to stop leakage of H ₂ and CO into tank. It should be noted that the stored catalyst slurry in the slurry prep tank has seen some syngas.
	1200	214.6	GC #1 appears to be malfunctioning. Lab personnel investigating.
	1230	215.1	Slurry valve between reactor and primary vapor/liquid separator was greased and attempted to be shut tighter. It appeared that there was a slight leak of slurry from the reactor to the separator.
4 Sept 88	0300	229.6	NDG scan shows gas holdup to be stabilizing.
	1100	237.6	Slurry prep tank pumped with H ₂ and N ₂ .
5 Sept 88	1100	261.6	PDU running stable.

TABLE V.1

RUN E-7 CHRONOLOGY

<u>Date</u>	<u>Time</u>	<u>Cumulative Time On Production Gas (hours)</u>	<u>Notes and Observations</u>
6 Sept 88	0700	281.6	Preliminary results for first five days of Run E-7 show the percent methanol in the reactor effluent has been holding at 8.8 mol% with a reactor feed rate of 138,000 SCFH of CO-Rich gas, methanol production is 10.0 TPD, and the PDU reactor is running at 101% of autoclave.
	1400	288.6	Blinds swung on the valves to slurry prep tank that were identified on 3 Sept 88 to isolate tank from syngas loop. Prep tank will be pressurized with H ₂ and N ₂ and will be analyzed within two days for presence of syngas.
	1500	289.6	Added 100 gallons of Drakeol-10 oil to Primary Vapor/Liquid Separator from process oil storage vessel.
7 Sept 88	1200	310.6	PDU continued smooth operation over the last 24 hours.
8 Sept 88	1000	332.6	Run E-7 continues to go smoothly. The stable methanol production over the past 7 days indicates a low catalyst deactivation rate.
	1200	334.6	GC's off line for 9 hours today to install oxygen traps on the nitrogen carrier gas lines.
9 Sept 88	1100	357.6	Smooth operation continues. Production of methanol is holding steady at 10.2 TPD.
10 Sept 88	1300	383.6	Feed gas trip to reactor due to malfunctioning thermocouple in reactor.
	1330	383.6	Normal feed flow to the reactor returned.
	2100	391.1	GC #1 erratic again.
11 Sept 88	0230	396.6	32.3 gal of oil added to the Intermediate Oil Separator.
12 Sept 88	1400	432.1	Production of methanol steady at 10.1 TPD. All process conditions steady as well.
13 Sept 88	0900	451.1	Methanol production holding steady with no apparent signs of catalyst deactivation.

TABLE V.1

RUN E-7 CHRONOLOGY

<u>Date</u>	<u>Time</u>	<u>Cumulative Time On Production Gas (hours)</u>	<u>Notes and Observations</u>
14 Sept 88	1200	478.1	New controller installed in GC #1. GC #1 put back on line.
	1500	481.1	Bumped recycle up to increase total feed to 145,600 SCFH. Fresh feed is 37,000 SCFH.
15 Sept 88	1300	503.1	Production of methanol continues at 10.0 TPD.
	1500	505.1	Preparations begin for Hurricane Gilbert.
	1615	506.3	Gas flow to reactor stopped.
	1700		Reactor depressurization. Reaction bed temperature maintained with utility oil heater.
	1840		Begin purging syngas from reactor.
	2050		Reactor purged. Began decreasing slurry temperature from 470°F to 295°F with 1 mol% H ₂ in N ₂ .
	2215		Reactor pressurized to 285 psig and 295°F with N ₂ . Reactor isolated.
17 Sept 88	0800		Started N ₂ feed of 6000 SCFH to reactor via reduction gas circuit after 33 hour isolation period. Heating reaction bed to 200°F.
18 Sept 88	0600		Beginning to ramp up reactor to 300°F on N ₂ feed.
	0930		Reactor at 300°F. Switching to reduction gas of 1 mol% H ₂ in N ₂ .
	1215	506.3	Reactor at 465°F. Blending syngas into feed.
	1220	506.4	Started once thru syngas feed at 15,000 SCFH.
	1300	507.1	Reactor at 482°F and 750 psig.
	1330	507.6	Recycle gas flow restarted.
	1800	512.1	Reactor lined out at pre-shutdown conditions. The total time not on syngas for this shutdown period was 68 hours.
19 Sept 88	0800	526.1	GC #1 still stopping intermittently.

TABLE V.1

RUN E-7 CHRONOLOGY

<u>Date</u>	<u>Time</u>	<u>Cumulative Time On Production Gas (hours)</u>	<u>Notes and Observations</u>
20 Sept 88	0000	542.1	HYCO steam outage caused the CO ₂ composition in the feed to fall from 13 mol% to 7.4 mol%. Outage continues for 1 hour.
	0930	551.6	Methanol production at 9.9 TPD.
21 Sept 88	1200	578.1	Production down due to fluctuating line pressure from the HYCO plant.
	1725	583.5	30 gal of oil added to the Intermediate Oil Separator.
22 Sept 88	0100	591.1	HYCO cut the CO feed pressure.
	0130	591.5	Reactor feed flow reduced to 72,000 SCFH.
	0600	596.1	Feed gas flow returned to 145,000 SCFH.
	0900	599.1	GC #1 continuing to power down.
23 Sept 88	0830	622.6	Run E-7 continued smoothly with methanol production at 9.7 TPD, indicating possible catalyst deactivation.
24 Sept 88	0930	647.6	Demister pressure drop up to 3.5 psi. Will be bypassed when drop is 4 psi.
25 Sept 88	0045	662.8	Demister bypass opened 2 rounds. Pressure drop falls from 4 to 2.88 psi
	2000	682.1	Demister bypass opened to 3 rounds.
26 Sept 88	0800	694.1	Over the last three days, methanol production constant at 9.95 TPD. Catalyst is slowly deactivating.
	1030	696.6	40 gal of oil added to Intermediate Oil Separator.
	1400	700.1	All flow to demister diverted through bypass. 27.10 Demister blocked in.
27 Sept 88	0830	718.6	GC #1 on stream for 24 hours with SOLA transformer. Oil samples taken at the Slurry Carryover Surge Pot (black) and at the Intermediate Oil Separator (clear).
	0930	719.6	Demister washed for 8 minutes.
	0940	719.8	All flow sent through the Demister. Bypass closed, pressure drop of 2.56 psi.

TABLE V.1

RUN E-7 CHRONOLOGY

<u>Date</u>	<u>Time</u>	<u>Cumulative Time On Production Gas (hours)</u>	<u>Notes and Observations</u>
27 Sept 88	2000	730.1	Oil return rate to reactor determined to be 0.232 gpm over 8 hours.
28 Sept 88	0530	739.6	Demister pressure drop increased rapidly to 3.2 psi from 2.85 psi, then quickly dropped back to 2.53 psi.
	0800	742.1	Demister taken off line due to concerns over sudden pressure drop changes that may indicate the Demister support rings are broken.
29 Sept 88	0830	766.6	Intermediate Oil Separator oil sample was murky black and contained catalyst.
	1000	768.1	Production rate of 9.6 TPD. Drop in production caused by inaccurate GC data and HYCO line pressure fluctuations. Average oil return rate to reactor was 0.226 gpm over 24 hours. Oil return was 0.973 wt% methanol.
	1100	769.1	Intermediate Oil Separator temperature set to 260°F. Production falls to 9.59 TPD.
30 Sept 88	0830	790.6	Intermediate Oil Separator samples becoming increasingly thick and black.
	1000	792.1	Methanol production 9.73 TPD.
1 Oct 88	0830	814.6	Production down to 9.47 TPD due to increased methanol in the oil return.
	1300	819.1	Carbonyl numbers checked and found to be stable over last 10 days at 3-4 ppb Ni and 1-2 ppb Fe.
	1330	819.6	Intermediate Oil Separator samples increasingly filled with catalyst since demister taken out of service. They now resemble Slurry Surge Pot samples.
2 Oct 88	0830	838.6	Production picked up to 9.60 TPD.
3 Oct 88	0830	862.6	Catalyst reported on Oil Condensate Pump shafts.
	0900	863.1	Methanol production 9.59 TPD.
	0950	864.0	Intermediate Oil Separator temperature reset to 270°F to improve methanol production.

TABLE V.1

RUN E-7 CHRONOLOGY

<u>Date</u>	<u>Time</u>	<u>Cumulative Time On Production Gas (hours)</u>	<u>Notes and Observations</u>
3 Oct 88	1000	864.1	Upper spray nozzles of Cyclone Separator opened to knock more slurry out of outlet gas.
4 Oct 88	0930	887.6	Intermediate Oil Separator samples considerably clearer with spray nozzles open.
	2330	901.6	Methanol production was 9.61 TPD today.
5 Oct 88	0000	902.1	GC #1 malfunctioned resulting in erroneous compositions
	1030	912.6	Run E-7 running smoothly with methanol production at 9.51 TPD.
	1400	916.1	GC #1 functioning properly after its electronic controller was replaced.
6 Oct 88	0930	935.6	Production and outlet methanol concentration up slightly to 9.61 TPD and 8.07 mol%, respectively.
	1645	942.8	Product Separator level controller determined to be bad, causing fluctuations in inventory.
	1720	943.5	Reactor temperature over 486°F for 20 minutes and swinging greatly.
7 Oct 88	0845	958.8	Production down to 9.52 TPD due to fluctuations in Product Separator inventory, but outlet methanol concentration up to 8.21 mol%. GC #1 working reliably.
	0930	959.6	Pinhole leak found in the rupture disk at the Internal Heat Exchanger outlet.
	1025	960.6	Began cooling reactor to 440°F.
	1110	961.3	Reactor temperature is 430°F. Feed gas flow to reactor stopped.
	1220		Reactor depressurized to 107 psig. N ₂ /H ₂ started through reduction gas circuit.
	1240		Reduction gas (1.5 mol% H ₂) flow of 20,000 SCFH to reactor at 200°F.
	1305		Gas flow stopped.
	1330		Rupture disk pulled. Teflon liner had deteriorated.

