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

Topical Report

Task 2.2: Process Variable Scan Run E-8
and In-Situ Activation with Syngas Run E-9

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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 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
lbmol	Pound moles
m^2	Square meters
min	Minutes
mol %	Mole percent
ppb	Parts per billion by volume for gas by weight for liquid
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

ABSTRACT

Liquid-entrained operations at the LaPorte LPMEOH Process Development Unit (PDU) continued from January 1989 through March 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 primary operating objectives of this activity were to develop a broad operating experience base at a variety of potential commercial applications and to test an in-situ catalyst activation procedure using readily available syngas in place of hydrogen. Secondary objectives were to further test the limits of the LPMEOH slurry reactor operating range to assist in the future evaluation of optimum process configurations and examine the potential of water injection as a means to enhance reactor performance.

The Process Variable Run E-8 began in January 1989 as a continuation of the 127-day Catalyst Activity Maintenance Run E-7, and continued until the end of February 1989 using the alternate commercial catalyst (F21/0E75-43). Twenty-eight different process conditions examined the effects of feed gas composition, pressure, temperature, space velocity, superficial inlet gas velocity, slurry concentration and slurry liquid level. In addition, there were five repeats of baseline operating conditions as a check on catalyst activity maintenance during this 50-day run. One of the more notable accomplishments was flawless operations at a 50 wt% catalyst slurry concentration.

In March 1989, Run E-9 demonstrated the ability to activate the catalyst in-situ using a dilute syngas in place of dilute hydrogen. The successful activation was followed by a small series of process variable studies designed to evaluate the effectiveness of the activation procedure and further expand the operating experience base of the LPMEOH slurry reactor. The most notable accomplishments in this 14-day run included a record methanol production rate of 12.8 TPD and operating at a precedent-setting inlet superficial gas velocity of 0.72 ft/sec.

A mixing study on the slurry reactor was done in February and March, 1989 using radioactive gas and liquid tracers. The results of that work have been previously published as a DOE Topical Report entitled "Task 2.3: Tracer Studies in the LaPorte LPMEOH PDU" and is not reported here.

I. EXECUTIVE SUMMARY

The effort to prove the technical feasibility of the LPMEOH process at the Process Development Unit (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 developing process economics. 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 to define the limits of performance of the slurry system, in an effort to provide data for commercialization activities, and to demonstrate a simplified procedure to activate the catalyst with dilute syngas and without the use of the slurry circulation pump. These aggressive conditions and process simplifications have the potential to significantly impact commercial capital and operating costs and are important for improving process economics.

A. Process Variable Scan Run E-8

The Process Variable Run E-8 was conducted from 10 January through 28 February 1989 as a continuation of the 127-day Catalyst Activity Maintenance Run E-7. The run objective was to define the limits of performance of the slurry system, in an effort to provide data for commercialization activities. Twenty-eight different process conditions examined the effects of feed gas composition, pressure , temperature, space velocity, superficial inlet gas velocity, slurry concentration, and slurry liquid level. The cases maximizing gas linear velocity and catalyst concentration were particularly important to improved process economics. In addition, there were five repeats of baseline operating conditions as a check on catalyst activity maintenance.

The LP-III operating plan for Run E-8 called for a PDU shutdown following the Catalyst Activity Maintenance Run E-7. The stability of the catalyst activity and the success of the addition/withdrawal procedure, however, resulted in a highly active catalyst slurry at the end of Run E-7 with a methanol production rate of 9.5 TPD. This excellent residual level of catalyst activity allowed Run E-8 to begin immediately after the completion of Run E-7, without performing the scheduled two-week turnaround.

Run E-8 consisted of a series of 34 different process conditions or cases, of which the majority had been previously tested in the laboratory autoclaves, to determine the impact on methanol productivity and catalyst deactivation. The purpose of the PDU operations was to confirm that data and to expand the information base to include the impact on hydrodynamics, mass transfer and gas holdup. Several operating parameters, including inlet superficial gas velocity, slurry catalyst weight percent, and slurry liquid level, can only be tested reliably in the PDU.

The PDU performed well at all of the tested conditions and all of the cases proposed in the process variable scan matrix for Run E-8 were completed with the exception of case E-8.10. This case was postponed to Run E-9 since the maximum achievable inlet superficial gas velocity for E-8.10 was not substantially greater than previous runs (0.56 ft/sec) with the 01.20 Recycle Compressor running at its maximum throughput.

Run E-8 concluded over six months of continuous operation at the LaPorte LPMEOH PDU covering three different runs: Run E-6--the alternate catalyst run, Run E-7--the catalyst activity maintenance run, and Run E-8--the process variable scan run. At the conclusion of Run E-8, the reactor, oil separation section, and slurry pump were opened and inspected. The PDU equipment and vessels were in good condition. Catalyst buildup was minimal on most surfaces and heat exchanger fouling was very limited.

The PDU accumulated 1194 hours of methanol synthesis operation while producing 382 tons of methanol at an average purity of 97.1 wt% during the in-situ catalyst activation run E-8. The results from this run provide a broad operating experience background that serves as a basis for future commercial demonstrations and the trends observed in several of the runs defined the performance constraints of the LPMEOH process.

B. In-Situ Activation with Syngas Run E-9

The final 10-day run of the LP-III program began on 14 March 1989 with a fresh batch of the alternate catalyst. The main objective of this run was to demonstrate a simplified procedure to activate the catalyst with dilute syngas in place of dilute hydrogen and without the use of the slurry circulation pump. These process simplifications have the potential to significantly impact commercial capital and operating costs. The activation was followed by a small series of process variable studies designed to evaluate the effectiveness of the activation procedure and further expand the operating experience base of the LPMEOH slurry reactor.

The new catalyst activation procedure went smoothly and was completed on schedule. Run ER-6 was clearly the simplest and most uneventful of any PDU catalyst activation and resulted in fully activated catalyst slurry.

The transition from reduction gas (ER-6) to synthesis gas (E-9), however, was troublesome but manageable. The initial low reactor feed flow rates resulted in nonuniform temperature and gas holdup profiles within the reactor, and the liquid/vapor interface at the top of the slurry level was indiscernible with the nuclear density gauge. The initial behavior of the slurry on synthesis gas can best be described as a froth with substantial slurry carryover from the reactor. However, methanol samples remained clear. This operating condition was corrected by reducing the reactor feed flowrate which resulted in the formation of a distinct vapor/liquid interface while maintaining uniform temperature and gas holdup profiles within the reactor. Normal operating conditions were obtained within 48 hours of the beginning of the run. The remainder of the operations were uneventful and executed according to plan.

Run E-9 consisted of a series of eight different process conditions or cases. The majority of the cases were chosen to evaluate the effectiveness of the activation procedure, but four cases were included to further expand the operating experience base of the LPMEOH slurry reactor. Two cases examined the effect of water injection on reactor performance and a final case tested the maximum attainable superficial inlet gas velocity to the slurry reactor. The PDU accumulated 330 hours of methanol synthesis operation while producing 122 tons of methanol at an average purity of 96.5 wt% during the in-situ catalyst activation run E-9.

In addition to the activities described above, Runs E-8 and E-9 included three periods of reactor mixing studies using radioactive gas and liquid tracers. The details and results of that work have been previously published as a DOE Topical Report entitled "Task 2.3: Tracer Studies in the LaPorte LPMEOH PDU" and are not discussed in this report.

C. Overall LP-III Program

The PDU performed very well over the wide range of process conditions for the 64 operating days of Runs E-8 and E-9. Worthy of special note are successful operations at slurry concentrations of 50 wt% oxide, operation at inlet superficial gas velocities of 0.72 ft/sec and a sustained production rate of 12.8 TPD. Five-hundred and four tons of methanol were produced with an average product purity of 97.0 wt% methanol and 98.0 wt% total alcohols. Total lost time was 21 out of 1546 hours for an overall 98.6% on-stream factor.

Run E-9 was the completion of PDU operations under the DOE LP-III contract (DE-AC22-87PC90005). Overall, this was a tremendously successful series of runs producing over 1/2 million gallons of methanol (1677 tons) during 212 operating days. The average production rate of 8 TPD exceeded the PDU design nameplate capacity of 5 TPD by 60%. As a result of these tests, the LPMEOH technology is ready to be economically demonstrated at a commercial scale.

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 1989 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:

Date	Development Scale and Key Results
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 - 1989	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 ft. 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
1988 - 1989	2 ft. ID x 20 ft. tall LaPorte PDU (up to 13 TPD MeOH) Isolated Reactor Design Proven Catalyst Addition/Withdrawal Demonstrated Load Following Demonstrated Improved Reactor Productivity Improved Catalyst Life Improved Oil Recovery

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

	Minimum	"Typical"	Maximum
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 CGCC plant configured to make electric power and coproduct methanol.

- Balanced Type, representative of CO-Rich gas which has undergone shift and O_2 rejection so that the hydrogen and carbon oxide concentrations are approximately stoichiometrically balanced (2:1) in order to achieve an "all-methanol" product.

- H_2-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 H_2, CO, N_2, and CH_4 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

Component (mol%)	CO-Rich Gas	Balanced Gas	H_2-Rich Gas
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

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.

TABLE II.3

LAPORTE PDU OPERATIONS SUMMARY

Run #	Date	Objective	Operation Mode	Catalyst Type	Hours On Syngas
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	231
					2536

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.

C. LPMEOH III Operations

Additional major synthesis runs under the LP-III contract were conducted from June 1988 through early January 1989.

TABLE II-4

LAPORTE PDU OPERATIONS SUMMARY

Run #	Date	Objective	Operation Mode	Catalyst Type	Hours On Syngas
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
E-6	Aug 88	Alternate Catalyst Evaluation	Slurry Loop for Reduction; Internal Only for Syngas	Powder	161
E-7	Sep/Jan 89	Catalyst Activity Maintenance	Internal	Powder	3139 3559

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.

Run E-6 was started in late August to evaluate an alternate commercial catalyst as a possible substitute for the previously used baseline catalyst. Run E-6 consisted of a series of process variable scans to determine the behavior of the catalyst slurry under various operating conditions. The initial condition of 5,600 SL/hr-kg 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 36 wt% and the catalyst productivity increased from 79 to 100% of autoclave performance. A comparison of the baseline and alternate catalysts at equal feed rates and reactor volumes showed that the alternate catalyst produces 9% more methanol at 35 wt% than the previous catalyst at 40 wt%.

The alternate catalyst run was continued as the Activity Maintenance Run E-7 for a 120-day catalyst life study at nominal conditions of 10,000 sl/kg-hr, 482°F, 750 psig and 35 wt% oxide catalyst. The PDU produced a record 10.1 tons per day of methanol during the first 2 weeks of Run E-7. After 120 days of operation, the methanol production rate was still in excess of 8 TPD, indicating a baseline (poison-free) deactivation rate of no more than 0.2%/day. This was half the rate of that in Run E-3 in 1985. Although the Activity Maintenance Run was only four months in duration, the high productivity resulted in a cumulative methanol production of over 2500 lb of methanol per lb of catalyst. This corresponds to approximately 30-40% of the typical gas phase catalyst life on a catalyst consumption basis.

At the end of Run E-7 a series of tests were carried out to define the response of the LPMEOH unit to fast and major changes in the feed rate. These tests parallel what would be expected in load-following of commercial gasification systems. Cuts of 80% in the feed flow were accommodated easily and resulted in process fluctuations lasting only a few minutes. In every case the temperature response of the reactor was very good, the maximum difference being 5°F.

Following these tests, the potential for catalyst addition and withdrawal was investigated. Approximately half of the aged catalyst slurry was removed from the reactor and replaced by fresh catalyst which had been held in the slurry preparation vessel, where it had been activated 120 days previously as part of the original batch (for Run E-6). The new production level was within 5% of that predicted, assuming the added catalyst had the same activity as that used initially in Run E-6. This significant result answered two key questions. One, it is possible to store activated catalyst for long periods of time and two, catalyst addition/withdrawal seems a viable means of maintaining catalyst "activity" (production rate).

Overall, Run E-7 was tremendously successful. Over 1,000 tons of methanol were produced and the unit responded superbly to the ups and downs of normal operation. Total lost time was 137 out of 3,100 hours, of which 130 hours were the result of electrical or gas supply outages unrelated to the LPMEOH PDU. The high level of residual catalyst activity resulting from the low rate of catalyst deactivation and the success of the addition/withdrawal procedure allowed Run E-7 to be continued as Run E-8, eliminating the requirement for the activation of a fresh batch of catalyst slurry.

LaPorte PDU operations successfully demonstrated LPMEOH process technology at a representative engineering scale. The more notable achievements include:

- Over 6,000 hours of methanol synthesis operation with an on-stream factor of 96-100%.
- Low catalyst deactivation while operating with a 35 wt% catalyst slurry for an extended period of time on CO-rich synthesis gas.
- The ability to activate methanol synthesis catalyst powders in an inert liquid at high concentrations.
- Methanol production levels above 10 TPD with a purity of the methanol product from CO-rich gas consistently higher than 97 wt%.
- Optimization of the process by eliminating the external slurry loop while simultaneously increasing productivity.

III. LAPORTE LPMEOH PDU

A. Process Description

A simplified flowsheet for the process configuration used at the LaPorte PDU for Runs E-8 and E-9 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 an external cyclone for slurry carryover disengagement which 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 does not significantly impact the reactor hydrodynamics.

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

Figure III.1

SIMPLIFIED PROCESS FLOWSHEET FOR LAPORTE PDU

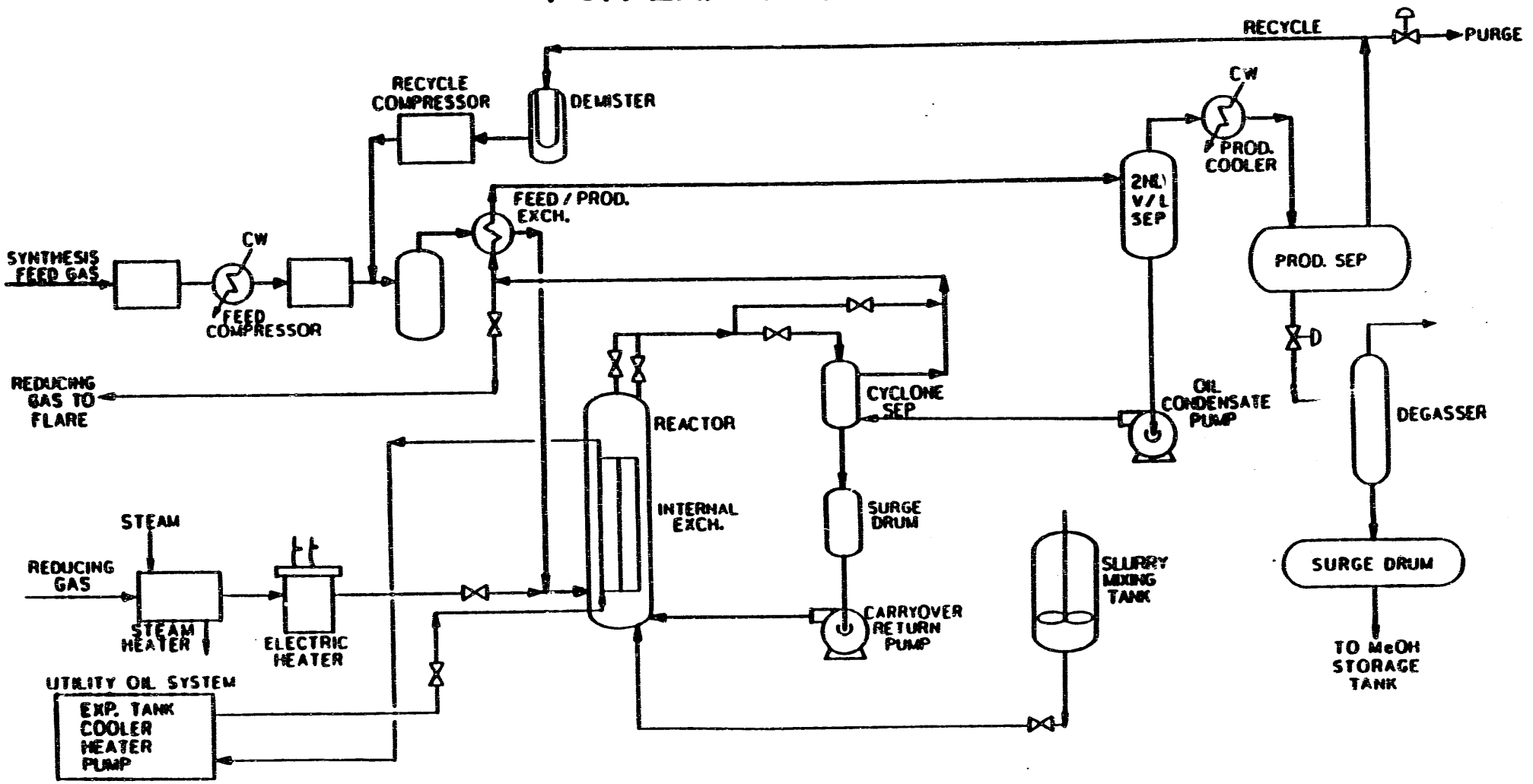
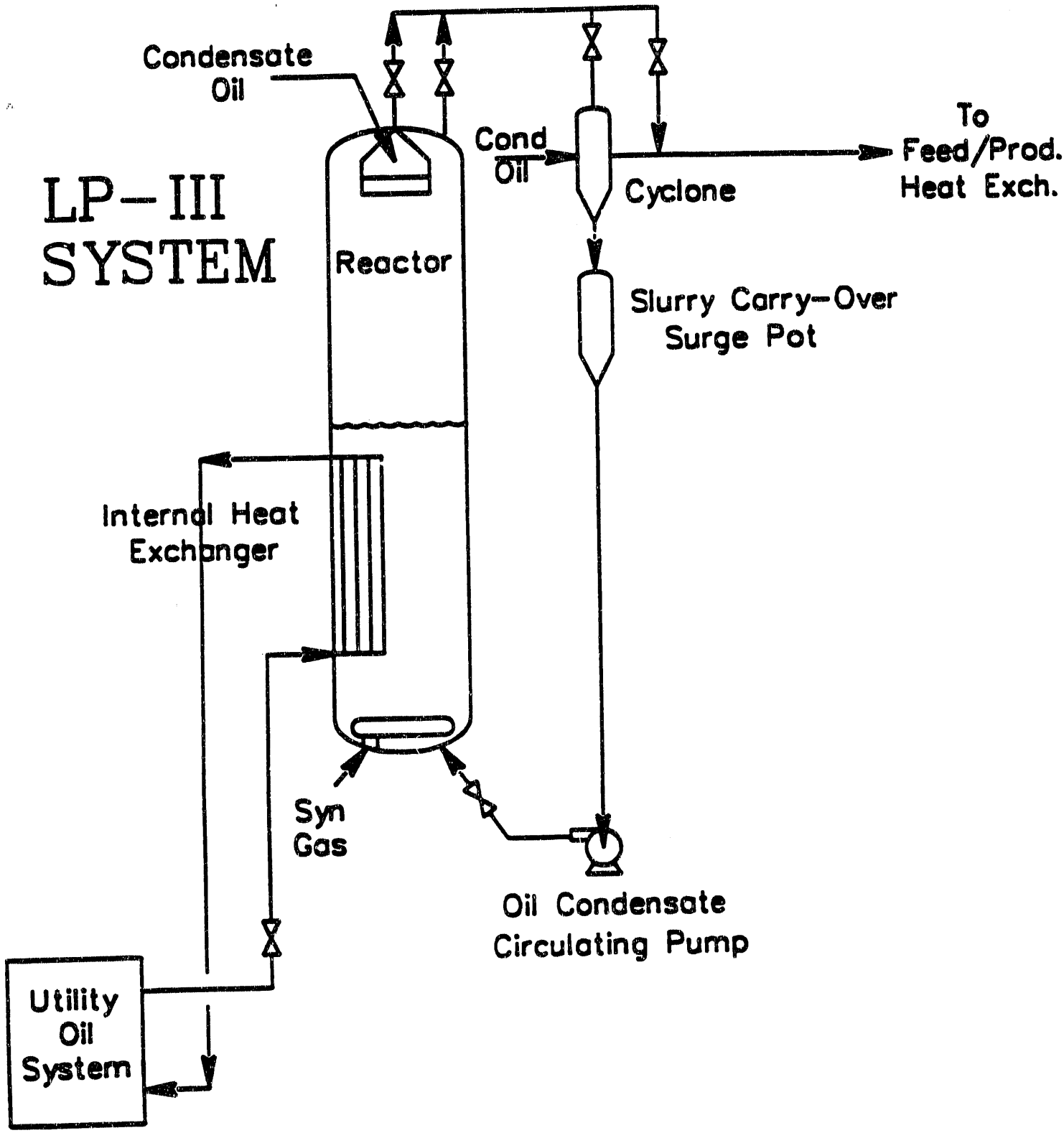