TABLE V.1

RUN E-7 CHRONOLOGY

<u>Date</u>	<u>Time</u>	<u>Cumulative Time On Production Gas (hours)</u>	<u>Notes and Observations</u>
7 Oct 88	1410		Utility oil circulating, reheating slurry.
	1455		Reduction gas flow restarted at 20,000 SCFH.
	1725	961.3	Once through syngas feed started to reactor.
	1845	962.6	Recycle gas flow started.
	2100	964.8	Reactor feed at 144,000 SCFH. Conditions stabilized.
8 Oct 88	0630	974.3	Cumulative methanol production topped 100,000 gallons today. GC #1 and Product Separator level controller working well.
9 Oct 88	1200	1003.8	Run E-7 continued smoothly. Production better than pre-shutdown levels, 9.68 TPD.
	1930	1011.3	A 10 minute swing in plant pressure and loop flows was caused by malfunctioning CO ₂ controller which allowed CO ₂ to buildup in the loop and resulted in a 15,000 SCFH high purge rate. CO ₂ feed put on manual control, but several hours were necessary to return CO ₂ compositions to normal.
10 Oct 88	1300	1028.8	40 gal of oil added to Intermediate Oil Separator.
11 Oct 88	0830	1048.3	Production at 9.51 TPD of methanol.
	1400	1053.8	GC numbers for carbonyls remained good, 4.5 ppb Ni, <2 ppb Fe.
12 Oct 88	0830	1072.3	Methanol production at 9.53 TPD.
	1300	1076.8	Added 30 gal of Drakeol 10 to Intermediate Oil Separator.
13 Oct 88	0845	1096.6	Methanol production at 9.59 TPD.
	1200	1099.8	Intermediate Oil Separator temperature gradually increased to 280°F.

TABLE V.1

RUN E-7 CHRONOLOGY

<u>Date</u>	<u>Time</u>	Cumulative Time On Production <u>Gas (hours)</u>	<u>Notes and Observations</u>
14 Oct 88	0830	1120.3	Intermediate Oil Separator samples appear good - grey and translucent.
	0900	1120.8	Production increased to 9.65 TPD, but most of this increase was due to changes in the inventories of the methanol accumulators stemming from the installation of a new FQ-241 controller.
15 Oct 88	0800	1143.8	PDU running well. Production down slightly to 9.41 TPD, probably due to lower flow rates.
16 Oct 88	0830	1168.3	Production steady at 9.39 TPD. Intermediate Oil Separator samples still appear good.
17 Oct 88	0800	1191.8	Production at 9.37 TPD of methanol.
18 Oct 88	0845	1216.6	Methanol production at 9.39 TPD.
19 Oct 88	1045	1242.6	Production steady at 9.36 TPD. Methanol outlet composition was 8.03 mol%.
	1500	1246.8	Replaced level transmitter on the Product Separator
20 Oct 88	1230	1268.3	Both the methanol outlet concentration and the daily production were down to 7.98 mol% and 9.19 TPD, respectively.
21 Oct 88	1700	1296.8	Methanol density calculation changed, will result in 1% 'loss' in production.
	2130	1301.3	Steady operation with production of 9.29 TPD.
22 Oct 88	1300	1316.8	Both GC's went down.
	1530	1319.3	Both GC's put on line.
23 Oct 88	1000	1337.8	Deactivation continuing with methanol production declining to 9.35 TPD, and methanol outlet concentration to 7.91 mol%.
	1630	1344.3	PDU shut down to install auxiliary inlets on the main cooling water lines in preparation for the shutdown of HYCO-1 cooling tower.
	1830		Temporary lines now available to HYCO-2 cooling tower.

TABLE V.1

RUN E-7 CHRONOLOGY

<u>Date</u>	<u>Time</u>	Cumulative Time On Production <u>Gas (hours)</u>	<u>Notes and Observations</u>
23 Oct 88	1900	1344.3	Syngas feed to reactor initiated.
	2000	1345.3	PDU reactor lined out.
	2100	1346.3	Switched to alternate cooling water supply. Unable to keep vapor exiting Product Separator below 100°F.
24 Oct 88	0100	1350.3	Shut down PDU until morning. Switching feed to reduction gas.
	1730		Installation of booster pump on the alternate cooling water supply completed.
	1815		Reactor temperature being increased to 450°F.
	1915	1350.3	Once through CO rich gas feed to the reactor.
	2130	1351.6	Started recycle gas flow.
	2330	1353.6	Process lined out.
25 Oct 88	0700	1361.1	Operation of Product Gas Cooler marginal due to low cooling water supply pressure. Product flow temperature averaged 10°F high. As a result of this inability to condense methanol, production dropped to 9.1 TPD.
	1300	1367.1	Reactor feed rate reduced to 72,800 SCFH to decrease system temperatures.
	1400	1368.1	PDU lined out at new conditions which will be maintained until HYCO-1 cooling tower is back in service.
26 Oct 88	0600	1384.1	Cooling reactor for shutdown.
	0645	1384.8	Depressurizing reactor.
	0730	1385.6	Reduction gas flow to reactor begun.
	0800		Daily production rate of 5.63 TPD, 100% of autoclave at current low space velocity of 4748 Sl/hr kg.
	1320		Power returned to PDU.
27 Oct 88	0930	1385.6	CO rich gas feed resumed in OTM mode.
	1100	1387.1	Recycle flow begun.

TABLE V.1

RUN E-7 CHRONOLOGY

<u>Date</u>	<u>Time</u>	<u>Cumulative Time On Production Gas (hours)</u>	<u>Notes and Observations</u>
27 Oct 88	1330	1389.6	PDU lined out at 72,800 SCFH feed due to restricted cooling water supply.
28 Oct 88	0900	1409.1	Methanol outlet concentration at 9.84 mol%. Productivity was 97% of autoclave.
	1800	1418.1	Normal cooling water service returned.
29 Oct 88	0800	1432.1	Bringing reactor up to full feed flow.
	1100	1435.1	PDU lined out at 10,000 GHSV. Reactor had been run for 38 continuous hours at nominal 5000 GHSV.
30 Oct 88	1800	1466.1	Due to low CO ₂ tank pressure, the CO ₂ feed concentration dropped to 10.7 mol%.
	2100	1469.1	Normal production rates of 9.1 TPD recovered. Outlet concentration of methanol running 7.7 mol%.
31 Oct 88	0530	1477.6	CO ₂ tank refilled. CO ₂ feed concentration returned to 12.5 mol%.
	0900	1481.1	Change in feed gas composition did not affect methanol production which remained at 9.0 TPD or outlet concentration at 7.7 mol%.
1 Nov 88	0800	1504.1	Production rate steady at 9.0 TPD, but the methanol concentration in the reactor effluent dropped to 7.5 mol%. The current deactivation rate for both production and concentration was 0.2%/day. Over the past week, both dropped about 2%, probably due to changing feed gas compositions resulting from recycle of lower conversion outlet gas.
2 Nov 88	1130	1531.6	Production and concentration steady.
3 Nov 88	0900	1553.1	Intermediate Oil Separator sample was darker but still transparent.
	1000	1554.1	Production rate and methanol concentration in the reactor effluent were 8.9 TPD and 7.6 mol%, respectively.
4 Nov 88	1100	1579.1	Operating smoothly with methanol production of 8.9 TPD.
5 Nov 88	0800	1600.1	Production at 8.96 TPD.

TABLE V.1

RUN E-7 CHRONOLOGY

<u>Date</u>	<u>Time</u>	<u>Cumulative Time On Production Gas (hours)</u>	<u>Notes and Observations</u>
5 Nov 88	1230	1604.6	Intermediate Oil Separator operating temperature reduced to 260°F.
6 Nov 88	0800	1624.1	Methanol production was 9.06 TPD.
7 Nov 88	0800	1648.1	Concentration of methanol in reactor effluent continued its slow decline. Methanol production was 9.00 TPD.
8 Nov 88	0830	1672.6	Methanol production rate down to 8.86 TPD.
	1500	1679.1	Feed gas pressure transmitter bad for 2 hours until card changed.
9 Nov 88	0900	1697.1	Operating smoothly with production of 8.89 TPD of methanol.
10 Nov 88	0800	1720.1	Production rate down slightly to 8.86 TPD.
	1400	1726.1	Computer crashed, down for 2 hours. No balances for this period.
11 Nov 88	0800	1744.1	Steady operation with 8.85 TPD production of methanol.
12 Nov 88	0800	1768.1	Production rate steady at 8.86 TPD. Methanol effluent concentration was 7.64 mol%.
	1230	1772.6	Oil in methanol product leveled at 0.10 wt%, a 38% drop in one week due to the decrease in the Intermediate Oil Separator temperature.
13 Nov 88	0800	1792.1	Methanol production 8.82 TPD, concentration 7.60 mol%.
14 Nov 88	0800	1816.1	Production continued at a rate of 8.84 TPD.
	1444	1822.8	All gas flow to the reactor stopped. Three nuclear density gauge scans were taken to verify catalyst loading in the reactor.
	1503	1822.8	Gas flow to reactor reinstated. Catalyst loading determined to be 393.7 kg, as expected.
15 Nov 88	0800	1839.8	PDU recovered quickly from previous day's interruption of feed gas. Production quickly returned to 8.84 TPD with methanol concentration of 7.64 mol%.