Figure III.2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Feed/Prod.
Heat Exch.
Slurry Carry–Over
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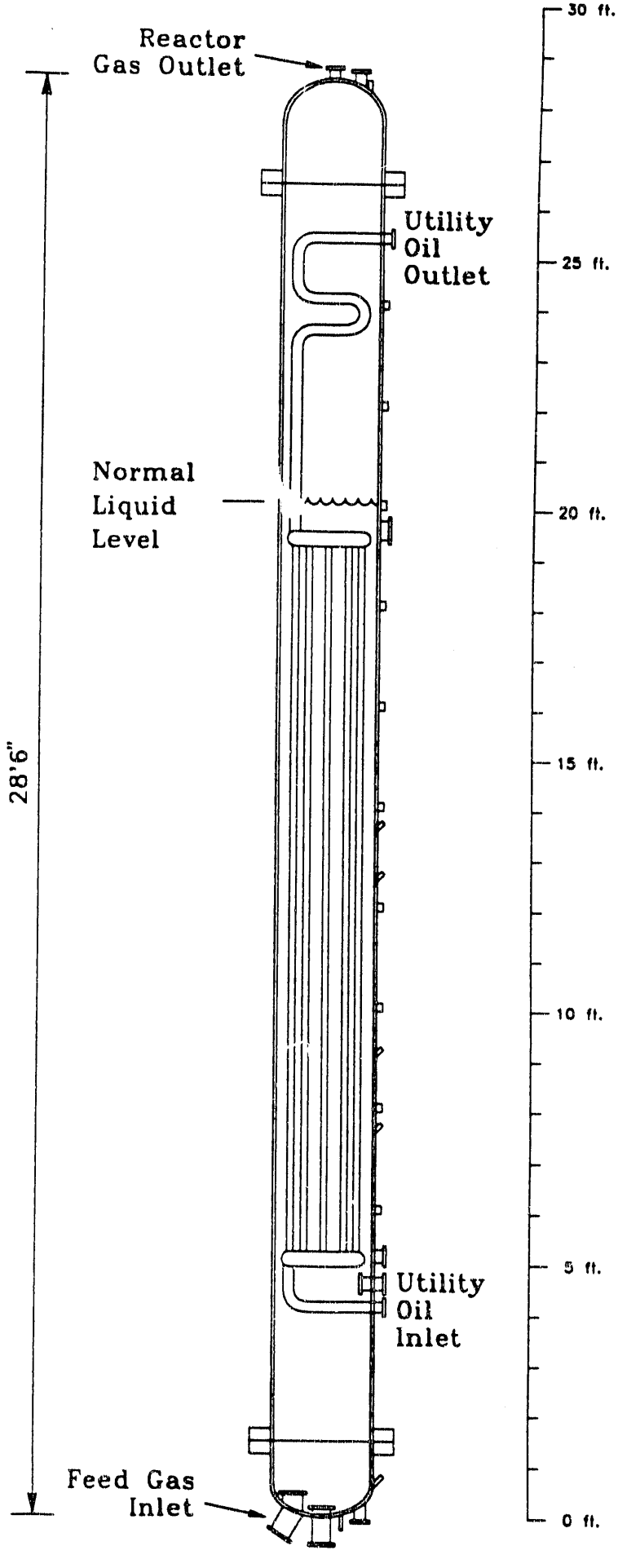
Exchanger
Syn
Gas
Oil Condensate
Circulating Pump
Utility
Oil
System

Figure III.3

LPMEOH REACTOR AT LAPORTE PDU



IV. PROCESS VARIABLE SCAN RUN E-8

A. Introduction

The Process Variable Run E-8 began in January 1989 as a continuation of the 127-day Catalyst Activity Maintenance Run E-7, and continued until the end of February 1989 using the alternate commercial catalyst (F21/0E75-43). The run objective was to define the limits of performance of the slurry system, in an effort to provide data for commercialization activities. Twenty-eight different process conditions examined the effects of feed gas composition, pressure, temperature, space velocity, superficial inlet gas velocity, slurry concentration, and slurry liquid level. The cases maximizing gas linear velocity and catalyst concentration were particularly important to improved process economics. In addition, there were five repeats of baseline operating conditions as a check on catalyst activity maintenance.

B. Methanol Synthesis Operation

The LP-III operating plan for Run E-8 called for a PDU shutdown following the Catalyst Activity Maintenance Run E-7. The catalyst slurry was to be drained from the reactor and the PDU equipment disassembled, inspected and cleaned. A fresh batch of catalyst slurry would then be activated prior to the start of Run E-8. The anticipated rate of catalyst deactivation and the need to replace the largely deactivated catalyst slurry had necessitated this scheduled turnaround. The stability of the catalyst activity and the success of the addition/withdrawal procedure, however, resulted in a highly active catalyst slurry at the end of Run E-7 with a methanol production rate of 9.5 TPD. This excellent residual level of catalyst activity allowed Run E-8 to begin immediately after the completion of Run E-7, without performing the scheduled two-week turnaround. This program modification resulted in an operating efficiency and allowed the scope and length of the Process Variable Scan Run E-8 to be expanded from the original plan at no cost.

Run E-8 consisted of a series of 34 different process conditions or cases. These cases were chosen to systematically examine the effects of feed gas composition, CO_2 effects, pressure, temperature, space velocity, superficial inlet gas velocity, slurry concentration, and slurry liquid level. The majority of these conditions had been tested previously in the laboratory autoclaves to determine the impact on methanol productivity and catalyst deactivation. The purpose of the PDU operations was to confirm that data and to expand the information base to include the impact on hydrodynamics, mass transfer, and gas holdup. Several operating parameters, including inlet superficial gas velocity, slurry catalyst weight percent and slurry liquid level, can only be tested reliably in the PDU.

The feed gas types tested in Run E-8 are defined in Table IV.1. Overall, the feed gases represented the entire range of synthesis gas compositions that could be expected from most modern gasifier, partial oxidation or reformer technologies. The gas compositions ranged from CO-rich to H_2-rich with H_2/CO ratios varying from 0.49 for a Shell gasifier type feed to 3.94 for a natural gas reformer type feed. Carbon dioxide levels varied from 1 to 16 mol% and inert levels from 1 to 21 mol% were tested.

TABLE IV.1

RUN E-8 TARGET GAS COMPOSITIONS

Gas Type	H2	CO	CO2	N2	CH4	H2/CO	(H2-CO2)/(CO+CO2)
CO-Rich	35	51	13	1		0.69	0.34
H2-Rich	71	18	7	4		3.94	2.56
Balanced	54	23	2	21		2.35	2.08
Dow	41	41	16	2		1.00	0.44
Shell	32	65	2	1		0.49	0.45
G. Plains	60	21	1	1	17	2.86	2.68
*CO-Rich	37	54	8	1		0.69	0.47

The planned range of the operating variables to be tested in Run E-8 are listed in Table IV.2. The maximum target superficial gas velocity (1.0 ft/sec) and catalyst loading (50 wt% ox.) were very aggressive and previously untested operating conditions. The slurry level variation was the first test of the impact of the reactor liquid/diameter ratio (L/D) on reactor performance.

TABLE IV.2

PLANNED RANGE OF OPERATING VARIABLES FOR RUN E-8

	Minimum	Maximum
Reactor Pressure, psig	500	900
Reactor Temperature, °C	235	285
°F	455	545
Space Velocity, liter/hr-kg cat	2,000	14,000
Superficial Gas Velocity, ft/sec	0.1	1.0
Catalyst Loading, wt% ox.	35	50
Slurry Level, %	64	100
, L/D	6.8	10.6

The full matrix of nominal operating conditions for Run E-8 is shown in Table IV.3. The operation of the PDU was very stable for all of the cases tested and there were no constraints on the process caused by the design or limitations within the slurry reactor. The Run Chronology in Table IV.4 gives the detailed account of the run.

In addition to the 34 process variable conditions, Run E-8 included two operating periods of reactor mixing studies using radioactive gas tracer tests. The details and results of that work have been previously published as a DOE Topical Report entitled "Task 2.3 Tracer Studies in the LaPorte LPMEOH PDU" and are not discussed here.

TABLE IV.3

MATRIX OF NOMINAL TARGET PVS RUN CONDITIONS FOR RUN E-8

Run No.	Gas Type	Pres. psig	Temp. °C	Space Vel. L/hrkg	Gas Vel. ft/sec	Slurry Conc. wt. %	Slurry Height %	Comment
127	CO-Rich	750	250	9000	0.5	40	100	Run E7:Day 127
	24 hour concentration period before beginning Run E-8							
1	CO-Rich	750	250	7000	0.5	45	100	
2	CO-Rich	750	250	7000	0.5	50	83	Est. Max Conc.
3	CO-Rich	750	250	3000	0.2	50	71	
4	CO-Rich	750	250	3000	0.2	45	87	
5	CO-Rich	900	250	5000	0.3	40	100	
6	CO-Rich	750	250	9000	0.5	40	100	Baseline
7	CO-Rich	900	250	9000	0.5	40	100	
8	CO-Rich	750	250	4000	0.2	40	92	
9	CO-Rich	500	250	7000	0.5	40	100	
10	CO-Rich	500	250	13000	1.0	40	100	Max. Gas Vel.
11	CO-Rich	750	250	11000	0.5	35	100	Baseline
12	CO-Rich	750	250	6000	0.3	35	92	
13	CO-Rich	750	250	14000	0.6	35	100	
14	CO-Rich	750	250	3000	0.1	35	77	
15	H2-Rich	500	250	7000	0.5	35	100	
16	H2-Rich	750	250	7000	0.3	35	100	
17	H2-Rich	750	250	11000	0.5	35	100	
18	Balanced	750	250	7000	0.3	35	88	
19	Dow Gas	750	250	7000	0.3	35	87	
20	Dow Gas	900	250	7000	0.3	35	85	
21	CO-Rich	750	250	11000	0.5	35	100	Baseline
22	Balanced	750	250	11000	0.5	35	100	
23	Balanced	900	250	11000	0.4	35	95	
24	CO-Rich*	750	250	11000	0.5	35	100	Optim. CO2
25	CO-Rich*	900	250	11000	0.4	35	95	Optim. CO2
26	Shell Gas	750	250	11000	0.5	35	100	
27	Shell Gas	900	250	11000	0.4	35	95	
28	CO-Rich	750	250	11000	0.5	35	100	Baseline
29	CO-Rich	750	235	11000	0.5	35	99	Temp. Effect
30	G. Plains	900	250	7000	0.3	35	85	
31	CO-Rich	750	270	11000	0.5	35	101	Temp. Effect
32	CO-Rich	750	285	2000	0.1	35	73	Temp. Effect
33	CO-Rich	750	250	11000	0.5	35	100	Baseline
	Drain 30% of Slurry Inventory							
34	CO-Rich	750	250	10000	0.4	35	64	L/D Effect

Note: * CO-Rich gas matrix with reduced (8 mol%) CO2

TABLE IV.4

RUN E-8 CHRONOLOGY

Date	Time	Cumulative Time On Production Gas (hours)	Notes and Observations
09 Jan 89	0800	0.0	Run E-7 officially ended after 124 days on stream at the nominal conditions of: 482°F, 750 psig, 10,000 Sl/hr-kg space velocity and CO-Rich feed gas.
	0950	1.8	Began continuous addition of slurried catalyst from the slurry prep tank to the reactor via 10.56 pumps.
	1530	7.5	A 10.56 check valve momentarily plugged so for a brief time there was no slurry flow to the reactor.
	1700	9.0	Both 10.56 pumps in service. Both north side 10.56 pump check valves leak. Pumps require constant attention in order to maintain discharge pressure. This is slowing the rate of slurried catalyst addition.
	2100	13.0	First signs of a significant increase in reaction. The utility oil temperature to the internal heat exchanger continues to drop.
	2150	13.8	Stop catalyst addition for the evening. Added slurried catalyst from the prep tank to the reactor for approximately 12 hours.
10 Jan 89	0000	16.0	Lined plant out for the evening at the nominal conditions of: 482°F, 750 psig, 7,000 Sl/hr-kg and CO-Rich feed gas.
	0630	22.5	The plant ran well over the early morning hours. The temperature and gas profiles in the reactor were both steady. The operator was unable to get the hydrogen concentration in the reactor feed above 34 mol%, because the reaction rate was so fast.
	0740	23.7	HV-150-2-S closed for a shut down test to determine catalyst loading after 09 Jan 89 continuous addition. The catalyst loading according to this test was 567 kg.
	0925	25.2	A sample was taken from the slurry prep tank. Only ½ gallon oil and gas was extracted.

TABLE IV.4

RUN E-8 CHRONOLOGY

Date	Time	Cumulative Time On Production Gas (hours)	Notes and Observations
	1300	28.8	With the 28.30 catalyst prep tank apparently empty it was decided to start Run E-8.1. The nominal conditions for this case were: 482°F, 750 psig, 7000 Sl/hr-kg space velocity, 45 wt%, and CO-Rich feed gas.
	1500	30.8	Able to control reactor temperature with TIC-188 set at 280°F which results in a colder feed gas temperature to the reactor.
11 Jan 89	1900	58.8	End of Case E-8.1. With no problems operating at 45 wt% catalyst, it was decided to thicken up further boiling off oil and reducing liquid level. To help with reactor temperature control, TIC-188 was moved to 290°F to further cool the reactor feed gas temperature. Oil return to the reactor was stopped.
12 Jan 89	0000	63.8	Slurry concentration at 49.95 wt%. Some instability in the nuclear density gauge readings in position number eight near the top of the reactor liquid level.
	0200	65.8	Temperature, flow, and compositions lined out for Case E-8.2 conditions. The nominal conditions for this case are: 482°F, 750 psig, 7,000 Sl/hr-kg space velocity, 50 wt% and CO-Rich gas composition.
13 Jan 89	0700	94.8	End of Case E-8.2. Reducing feed gas rates for Case E-8.3. Because of the expected lower methanol production rate and resulting lower heat load, it will be possible to return TIC-188 to 280°F during the rate reduction.
	1000	97.8	The conditions for Case E-8.3 reached easily. These conditions were: 482°F, 750 psig, 50 wt%, 3,000 Sl/hr-kg space velocity, and CO-Rich feed gas composition.
14 Jan 89	1000	121.8	The 0700 methanol product sample was found to be cloudy.

TABLE IV.4

RUN E-8 CHRONOLOGY

Date	Time	Cumulative Time On Production Gas (hours)	Notes and Observations
	1400	125.8	Opened the slurry prep tank for inspection and found 3-5 inches of settled slurry covering the bottom of the vessel. Two pint bottle samples were taken and one quart size sample was taken for analysis. These samples did not flow. They resembled paste or mud. Estimated that these samples were approximately 65 wt% solids.
	1900	130.8	Case E-8.3 ended. Started to add oil from the intermediate oil separator to the reactor to dilute slurry down to 45 wt% for Case E-8.4.
	2006	131.8	Noticed an immediate 20% increase in production by dilution of the 50 wt% slurry.
	2115	133.0	The three phase gas hold up data indicates that the concentration of solids is roughly 46 wt%. Waiting for temperature and flow composition to stabilize.
15 Jan 89	0100	136.8	Beginning of Case E-8.4. Nominal conditions for this case are: 482°F, 750 psig, 3,000 Sl/hr-kg space velocity, 45 wt% catalyst, and CO-Rich feed gas composition.
	0800	142.8	Operation smooth. The methanol in the reactor effluent reached as high as 10 mol%.
16 Jan 89	0700	166.8	Case E-8.4 ended.
	0941	169.4	The blind between the slurry prep tank and the reactor was swung. The gas flow to the reactor was stopped and the pre-transfer shutdown NDG scan was taken.
	1023		Plant depressurization complete. The slurry in the reactor was agitated using high pressure nitrogen.
	1050		High pressure nitrogen flow stopped and a set of NDG scans were taken to verify original set. Nitrogen flow resumed.

TABLE IV.4

RUN E-8 CHRONOLOGY

Date	Time	Cumulative Time On Production Gas (hours)	Notes and Observations
	1103		Stop nitrogen flow to reactor and begin catalyst draining from the reactor to the slurry prep tank. Three consecutive openings of valve HV-1509-S lowered the degassed slurry level from 143.5 inches on the tape to 131.75 inches on the tape. The target slurry height was 132 inches.
	1208	169.4	Started once through syngas blending to the flare.
	1738	174.9	Plant finally at 750 psig, but composition still not close.
16 Jan 89	1845	176.0	Finding it difficult to get enough hydrogen into the plant because of the high conversion across the reactor. TIC-188 moved to 270°F because the utility oil temperature to the internal heat exchanger was too low (294°F).
	1900	176.3	Plant finally lined out at Case E-8.5 conditions. The reason for the extended line out period was to purge out nitrogen because we used nitrogen to stir the catalyst slurry instead of syngas. The nominal conditions of this case were: 482°F, 750 psig, 40 wt%, 5,000 Sl/hr-kg, and CO-Rich gas.
17 Jan 89	1900	200.3	End of Case E-8.5. Preparations begun for next catalyst draining.
	1922	200.7	HV-150-2-S closed and gas flow to the reactor stopped in order to conduct reactor isolation shutdown test. The NDG scan results showed a catalyst loading for Case E-8.5 to be 530 kg.
	1945		Plant being depressurized while maintaining a small flow of syngas.
	2038		Beginning slurry transfer from reactor to slurry prep tank at 350 psig.
	2043		On third opening of valve HV-1509-S the valve stuck open. The three backup valves between the reactor and the prep tank also stuck open. Finally closed with a liquid level 126.5 inches. target was 125 inches. Did not risk reopening valve and overshooting catalyst withdrawal.

TABLE IV.4

RUN E-8 CHRONOLOGY

Date	Time	Cumulative Time On Production Gas (hours)	Notes and Observations
	2050	200.7	HV-150-2-S reopened. Began syngas blending.
18 Jan 89	0100	208.4	The PDU lined out at the nominal conditions of Case E-8.6: 482° F, 750 psig, 40 wt% catalyst, 9,000 Sl/hr-kg and CO-Rich feed gas composition.
19 Jan 89	0700	224.8	Plant ran very smoothly for this base line condition. Case E-8.6 ended. Moved TIC-188 to 280°F in anticipation of an increasing heat duty from heat of reaction as the plant pressure was raised to 900 psig.
	0805	235.9	Had to move TIC-188 to 290°F.
	1020	238.2	Plant pressure at 890 psig and TIC-188 at 300°F.
	1200	239.8	Set TIC-188 at 310°F. The PDU will run at this setting for the duration of this high production case. It is difficult to get enough hydrogen into the front end of the plant with these high production rates .
20 Jan 89	0500	256.8	The concentration of hydrogen finally above 34.5 mol%. Official start of Case E-8.7. The conditions for this case are: 482°F, 900 Psig, 40 wt% catalyst, 9,000 Sl/hr-kg space velocity and CO-Rich feed gas. The 22 hour line out period was because of the low mol% hydrogen in the feed.
	0830	260.3	Found that FQI-241, methanol product flow meter, was over range on the computer. Re-spanned the computer to be accurate at a higher voltage signal.
	0930	261.3	Began flowing the methanol product to the product day tank to verify the 12 TPD production numbers being calculated from the re-spanned FQI-241.
	1900	270.8	Stopped flow to the product day tank. The day tank measured a production rate of 12.08 TPD and the FQI-124, product flow meter, calculated a production rate of 12.03 TPD.
	1930	271.3	Production and conversion of feed gas was so high, coupled with heavy rain, caused the flare to go out.

TABLE IV.4

RUN E-8 CHRONOLOGY

Date	Time	Cumulative Time On Production Gas (hours)	Notes and Observations
21 Jan 89	0700	282.8	Case E-8.7 ended after 26 hours of record breaking production rates of 12.04 TPD. Started backing down plant pressure and flows.
	1400	289.8	Beginning of Case E-8.8. Nominal conditions for this case were: 482°F, 750 psig, 5000 Sl/hr-kg space velocity, 40 wt% catalyst and CO-Rich feed gas composition.
22 Jan 89	0630	306.3	Plant running well even at reduced CO line pressure. CO flow control valve open wide for a short period of time until line pressure from HYCO was restored.
23 Jan 89	0700	330.8	End of Case E-8.8. Preparing for catalyst withdrawal.
	0730	331.3	HV-150-2-S closed for reactor isolation shutdown test and NDG scans begun. This set of scans showed a catalyst loading of 460 kg.
	0800		Plant depressurization to 350 psig begun.
	0807		Stirring slurry with syngas at 350 psig.
	0835		Second set of uclear density gauge scans verified that the height to drain the reactor to was 119.25 inches.
	0840		Transfer of slurry form the reactor to the slurry prep tank.
	0857	331.3	Transfer completed. Final height at 119.5 inches. HV-150-2-S opened and once through syngas flow started.
	0905	331.5	Plant coming on line and recycle was started. Began line out period for Case E-8.9 nominal conditions of 482°F, 750 psig, maximum flow, and 38 wt% catalyst. (note: maximum flow was 6,800 Sl/hr-kg cat under these conditions)
	1245	335.1	Waiting on feed gas composition and temperature to line out.
	1300	335.4	Plant lined out at E-8.9 nominal conditions.

TABLE IV.4

RUN E-8 CHRONOLOGY

Date	Time	Cumulative Time On Production Gas (hours)	Notes and Observations
	1640	339.0	Oil samples drawn from intermediate oil separator and slurry carry-over surge pot. No visible signs of catalyst carryover.
24 Jan 89	1900	365.4	End of Case E-8.9. Preparing for reactor isolation shutdown test.
	1910	365.5	HV-150-2 valve closed. No flow to reactor. NDG scans started.
	1921	365.4	HV-150-2 valve opened. Flow to reactor resumed. The NDG scan results during the shutdown test indicate a catalyst loading of 401 kg.
	1943	365.9	Attempting to increase flowrate to the reactor to obtain conditions designated for Case E-8.10 of 12,600 Sl/hr-kg cat space velocity, 482°F, and 500 psig. This means feeding 194,617 SCFH of feed gas to reactor to achieve 1 ft/sec linear velocity.
	2000	366.2	Due to compressor capacity constraints the feed gas to the reactor was only able to be raised to 142,000 SCFH. Conditions for Case E-8.10 are unattainable. It was decided to return plant back to conditions of Case E-8.9 until 0700 on 25 Jan 89.
25 Jan 89	0700	377.2	Preparing for reactor shutdown test to determine catalyst loading.
	0704	377.3	Closed H_2 bypass valve. Closed HIC-636 oil return valve. Lowering plant pressure to 300 psig.
	0733	377.7	HV-150-2 valve closed. No flow to reactor. NDG scans taken. Results of NDG scans show 400.1 kg of catalyst loading.
	0750		Slurry transfer from reactor to slurry prep tank started. Beginning slurry level is at 136 inches on the tape.
	0752		Slurry transfer valve stuck open.
	0801		Transfer complete. Slurry transfer flow stopped by closing the valves on the inlet of the slurry prep tank. Final slurry level in reactor is at 118.75 inches. Target was 118.0 inches.

TABLE IV.4

RUN E-8 CHRONOLOGY

Date	Time	Cumulative Time On Production Gas (hours)	Notes and Observations
	0807	377.7	HV-150-2 is opened to allow slurry mixing with syngas as plant pressure is brought up to 750 psig.
	0821	378.0	H_2 bypass valve opened.
	0838	378.3	HV-150-2 is closed again in order to determine catalyst loading after slurry transfer.
	0840		NDG scans taken.
	0852	378.3	HV-150-2 valve opened. Feed gas to reactor. Shutdown test results indicate a catalyst loading of 361 kg. (Target loading: 353-354 kg)
	0900	378.4	Attempting to line out plant at Case E-8.11 nominal conditions of 482°F, 750 psig, 11,100 Sl/hr-kg space velocity, 35 wt% catalyst, and CO-Rich feed gas.
	1108	380.5	Plant lined out in flow, pressure, and temperature, but not in feed gas composition.
	1300	382.4	Plant lined out. Beginning of Case E-8.11 balance period.
	2300	392.4	Feed fell off, recycle was out of control, and temperature was fluctuating until 0000 hours.
26 Jan 89	0000	393.4	Composition and temperature stabilized.
	1530	408.9	Leak discovered around recycle compressor discharge.
	1600	409.4	End of Case E-8.11. Preparing to depressurize compressor in order to repair leak.
	1620	409.7	Block in HIC-636.
	1621	409.7	H_2 bypass blocked in.
	1623	409.8	HV-150-2 closed. No flow to reactor. Purge gas to flare flow (PV-201) blocked in.
	1650		Compressor depressurized. Changing recycle discharge pipe.
	1715		Compressor discharge line changed out.

TABLE IV.4

RUN E-8 CHRONOLOGY

Date	Time	Cumulative Time On Production Gas (hours)	Notes and Observations
	1728		Attempting to restart compressor. Oil pump is stuck.
	1820		Compressor restarted.
	1837	409.8	HV-150-2 open. Syngas flow to reactor resumed.
	1841	409.8	HIC-636 unblocked.
	2012	411.4	After finding that the recycle valve (PIC-247) on the recycle compressor would not completely close under normal instrument air pressure, the valve was closed as tightly as possible and an attempt to bring up rates to the high superficial gas velocity case (Case E-8.10), which had to be aborted on 24 Jan 89, was done.
	2300	414.2	In the attempt to bring the reactor feed flowrate up, the pressure was allowed to go up to 800 psig (and thus increase recycle capacity). The flow to the reactor became over the range of the transmitters and the plant was not able to be lined out. It was decided to return the plant to the nominal conditions for Case E-8.12 of 482°F, 750 psig, 6,600 Sl/hr-kg cat space velocity, and 35 wt% catalyst.
27 Jan 89	0008	415.3	NDG scan shows slurry level in reactor at 191.75 inches on the tape.
	0100	416.2	Plant lined out at Case E-8.12 conditions.
	1200	427.2	Plant running smooth. Will hold conditions until 0800 on 28 Jan 89.
28 Jan 89	0800	447.2	End of Case E-8.12. Preparing to attempt to close recycle valve (PIC-2457) completely so the maximum gas velocity Case E-8.13 will be attainable.
	0820	447.5	HV-150-2 closed. No flow to reactor. Recycle compressor recycle line isolated. Recycle valve (PIC-247) still will not close completely.
	0840	447.5	HV-150-2 opened. Syngas flow to reactor resumed.

TABLE IV.4

RUN E-8 CHRONOLOGY

Date	Time	Cumulative Time On Production Gas (hours)	Notes and Observations
	1000	448.8	Spanning reactor feed gas flowmeter (FT-187A) DP to 350 inch H_2O so it will be in the range of the flows which will be obtained in Case E-8.13.
	1445	453.6	Starting to bring flowrates up and attempting to line plant conditions out to the maximum gas velocity Case E-8.13 nominal conditions of 482°F, 750 psig, 14,000 Sl/hr-kg cat, 35 wt% catalyst, and CO-Rich feed gas.
	1600	454.8	Reactor feed rate up to 184,000 SCFH. Adjusting feed gas to CO-Rich composition.
	1700	455.8	Attempting to bring reactor feed flowrate up to 190,000 SCFH, but the recycle valve (PIC-257) on the recycle compressor is still open 15%. 185,000 SCFH may be the highest reactor feed flowrate that will be attainable.
	1800	456.8	Plant is lined out with 185,000 SCFH reactor feed flowrate. Beginning of Case E-8.13 balance period.
29 Jan 89	0600	468.8	Oil samples taken from slurry carry-over surge pot and intermediate oil separator. Samples showed little or no signs of slurried catalyst carry-over.
	0800	470.8	Methanol product samples show no signs of catalyst carry-over.
	1800	480.8	Methanol product sample shows no sign of catalyst carry-over. Oil samples from slurry carry-over surge pot and intermediate oil separator show slight signs of slurried catalyst carry-over.
	1900	481.8	End of Case E-8.13. Starting to back off to Case E-8.14 nominal conditions of 482°F, 750 psig, 3,000 Sl/hr-kg cat, 35 wt%, and CO-Rich feed gas. Reactor feed flowrate being backed down to 40,400 SCFH.
	2130	484.3	Reactor feed flowrate, temperature, and pressure are lined out. Adjusting composition to CO-Rich feed gas.
30 Jan 89	0000	486.8	Plant lined out. Begin Case E-8.14 balance period.
	1200	498.8	PDU running smooth.

TABLE IV.4

RUN E-8 CHRONOLOGY

Date	Time	Cumulative Time On Production Gas (hours)	Notes and Observations
31 Jan 89	0700	517.8	End of Case E-8.14. Preparing for reactor isolation shutdown test to check catalyst loading.
	0712	518.0	HV-150-2 closed. No flow to reactor.
	0720		Taking reactor NDG scans. The scan results indicate 355.2 kg of catalyst in reactor. This is a drop in catalyst inventory of 6.1 kg over the last check.
	0742		Depressurizing plant to 300 psig to quickly purge out plant in preparation for gas composition change.
	0900		Bringing up plant pressure to 500 psig.
	0930	518.0	HV-150-2 opened. Starting once-thru balanced feed gas to the reactor at 444°F and 500 psig. Reactor feed gas flowmeter (FT-187A) respanned to 150 inches of H_2O.
	1035	519.1	Started recycle flow to reactor. Begin to line plant out to Case E-8.15 nominal conditions of 482°F, 500 psig, 7,000 Sl/hr-kg cat, 35 wt% catalyst, and H_2-Rich reactor feed gas.
	1100	519.5	Added 32 gallons of Drakeol-10 oil to intermediate oil separator. Increased oil return flowrate to reactor from intermediate oil separator to dilute slurried catalyst down to 35 wt%.
	1400	522.5	Added 28 more gallons of oil to 27.14 intermediate oil separator.
	1800	526.5	Reactor NDG scan taken. Results indicate 33 wt% catalyst in reactor.
	1900	527.2	Plant lined out at Case E-8.15 conditions.
1 Feb 89	1900	551.2	Case E-8.15 ended without incident. Start to bring plant pressure up to 750 psig for Case E-8.16 conditions.
2 Feb 89	0000	556.2	Plant lined out at E-8.16 conditions of 482°F, 750 psig, 7,000 Sl/hr-kg cat, and H_2-Rich feed gas.

TABLE IV.4

RUN E-8 CHRONOLOGY

Date	Time	Cumulative Time On Production Gas (hours)	Notes and Observations
	0830	564.7	Having difficulty holding reactor temperature down to 482°F. Utility oil to internal heat exchanger is at 290°F and fin-fan is 100% open. Temperature to intermediate oil separator is increased to 300°F (TIC-188). Utility oil temperature increases to 330°F. Ambient temperature is 80°F.
	1000	566.2	Blew residual slurry from the external loop to the slurry prep tank (28.30) with nitrogen. The slurry in the prep tank will be kept at 200°F and under agitation in an attempt to dislodge the caked slurry that was found on the bottom head of the tank after catalyst addition on 14 January.
3 Feb 89	0630	586.7	Ambient temperature has dropped from 80°F to 35°F overnight. No problem holding reactor temperature down to 482°F. Utility oil temperature to reactor at 350°F and fin-fan only 20% open.
	0700	587.2	End of Case E-8.16. Increasing reactor feed flowrate to 148,900 SCFH to obtain Case E-8.17 nominal conditions of 482°F, 750 psig, 11,100 Sl/hr-kg cat space velocity and H_2-Rich feed gas.
	0930	589.7	Plant lined out on flow and temperature. Working on lining out composition.
	1500	595.2	Plant lined out on E-8.17 conditions.
	1830	598.7	Cutting N_2 feed back to 2-3 mol% of total feed due to Air Plant shutdown. Desired N_2 feed composition is 4 mol% for H_2-Rich feed gas.
4 Feb 89	0300	607.2	H_2 feed dropping off due to HYCO Plant upset. Reactor temperature dropping off; utility oil heaters firing in attempt to hold reactor temperature.
	0400	608.2	Plant lined out on temperature and pressure, but losing feed as HYCO Plant is shutting down.
	0530	609.7	PDU shutdown due to loss of feed from Air Plant and HYCO Plant. Will try to hold reactor temperature with utility oil system.