TABLE V.1

RUN E-7 CHRONOLOGY

<u>Date</u>	<u>Time</u>	Cumulative Time On Production <u>Gas (hours)</u>	<u>Notes and Observations</u>
16 Nov 88	0830	1864.3	Methanol production dropped slightly to 8.79 TPD.
	1330	1869.3	Plant temperatures fluctuated as cold weather arrived.
	1500	1870.8	Temperatures under control.
17 Nov 88	0830	1888.3	Due to weather change, methanol concentration dropped to 7.40 mol%. Production at 8.90 TPD.
	0843	1888.6	Feed gas to the reactor stopped. Feed gas compressor drive belts were tightened.
	0925	1888.6	Feed gas flow to the reactor resumed.
	1000	1889.1	Flows and temperatures constant throughout process. Only 42 minutes off syngas.
	1300	1892.1	Computer down for 1 hour.
18 Nov 88	0900	1912.1	Methanol production virtually unchanged at a daily rate of 8.87 TPD.
19 Nov 88	0830	1935.6	PDU producing 8.78 TPD of methanol with the reactor effluent 7.62 mol% methanol.
20 Nov 88	0830	1959.6	Methanol production steady at 8.80 TPD.
21 Nov 88	0830	1983.6	PDU methanol production rate was 8.86 TPD. Reactor effluent methanol concentration was 7.46 mol%.
22 Nov 88	0830	2007.6	PDU performed at the same levels it had for the previous 3 weeks.
23 Nov 88	0730	2030.6	Production rate was 8.83 TPD. Reactor effluent was 7.44 mol% methanol.
24-28 Nov 88			PDU ran smoothly.
29 Nov 88	0830	2175.6	Daily production average was 8.73 TPD.
30 Nov 88	0900	2200.3	Methanol production up slightly to 8.77 TPD. Reactor effluent was 7.39 mol% methanol.
1 Dec 88	0705	2222.4	Relay malfunction caused shutdown trip. Feed gas flow interrupted and utility oil heater stopped.
	0720	2222.4	Feed gas flow returned.

TABLE V.1

RUN E-7 CHRONOLOGY

<u>Date</u>	<u>Time</u>	<u>Cumulative Time On Production Gas (hours)</u>	<u>Notes and Observations</u>
1 Dec 88	0800	2223.1	Normal operating conditions restored.
	0945	2224.8	Intermediate Oil Separator operating temperature lowered to 250°F.
2 Dec 88	0845	2247.8	Methanol production was 8.69 TPD. Concentration in reactor effluent was 7.25 mol%.
3 Dec 88	0815	2271.3	Production at 8.59 TPD.
4 Dec 88	1100	2298.1	Lab temperature discovered to be out of control for at least 2 hours, causing GC baselines to drift.
	1200	2299.1	Lab temperature returned to normal.
	1400	2301.1	Normal GC operation restored.
5 Dec 88	0815	2319.3	PDU running smoothly with daily production level of 8.61 TPD.
	1200	2323.1	40 gal of Drakeol 10 added to the Intermediate Oil Separator.
6 Dec 88	0840	2343.7	Methanol production essentially unchanged. Data analysis indicated that the catalyst activity was exhibiting an exponential decay with respect to cumulative methanol production.
7 Dec 88	0940	2368.7	Methanol production rate averaged 8.61 TPD over the last 24 hours.
	1030	2369.6	Total power failure in LaPorte HYCO facility shut down methanol unit.
	1100		Power restored but no feed gas from HYCO.
	1130		Plant held at 115 psig and 360°F with a slow N ₂ purge for 4.5 hours.
	1600		Reactor reheating begun.
	1810		N ₂ purge replaced with 5,000 SCFH of reduction gas.
	1950	2369.6	Once through syngas fed to reactor.
	2030	2370.3	Recycle gas flow started.
	2200	2371.8	Normal operating conditions restored.

TABLE V.1

RUN E-7 CHRONOLOGY

<u>Date</u>	<u>Time</u>	<u>Cumulative Time On Production Gas (hours)</u>	<u>Notes and Observations</u>
8 Dec 88	1030	2384.3	PDU once again successfully recovered from an unplanned outage. Production back to 8.68 TPD.
	1400	2387.8	Latest carbonyls numbers were good, Ni 5.1 ppb or less, Fe <1 ppb.
9 Dec 88	0830	2406.3	Methanol production at 8.47 TPD, effluent concentration at 7.15 mol%.
10-11 Dec 88			Plant ran without incident.
12 Dec 88	0830	2478.3	Rate of methanol production was 8.45 TPD.
13 Dec 88	0800	2501.8	Methanol production and reactor effluent concentration down slightly to 8.41 TPD and 7.11 mol%, respectively.
14 Dec 88	0900	2526.8	Catalyst continuing to deactivate normally with production at 8.31 TPD.
15 Dec 88	0900	2550.8	PDU running smoothly at 8.36 TPD of methanol.
	1702	2558.8	Life run E-7 achieved 100 days on synthesis gas.
16 Dec 88	1030	2576.3	Methanol production was 8.3 TPD over the past 24 hours. The production has been decreasing at a rate of 0.19%/day over the 100 days of this run.
17 Dec 88	0430	2594.3	CO ₂ control valve went wide open causing the CO ₂ level in the reactor loop to be high (16 mol%) for about 2 hours.
	0630	2596.3	Normal CO ₂ levels restored. Upset caused no observable change in productivity.
	1100	2600.8	Daily production rate was 8.38 TPD.
18 Dec 88	1000	2623.8	PDU ran flawlessly, 8.34 TPD methanol production.
19 Dec 88	1200	2649.8	Oil condensation temperature raised to 260°F in preparation for ramping tests. Methanol production at 8.27 TPD.
	1500	2652.8	Began ramping space velocity down from 9700 to 2000 at a rate of 0.44%/min.
	1800	2655.8	Space velocity 2000.

TABLE V.1
RUN E-7 CHRONOLOGY

<u>Date</u>	<u>Time</u>	Cumulative Time On Production <u>Gas (hours)</u>	<u>Notes and Observations</u>
19 Dec 88	1900	2656.8	Methanol in effluent at 11 mol%. The 80% reduction in feed gas flow caused a 67% reduction in methanol production.
	1910	2657.0	Began rapidly ramping up space velocity at a rate of 3.5%/min.
	1933	2657.3	PDU stable at 9700 GHSV. Ramping accomplished keeping reactor temperature within 4°F of 482°F.
20 Dec 88	0815	2670.1	Started next ramping test. Feed gas flow being dropped from 145,000 SCFH at a rate of 2%/min.
	0855	2670.8	Attained 29,000 SCFH feed flow. Uneventful ramp with steady temperature.
	1605	2677.8	Began ramp up. Methanol concentration in the reactor effluent rose from 6.96 mol% to 10.46 mol% as a result of lower feed gas flow.
	1645	2678.6	End ramping to 145,000 SCFH feed.
21 Dec 88	0720	2693.1	Feed gas was ramped down at 2%/min.
	0800	2693.8	Reactor operating at 29,000 SCFH feed.
	1600	2701.8	PDU performed flawlessly during the rate hold, producing methanol at the rate of 2.34 TPD. Began ramp up at 10%/min. No problems, very smooth.
22 Dec 88	0730	2717.3	Began ramping feed rate down from 145,000 SCFH at 8.9%/min.
	0739	2717.5	Reactor operating at 29,000 SCFH.
	1200	2721.8	Ramping feed gas flow back up at 2%/min.
	1240	2722.5	PDU running smoothly at 145,000 SCFH.
	1300	2722.8	Rigorous (instantaneous) ramp down to 73,000 SCFH begun.
	1302:30	2722.8	Reactor reached 73,000 SCFH feed after 16%/min. decrease.
	1600	2725.8	Ramping up feed at 3.3%/min.

TABLE V.1

RUN E-7 CHRONOLOGY

<u>Date</u>	<u>Time</u>	<u>Cumulative Time On Production Gas (hours)</u>	<u>Notes and Observations</u>
22 Dec 88	1615	2726.1	Reactor operating normally at nominal 10,000 GHSV. End of ramping tests. Methanol production rate responded very quickly to changing feed rates, closely tracking its progress.
	1800	2727.8	Oil condenser temperature reset to 250°F.
	2300	2732.8	Ramping tests deemed successful after simulating slow and instantaneous ramping with 5°F temperature variance or less and consistent quick return of the process to original production levels.
23-27 Dec 88			PDU ran smoothly with no perturbations.
28 Dec 88	1815	2872.1	Methanol production rate steady around 8.15 TPD since ramping tests.
29 Dec 88	0730	2885.3	Began preparations for 50% catalyst changeout.
	0803	2885.8	Syngas flow to the reactor was stopped, and a NDG scan was done to determine catalyst inventory (388.05 kg of oxide).
	0840		Began N ₂ feed to reactor.
	1330		Reactor and prep tank temperatures in line.
	1338		All gas feed to reactor stopped.
	1400		Reactor slurry emptied into the Primary Vapor/Liquid Separator.
	1420		Total of 131.5 gal of slurry (54.2% of catalyst inventory) was removed from reactor. Dropping reactor pressure.
	1445		145.0 gal of fresh slurry added to reactor from the Slurry Prep Tank.
	1500		Withdrawal/addition process complete. Standard restart procedures initiated.
	1810	2885.8	Reactor now on once through syngas.
	1900	2886.6	Recycle gas flow started.
	2400	2891.6	Stable reactor flows, compositions, and temperatures.