TABLE IV.4

RUN E-8 CHRONOLOGY

Date	Time	Cumulative Time On Production Gas (hours)	Notes and Observations
	0930		Attempting to hold reactor temperature at 420°F.
	1100		Reactor temperature has dropped to 408°F. HYCO Plant starting to come back on line; should be getting feed gas soon.
	1110		Coming back on line with H_2 and CO feed to reactor. Reactor temperature starting to come up after dropping to 407°F.
	1130	609.7	Syngas to reactor. Reactor temperature at 438°F.
	1145	609.9	Reactor temperature at 452°F and pressure at 850 psig.
	1159	610.2	Reactor temperature coming up smoothly. Temperature at 486°F and pressure at 770 psig.
	1700	615.2	Reactor lined out at same conditions as before shutdown. Continue Case E-8.17. Productivity comparison of before and after shutdown is 39.0 versus 38.5 gmol/hr-kg cat respectively.
5 Feb 89	0700	629.2	End of Case E-8.17. Moving conditions to those of Case E-8.18: 482°F, 750 psig, 6,600 Sl/hr-kg cat, 35 wt%, and Balanced feed gas.
	0805	630.3	Dropped reactor slurry level down to 182 inches on the tape in order to concentrate slurry up to 35 wt% catalyst.
	1200	634.2	Plant lined out at Case E-8.18 conditions.
6 Feb 89	0045	646.9	N_2 feed pressure and flow unstable due to Air Plant upset. H_2 and CO feed line pressures down due to HYCO Plant trip. Composition to reactor fluctuating ever since 0000 hours.
	0600	652.2	End of Case E-8.12. H_2, CO, and N_2 feed line pressures fluctuated all night due to power failures at HYCO and ASU.

TABLE IV.4

RUN E-8 CHRONOLOGY

Date	Time	Cumulative Time On Production Gas (hours)	Notes and Observations
	0800	654.2	Cutting back on N_2 per Air Plant's request. It is decided to move to a Dow Gas reactor feed case which only requires 2 mol% N_2 instead of the 21 mol% N_2 required for the current Balanced gas case.
	0910	655.4	Feed line pressures very low. Trying to stabilize reactor conditions at 482°F, 900 psig, 6,600 Sl/hr-kg cat, and balanced feed gas.
	1000	656.2	Can not get enough feed flow to reactor due to low line pressure. Dropping plant pressure to 750 psig. Attempting to line out plant conditions.
	1130	657.7	Switch on Nuclear Density Gauge traverse motor malfunctioning. No indication of slurry level can be obtained. Holding conditions.
	1230	658.7	NDG switch repaired. Adjusting to Dow feed gas composition.
	1400	660.2	PDU lined out at Case E-8.19 conditions which have been revised to 482°F, 750 psig, 6,600 Sl/hr-kg cat, and Dow feed gas.
	2330	669.7	Dip in power supply. Utility oil heaters out for approximately 10 minutes.
7 Feb 89	0500	675.2	Difficulty holding reactor composition all night due to fluctuating pressure in feed lines.
	1400	684.2	End of Case E-8.19. Starting to move plant to Case E-8.19 conditions: 482°F, 900 psig, 6,600 Sl/hr-kg cat, and Dow feed gas.
	1445	684.9	Reactor pressure at 900 psig. Attempting to line out temperature and feed gas composition.
	1600	686.2	PDU lined out at Case E-8.20 conditions.
8 Feb 89	1330	707.7	Drained 4,563 lbs of slurry from the slurry prep tank. Several samples of the slurry were taken for solids and methanol concentration analyses. This is the slurry which was transferred to the prep tank on 2 Feb 89.

TABLE IV.4

RUN E-8 CHRONOLOGY

Date	Time	Cumulative Time On Production Gas (hours)	Notes and Observations
	1915	713.4	End of Case E-8.20. Changing PDU conditions to Case E-8.21 specified conditions, which are the baseline conditions of 482°F, 750 psig, 11,100 Sl/hr-kg cat, and CO-Rich feed gas.
	2000	714.2	Pressure, temperature, and reactor feed flowrate lined out. Making moves to line out composition.
	2300	717.2	Lined out at Case E-8.21 conditions.
9 Feb 89	1030	728.7	Slurry prep tank inspection reveals very thin (less than 1/16") coating of slurried catalyst on walls, bottom head and stirrer. Overall very clean.
	1345	731.9	PDU is running smoothly at Case E-8.21 conditions.
10 Feb 89	0700	749.2	End of baseline Case E-8.21. Changing conditions to Case E-8.22 conditions of 482°F, 750 psig, 11,100 Sl/hr-kg cat, and balanced feed gas. GC gas standard being switched for balance gas.
	1400	756.2	Plant lined out at Case E-8.22 conditions.
11 Feb 89	1000	776.2	Lab is analyzing flash gas samples on GC #2, therefore, no GC #2 analyses on reactor effluent for next two hours.
	1900	785.2	End of Case E-8.22.
	1915	785.4	Raising pressure for Case E-8.23. Nominal conditions for Case E-8.23: 482°F, 900 psig, 11,000 Sl/hr-kg cat, and balanced feed gas.
	2200	788.2	Plant lined out at Case E-8.23 conditions.
12 Feb 89	0800	798.2	PDU running without incident at Case E-8.23 conditions.
13 Feb 89	0800	788.2	Informed that lab will not have GC standard for upcoming CO-Rich* (optimum 8 mol% CO2) case until 1400 hours today. Therefore, holding present conditions until 1300 hours.
	1300	827.2	End of Case E-8.23.

TABLE IV.4

RUN E-8 CHRONOLOGY

Date	Time	Cumulative Time On Production Gas (hours)	Notes and Observations
	1315	827.4	Begin to change conditions to Case E-8.24 nominal conditions of 482°F, 750 psig, 11,100 Sl/hr-kg cat, and CO-Rich* feed gas.
	1530	829.7	GC's calibration with CO-Rich* gas complete.
	1800	832.2	Plant lined out at Case E-8.24 conditions.
14 Feb 89	1900	857.2	End of Case E-8.24.
	1915	857.4	Raising plant pressure to 900 psig for Case E-8.25. Nominal conditions for Case E-8.25: 482°F, 750 psig, 11,100 Sl/hr-kg cat, and CO-Rich* feed gas.
	2200	860.2	Pressure, temperature, and flowrate lined out. Attempting to line out on composition.
15 Feb 89	0200	864.2	Having difficulty feeding over 35 mol% H_2 to reactor due to inability to hold temperature down to 482°F. Reaction is taking off with this optimum CO_2 feed gas composition.
	0730	869.7	Moved TIC-188 (reactor feed temperature control) to 295°F.
	0830	870.7	TIC-188 moved to 300°F.
	1010	872.4	TIC-188 moved to 305°F. Finally able to get 37 mol% H_2 in reactor feed and control reactor temperature at 482°F. PDU finally lined out at Case E-8.25 conditions: 482°F, 900 psig, 11,100 Sl/hr-kg cat, CO-Rich* feed gas (optimum CO_2%).
16 Feb 89	0730	893.7	PDU ran smoothly overnight.
	1100	897.2	End of Case E-8.25
	1115	897.4	Moving PDU to Case E-8.26 conditions of 482°F, 750 psig, 11,000 Sl/hr-kg cat, and Shell feed gas. TIC-188 was moved back to 290°F.
	1525	901.6	Noticed GC #2 has missed methanol peak in reactor feed analysis since approximately 1200 hours today.

TABLE IV.4

RUN E-8 CHRONOLOGY

Date	Time	Cumulative Time On Production Gas (hours)	Notes and Observations
	1545	901.9	Both GC's recalibrated with Shell gas standard. Methanol peak is now being picked up by both GC's.
	1900	905.2	PDU lined out at case E-8.26 conditions.
17 Feb 89	1900	929.2	End of Case E-8.26. Moving to Case E-8.27 conditions. The conditions for Case E-8.27 are the same as E-8.26 except that the pressure is raised to 900 psig.
18 Feb 89	0300	937.2	Lined out at Case E-8.27 conditions.
19 Feb 89	0700	965.2	End of Case E-8.27 without incident. Moving to Case E-8.28 baseline CO-Rich feed gas conditions. GC's are being recalibrated with CO-Rich standard gas. Noticed GC #1 has been missing methanol peak in reactor feed gas.
	1200	970.2	Lined out at Case E-8.28 baseline conditions of 482°F, 750 psig, 11,000 Sl/hr-kg cat, and CO-Rich feed gas.
20 Feb 89	0715	989.4	No problems overnight except GC #1 missed methanol peak in reactor feed since 1800 hours last night.
	1300	995.2	End of Case E-8.28. Preparing for reactor shutdown test.
	1315	995.4	Start reactor isolation shutdown test.
	1345	995.4	End of reactor isolation shutdown test. Making moves to Case E-8.29 conditions of 455°F, 750 psig, 11,000 Sl/hr-kg cat, and CO-Rich feed gas. The shutdown test results showed 367 kg of catalyst loading. This is 3% higher than that calculated from the last shutdown test, within the error inherent in the method. For the sake of consistency, the previous value of 355 kg will be used.
	1700	998.7	PDU lined out at Case E-8.29 conditions.
21 Feb 89	0800	1013.7	Reactor temperature unstable through t this case. Composition is holding steady.

TABLE IV.4

RUN E-8 CHRONOLOGY

Date	Time	Cumulative Time On Production Gas (hours)	Notes and Observations
	1620	1022.0	Noticed GC #2 reported 0.0 mol% methanol in reactor feed gas for 1000, 1200, 1300, and 1400 hours.
	1700	1022.7	End of Case E-8.29.
	1715	1022.9	Raising temperature back up to 482°F. Moving PDU to Case E-8.30 Great Plains feed gas conditions of 482°F, 900 psig, and 6,600 Sl/hr-kg cat.
	1723	1023.1	Opened methane feed to reactor.
	2400	1029.7	PDU lined out at Case E-8.30 conditions.
22 Feb 89	0545	1035.4	Some trouble holding reactor feed composition stable overnight. GC #2 has missed methanol peak since 1000 hours last night. GC #1 also missed methanol peak in reactor feed analysis at 0300 hours.
	0900	1038.7	Investigating cause and solution to GC problems. Lab attributes problem to sawtooth in the methanol peak which causes it to cut off integration early.
	1200	1041.7	Running smoothly at Case E-8.30 conditions.
23 Feb 89	0700	1060.7	End of Case E-8.30.
	0703	1060.7	Moving to Case E-8.31 conditions. Methane feed to reactor stopped and plant pressure being lowered to 750 psig.
	0724	1061.1	Plant pressure down to 770 psig and starting to change reactor feed composition to CO-Rich gas.
	1100	1064.7	Lined out at Case E-8.31 conditions of 518°F, 750 psig, 11,000 Sl/hr-kg cat, and CO-Rich feed gas. Preparations begun for gas phase tracer studies which will be performed tomorrow. ICI TRACERCO is installing detectors and plans are being made to conduct pressure test and sample injections of nitrogen later this afternoon.
	2100	1074.7	The traversing cable on the Nuclear Density Gauge snapped.

TABLE IV.4

RUN E-8 CHRONOLOGY

Date	Time	Cumulative Time On Production Gas (hours)	Notes and Observations
24 Feb 89	0730	1085.2	Attempting to fix cable which failed last night.
	0900	1086.7	Cable repaired. Currently recalibrating NDG gauge with level transmitter on the Yokogawa recorder.
	1200	1089.7	End of Case E-8.31 and moving conditions to Case E-8.32.
	1420	1092.0	Tracer studies begun. See Tracer Study topical report for details.
25 Feb 89	0030	1102.2	Test #3 of tracer studies finished.
	0045	1102.4	Closed H_2 bypass valve. Raising gas flow to determine maximum linear velocity.
	0050	1102.5	Maximum reactor feed flow is 201,800 SCFH (FT-187A) at a superficial inlet gas velocity of 0.66 ft/sec.
	0400	1105.7	Case E-8.32 begins.
26 Feb 89	0655	1132.6	Plant tripped due to high reactor temperature of 545°F. Case E-8.32 ends.
	0730	1132.6	Plant restarted and conditions being brought up to baseline.
	0900	1134.2	Run E-8.33 begins.
27 Feb 89	0915	1158.4	Pre-shutdown nuclear scan completed.
	0928	1158.7	Feed gas flow to reactor stopped. Case E-8.33 ends.
	1028		Draining slurry from reactor.
	1044		Plant pressure lowered to less than 100 psig because too much slurry was drained and some must be returned to the reactor.
	1107		Slurry level at 75.5" after transfer of slurry back to reactor completed.
	1128	1158.7	Feed gas flow restarted. Flows being calculated.
	1400	1161.2	Plant lined out in flow and composition. Case E-8.34 begins.

TABLE IV.4

RUN E-8 CHRONOLOGY

Date	Time	Cumulative Time On Production Gas (hours)	Notes and Observations
28 Feb 89	0145	1172.9	GC #1 locked up until after 0900.
	1408	1185.3	End of case E-8.34. Preparations begin for further tracer studies. See Tracer Studies Topical Report for details.
	2300	1194.3	End of second set of tracer studies. Feed gas to reactor stopped. End of Run E-8.

C. Discussion of Results

1. Catalyst Activity Maintenance

Throughout the run, operating conditions were returned to a standard baseline condition to check on changes in catalyst activity. Baseline cases E-8.6 through E-8.28 in Table IV.5 are at essentially equivalent conditions and suggest healthy catalyst activity throughout the run with an average catalyst productivity consistently at 96% of fresh catalyst autoclave results. Baseline case E-8.33 was also done at these conditions but followed the high slurry temperature (285°C) case E-8.32. As expected there appears to have been some (approximately 3%) loss in catalyst activity as a result of that 25-hour operating period.

TABLE IV.5

LAPORTE LPMEOH PDU
RUN E-8 CATALYST ACTIVITY MAINTENANCE

CO-Rich Gas, 750 psig, 482°F

Case	Days From Run E-8 Start	Space Velocity Sl/hr kg	Slurry Conc. wt% ox.	Percent of Autoclave
E-8.6	9.79	8,525	41.1	95
E-8.11	17.06	10,841	36.5	96
E-8.21	31.22	11,006	35.8	97
E-8.28	41.47	10,962	35.5	96
E-8.33	48.28	11,024	35.6	93

The results of this catalyst evaluation are consistent with previous results and indicate that the results obtained from the process variable scans are representative behavior of the LPMEOH PDU to changing process conditions and do not require correction for declining catalyst activity.

2. PVS Conditions

All of the cases proposed in the process variable scan matrix were completed with the exception of case E-8.10. The maximum achievable inlet superficial gas velocity for E-8.10 was not substantially greater than previous runs with the 01.20 Recycle Compressor running at its maximum throughput. As a result, that case was abandoned and the maximum superficial gas velocity was achieved in Case E-8.13 at 0.64 ft/sec. Ongoing minor modifications were done on the 01.20 compressor during the remainder of the run, in an effort to increase the output capacity. The results of this work are demonstrated in the Run E-9 results.

Run E-8 provides a broad operating experience background that serves as a basis for future commercial demonstrations and the trends observed in several of the runs demonstrate the performance constraints of the LPMEOH process. As stated earlier, the PDU performed well at all of the tested conditions. The complete run summary is provided in Table IV.6 and the detailed data acquisition sheets are included as Appendix A.