TABLE V.1

RUN E-7 CHRONOLOGY

<u>Date</u>	<u>Time</u>	<u>Cumulative Time On Production Gas (hours)</u>	<u>Notes and Observations</u>
30 Dec 88	0840	2900.3	Gas flow to reactor stopped for NDG scan.
	0905	2900.3	Syngas feed reinstated.
	0945	2901.1	PDU approaching normal operating conditions. 58.2 wt% of catalyst was replaced, reactor contained 425.5 kg of oxide. Nominal operating conditions now were 39 wt% catalyst, 9000 GHSV, and 33 vol% gas holdup.
31 Dec 88	1100	2926.3	PDU production up to 9.52 TPD average with 8.11 mol% methanol in the reactor effluent. Performance jumped to Day 35 levels.
1 Jan 89	0600	2945.3	Plant running smoothly at production rate of 9.58 TPD of methanol.
2 Jan 89	1100	2974.3	Production improved to 9.64 TPD.
3 Jan 89	1730	3004.8	Oil condensation temperature raised to 260°F to keep recovered oil free of methanol.
4 Jan 89	0800	3019.3	PDU operating steadily with methanol production at 9.48 TPD. Methanol concentration of 8.21 mol% in the reactor effluent.
5 Jan 89	0800	3043.3	Cumulative methanol production topped 325,000 gal as daily production now averaging 9.56 TPD. 120 days of life run reached. The steep drop in the reaction rate constant seen immediately after catalyst changeout ended. Carbonyl levels still low, 1.8 ppbv Ni and <1 ppbv Fe in the reactor effluent.
6 Jan 89	0600	3065.3	Methanol production at 9.50 TPD.
7 Jan 89	0600	3089.3	Methanol production at 9.44 TPD.
8 Jan 89	0600	3113.3	Continued smooth operation. Methanol production steady at 9.42 TPD. Concentration of methanol in reactor effluent was 8.15 mol%.
9 Jan 89	0800	3139.3	Run E-7 ends after 124.2 days on syngas and cumulative production of 337,405 gal of methanol.

Figure V.1

SLURRY PROPERTIES AT INITIAL STAGES OF RUN E-7 Gradual Change in Gas Holdup and Slurry Conc. with Time

Figure V.2

LAPORTE PDU METHANOL PRODUCTION VS TIME

CO-Rich gas, 482°F, 750 psig

Overall, Run E-7 was tremendously successful. Over 1000 tons of methanol were produced at high purity and the unit responded superbly to the variations of normal everyday operation. Total lost time was 137 out of 3100 hours, of which 130 were the result of electrical or gas supply outages unrelated to the LPMEOH PDU.

The PDU shutdown and turn-around scheduled for the end of Run-E7 was not performed because of the sustained high level of catalyst activity at the end of the run. Rather than shutting down and activating a fresh batch of catalyst, the run was instead continued as the Process Variable Run E-8.

C. Discussion of Results

1. Catalyst Activity Maintenance

The LaPorte LPMEOH PDU data from Run E-7 was analyzed to determine a catalyst deactivation rate for the F21/OE75-43 catalyst. Deactivation was observed under the nominal conditions for Run E-7 of CO-Rich feed gas, 10,000 SI/hr-kg cat, 750 psig, and 482°F.

As shown in Figure V.2 the initial production rate of 10 TPD slowly decreased to 8 TPD over 120 days of operation indicating a baseline (poison-free) deactivation rate of no more than 0.2%/day. This was half the rate of decay in Run E-3 in 1985. The differences in deactivation rate between Run E-1 and E-3 are attributable to the reduction in metal carbonyl poisoning brought about by the partial replacement of carbon steel with stainless steel. The differences between Run E-7 and E-3 are much less, but are probably the result of an improved catalyst stability and removal of the last of the carbon steel in the PDU system (new stainless steel reactor). Improvements to the reactor gas distribution system may also have had an effect.

The methanol productivity was also excellent throughout the life run, declining slowly from 30 gmol/hr-kg cat to 24 gmol/hr-kg cat (Figure V.3). This was also a significant improvement over previous catalyst life runs as shown in Figure V.4. The complete daily run summary is provided in Table V.2.

The temperature approach to methanol equilibrium for Run E-7 was as expected. The approach began at about 15°C and increased relatively linearly to 28°C just prior to catalyst addition/withdrawal (Figure V.5), indicating slow deactivation of the catalyst. After the catalyst changeout, the temperature approach dropped to near 16°C; however, the corresponding rate of increase seemed greater over the short test period. The temperature approach to water-gas shift reaction equilibrium results were more scattered (Figure V.6). Generally, the approach began near zero and slowly increased until day 40. After day 40 the approach varied between 5 and 15°C. It should be noted that near day 60, short term reductions in feed gas flow caused both equilibrium temperature approaches to drop sharply.

A more fundamental characterization of catalyst deactivation requires an estimation of the decrease in the reaction rate constant over time. The kinetic expression for methanol synthesis was defined in the previous DOE contract (DE-AC22-85PC80007) and is listed below.

Figure V.3

RUN E-7 PRODUCTIVITY VS TIME
750 psig, 250 °C, 10,000 SI/hr-kg cat, CO-rich gas

Figure V.4

LAPORTE PDU PRODUCTIVITY vs TIME

750 psig, 250°C, CO-rich gas

LEGEND

○ Run E7 - 1983

□ Run E3 - 1985

△ Run E1 - 1984

Table V.2

LAPORTE LPMEOH PDU

DATA SUMMARY FOR RUN E-7

Day Number	Balance Period Date & Time	Cumulative		Temp (°C)	Pres. (psig)	Inlet Gas Velocity (ft/s)	Space Velocity (1/hr-kg)	Slurry Conc. (wt% ox.)	Gas Holdup (vol %)	Catalyst Inventory (kg)	CO Conv. (%)	MeOH Productivity (gmol/hr-kg)	Pct. of Net MeOH Autocl. Production (%)	Net MeOH Production (TPD)
		Gas Type	Days on Syngas											
1	09/01 0600 - 09/02 0600	CO-Rich	7.70	250.1	751.7	0.50	9462	36.7	30.0	403	13.6	28.7	100	9.99
2	09/02 0600 - 09/03 0600	CO-Rich	8.70	249.9	751.7	0.51	9499	37.2	31.6	403	14.0	29.0	102	10.08
3	09/03 0600 - 09/04 0600	CO-Rich	9.70	249.8	751.6	0.51	9516	37.7	32.7	403	13.7	29.4	103	10.20
4	09/04 0600 - 09/05 0600	CO-Rich	10.70	249.8	751.9	0.50	9520	37.7	32.9	402	13.7	29.4	103	10.19
5	09/05 0600 - 09/06 0600	CO-Rich	11.70	250.0	751.9	0.50	9502	38.0	33.6	402	13.5	28.9	101	10.01
6	09/06 0600 - 09/07 0600	CO-Rich	12.70	249.9	752.0	0.51	9569	37.8	33.3	402	13.7	29.4	102	10.18
7	09/07 0600 - 09/08 0600	CO-Rich	13.70	249.8	752.0	0.51	9535	37.9	33.5	402	14.0	29.7	103	10.25
8	09/08 0600 - 09/09 0600	CO-Rich	14.70	249.8	752.0	0.51	9604	37.9	33.7	402	13.7	29.7	103	10.25
9	09/09 0600 - 09/10 0600	CO-Rich	15.70	249.8	752.0	0.51	9590	37.9	33.6	401	13.4	28.7	100	9.93
10	09/10 0600 - 09/11 0600	CO-Rich	16.70	249.9	752.3	0.50	9569	37.9	33.6	401	13.9	29.5	103	10.19
11	09/11 0600 - 09/12 0600	CO-Rich	17.70	250.0	752.3	0.51	9542	37.8	33.5	401	13.6	29.2	102	10.07
12	09/12 0600 - 09/13 0600	CO-Rich	18.70	249.7	752.2	0.51	9555	37.8	33.6	401	13.5	29.1	101	10.01
13	09/13 0600 - 09/14 0600	CO-Rich	19.70	249.9	752.3	0.51	9601	37.8	33.7	400	13.6	29.3	102	10.07
14	09/14 0600 - 09/15 0600	CO-Rich	20.70	249.7	752.3	0.50	9544	37.7	33.4	400	13.7	29.4	102	10.10
15	09/15 0600 - 09/16 0600	CO-Rich	21.13	250.0	752.3	0.51	9580	37.7	33.4	400	13.6	29.1	101	9.98
16	09/16 0600 - 09/17 0600	CO-Rich	21.87	249.8	751.9	0.51	9615	38.0	34.3	400	13.5	29.2	101	10.04
17	09/17 0600 - 09/18 0600	CO-Rich	22.87	249.7	751.7	0.51	9605	38.0	34.2	400	13.2	28.7	100	9.87
18	09/18 0600 - 09/19 0600	CO-Rich	23.87	249.7	751.7	0.51	9607	38.0	34.2	400	13.6	29.1	101	10.00
19A	09/19 0600 - 09/20 0600	CO-Rich	24.62	249.7	751.7	0.51	9638	37.7	33.6	399	13.4	28.9	100	9.92
19B	09/20 0600 - 09/21 0600	CO-Rich	24.87	248.5	751.7	0.31	5978	37.3	24.7	399	15.0	20.3	99	6.95
20	09/21 0600 - 09/22 0600	CO-Rich	25.87	249.5	751.4	0.50	9427	37.8	33.9	399	13.3	28.0	99	9.67
21	09/22 0600 - 09/23 0600	CO-Rich	26.87	249.6	751.4	0.51	9617	37.9	34.1	399	13.5	28.9	100	9.93
22	09/23 0600 - 09/24 0600	CO-Rich	27.87	249.6	751.4	0.51	9622	37.9	34.1	399	13.6	29.0	101	9.93
23	09/24 0600 - 09/25 0600	CO-Rich	28.87	249.6	751.6	0.51	9659	37.9	34.1	398	13.5	29.1	101	9.95
24	09/25 0600 - 09/26 0600	CO-Rich	29.87	249.6	751.4	0.51	9712	37.8	34.1	398	13.3	29.0	100	9.93
25	09/26 0600 - 09/27 0600	CO-Rich	30.87	249.6	751.9	0.51	9696	37.7	33.8	398	13.6	29.4	101	10.00
26	09/27 0600 - 09/28 0600	CO-Rich	31.87	249.8	752.0	0.51	9634	37.7	33.7	398	12.8	28.1	97	9.57