TABLE IV.6

DATA SUMMARY FOR LAPORTE LPMEOH PDU RUN E-8

Case	Balance Period Date & Time	Gas Type	Days On Syngas	Temp (deg C)	Pres. (psig)	Inlet Gas Velocity (ft/sec)	Space Velocity (l/hr-kg)	Slurry Conc. (wt% ox.)	Gas Holdup (vol%)	Slurry Height (%)	Catalyst Inventory (kg)	CO Conv. (%)	MeOH Productivity (gmol/hr-kg)	Pct. of Autocl. (%)	Net MeOH Production (TPD)	Comments
E-8.1	10 JAN 1300 - 11 JAN 1900	CO-Rich	2.45	250.3	753.2	0.50	6729	45.3	29.5	100	567	13.5	20.5	92	10.03	
E-8.2	12 JAN 0200 - 13 JAN 0700	CO-Rich	3.95	249.6	753.3	0.51	6767	49.6	27.0	83	567	12.1	18.5	82	9.06	
E-8.3	13 JAN 1000 - 14 JAN 1900	CO-Rich	5.45	249.9	753.3	0.23	3081	50.0	16.0	74	567	14.1	9.5	62	4.74	
E-8.4	15 JAN 0100 - 16 JAN 0700	CO-Rich	6.95	249.9	753.3	0.23	3112	45.6	19.6	87	567	15.8	10.9	93	5.41	
E-8.5	16 JAN 1900 - 17 JAN 1900	CO-Rich	8.35	250.2	893.0	0.29	4914	42.1	25.8	100	530	17.3	19.1	95	8.79	
E-8.6	18 JAN 0100 - 19 JAN 0700	CO-Rich	9.79	250.0	753.3	0.52	8525	41.1	32.9	100	460	13.0	25.2	95	9.96	Baseline
E-8.7	20 JAN 0500 - 21 JAN 0700	CO-Rich	11.79	250.6	893.6	0.47	9151	41.1	32.9	100	460	14.8	30.3	94	12.04	Record Production
E-8.8	21 JAN 1400 - 23 JAN 0700	CO-Rich	13.79	250.1	752.9	0.24	4331	40.4	25.2	92	460	15.6	15.2	97	6.09	
E-8.9	23 JAN 1400 - 24 JAN 1900	CO-Rich	15.22	250.0	502.3	0.53	6819	37.5	32.8	100	401	9.6	14.9	96	5.11	Maximum Flow
E-8.10		CO-Rich		250.0	500.0		12600	40.0				THIS CONDITION WAS UNATTAINABLE				
E-8.11	25 JAN 1300 - 26 JAN 1600	CO-Rich	17.06	250.2	752.4	0.52	10841	36.5	36.7	100	361	12.3	30.0	96	9.28	Baseline
E-8.12	27 JAN 0100 - 28 JAN 0800	CO-Rich	18.63	250.0	753.0	0.30	6168	36.5	31.0	92	361	14.9	20.6	98	6.42	
E-8.13	28 JAN 1800 - 29 JAN 1900	CO-Rich	20.08	250.1	783.6	0.64	13684	37.0	36.7	100	358	11.0	34.3	95	10.47	Max Gas Vel.
E-8.14	30 JAN 0000 - 31 JAN 0700	CO-Rich	21.58	250.2	752.6	0.14	2985	36.5	19.0	77	355	17.0	11.4	101	3.52	
E-8.15	31 JAN 1900 - 01 FEB 1900	H2-Rich	22.97	250.2	503.0	0.46	6819	33.2	28.8	100	355	36.9	19.6	--	5.67	
E-8.16	01 FEB 2200 - 03 FEB 0700	H2-Rich	24.47	250.5	753.0	0.31	6800	32.2	25.6	100	355	57.4	29.4	--	6.83	
E-8.17	03 FEB 1500 - 05 FEB 0700	H2-Rich	26.22	250.1	753.0	0.52	11086	33.7	30.2	100	355	43.0	36.4	--	11.55	
E-8.18	05 FEB 1200 - 06 FEB 0600	Balanced	27.17	249.7	753.2	0.33	6634	36.0	27.6	88	355	29.9	20.0	--	6.20	
E-8.19	06 FEB 1400 - 07 FEB 1400	Dow Gas	28.51	250.0	753.2	0.31	6573	36.4	27.9	87	355	21.8	25.4	--	7.75	
E-8.20	07 FEB 1600 - 08 FEB 1900	Dow Gas	29.73	250.4	893.0	0.26	6557	36.8	27.0	85	355	24.1	28.6	--	8.72	
E-8.21	08 FEB 2300 - 10 FEB 0700	CO-Rich	31.22	249.8	752.9	0.52	11006	35.8	36.1	100	355	12.1	30.1	97	9.15	Baseline
E-8.22	10 FEB 1400 - 11 FEB 1900	Balanced	32.72	250.2	752.9	0.52	11024	34.8	33.4	100	355	24.8	28.5	--	8.58	
E-8.23	11 FEB 2200 - 13 FEB 1300	Balanced	34.47	249.7	893.5	0.44	11085	35.8	32.4	95	355	28.0	31.1	--	9.35	
E-8.24	13 FEB 1800 - 14 FEB 1900	CO-Rich *	35.72	250.1	752.9	0.52	11022	35.8	36.0	100	355	12.2	31.7	94	9.59	Optim. CO2
E-8.25	15 FEB 1000 - 16 FEB 1100	CO-Rich *	37.38	249.9	893.8	0.44	11156	37.0	35.5	95	355	13.5	36.1	92	10.95	Optim. CO2
E-8.26	16 FEB 1900 - 17 FEB 1900	Shell Gas	38.72	249.8	753.3	0.52	11039	36.2	37.1	100	355	7.1	22.1	--	6.79	
E-8.27	18 FEB 0300 - 19 FEB 0700	Shell Gas	40.22	250.0	893.6	0.44	11114	37.3	36.4	95	355	8.2	25.8	--	7.89	
E-8.28	19 FEB 1200 - 20 FEB 1300	CO-Rich	41.47	249.6	752.7	0.51	10962	35.5	35.4	100	355	12.0	29.6	96	8.94	Baseline
E-8.29	20 FEB 1700 - 21 FEB 1700	CO-Rich	42.81	235.3	753.0	0.50	10958	35.9	36.4	99	355	9.6	24.1	84	7.24	
E-8.30	22 FEB 0000 - 23 FEB 0700	G.Plains	44.20	249.7	893.3	0.27	6711	36.3	26.0	85	355	38.5	24.2	--	7.25	
E-8.31	23 FEB 1100 - 24 FEB 1200	CO-Rich	45.40	270.1	753.3	0.53	10959	35.2	33.7	101	355	11.4	27.8	89	8.55	
E-8.T1	24 FEB 1200 - 24 FEB 2400	CO-Rich	45.92	251.1	752.9	Variable Conditions										Gas Tracer Tests
E-8.32	25 FEB 0400 - 26 FEB 0700	CO-Rich	47.19	265.0	753.0	0.13	2076	36.6	11.2	73	355	10.5	4.2	52	1.39	
E-8.33	26 FEB 0900 - 27 FEB 0900	CO-Rich	48.26	249.8	752.7	0.52	11024	35.6	35.5	100	355	11.6	29.2	93	8.80	Baseline
E-8.34	27 FEB 1400 - 28 FEB 1400	CO-Rich	49.39	249.6	753.0	0.35	10327	37.6	31.9	84	256	11.1	26.4	87	5.75	L/D Effect
E-8.T2	28 FEB 1400 - 28 FEB 2300	CO-Rich	49.76	250.0	753.0	Variable Conditions										Gas Tracer Tests

*CO-Rich gas matrix with 7-8 mol% CO2 in the reactor feed

Figure IV.1 shows the methanol productivity performance as a function of space velocity. The data are very consistent throughout the run and reflect the expected behavior predicted from autoclave experience. It should be noted that the PDU data in Figure IV.1 are very close to the autoclave prediction for fresh catalyst, in spite of the fact that this catalyst slurry had been partially used for 4 1/2 months prior to the start of Run E-8. This can be attributed both to the stable nature of the catalyst slurry and the enhanced performance of the partially back-mixed bubble column reactor as compared to a well mixed autoclave reactor.

Figure IV.2 is a plot of the PDU methanol productivity, relative to the autoclave prediction, as a function of catalyst loading in the slurry. The results shown in Figure IV.2 are consistent with previous PDU operating experience which indicated that there was not a significant change in catalyst productivity at slurry concentrations varying from 34 to 40 wt%. The data, however, do begin to show a significant drop-off in productivity at slurry concentrations somewhere in excess of 42 to 45 wt%, which is attributed to the onset of a mass transfer controlled regime in the slurry reactor at the higher catalyst concentrations.

Although the transition from a kinetically controlled system may be occurring in cases E-8.1 through E-8.4, this could be a more optimum operating point. The behavior of the system was very stable and the methanol volumetric productivity continued to improve with increasing slurry concentration, as shown in Table IV.7 below.

TABLE IV.7

RUN E-8 REACTOR VOLUMETRIC PRODUCTIVITY
CO-Rich Gas, 750 psig, 482°F

Case	Space Velocity Sl/hr kg	Slurry Conc. wt% ox.	Slurry Height Percent	Methanol Product. TPD	Volumetric Productivity lb-MeOH/hr cu ft
E-8.12	6,168	36.5	92	6.42	11.0
E-8.1	6,729	45.3	100	10.03	15.8
E-8.2	6,767	49.6	83	9.06	17.2
E-8.14	2,985	36.5	77	3.52	7.2
E-8.4	3,112	45.6	87	5.41	9.8
E-8.3	3,081	50.0	74	4.74	10.1

The typical dependence of catalyst productivity on temperature is shown in Figure IV.3 with an optimum reactor temperature of approximately 490°F. The productivity decreases at lower temperatures due to a decrease in catalyst activity, and the productivity decreases at higher temperatures due to a less favorable methanol reaction equilibrium constant.

The effect of feed gas composition on the LPMEOH reactor performance was tested in 13 separate runs. The laboratory autoclave program under Subtask 3.2 showed that, for a CO-Rich gas matrix at 750 psig, there is a well defined optimum in the methanol productivity with 8 mol% CO_2 in reactor feed gas.

Figure IV.1

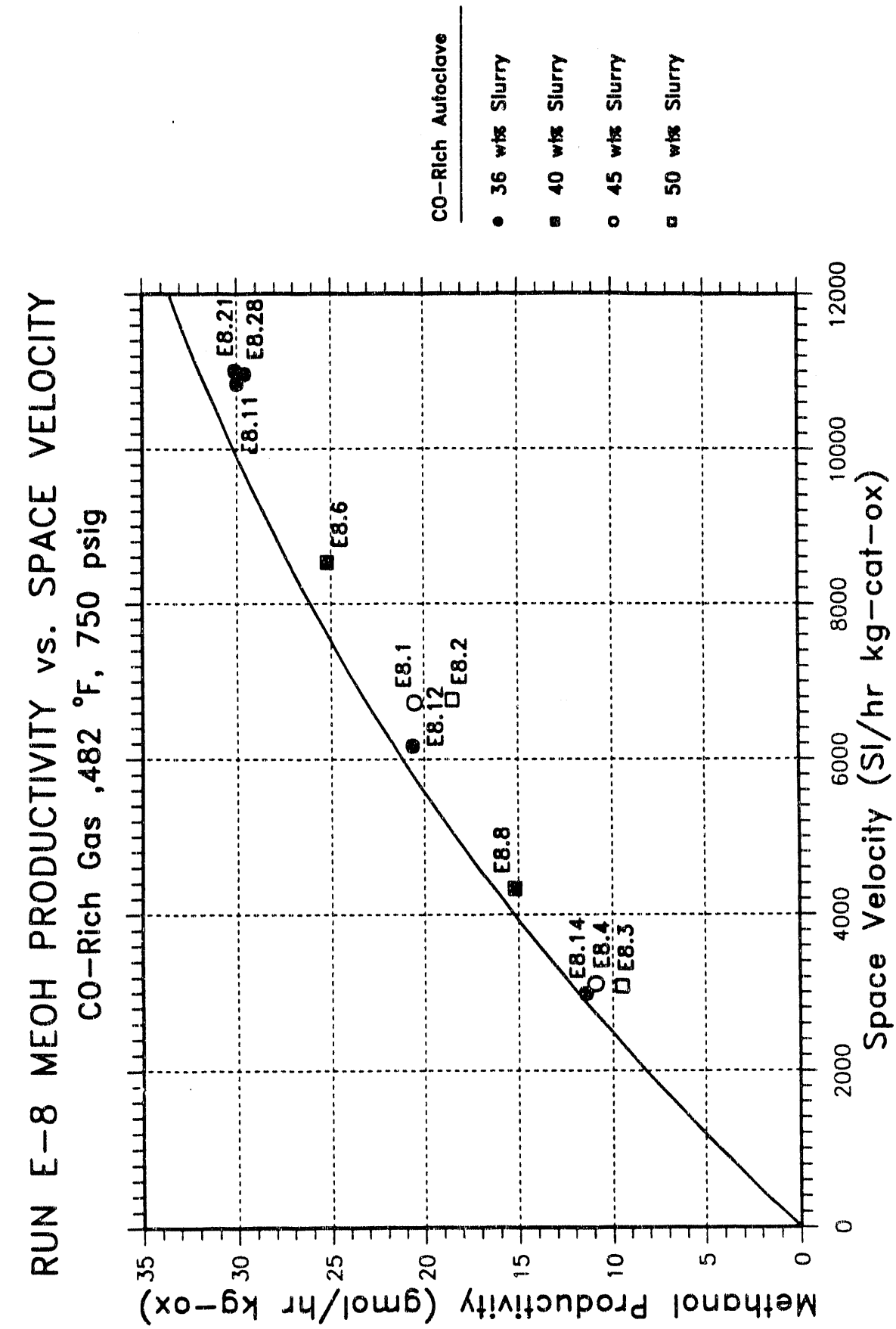

RUN E-8 MEOH PRODUCTIVITY vs. SPACE VELOCITY
CO-Rich Gas ,482 °F, 750 psig
CO-Rich Autoclave
36 wt% Slurry
40 wt% Slurry
45 wt% Slurry
50 wt% Slurry
E8.21
E8.28
E8.11
E8.6
E8.1
E8.12
E8.2
E8.8
E8.14
E8.4
E8.3
Methanol Productivity (gmol/hr kg-ox)
Space Velocity (Sl/hr kg-cat-ox)
0
5
10
15
20
25
30
35
0
2000
4000
6000
8000
10000
12000

Figure IV.2

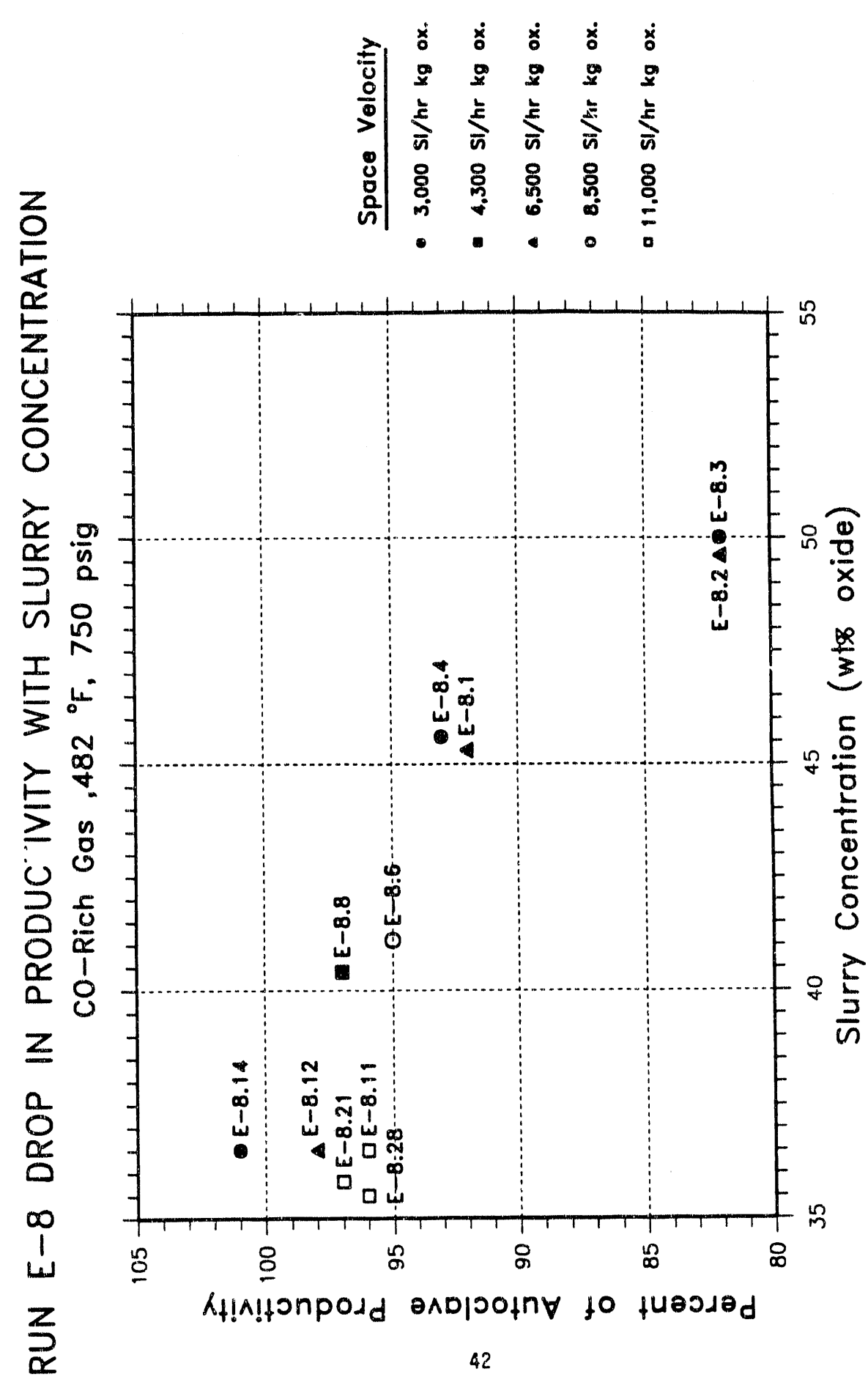
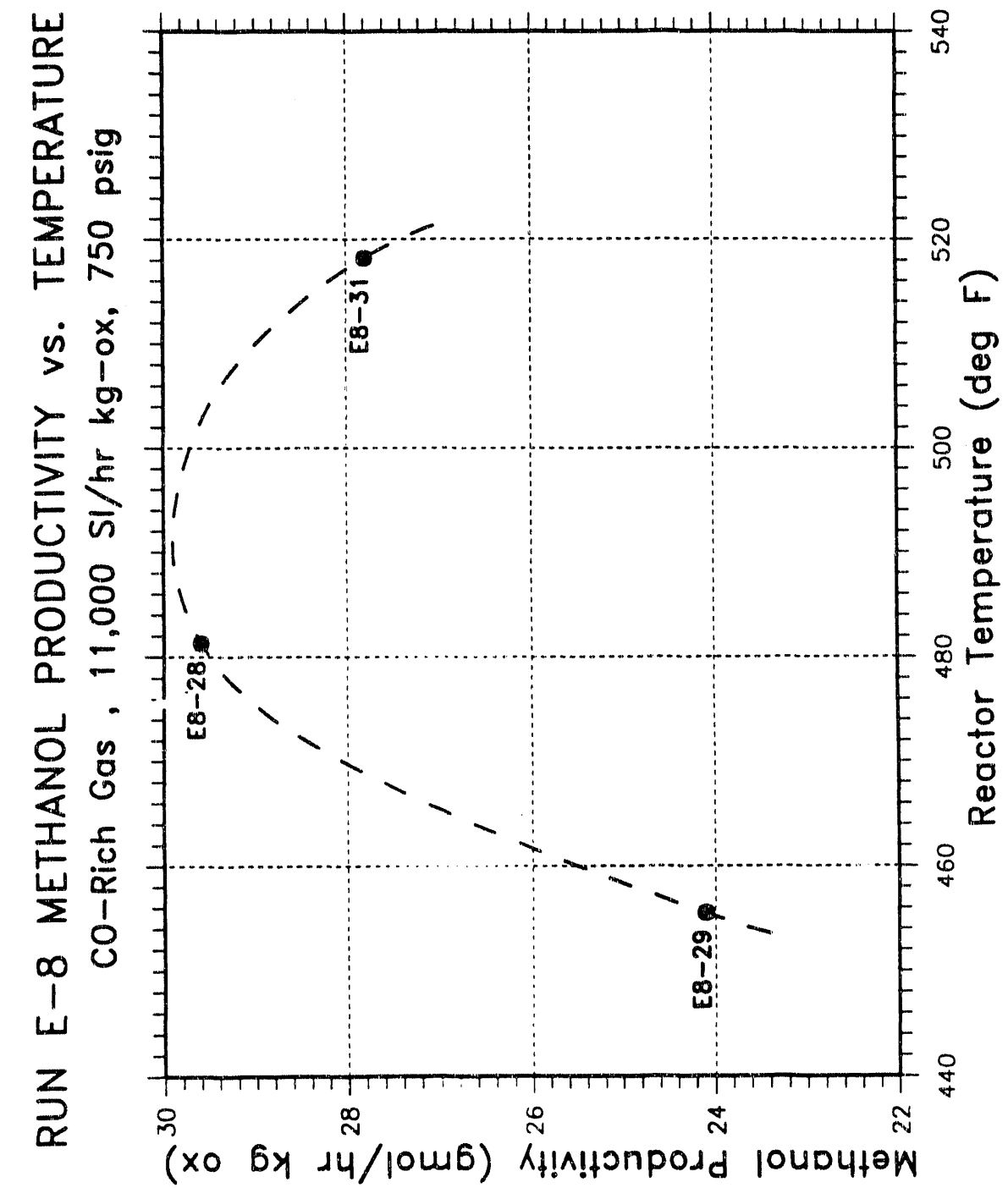