Table V.2

LAPORTE LPMEOH PDU

DATA SUMMARY FOR RUN E-7

Day Number	Balance Period Date & Time	Cumulative Days on Syngas	Temp (°C)	Pres. (psig)	Inlet Gas Velocity (ft/s)	Space Velocity (1/hr-kg)	Slurry Conc. (wt% ox.)	Gas Holdup (vol %)	Catalyst Inventory (kg)	CO Conv. (%)	MeOH Productivity (gmol/hr-kg)	Pct. of Autocl. Production (%)	Net MeOH Production (TPD)
27	09/29 0600 - 09/30 0600	CO-Rich 32.87	249.6	751.9	0.51	9645	37.7	33.8	397	13.2	28.6	99	9.73
28	09/30 0600 - 10/01 0600	CO-Rich 33.67	249.6	751.9	0.50	9602	37.6	33.7	396	12.9	27.9	97	9.47
29	10/01 0600 - 10/02 0600	CO-Rich 34.87	249.6	752.0	0.51	9714	37.5	33.7	395	12.9	28.3	98	9.60
30	10/02 0600 - 10/03 0600	CO-Rich 35.87	249.5	751.9	0.51	9754	37.4	33.5	395	12.9	28.4	98	9.63
31	10/03 0600 - 10/04 0600	CO-Rich 36.87	249.6	752.0	0.51	9810	37.4	33.5	394	12.9	28.6	98	9.66
32	10/04 0600 - 10/04 2400	CO-Rich 37.87	249.7	752.0	0.51	9761	37.3	33.5	394	12.7	28.1	96	9.49
33	10/05 0600 - 10/06 0600	CO-Rich 38.87	249.6	752.0	0.51	9796	37.3	33.4	394	12.9	28.6	98	9.67
34	10/06 0600 - 10/07 0600	CO-Rich 39.87	250.1	752.2	0.51	9725	37.3	33.4	394	13.1	28.4	98	9.60
35	10/07 0600 - 10/08 0600	CO-Rich 40.60	249.5	751.5	0.51	9746	37.3	33.3	394	12.1	29.2	100	9.85
36	10/08 0600 - 10/09 0600	CO-Rich 41.60	249.9	751.5	0.51	9796	37.5	33.9	394	12.5	28.8	99	9.72
37	10/09 0600 - 10/10 0600	CO-Rich 42.60	249.9	751.3	0.50	9701	37.5	33.8	394	13.0	28.3	98	9.55
38	10/10 0600 - 10/11 0600	CO-Rich 43.60	249.9	751.2	0.51	9745	37.4	33.7	394	12.8	28.3	97	9.55
39	10/11 0600 - 10/12 0600	CO-Rich 44.60	249.9	751.2	0.51	9739	37.5	33.9	394	12.9	28.4	98	9.59
40	10/12 0600 - 10/13 0600	CO-Rich 45.60	249.8	750.8	0.51	9779	37.4	33.7	394	13.0	28.6	98	9.66
41	10/13 0600 - 10/14 0600	CO-Rich 46.60	249.5	751.3	0.51	9762	37.5	33.9	394	13.0	28.8	99	9.72
42	10/14 0600 - 10/15 0600	CO-Rich 47.60	249.8	751.0	0.51	9744	37.4	33.7	394	12.7	28.0	96	9.44
43	10/15 0600 - 10/16 0600	CO-Rich 48.60	250.2	751.3	0.51	9766	37.4	33.7	394	12.6	27.9	96	9.41
44	10/16 0600 - 10/17 0600	CO-Rich 49.60	249.9	751.2	0.51	9734	37.4	33.6	394	12.6	27.8	96	9.37
45	10/17 0600 - 10/18 0600	CO-Rich 50.60	250.0	751.3	0.51	9729	37.3	33.3	394	12.6	27.8	96	9.39
46	10/18 0600 - 10/19 0600	CO-Rich 51.60	249.9	751.7	0.51	9736	37.3	33.4	394	12.6	27.8	96	9.36
47	10/19 0600 - 10/20 0600	CO-Rich 52.60	249.7	751.7	0.50	9668	37.7	33.6	394	12.4	27.3	94	9.18
48	10/20 0600 - 10/21 0600	CO-Rich 53.60	249.8	751.9	0.51	9736	37.3	33.4	394	12.5	27.6	95	9.29
49	10/21 0600 - 10/22 0600	CO-Rich 54.60	249.6	751.6	0.51	9746	37.3	33.4	394	12.6	27.9	96	9.38
50	10/22 0600 - 10/23 0600	CO-Rich 55.60	249.8	751.6	0.51	9805	37.3	33.3	394	12.5	27.7	95	9.32
51	10/23 0600 - 10/23 1600	CO-Rich 56.28	250.0	751.7	0.51	9786	37.4	33.5	394	12.5	27.6	95	9.30
52	10/25 0000 - 10/25 0600	CO-Rich 56.74	250.4	752.2	0.51	9747	37.5	34.0	394	12.4	27.1	93	9.10
53A	10/25 0600 - 10/25 1300	CO-Rich 57.03	250.1	752.2	0.51	9765	37.5	34.0	394	12.2	27.0	93	9.07

Table V.2

LAPORTE LPMEOH PDU

DATA SUMMARY FOR RUN E-7

Day Number	Balance Period Date & Time	Cumulative		Temp (°C)	Pres. (psig)	Inlet Gas Velocity (ft/s)	Space Velocity (1/hr-kg)	Slurry Conc. (wt% ox.)	Gas Holdup (vol %)	Catalyst Inventory (kg)	CO Conv. (%)	MeOH Productivity (gmol/hr-kg)	Pct. of Net MeOH Autocl. Production (%)	Net MeOH Production (TPD)
		Gas Type	Days on Syngas											
53B	10/25 1400 - 10/26 0600	CO-Rich	57.74	249.7	752.2	0.25	4748	36.9	26.7	394	15.5	16.8	99	5.84
54	10/27 1000 - 10/28 0600	CO-Rich	58.60	250.3	751.7	0.25	4889	37.5	28.4	394	15.1	16.7	96	5.87
55	10/28 0600 - 10/29 0800	CO-Rich	59.68	249.8	751.7	0.25	4877	37.6	28.9	394	15.1	16.6	96	5.62
56	10/29 1100 - 10/30 0600	CO-Rich	60.64	249.7	751.6	0.51	9788	37.8	34.7	394	12.3	27.0	93	9.18
57A	10/30 0600 - 10/30 1800	CO-Rich	61.14	249.9	751.6	0.51	9707	37.7	34.5	394	12.3	26.6	92	9.03
57B	10/30 1800 - 10/31 0600	CO-Rich	61.64	249.8	751.6	0.51	9714	37.7	34.5	394	11.8	26.4	91	8.99
58	10/31 0600 - 11/01 0600	CO-Rich	62.64	249.6	751.6	0.51	9698	37.6	34.2	394	12.0	26.5	91	8.98
59	11/01 0600 - 11/02 0600	CO-Rich	63.64	249.9	751.7	0.51	9717	37.7	34.5	394	12.1	26.5	91	8.96
60	11/02 0600 - 11/03 0600	CO-Rich	64.64	249.9	751.7	0.51	9716	37.6	34.2	393	12.1	26.5	91	8.94
61	11/03 0600 - 11/04 0600	CO-Rich	65.64	249.8	751.7	0.50	9665	37.6	34.3	393	12.2	26.5	92	8.93
62	11/04 0600 - 11/05 0600	CO-Rich	66.64	249.9	752.0	0.50	9679	37.5	34.1	393	12.2	26.6	92	8.96
63	11/05 0600 - 11/06 0600	CO-Rich	67.64	249.9	752.0	0.50	9684	37.5	34.0	393	12.3	26.9	93	9.06
64	11/06 0600 - 11/07 0600	CO-Rich	68.64	250.0	752.0	0.50	9677	37.6	34.1	393	12.2	26.7	92	9.00
65	11/07 0600 - 11/08 0600	CO-Rich	69.64	250.2	752.0	0.50	9668	37.7	34.4	393	12.1	26.3	91	8.86
66	11/08 0600 - 11/09 0600	CO-Rich	70.64	250.2	751.9	0.50	9682	37.6	34.3	393	12.0	26.4	91	8.89
67	11/09 0600 - 11/10 0600	CO-Rich	71.64	250.0	751.7	0.50	9680	37.6	34.2	393	12.0	26.3	91	8.86
68	11/10 0600 - 11/11 0600	CO-Rich	72.64	250.1	751.7	0.50	9651	37.4	33.7	393	12.2	26.3	91	8.85
69	11/11 0600 - 11/12 0600	CO-Rich	73.64	249.9	751.7	0.50	9685	37.5	34.0	393	12.2	26.3	91	8.86
70	11/12 0600 - 11/13 0600	CO-Rich	74.64	249.9	751.7	0.50	9671	37.5	34.0	393	12.0	26.2	91	8.82
71	11/13 0600 - 11/14 0600	CO-Rich	75.64	250.0	751.7	0.50	9664	37.5	34.0	393	12.1	26.3	91	8.84
72	11/14 0600 - 11/15 0600	CO-Rich	76.61	250.0	751.9	0.50	9691	37.5	34.0	393	12.1	26.3	91	8.84
73	11/15 0600 - 11/16 0600	CO-Rich	77.61	249.7	752.2	0.51	9708	37.4	33.8	393	12.0	26.1	90	8.79
74	11/16 0600 - 11/17 0600	CO-Rich	78.61	249.7	752.0	0.51	9762	37.6	34.3	393	12.0	26.5	91	8.90
75	11/17 0600 - 11/18 0600	CO-Rich	79.58	249.7	752.3	0.50	9644	37.6	34.0	393	12.2	26.6	92	8.87
76	11/18 0600 - 11/19 0600	CO-Rich	80.58	249.9	752.2	0.50	9693	37.5	33.8	393	11.9	26.2	90	8.78
77	11/19 0600 - 11/20 0600	CO-Rich	81.58	249.7	752.2	0.51	9753	37.5	34.1	393	11.9	26.2	90	8.80
78	11/20 0600 - 11/21 0600	CO-Rich	82.58	249.9	752.3	0.50	9686	37.5	33.9	393	12.1	26.3	91	8.86

Table V.2

LAPORTE LPMEOH PDU

DATA SUMMARY FOR RUN E-7

Day Number	Balance Period		Cumulative Days on Syngas	Temp (°C)	Pres. (psig)	Inlet Gas Velocity (ft/s)	Space Velocity (1/hr-kg)	Slurry Conc. (wt% ox.)	Gas Holdup (vol %)	Catalyst Inventory (kg)	CO Conv. (%)	MeOH Productivity (gmol/hr-kg)	Pct. of Net MeOH Autocl. Production (%)	
	Date	Time	Gas Type											
79	11/21	0600 - 11/22 0600	CO-Rich	83.58	752.3	0.51	9711	37.3	33.5	393	12.1	26.2	90	8.81
80	11/22	0600 - 11/23 0600	CO-Rich	84.58	752.3	0.51	9715	37.4	33.8	393	12.0	26.3	90	8.83
81	11/23	0600 - 11/24 0600	CO-Rich	85.58	752.4	0.50	9649	37.5	34.0	393	12.0	25.9	90	8.70
82	11/24	0600 - 11/25 0600	CO-Rich	86.58	752.4	0.50	9703	37.4	33.7	393	11.8	25.7	89	8.65
83	11/25	0600 - 11/26 0600	CO-Rich	87.58	752.2	0.51	9711	37.5	34.1	393	11.8	25.7	88	8.62
84	11/26	0600 - 11/27 0600	CO-Rich	88.58	752.3	0.50	9656	37.4	33.7	393	11.5	25.3	88	8.51
85	11/27	0600 - 11/28 0600	CO-Rich	89.58	752.4	0.50	9673	37.5	33.8	393	11.7	25.5	88	8.55
86	11/28	0600 - 11/29 0600	CO-Rich	90.58	750.0	0.51	9690	37.4	33.6	393	12.0	26.0	90	8.73
87	11/29	0600 - 11/30 0600	CO-Rich	91.58	752.2	0.51	9642	37.5	34.0	393	12.0	26.1	90	8.73
88	11/30	0600 - 12/01 0600	CO-Rich	92.58	752.6	0.51	9719	37.5	33.9	393	11.8	25.8	89	8.68
89	12/01	0600 - 12/02 0600	CO-Rich	93.57	751.9	0.51	9604	37.4	33.7	393	11.9	25.8	90	8.69
90	12/02	0600 - 12/03 0600	CO-Rich	94.57	752.3	0.51	9642	37.5	33.8	393	11.8	25.5	88	8.59
91	12/03	0600 - 12/04 0600	CO-Rich	95.57	752.2	0.50	9620	37.4	33.8	393	11.7	25.4	88	8.55
92	12/04	0600 - 12/05 0600	CO-Rich	96.57	751.9	0.51	9684	37.4	33.7	393	11.7	25.6	89	8.61
93	12/05	0600 - 12/06 0600	CO-Rich	97.57	751.9	0.52	9633	37.4	33.7	393	11.7	25.5	88	8.59
94	12/06	0600 - 12/07 0600	CO-Rich	98.57	751.6	0.52	9643	37.4	33.8	393	11.9	25.6	89	8.61
95	12/07	0600 - 12/08 0600	CO-Rich	99.24	751.6	0.51	9676	37.4	33.7	393	11.9	25.8	89	8.68
96	12/08	0600 - 12/09 0600	CO-Rich	100.24	753.5	0.51	9723	37.4	33.6	393	11.4	25.2	87	8.48
97	12/09	0600 - 12/10 0600	CO-Rich	101.24	753.5	0.51	9744	37.3	33.5	393	11.5	25.3	87	8.51
98	12/10	0600 - 12/11 0600	CO-Rich	102.24	753.5	0.51	9732	37.3	33.3	393	11.5	25.3	87	8.52
99	12/11	0600 - 12/12 0600	CO-Rich	103.24	753.5	0.50	9664	37.2	33.1	393	11.5	25.1	87	8.45
100	12/12	0600 - 12/13 0600	CO-Rich	104.24	753.5	0.50	9621	37.2	33.2	393	11.6	25.0	87	8.41
101	12/13	0600 - 12/14 0600	CO-Rich	105.24	753.5	0.50	9630	37.3	33.3	393	11.3	24.7	86	8.31
102	12/14	0600 - 12/15 0600	CO-Rich	106.24	753.5	0.50	9667	37.2	33.2	393	11.5	24.8	86	8.36
103	12/15	0600 - 12/16 0600	CO-Rich	107.24	753.5	0.50	9669	37.2	33.3	393	11.3	24.7	85	8.32
104	12/16	0600 - 12/17 0400	CO-Rich	108.24	753.5	0.50	9666	37.2	33.2	393	11.4	24.9	86	8.38
105	12/17	0700 - 12/18 0600	CO-Rich	109.24	753.5	0.50	9704	37.2	33.3	393	11.3	24.8	85	8.34

Table V.2

LAPORTE LPMEOH PDU

DATA SUMMARY FOR RUN E-7

Day Number	Balance Period Date & Time	Cumulative		Temp (°C)	Pres. (psig)	Inlet Gas Velocity (ft/s)	Space Velocity (/hr-kg)	Slurry Conc. (wt% ox.)	Gas Holdup (vol %)	Catalyst Inventory (kg)	CO Conv. (%)	MeOH Productivity (gmol/hr-kg)	Pct. of Net MeOH Autocl. Production (%)	Net MeOH Production (TPD)
		Gas Type	Days on Syngas											
106	12/18 0600 - 12/19 0600	CO-Rich	110.24	249.9	753.5	0.50	9674	37.0	32.6	393	11.2	24.6	85	8.27
107	12/19 0600 - 12/20 0800	CO-Rich	111.32	250.0	753.0	0.51	9724	37.2	33.2	393	11.2	24.6	85	8.28
108A	12/20 1000 - 12/20 1600	CO-Rich	111.65	249.0	752.7	0.10	2012	36.7	13.2	393	15.8	7.3	94	2.44
108B	12/20 1600 - 12/21 0700	CO-Rich	112.28	250.1	752.7	0.50	9692	37.1	32.9	393	11.2	24.5	85	8.24
109A	12/21 0700 - 12/21 1600	CO-Rich	112.65	249.8	752.7	0.09	1776	36.3	11.8	393	17.3	7.1	101	2.34
109B	12/21 1600 - 12/22 0700	CO-Rich	113.28	250.2	752.7	0.50	9688	37.0	32.6	393	11.1	24.4	84	8.21
110A	12/22 0700 - 12/22 1200	CO-Rich	113.49	249.8	752.7	0.10	1880	36.5	12.4	393	16.8	7.3	99	2.43
110B	12/22 1200 - 12/22 1600	CO-Rich	113.65	250.1	752.7	0.26	4930	36.6	23.5	393	12.8	14.6	84	4.90
110C	12/22 1600 - 12/23 0600	CO-Rich	114.24	250.0	752.7	0.50	9687	37.1	32.8	393	11.1	24.4	84	8.19
111	12/23 0600 - 12/24 0600	CO-Rich	115.24	250.0	752.7	0.50	9709	37.0	32.6	393	11.0	24.3	84	8.16
112	12/24 0600 - 12/25 0600	CO-Rich	116.24	249.9	752.7	0.50	9711	37.0	32.6	393	10.9	24.2	83	8.14
113	12/25 0600 - 12/26 0600	CO-Rich	117.24	250.0	752.7	0.50	9713	37.1	32.8	393	10.9	24.1	83	8.11
114	12/26 0600 - 12/27 0600	CO-Rich	118.24	250.0	752.7	0.50	9670	37.1	33.0	393	10.9	23.9	83	8.03
115	12/27 0600 - 12/28 0600	CO-Rich	119.24	250.0	752.7	0.50	9691	37.1	32.8	393	10.8	24.0	83	8.08
116	12/28 0600 - 12/29 0600	CO-Rich	120.32	250.0	752.7	0.50	9753	36.9	32.4	393	10.7	23.9	82	8.03
117	12/30 0000 - 12/30 0600	CO-Rich	120.90	250.3	752.7	0.50	8970	39.1	33.0	426	18.0	26.3	96	9.59
118	12/30 0600 - 12/31 0600	CO-Rich	121.90	250.0	752.4	0.50	8902	39.4	33.8	426	13.1	26.0	95	9.52
119	12/31 0600 - 01/01 0600	CO-Rich	122.90	250.1	752.4	0.50	8961	39.5	34.1	426	12.9	26.1	95	9.58
120	01/01 0600 - 01/02 0600	CO-Rich	123.90	250.3	751.9	0.51	8980	39.3	33.4	426	13.0	26.2	95	9.64
121	01/02 0600 - 01/03 0600	CO-Rich	124.90	250.4	752.3	0.50	8844	39.2	33.3	426	12.7	25.5	94	9.36
122	01/03 0600 - 01/04 0600	CO-Rich	125.90	250.2	752.4	0.50	8940	39.3	33.4	426	12.7	25.8	94	9.48
123	01/04 0600 - 01/05 0600	CO-Rich	126.90	250.0	752.4	0.51	8987	39.1	33.1	426	12.9	26.1	95	9.56
124	01/05 0600 - 01/06 0600	CO-Rich	127.90	250.4	752.4	0.51	8992	39.1	33.0	426	12.8	26.0	94	9.50
125	01/06 0600 - 01/07 0600	CO-Rich	128.90	250.4	752.4	0.50	8963	39.0	32.8	426	12.7	25.8	94	9.44
126	01/07 0600 - 01/08 0600	CO-Rich	129.90	250.3	752.4	0.51	8982	38.9	32.5	426	12.6	25.8	94	9.42
127	01/08 0600 - 01/09 0800	CO-Rich	130.99	250.0	752.4	0.51	9031	39.0	32.7	426	12.8	26.2	95	9.57