RUN E-8 DROP IN PRODUCTIVITY WITH SLURRY CONCENTRATION
CO-Rich Gas ,482 °F, 750 psig
Space Velocity
3,000 Sl/hr kg ox.
4,300 Sl/hr kg ox.
6,500 Sl/hr kg ox.
8,500 Sl/hr kg ox.
11,000 Sl/hr kg ox.
E-8.14
E-8.12
E-8.21
E-8.11
E-8.28
E-8.8
E-8.6
E-8.4
E-8.1
E-8.2
E-8.3
Percent of Autoclave Productivity
105
100
95
90
85
80
35
40
45
50
55
Slurry Concentration (wt% oxide)

Figure IV.3


RUN E-8 METHANOL PRODUCTIVITY vs. TEMPERATURE
CO-Rich Gas , 11,000 Sl/hr kg-ox, 750 psig
Methanol Productivity (gmol/hr kg ox)
Reactor Temperature (deg F)
30
28
26
24
22
440
460
480
500
520
540
E8-28
E8-31
E8-29

The results obtained in Run E-8 are consistent with the previous laboratory observations and demonstrate the effect of CO_2 partial pressure on methanol productivity, as seen in Figure IV.4. The sharp drop-off in productivity below 2 mol% CO_2 suggests that commercial gas feeds with these compositions could significantly benefit from either CO_2 or water injection in the reactor feed.

The performance of the other gas types relative to CO-Rich gas are shown in Figure IV.5. Operation on H_2-Rich gas produced 30% more methanol than CO-Rich gas at equivalent conditions due to the more optimum H_2/CO ratio and a CO_2 concentration at 7 mol%. Operation on Shell type gas produced 30% less methanol than CO-Rich gas at equivalent conditions due to the low (2 mol%) CO_2 concentration, however, this performance would be equivalent to CO-Rich gas using either water or CO_2 injection as mentioned above. The methanol production rate for the other gas types tested varied less from the baseline performance on CO-Rich gas.

3. Product Methanol Composition

The product methanol compositions for all of the cases in Run E-8 are shown in Table IV.8. For the 482°F reactor cases, the methanol purity varied from 95.42 to 98.34 wt% and averaged 97.08 wt%. The average impurities were 0.89 wt% water, 0.26 wt% oil, 0.49 wt % ethanol, 0.42 wt% higher alcohols and 0.86 wt% other oxygenates. The concentration of mineral oil in the product varied from 0.12 to 0.67 wt% and was set by the PDU operating parameters and the methanol production rate.

The methanol purity decreased with increasing temperature, with the minimum purity occurring in case E-8.32 at 85.90 wt% methanol, 11.02 wt% other alcohols, and 1.54 wt% water for a reactor temperature of 545°F. The concentration of higher molecular weight byproducts in the methanol product also increased with longer reactor residence times. This is illustrated in Figures IV.6 and IV.7. Figure IV.6 is a plot of the methanol product purity from CO-Rich gas as a function of space velocity. The methanol concentration increases from 95.5 to 97.8 wt% as the space velocity increases (residence time decreases) from 3,000 to 14,000 Sl/hr kg-ox. Figure IV.7 shows the opposite trend for higher alcohols. The higher alcohol concentration decreases from 2.0 to 0.5 wt% as the space velocity increases (residence time decreases) from 3,000 to 14,000 Sl/hr kg-ox.

4. Reactor Internal Heat Exchanger

As in previous runs, the overall heat transfer coefficient for the internal heat exchanger was calculated from the utility oil data. 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. An operating fouling factor of 0.0015 hr-ft^2-°F/Btu was used for all of the heat transfer coefficient calculations based on the previous heat exchanger data analysis described in the topical report entitled "Task 2.2: Alternate Catalyst Run E-6 and Catalyst Activity Maintenance Run E-7".

A comparison of the predicted and measured overall coefficients indicated that the average absolute error was 5.7% for the 33 cases of Run E-8. With the exception of cases E-8.9, 32, and 34 none of the errors were greater than 9.0% (see Table IV.9). The typical calculated uncertainty in the measured coefficients was estimated at 11%. The high errors in cases E-8.9, 32, and 34 are caused by the lower methanol production rates which result in lower heat fluxes and less accuracy in the measured data.

Figure IV.4

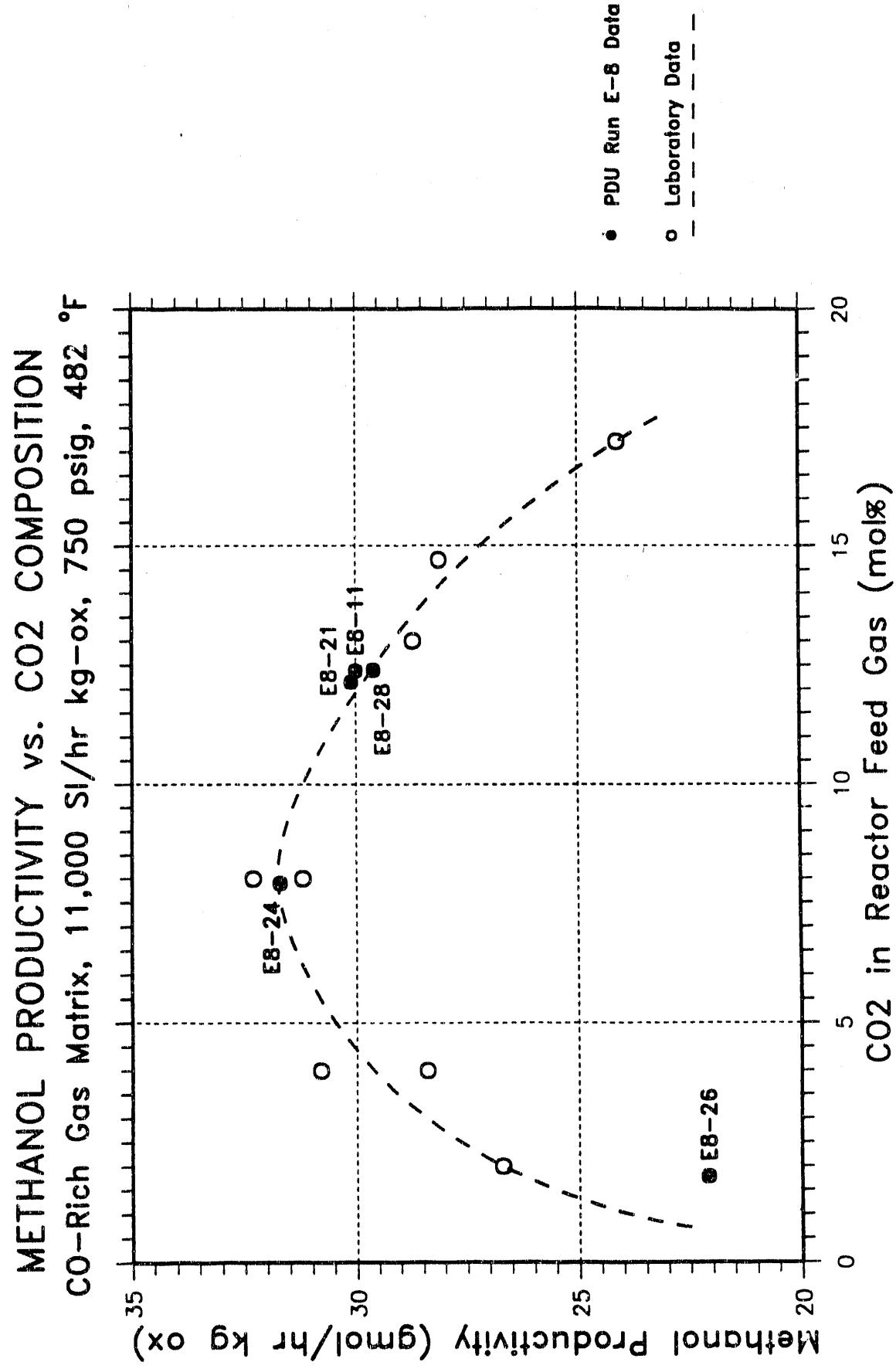

METHANOL PRODUCTIVITY vs. CO2 COMPOSITION
CO-Rich Gas Matrix, 11,000 Sl/hr kg-ox, 750 psig, 482 °F
PDU Run E-8 Data
Laboratory Data
E8-24
E8-21
E8-11
E8-28
E8-26
Methanol Productivity (gmol/hr kg ox)
CO2 in Reactor Feed Gas (mol%)
35
30
25
20
0
5
10
15
20

Figure IV.5

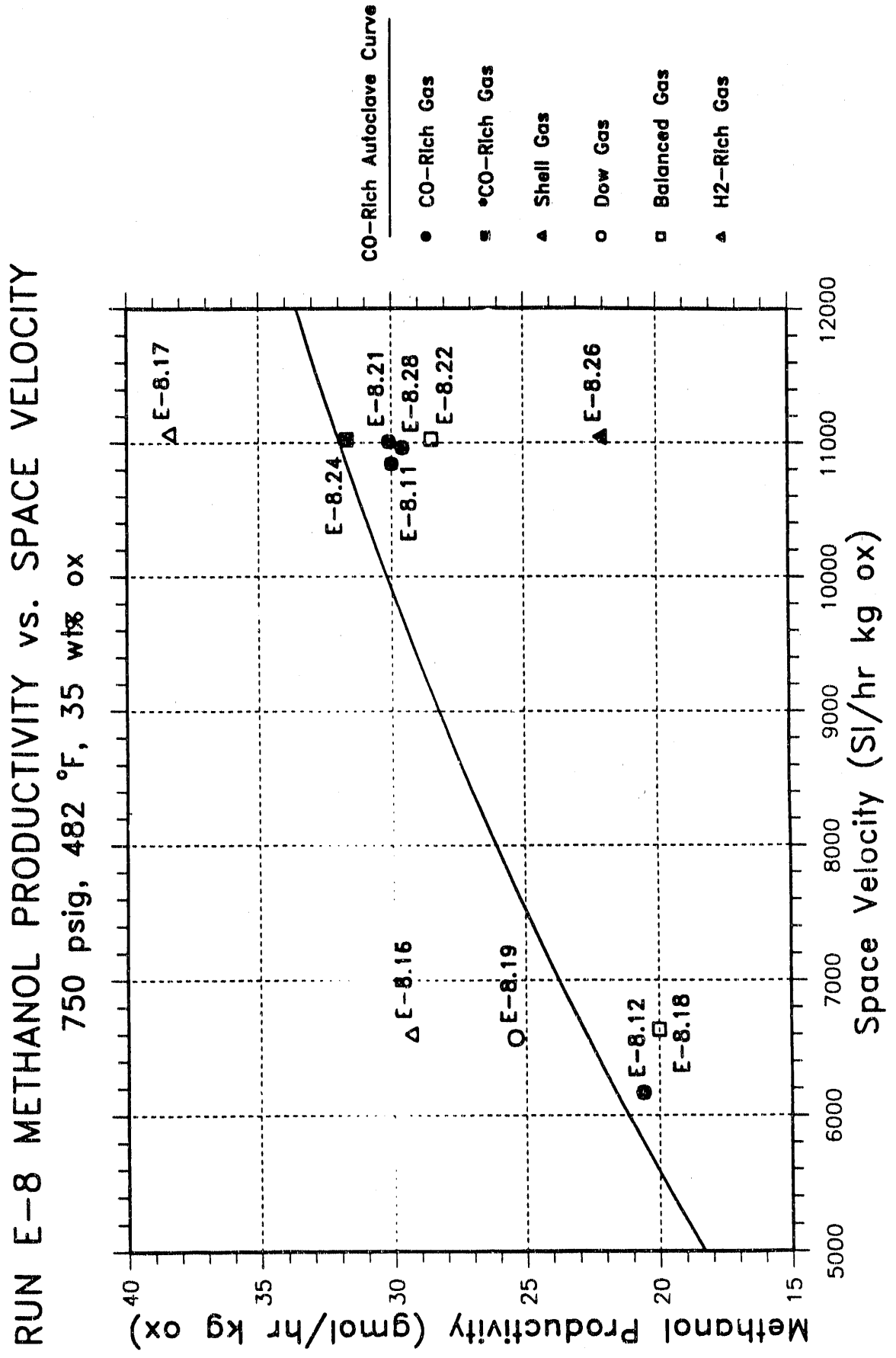

RUN E-8 METHANOL PRODUCTIVITY vs. SPACE VELOCITY
750 psig, 482 °F, 35 wt% ox
Methanol Productivity (gmol/hr kg ox)
Space Velocity (Sl/hr kg ox)
CO-Rich Autoclave Curve
CO-Rich Gas
•CO-Rich Gas
Shell Gas
Dow Gas
Balanced Gas
H2-Rich Gas
E-8.17
E-8.21
E-8.28
E-8.22
E-8.24
E-8.11
E-8.26
E-8.15
E-8.19
E-8.12
E-8.18
40
35
30
25
20
15
5000
6000
7000
8000
9000
10000
11000
12000

Table IV.8

Methanol Product Compositions for LaPorte PDU Run E-8

Case No.	E-8.1	E-8.2	E-8.3	E-8.4	E-8.5	E-8.6	E-8.7	E-8.8	E-8.9
Balance Period:									
Start Date	01/10/89	01/12/89	01/13/89	01/15/89	01/16/89	01/18/89	01/20/89	01/21/89	01/23/89
Start Time	13:00	02:00	10:00	01:00	19:00	01:00	05:00	14:00	14:00
End Date	01/11/89	01/13/89	01/14/89	01/16/89	01/17/89	01/19/89	01/21/89	01/23/89	01/24/89
End Time	19:00	07:00	19:00	07:00	19:00	07:00	07:00	07:00	19:00
Gas Type	CO-Rich	CO-Rich	CO-Rich	CO-Rich	CO-Rich	CO-Rich	CO-Rich	CO-Rich	CO-Rich
Temperature (deg F)	482.5	481.6	481.8	481.8	482.4	482.0	483.4	482.2	482.0
Pressure (psig)	753.2	753.3	753.3	753.3	893.0	753.3	893.6	752.9	502.3
Space Vel. (Sl/hr kg-cat-ox)	6729	6767	3081	3112	4914	8525	9151	4331	6819
Slurry Conc. (wt% oxide)	45.3	49.6	50.0	45.6	42.1	41.1	41.1	40.4	37.5
METHANOL PRODUCT COMPOSITION (wt%)									
Methanol	97.007	96.973	95.416	95.769	96.479	97.391	97.105	96.473	97.051
Water	0.686	0.698	0.565	0.479	0.409	0.692	0.585	0.467	0.861
Dimethyl ether	0.028	0.030	0.063	0.062	0.042	0.021	0.020	0.036	0.016
Methyl formate	0.792	0.789	1.014	1.184	1.390	0.734	1.111	1.207	0.451
Methyl acetate	0.156	0.155	0.399	0.373	0.252	0.097	0.092	0.250	0.109
Ethanol	0.633	0.612	1.066	0.959	0.709	0.491	0.421	0.766	0.594
Iso-propanol	0.000	0.000	0.019	0.000	0.000	0.000	0.000	0.000	0.000
N-propanol	0.244	0.238	0.442	0.389	0.266	0.182	0.157	0.300	0.234
Sec-butanol	0.027	0.028	0.036	0.033	0.027	0.022	0.020	0.027	0.031
Isobutanol	0.037	0.038	0.085	0.070	0.043	0.027	0.023	0.048	0.039
N-butanol	0.127	0.122	0.219	0.195	0.138	0.098	0.084	0.155	0.117
2&3-Pentanol	0.000	0.000	0.025	0.000	0.000	0.000	0.000	0.000	0.000
Isopentanol	0.039	0.037	0.074	0.064	0.040	0.029	0.024	0.045	0.036
1-Pentanol	0.073	0.073	0.130	0.115	0.083	0.057	0.048	0.091	0.068
Oil	0.151	0.207	0.450	0.308	0.122	0.159	0.310	0.135	0.393
Molecular wt of product	32.22	32.23	32.38	32.51	32.41	32.17	32.28	32.39	32.18