Figure V.5

TEMPERATURE APPROACH TO MeOH EQUILIBRIUM
Run E-7, 750 psig, 250°C, 10000 Sl/hr-kg cat

Figure V.6

TEMPERATURE APPROACH TO H₂O EQUILIBRIUM

Run E-7, 750 psig, 250°C, 10,000 SI/hr-kg cat

$$R_{\text{MeOH}} = K_f f^{1/3} \text{CO} f^{2/3} \text{H}_2 \left(1 - \frac{f_{\text{MeOH}}}{K_{\text{eq}} f_{\text{CO}} f_{\text{H}_2}^2}\right) \quad \text{Eq. 1}$$

where: R_{MeOH} = methanol productivity (gmol/hr kg-cat-ox)
 K_f = rate constant (gmol/hr kg-cat-ox atm)
 f_x = fugacity of component x (atm)
 K_{eq} = methanol equilibrium constant (atm⁻²)

The rate constant expression is a function of temperature and given by:

$$K_f = k_o(t) * \exp \frac{-E_{\text{act}}}{1.987 * T} \quad \text{Eq. 2}$$

where: $k_o(t)$ = constant value in rate constant expression at time t (gmol/hr kg-cat-ox atm)
 E_{act} = energy of activation (14380 cal/gmol)
 T = temperature in degrees Kelvin

The relative activity of the catalyst was characterized by the eta (η) value in the rate constant expression.

$$\eta(t) = \frac{k_o(t)}{k_o(\text{initial})} \quad \text{Eq. 3}$$

where: $k_o(\text{initial})$ = constant value in rate constant expression at time $t=0$ (gmol/hr kg-cat-ox atm)

The feed gas composition, space velocity, superficial gas velocity, reactor conditions and methanol productivity for each balance period of the 120-day run are known. The eta and reaction rate constant were determined from the plant data by using a two CSTR tanks in series model of the LPMEOH Reactor.

The equation modeling the relative activity eta value of the F21/OE75-43 catalyst was determined to be an exponential decay function of the number of days from catalyst reduction (Figure V.7).

$$\eta = e^{(-0.003948 * D)} \quad \text{Eq. 4}$$

where: D = number of days from catalyst activation

The relative $k_o(t)$ constant value for the deactivation period of Run E-7 (Figure V.8) can therefore be described as:

$$k_o(t) = e^{(-0.003948 * D)} * k_o(\text{initial}) \quad \text{Eq. 5}$$

where: $k_o(\text{initial})$ = 2.368E+6 gmol/hr kg-cat-ox atm

Figure V.7

ETA VALUE vs TIME

Run E-7, 750 psig, 250 °C, 10,000 SI/hr--kg cat, CO-rich gas

Figure V.8

Ko CONSTANT VS TIME

Run E-7, 750 psig, 250 °C, 10,000 SI/hr-kg cat, CO-rich gas

The typical $k_o(\text{initial})$ value determined from autoclave results with F21/OE75-43 catalyst under the conditions of 10,000 SI/hr-kg cat, 750 psig, and 482°F is $2.91\text{E}+6$ gmol/hr kg-cat-ox atm. The $k_o(\text{initial})$ value determined from PDU data in equation 5 above indicates the new catalyst was not fully reduced during the ER-5 reduction. The analysis with this model predicts that the catalyst was only 81% active after the ER-5 reduction. The expected catalyst deactivation curve (η) resulting from a fully reduced catalyst as compared to the data from Run E-7 is shown in Figure V.9.

2. Catalyst Analytical Results

Analytical results on the catalyst slurry samples taken during Run E-R5 and Run E-6/7 show that the growth of copper crystallite size was slow (Table V.3), indicating a small loss in surface area for the copper. This result correlates with the relatively slow deactivation observed at LaPorte during Run E-7. Impurities pickup on the catalyst were also minimal. The end-of-run sample of LaPorte Run E-7 (Sample ID: E7-07) and an activated sample from the prep tank (Sample ID: E7-06) were analyzed for particle size distribution by image analysis. The end-of run sample showed a smaller average particle size ($0.247\text{ }\mu\text{m}$ vs. $1.19\text{ }\mu\text{m}$), however, the particle aspect ratio (i.e., individual particle width to length ratio) remained constant at 0.5.

On 16 December, a catalyst slurry sample was obtained from the prep tank (28.30) at LaPorte and was subsequently tested in a 300 cc autoclave (Run #9397-77). The result showed a methanol productivity of 14.8 gmol/kg-hr at 4750 GHSV on CO-rich gas. The corresponding reaction temperature and pressure were 482°F and 750 psig, respectively. This productivity is approximately 90% of the expected value of 16.5 gmol/kg-hr. For verification, another catalyst sample was taken on 20 December from the prep tank and tested in the same autoclave at the same conditions (Run #9397-79). Activities were measured at 5500 GHSV and 7280 GHSV with respective productivities of 16.7 and 20.7 gmol/kg-hr, again about 90% of expected. These results are consistent with the level of catalyst activity determined from the LaPorte PDU data.

3. Reactor Internal Heat Exchanger

The results from Run E-7 indicated the possible presence of fouling in the internal exchanger (Figure V.10). The predicted shell-side coefficient was approximately 300 Btu/hr-ft²-°F for the duration of the run. The calculated coefficient, however, was much lower, starting near 240 Btu/hr-ft²-°F and settling at 210 Btu/hr-ft²-°F. Neglecting the large uncertainty of 35% in the measured values, the results appear low. When the predicted and calculated lines are extrapolated, they reach a common value of approximately 300 Btu/hr-ft²-°F at zero time, indicating that fouling was possibly occurring during the beginning of the run.

An external fouling factor (or external resistance to heat transfer) of approximately 0.0015 hr-ft²-°F/Btu would bring the calculated and predicted values quite close. (Note: An external fouling factor of 0.001 hr-ft²-°F/Btu was assumed in the design of the exchanger.) Most of this fouling would have been generated during Run E-6, since the exchanger had been cleaned prior to Run E-6. Data from the following Run E-8 was also consistent with this amount of fouling. Based on these results, an operating fouling factor of 0.0015 hr-ft²-°F/Btu has been used for any subsequent analysis of the clean surface heat transfer coefficients for Runs E-7 and E-8. It should also be noted however, that a systematic problem with

FIGURE IV.9

CATALYST LIFE RUN K_o CONSTANT VALUE vs TIME
Comparison - Run E-7 to Fully Activated Catalyst
 750 psig, 250 °C, 10,000 SI/hr-kg cat, CO-rich gas

Table V.3

LAPORTE CATALYST SAMPLES FROM RUNS ER-5, E-6, AND E-7

Sample ID	BET		Crystallite Size		XPS Analysis				Catalyst Loading wt% ox.	AAS or ICP Analysis, ppmw								
	Date	Time	Location	Surf. Area m²/g	XRD, Angstroms		Atomic Percent			Ratio Cu/Zn	Fe		Ni					
					Cu	ZnO	Cu+2	Cu+1			Cu	Cu	S	Cl				
ER5-00	8/22/88	17:00	Drums															
ER5-01	8/23/88	12:00	Loop	89.3	amorphous		64	35	-	1.63	44.8	86	37					
ER5-02	8/23/88	16:30	Loop		amorphous		52	50	-	1.70								
ER5-03	8/23/88	19:30	Loop		amorphous		36	65	-	1.56								
ER5-04	8/23/88	23:30	Loop	85.3			18	82	-	1.09		57	49	<1000	<500			
ER5-05	8/24/88	9:30	Loop			60.0	-	50	50	0.42								
ER5-06	8/24/88	24:00	Loop	92.4	129	54.0	-	55	45	0.35								
ER5-EOR	8/25/88	8:30	Loop	83.3	133	56.9	-	60	40	0.25	43.2	93	45	<500	<500			
Syngas on at 11:00 on 25 August 1988																		
E6-01	8/26/88	5:00	27.10	75.5	195	58.8	-	45	55	0.13		83	<10	<250	<500			
E6-02	8/31/88	16:00	27.10															
E7-01	9/2/88	9:40	27.10	73.4	183	63.4	-	30	70	0.15		79.4	53.1	<300	<200			
E7-02	9/15/88	16:00	27.10	43.5 *	185	76.6	-	40	60	0.11		85.2	56.4	<300	<200			
E7-02b	10/3/88	16:20	27.10															
E7-03	11/2/88	16:00	27.10	not enough sample for any analysis														
E7-04	12/15/88	14:30	28.30	40.4	151	89	25	20	55	0.33	36.2	58	46	280	2000 **			
E7-05	12/20/88	14:00	28.30								38.0							
E7-06***	12/19/88	14:30	27.10	146	81.2	-	-	45	55	0.11		110	38	<200	630			
E7-07	12/29/88	14:50	28.30	duplicate set of analytical tests										35.2	122	48	<1780	<400
E7-07	12/29/88	14:50	28.30								42.0	55	50	<335	<310			
E7-08	1/5/89	9:20	27.10															

not enough sample for any analysis

duplicate set of analytical tests

* Probably reflects incomplete washing of the residual oil from the catalyst
 ** XPS results also show 0.8 atomic percent Cl on this catalyst (contaminated sample bomb confirmed)
 *** The last sample before catalyst addition and withdrawal

LABORATORY AUTOCLAVE CATALYST ACTIVITY TESTING RESULTS

CO-Rich gas, 750 psig, 482 F

Test No.	Sample	Space Vel.		MeOH Productivity	
		SI/hr	kg-ox.	gmole/hr	kg-ox.
1	E7-04	4750		14.8	
2	E7-05	5500		16.7	
3	E7-05	7270		20.7	

Figure V.10

SHELL-SIDE COEFFICIENT vs. TIME **Run E-7, 27.10B Internal Heat Exchanger, No Fouling**

applying the Deckwer correlation to the LPMEOH slurry may have also accounted for part of the difference between the actual and predicted values.