Methanol Product Compositions for LaPorte PDU Run E-8

Case No.	E-8.11	E-8.12	E-8.13	E-8.14	E-8.15	E-8.16	E-8.17	E-8.18	E-8.19
Balance Period:									
Start Date	01/25/89	01/27/89	01/28/89	01/30/89	01/31/89	02/01/89	02/03/89	02/05/89	02/06/89
Start Time	13:00	01:00	18:00	00:00	19:00	22:00	15:00	12:00	14:00
End Date	01/26/89	01/28/89	01/29/89	01/31/89	02/01/89	02/03/89	02/05/89	02/06/89	02/07/89
End Time	16:00	08:00	19:00	07:00	19:00	07:00	07:00	06:00	14:00
Gas Type	CO-Rich	CO-Rich	CO-Rich	CO-Rich	H2-Rich	H2-Rich	H2-Rich	Balanced	Dow
Temperature (deg F)	482.4	482.0	482.2	482.4	482.4	482.9	482.2	481.5	482.0
Pressure (psig)	752.4	753.0	763.6	752.6	503.0	753.0	753.0	753.2	753.2
Space Vel. (Sl/hr kg-cat-ox)	10841	6168	13684	2985	6819	6600	11066	6634	6573
Slurry Conc. (wt% oxide)	36.5	36.5	37.0	36.5	33.2	32.2	33.7	36.0	36.4
METHANOL PRODUCT COMPOSITION (wt%)									
Methanol	97.484	96.769	97.727	95.840	96.285	96.597	96.134	95.840	97.282
Water	0.774	0.646	0.895	0.423	3.341	3.084	3.471	0.423	0.855
Dimethyl ether	0.013	0.023	0.010	0.041	0.007	0.009	0.006	0.041	0.017
Methyl formate	0.734	1.013	0.575	1.241	0.000	0.000	0.160	1.241	1.045
Methyl acetate	0.061	0.141	0.043	0.340	0.000	0.000	0.000	0.340	0.079
Ethanol	0.354	0.553	0.316	0.957	0.091	0.057	0.049	0.957	0.334
Iso-propanol	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
N-propanol	0.133	0.212	0.117	0.386	0.037	0.021	0.000	0.386	0.119
Sec-butanol	0.019	0.024	0.017	0.038	0.000	0.000	0.000	0.038	0.015
Isobutanol	0.000	0.032	0.000	0.068	0.000	0.000	0.000	0.068	0.000
N-butanol	0.072	0.107	0.064	0.200	0.000	0.000	0.000	0.200	0.062
2&3-Pentanol	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Isopentanol	0.000	0.031	0.000	0.061	0.000	0.000	0.000	0.061	0.003
1-Pentanol	0.044	0.068	0.039	0.120	0.000	0.000	0.000	0.120	0.040
Oil	0.352	0.381	0.197	0.285	0.238	0.233	0.180	0.285	0.152
Molecular wt of product	32.17	32.18	32.04	32.52	31.24	31.30	31.23	32.52	32.07

Methanol Product Compositions for LaPorte PDU Run E-8

Case No.	E-8.20	E-8.21	E-8.22	E-8.23	E-8.24	E-8.25	E-8.26	E-8.27	E-8.28
Balance Period:									
Start Date	02/07/89	02/08/89	02/10/89	02/11/89	02/13/89	02/15/89	02/16/89	02/18/89	02/19/89
Start Time	16:00	23:00	14:00	22:00	18:00	10:00	19:00	03:00	12:00
End Date	02/08/89	02/10/89	02/11/89	02/13/89	02/14/89	02/16/89	02/17/89	02/19/89	02/20/89
End Time	19:00	07:00	19:00	13:00	19:00	11:00	19:00	07:00	13:00
Gas Type	Dow	CO-Rich	Balanced	Balanced	CO-Rich*	CO-Rich*	Shell	Shell	CO-Rich
Temperature (deg F)	482.7	481.6	482.4	481.5	482.2	481.8	481.6	482.0	481.3
Pressure (psig)	893.0	752.9	752.9	893.5	752.9	893.8	753.3	893.6	752.7
Space Vel. (Sl/hr kg-cat-ox)	6557	11006	11024	11085	11022	11156	11039	11114	10962
Slurry Conc. (wt% oxide)	36.8	35.8	34.8	35.8	35.8	37.0	36.2	37.3	35.5
METHANOL PRODUCT COMPOSITION (wt%)									
Methanol	97.293	97.499	98.039	98.713	97.777	97.644	96.835	96.945	97.627
Water	0.871	0.772	0.691	0.627	0.524	0.448	0.212	0.191	0.819
Dimethyl ether	0.017	0.011	0.010	0.009	0.012	0.012	0.018	0.020	0.012
Methyl formate	1.045	0.741	0.162	0.185	0.672	0.879	0.554	0.774	0.661
Methyl acetate	0.076	0.063	0.000	0.000	0.059	0.056	0.094	0.088	0.051
Ethanol	0.308	0.383	0.218	0.180	0.416	0.397	0.996	0.844	0.333
Iso-propanol	0.000	0.000	0.000	0.000	0.000	0.000	0.019	0.000	0.000
N-propanol	0.114	0.133	0.076	0.061	0.154	0.142	0.395	0.330	0.123
Sec-butanol	0.016	0.020	0.021	0.000	0.021	0.015	0.041	0.035	0.015
Isobutanol	0.000	0.020	0.000	0.000	0.000	0.000	0.053	0.045	0.000
N-butanol	0.061	0.071	0.041	0.032	0.089	0.075	0.212	0.180	0.066
2&3-Pentanol	0.000	0.000	0.000	0.000	0.000	0.000	0.026	0.021	0.000
Isopentanol	0.000	0.021	0.000	0.000	0.022	0.022	0.050	0.044	0.000
1-Pentanol	0.036	0.044	0.025	0.000	0.051	0.048	0.128	0.109	0.039
Oil	0.163	0.222	0.418	0.193	0.203	0.262	0.366	0.372	0.254
Molecular wt of product	32.11	32.13	31.94	32.00	32.18	32.24	32.34	32.34	32.10

*CO-Rich gas matrix with 7-8% CO2 in the reactor feed

Methanol Product Compositions for LaPorte PDU Run E-8

Case No.	E-8.29	E-8.30	E-8.31	E-8.32	E-8.33	E-8.34
Balance Period:						
Start Date	02/20/89	02/22/89	02/23/89	02/25/89	02/26/89	02/27/89
Start Time	17:00	00:00	11:00	04:00	09:00	14:00
End Date	02/21/89	02/23/89	02/24/89	02/26/89	02/27/89	02/28/89
End Time	17:00	07:00	12:00	07:00	09:00	14:00
Gas Type	CO-Rich	G Plains	CO-Rich	CO-Rich	CO-Rich	CO-Rich
Temperature (deg F)	455.5	481.5	518.2	545.0	481.6	481.3
Pressure (psig)	753.0	893.3	753.3	753.0	752.7	753.0
Space Vel. (SV/hr kg-cat-ox)	10958	6711	10959	2076	11024	10327
Slurry Conc. (wt% oxide)	35.9	36.3	35.2	36.6	35.6	37.6
METHANOL PRODUCT COMPOSITION (wt%)						
Methanol	97.735	98.893	95.641	85.896	97.628	97.475
Water	1.104	0.500	0.880	1.545	0.844	0.833
Dimethyl ether	0.006	0.025	0.035	0.148	0.013	0.012
Methyl formate	0.589	0.188	0.723	0.000	0.683	0.717
Methyl acetate	0.000	0.000	0.249	0.720	0.048	0.051
Ethanol	0.142	0.155	1.041	3.391	0.321	0.330
Iso-propanol	0.000	0.000	0.022	0.077	0.000	0.000
N-propanol	0.053	0.051	0.433	1.937	0.112	0.123
Sec-butanol	0.000	0.000	0.056	0.273	0.016	0.018
Isobutanol	0.000	0.000	0.091	2.180	0.000	0.000
N-butanol	0.032	0.028	0.208	0.862	0.061	0.071
2&3-Pentanol	0.000	0.000	0.048	0.495	0.000	0.000
Isopentanol	0.000	0.000	0.076	1.268	0.000	0.000
1-Pentanol	0.000	0.000	0.122	0.534	0.039	0.041
Oil	0.339	0.160	0.375	0.673	0.235	0.328
Molecular wt of product	31.98	32.02	32.38	33.50	32.08	32.02

Figure IV.6

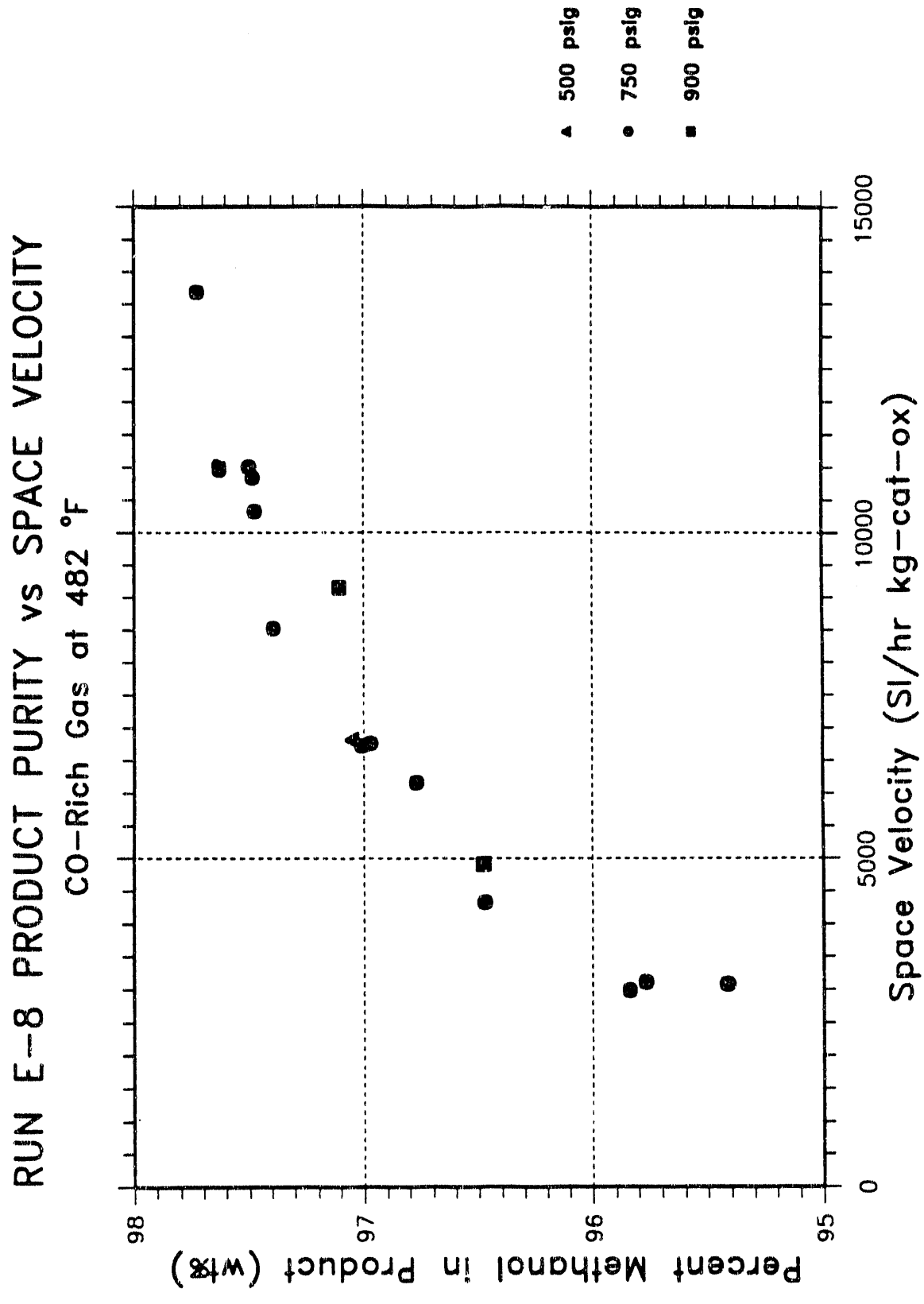
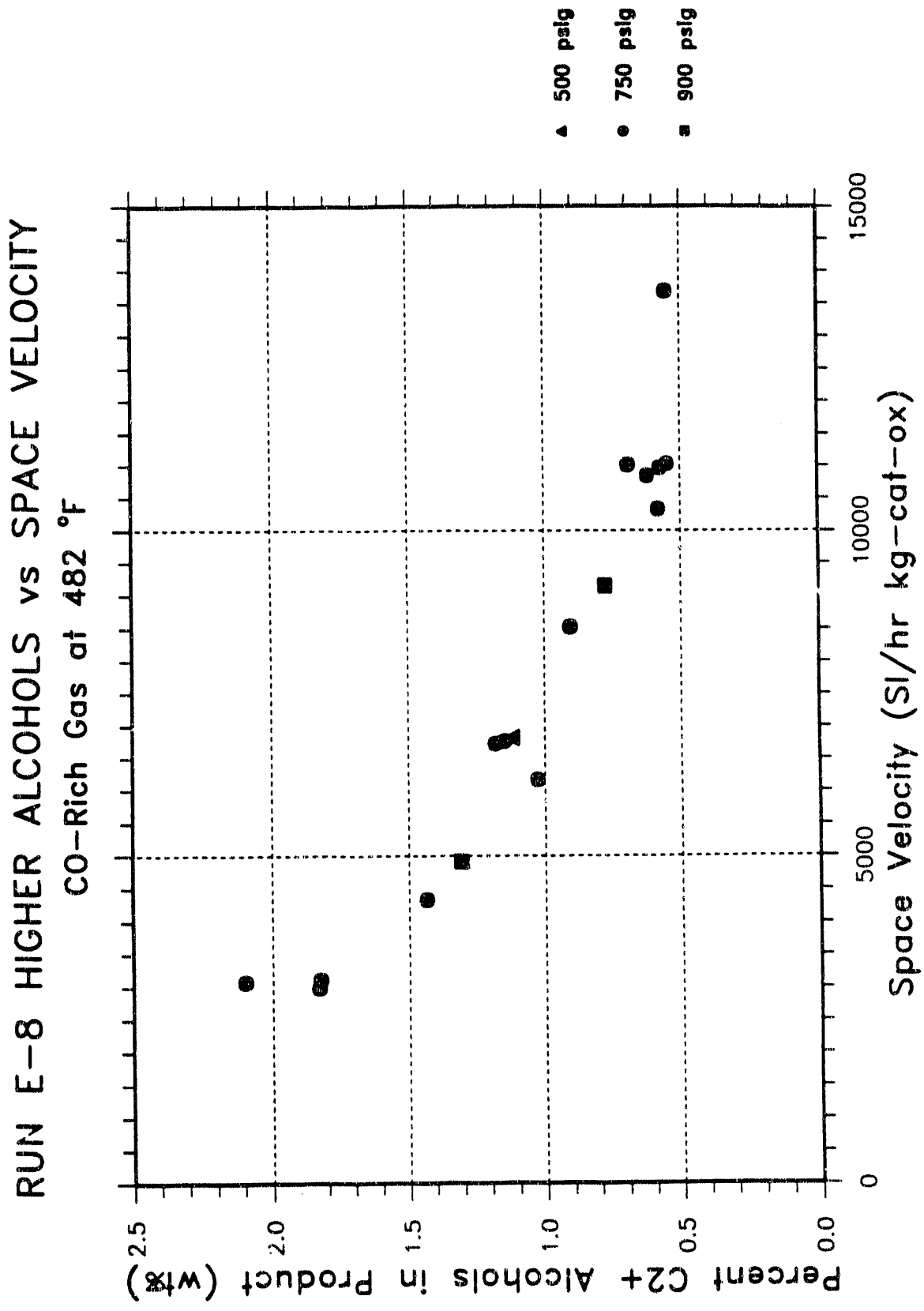

RUN E-8 PRODUCT PURITY vs SPACE VELOCITY
CO-Rich Gas at 482 °F
500 psig
750 psig
900 psig
Percent Methanol in Product (wt%)
98
97
96
95
Space Velocity (Sl/hr kg-cat-ox)
0
5000
10000
15000

Figure IV.7


RUN E-8 HIGHER ALCOHOLS vs SPACE VELOCITY
CO-Rich Gas at 482 °F
500 psig
750 psig
900 psig
Percent C2+ Alcohols in Product (wt%)
0.0
0.5
1.0
1.5
2.0
2.5
0
5000
10000
15000
Space Velocity (Sl/hr kg-cat-ox)

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).

$$St = h_o/(\rho_s * C_{ps} * v_g) = Beta * (Re_s * Fr_s * Pr_s^2)^{-0.25}$$

where:

St	=	Stanton number
h_o	=	shell-side heat transfer coefficient
ρ_s	=	slurry density
C_{ps}	=	slurry heat capacity
v_g	=	superficial gas velocity
Beta	=	Deckwer proportionality constant = 0.10
Re_s	=	slurry Reynolds number = $v_g * d_o * \rho_s / \mu_s$
Fr_s	=	slurry Froude number = $v_g^2/(g * d_o)$
Pr_s	=	slurry Prandtl number = $\mu_s * C_{ps}/k_s$
μ_s	=	slurry viscosity
g	=	gravitational acceleration
k_s	=	slurry thermal conductivity
d_o	=	tube outside diameter

A comparison of the predicted and measured slurry side coefficients are shown in Table IV.9. The average absolute error was 18% and again, with the exception of the low production cases E-8.9, 32, and 34, none of the errors exceeded 36%. The predictions of the heat transfer coefficients, using the Sieder-Tate and Deckwer correlations, were judged accurate within the range of uncertainty of the plant data.