4. Response to Process Upsets and Load Following

Operation of Run E-7 was suspended for three days beginning 15 September for safety reasons due to the threat of Hurricane Gilbert. The reactor was isolated for 33 hours without gas flow or heat control. The reactor was restarted without difficulty after the hurricane passed when the feed gas flow to the reactor was resumed after a 68-hour outage. Methanol production was 10 TPD for the 10-hour period prior to shutdown and 10.1 TPD for the 12-hour period after start-up. This unplanned outage clearly demonstrates the resilience of the LPMEOH process to upsets (Figure V.11).

At the end of the catalyst life-run, a series of tests were carried out aimed at defining the response to the LPMEOH unit to fast and major changes in feed rate. These tests parallel what would be expected in load-following for commercial gasification systems. The results are presented in Figure V.12 and Table V.4. In short, the unit responded exceptionally well to all changes. Cuts of 80% of flow were accommodated easily with transient conditions lasting only a few minutes. Feed gas flow ramping rates varied from 0.4%/min to 16.0%/min. In every case the temperature response of the reactor was excellent. The maximum difference between the target and actual slurry reaction temperature was 3°C for any of the test conditions.

5. Online Catalyst Addition/Withdrawal

The potential for catalyst addition and withdrawal was investigated following the load-following tests. At the conclusion of the catalyst activation ER-5, 874 l of catalyst slurry containing 395 kg of freshly activated catalyst was transferred to the 28.30 slurry prep tank for storage under a 1 mol% H₂: 99 mol% N₂ atmosphere. This unused slurry inventory was used for the fresh slurry changeout.

On 29 December, 54% of the aged catalyst slurry (210 kg cat oxide) was drained from the 27.10 reactor. Fresh catalyst slurry from the slurry prep tank was then pressure-transferred to the reactor. The resulting slurry consisted of 42% (178 kg) aged catalyst and 58% (248 kg) fresh catalyst at a slurry concentration of 39.1 wt%. The result of this changeout on the methanol productivity is shown in Figure V.13.

Assuming the fresh catalyst slurry from the slurry prep tank had the same activity as the measured productivity from the beginning of the run, the expected methanol production rate and relative catalyst activity (η) was 9.4 TPD and 0.814, respectively. The measured quantities were 9.7 TPD and 0.810, within 3% of the expected values. This close agreement between predicted quantity and measured quantity has two key conclusions. First, it is possible to store activated catalyst for long periods of time without significant loss of activity, and second, catalyst addition/withdrawal is a viable means of maintaining a constant level of catalyst "activity" (production rate) in the LPMEOH reactor.

Figure V.11

RESPONSE OF LPMEOH PDU TO HURRICANE GILBERT

Figure V.12

LAPORTE PDU RUN E-7 LOAD FOLLOWING TESTS Methanol Concentration in Reactor Outlet Stream

Table V.4

RAMPING TEST SUMMARY - LAPORTE PDU RUN E-7

<u>Ramp #</u>	<u>Date</u>	<u>Time</u>		<u>FT-187 Flow (MSCFH)</u>		<u>Rate % min.</u>
		<u>Initial</u>	<u>Final</u>	<u>Initial</u>	<u>Final</u>	
1	12/19	2:55	6:00	145	30	-0.4
2	12/19	19:10	19:33	30	145	+3.4
3	12/20	8:15	8:55	145	29	-2.0
4	12/20	16:05	16:45	29	145	+2.0
5	12/21	7:20	8:00	145	29	-2.0
6	12/21	16:00	16:08	29	145	+10.0
7	12/22	7:30	7:39	145	29	-8.9
8	12/22	12:00	12:40	29	145	+2.0
9	12/22	13:00	13:02:30	145	73	-16.0
10	12/22	16:00	16:15	73	145	+3.3

TEMPERATURE RESPONSE OF SLURRY REACTOR

<u>Ramp #</u>	<u>Temperature Range (°C)</u>			<u>Maximum Error (°C)</u>
	<u>Minimum</u>	<u>Target</u>	<u>Maximum</u>	
1	247	250	253	3
2	248	250	252	2
3	248	250	251	2
4	249	250	252	2
5	249	250	252	2
6	249	250	251	1
7	247	250	251	3
8	247	250	252	3
9	247	250	252	3
10	248	250	253	3

Figure V.13

6. Methanol Composition

Methanol purity was very consistent throughout Run E-7 (Figure V.14). Initially, methanol purity was near 97.00 wt% but increased gradually during the life of the run to 97.75 wt%. The only variances in product purity were caused by the sharp changes in feed gas flow caused by shutdown or ramping. Generally, these changes only lowered the purity by 0.7 wt%. After the catalyst changeout, product purity decreased to approximately 97.3 wt% methanol.

The level and change of byproducts in the product methanol is shown in Figure V.15. Water had an initial concentration of 0.6 wt% which rose to 0.9 wt%. Methyl esters concentrations are a reflection of the water composition, dropping from 1.0 wt% to 0.7 wt%. The heavier byproducts all decreased gradually throughout the course of the run. Oil in the product generally varied between 0.1 and 0.2 wt%, depending on the operating conditions. It is interesting to note that the compositions of all of the byproducts tended to return to near their initial levels after the catalyst changeout.

7. Conclusions

The rate constant expression for the deactivation period of Run E-7 was determined to be :

$$k_0(t) = e^{(-0.003948 \cdot D)} \cdot 2.368E+6 \text{ gmol/hr kg-cat-ox. atm}$$

where: k_0 = constant in the rate constant expression
D = number of days from catalyst activation

The initial k_0 value of $2.368E+6$ indicates the F21/OE75-43 catalyst was only 81% reduced after the ER-5 reduction. The autoclave results predicted an initial k_0 of $2.91E+6$.

The baseline catalyst deactivation rate was less than 0.2%/day, half the rate of Run E-3 in 1985. The improvement resulted from a better catalyst and from the further replacement of carbon steel with stainless steel in the PDU system. Productivity declined at only 0.05 gmol/hr kg-cat-ox day.

The temperature approach to methanol equilibrium increased relatively linearly from 15°C to 28°C just prior to catalyst changeout, indicating slow deactivation. The temperature approach to water equilibrium varied between 5° and 15°C during most of the run.

Analytical results on the catalyst slurry samples indicated slow crystallite size growth, a sign of relatively slow catalyst deactivation. Impurities pickup was also minimal. Activated catalyst slurry samples that were stored for up to three months and tested in an autoclave had productivities of approximately 90% of freshly activated catalyst.

A fouling factor of $0.0015 \text{ hr-ft}^2\text{-}^\circ\text{F/8tu}$ was estimated for Run E-7 heat transfer calculations based upon the difference between predicted and calculated shell-side heat transfer coefficients. Two-thirds of this fouling occurred during Run E-6 and the remainder during the first 20 days of Run E-7.

Figure V.14

PRODUCT METHANOL PURITY vs. TIME ON SYNGAS
Run E-7, 750 psig, 250 °C, 10,000 SI/hr-kg, CO-rich gas

Figure V.15

PRODUCT COMPOSITION vs. TIME
Run E-7, 750 psig, 250°C, 10,000 SI/hr-kg cat

The LPMEOH process demonstrated its resilience to upsets. Operations were suspended for three days for Hurricane Gilbert, yet startup was simple and productivity was unchanged. Similarly, for load-following, cuts of 80% in flow and changes in flow rates of up to 16.0%/min were accommodated easily with minimal temperature variance.

Approximately, half of the used catalyst slurry was replaced by fresh catalyst activated at the start of Run E-7. The new production level was within 3% of predicted, assuming the added catalyst had the same activity of the fresh catalyst in E-6. These results supported the viability of catalyst changeout and long term activated catalyst storage.

The product methanol purity was very consistent, rising gradually from 97.00 to 97.75 wt% prior to catalyst changeout. Water concentrations were below 1.0 wt%, and oil was generally below 0.2 wt%. Product compositions returned to near initial levels after the catalyst addition/withdrawal. Over 1000 tons of methanol were produced.

The PDU responded superbly to the variations of normal everyday operation. Total lost time was 137 out of 3100 hours, of which 130 were the result of electrical or gas supply outages unrelated to the LPMEOH PDU.

VI. RECOMMENDATIONS

A detailed process engineering study, alternate catalyst evaluation, and catalyst life run were performed under Task 2.2 of the new modification/operating program. Alterations to the PDU reduced oil impurity in the product. A new catalyst was adopted after proving to be more productive and better suited to continued operations. Heat transfer through the internal heat exchanger was measured and compared to correlations while exchanger fouling was estimated. Catalyst deactivation was quantified during a life run. System resilience was proven by upsets and load following. Consistent product compositions were achieved throughout the 120-day life run. Finally, catalyst addition/withdrawal was successfully demonstrated.

Several recommendations can be made from the results of these operations.

- Temperature ramping as well as hydrogen uptake must be closely controlled for complete in-situ activation of the catalyst.
- Catalyst activation at high slurry concentrations is difficult and should be avoided if possible. Activation of more dilute slurries followed by concentration while operating is preferred.
- The new catalyst (F21/OE75-43) is the preferred catalyst due to increased productivity and slower deactivation.
- Catalyst deactivation is relatively slow, and the activity can be maintained via periodic catalyst addition/withdrawal without major interruption of service.
- The Deckwer correlation should be used to predict the shell-side heat transfer coefficient in the reactor internal heat exchanger.
- Heat transfer within the reactor needs further study, but a fouling factor of $0.0015 \text{ hr-ft}^2\text{-}^\circ\text{F/Btu}$ for the shell-side of the internal heat exchanger is a conservative estimate.

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