The predicted shell side heat transfer coefficients are plotted versus the superficial gas velocity in Figure IV.8. These curves are based upon the average CO-Rich feed gas conditions at 482°F and 750 psig and are approximate for the other feed compositions and pressures. The predicted coefficients ranged from 200 to 220 Btu/hr-ft^2-°F at 0.10 ft/sec, to 340 to 370 Btu/hr-ft^2-°F at 0.80 ft/sec for slurry concentrations of 30 to 50 wt% oxide. The measured coefficients for the 482°F reactor temperature cases are also plotted in Figure IV.8 and are generally within 25% of the predicted values.

5. Post Run Inspection

Run E-8 ended on 28 February 1989. This concluded over six months of continuous operation at the LaPorte LPMEOH PDU. This six-month period covered three different runs: Run E-6--the alternate catalyst run from 8/25/88 through 9/01/88, Run E-7--the catalyst activity maintenance run from 9/01/88 through 1/10/1989, and Run E-8--the process variable scan run from 1/10/89 through 2/28/89. At the conclusion of Run E-8 the reactor, oil separation section, and slurry pump were opened and inspected. The down stream methanol vessels were not opened.

Overall, the PDU was in good shape. As was suspected, the 27.10 demister suffered the same damage as during Run E-5. The demister was dislodged, slightly crushed and plugged with catalyst. The internal heat exchanger and sparger were fouled more than at the end of Run E-5 but both were functional and in good condition considering the high concentration (50 wt%) tests

Table IV.9

RUN E-8
27.10B INTERNAL HEAT EXCHANGER COEFFICIENTS
(Btu/hr ft2 °F)

Case	Slurry Conc. (wt% oxide)	Overall Coefficient			Slurry Side Coefficient		
		Predicted	Measured	Pct. Error	Predicted	Measured	Pct. Error
E-8.1	45.3	79.5	73.8	-7.2	308.0	237.2	-23.0
E-8.2	49.6	81.0	75.0	-7.4	314.5	240.3	-23.6
E-8.3	50.0	78.9	74.2	-5.9	257.1	213.6	-16.9
E-8.4	45.6	78.3	73.2	-6.5	252.7	206.5	-18.3
E-8.5	42.1	75.5	70.6	-6.5	262.1	211.3	-19.4
E-8.6	41.1	80.4	76.7	-4.6	306.6	259.0	-15.5
E-8.7	41.1	78.5	74.0	-5.7	297.4	241.6	-18.7
E-8.8	40.4	78.3	74.2	-5.1	249.1	212.5	-14.7
E-8.9	37.5	86.1	74.4	-13.6	308.5	197.1	-36.1
E-8.11	36.5	82.5	82.0	-0.6	302.5	295.7	-2.2
E-8.12	36.5	80.0	79.4	-0.7	260.7	254.9	-2.2
E-8.13	37.0	83.0	83.6	0.7	320.1	328.8	2.7
E-8.14	36.5	76.1	74.9	-1.6	215.5	206.2	-4.3
E-8.15	33.2	84.0	80.8	-3.8	294.5	259.0	-12.0
E-8.16	32.2	73.6	67.4	-8.4	259.0	195.7	-24.4
E-8.17	33.7	80.0	83.2	4.1	296.5	347.2	17.1
E-8.18	36.0	81.0	82.4	1.7	264.5	279.5	5.7
E-8.19	36.4	79.1	83.4	5.4	262.3	315.5	20.3
E-8.20	36.8	75.8	80.9	6.8	250.0	315.9	26.4
E-8.21	35.8	82.8	84.7	2.3	301.6	328.8	9.0
E-8.22	34.8	82.9	86.0	3.8	301.3	347.4	15.3
E-8.23	35.8	80.7	82.1	1.7	289.8	307.9	6.2
E-8.24	35.8	81.5	84.1	3.2	301.1	340.3	13.0
E-8.25	37.0	78.3	79.1	1.1	289.2	300.9	4.0
E-8.26	36.2	85.3	80.3	-5.9	304.8	249.0	-18.3
E-8.27	37.3	83.5	80.2	-4.0	293.1	256.0	-12.7
E-8.28	35.5	83.1	84.7	1.9	301.0	322.6	7.2
E-8.29	35.9	84.2	77.2	-8.3	301.6	227.7	-24.5
E-8.30	36.3	79.2	86.3	8.9	255.0	345.8	35.6
E-8.31	35.2	85.5	86.1	0.7	304.0	311.7	2.5
E-8.32	36.6	78.7	53.8	-31.7	215.2	94.9	-55.9
E-8.33	35.6	83.4	85.2	2.1	302.0	325.9	7.9
E-8.34	37.6	82.0	94.8	15.6	275.8	503.8	82.7
Average Error				5.7			18.1

Figure IV.8

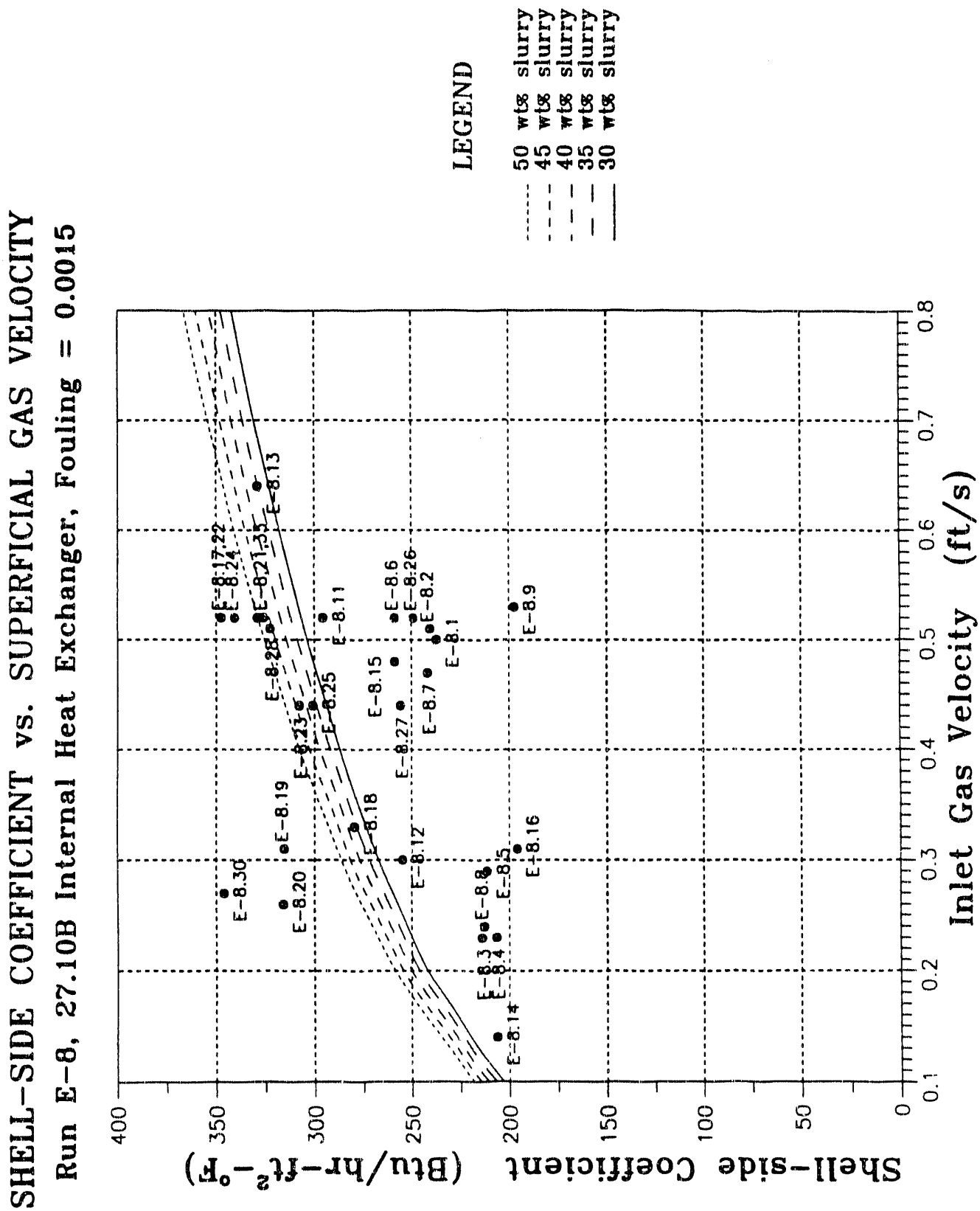

SHELL-SIDE COEFFICIENT vs. SUPERFICIAL GAS VELOCITY
Run E-8, 27.10B Internal Heat Exchanger, Fouling = 0.0015
LEGEND
50 wt% slurry
45 wt% slurry
40 wt% slurry
35 wt% slurry
30 wt% slurry
Shell-side Coefficient (Btu/hr-ft²-°F)
Inlet Gas Velocity (ft/s)
0
50
100
150
200
250
300
350
400
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
E-8.30
E-8.20
E-8.19
E-8.18
E-8.14
E-8.3
E-8.4
E-8.8
E-8.5
E-8.12
E-8.16
E-8.23
E-8.25
E-8.28
E-8.11
E-8.15
E-8.27
E-8.7
E-8.1
E-8.6
E-8.26
E-8.2
E-8.9
E-8.24
E-8.22
E-8.21
E-8.13

Table IV.10

RUNS E-6,7,8 CATALYST INVENTORY ACCOUNTING

Date	Estimated Catalyst Oxide Inventory (lbs) 27.10*	28.30	27.13 & Sl. Loop	Piping & Misc	Cummulative Removed (lbs)	Comments
8/22/88		2545				Initial charge to 28.30
8/24/88	1157		1320		68	68 lbs of residual slurry washed from 28.30
8/23/88- 8/31/88	1157		1263	48	77	9 samples pulled from 27.10 48 lbs lost to piping, demister and vessel walls
8/25/88	1157	1216	47	48	77	1215 lbs transferred from slurry loop to 28.30 9 lbs lost in 27.13 24 lbs lost in slurry pump cavity 14 lbs lost in slurry loop piping
8/28/88	1069	1216	135	48	77	88 lbs transferred from 27.10 to 27.13
8/31/88	887	1216	317	48	77	182 lbs transferred from 27.10 to 27.13
8/31/88- 10/3/88	867	1216	317	65	80	3 samples pulled from 27.10 17 lbs lost to piping, demister and vessel walls
10/3/88- 12/29/88	853	1213	317	77	85	3 samples pulled from 28.30 2 samples pulled from 27.10 12 lbs lost to piping and vessel walls
12/29/88	391	1213	779	77	85	462 lbs transferred from 27.10 to 27.13
12/29/88	937	667	779	77	85	546 lbs transferred from 28.30 to 27.10
1/10/89	1247	356	779	77	86	311 lbs transferred from 28.30 to 27.10 1 sample pulled from 27.10 on 1/5/90
1/16/89	1166	437	779	77	86	81 lbs transferred from 27.10 to 28.30
1/18/89	1012	591	779	77	86	154 lbs transferred from 27.10 to 28.30
1/23/89	882	721	779	77	86	130 lbs transferred from 27.10 to 28.30
1/25/89	794	809	779	77	86	88 lbs transferred from 27.10 to 28.30
1/27/89- 1/30/89	781	809	779	90	86	13 lbs lost to piping and vessel walls
2/2/89	781	1541	47	90	86	732 lbs transferred from 27.13 to 28.30
2/8/89	781	41	47	90	1586	1500 lbs drained from 28.30 to 12 drums
2/27/89	563	259	47	90	1586	218 lbs transferred from 27.10 to 28.30
2/28/89	0	822	47	90	1586	27.10 drained to 28.30
3/1/89	0	43	47	90	2365	779 lbs drained from 28.30 to 12 drums
Total Estimate					2545	Total of Estimated Inventories
Actual Found	0	14	47	90	2356	
					2507	Actual Total Catalyst Found: 38 lbs of catalyst unaccounted for

* Note: The catalyst solids accumulated on the 27.10 Reactor walls and internals is included under Piping & Misc.

performed during the PVS runs and the long time on stream. The equipment downstream of the reactor was in excellent shape. The 27.14 Secondary V/L Separator and the 27.14 demister were both clean and in good working condition. The slurry loop (27.13 Primary V/L Separator and 10.50 Slurry Pump) had the same accumulation of slurry as was seen in previous runs.

The following section is a detailed description of the condition of each piece of equipment at the time of inspection and the history of the catalyst over the six months of operation. Table IV.10 is the accounting of catalyst inventory over the last three runs. Overall, 2356 lbs of the original 2545 lb catalyst oxide charge was drained to drums or sampled, and 151 lbs were identified during the end of run vessel inspections. Only 38 lbs (1.5%) of the catalyst charged in August 1988 were not accounted for.

27.10 Reactor

The top head of the reactor was removed on 2 March after the reactor was drained and purged with nitrogen. The demister was in nearly the same condition as it was at the end of Run E-5, dislodged from its original position. Two to three inches of the demister were hanging below the support brackets and was compressed about one inch. It is estimated that 15 lbs of catalyst were lost on the demister. The performance of a demister in this service was generally unsatisfactory and should not be considered for a commercial design.

The top walls of the reactor (liquid level to top head) were found to be caked with as much as 1/2 inch of slurry. This was more than at the end of Run E-5 and is probably attributable to the length of this last run.

The internal heat exchanger was fouled more than in the previous run, but was in good shape, considering the high slurry concentrations achieved during a number of the PVS cases.

The sparger and the bottom head of the reactor were in excellent condition. There was about a 1/4 to 1/2 inch buildup of slurry on the sparger but it appeared to be open and functional.

The slurry inlet line from the 10.50 pump to the reactor was completely plugged with 65 wt% catalyst from slurry valve, V1509-S, to the slurry inlet nozzle.

The gas inlet line had a 1/8 inch coating of slurry from the gas shut off valve, HV-150-2-S, to the reactor inlet. During every shutdown, gas is shut off using valve HV-150-2-S and the line begins to fill with slurry. When gas flow is started the majority of the slurry is returned to the reactor leaving behind only the thin coating on the surface of the pipe.

In addition to the loss of catalyst to the demister, an estimated 79 lbs of catalyst was lost on the reactor walls and internals.

27.13 Primary Vapor Liquid Separator

The 27.13 manway was opened and 8 lbs of slurry with a somewhat reddish color was found. The walls were slightly coated with a black oily residue (less than 10 wt% catalyst). The vessel also had a slight odor of methanol. Catalyst losses in this vessel were estimated to be 9 lbs.

27.14 Secondary Vapor Liquid Separator

The 27.14 was found to be in excellent condition. The bottom 10 inch flange was removed and no significant catalyst buildup was observed. The 27.14 demister, installed after Run E-5, appeared to be undamaged and free of catalyst buildup.

Only 18 lbs of slurry were recovered from the vessel and it was estimated that 5 lbs of that was catalyst.

The standpipe at the bottom of the 27.14, originally intended to prevent solids from leaving the 27.14, was removed before the bottom flange was reinstalled.

21.10 Feed Product Exchanger

The feed product exchanger was opened and found to be clean and free from catalyst buildup. The tube sheet had a very thin coating of black oil and all heat exchanger tubes were unplugged.

10.50 Slurry Pump

The slurry pump was opened and found to be in the typical shutdown condition. Five gallons of slurry were found in the pump cavity and a small amount of slurry was on the rotating blades. Some of the slurry was a green color.

The pump was cleaned by hand and 52 lbs of roughly 45 wt% slurry was recovered, accounting for 24 lbs of catalyst.

28.30 Slurry Prep Tank

The prep tank was examined three times during this six-month period. The first examination was on 24 August 1988, while reduction (ER-05) was under way. It was necessary to wash the prep tank at this time to use it for catalyst storage during Run E-7. An estimated 68 lbs of catalyst were lost during this initial washing of the prep tank.

The prep tank was drained on 2 February 1989 and 4563 lbs of slurry were recovered. It was estimated that the catalyst concentration was 33 wt% as oxide. Therefore, roughly 1500 lbs of catalyst were recovered.

The prep tank was drained a final time on 1 March 1989 and 2072 lbs of slurry at 37.6 wt% were recovered. Thus, an estimated 779 lbs of catalyst were recovered at end of run.

A final inspection of the prep tank at the end of the run indicated that 14 lbs of catalyst remained in the prep tank after draining.

27.12 Slurry Carryover Surge Pot

The oil return lines from the 27.12 to the 10.52 Oil Makeup Pumps and the reactor were opened. There was about 1/4 of an inch of slurry that had settled out in the piping. It is estimated that 5 lbs of catalyst were lost in this piping. This accumulation was much more than was seen at the end of Run E-5, but again, the length of these runs is the likely cause.

V. IN-SITU ACTIVATION WITH SYNGAS RUN E-9

A. Introduction

The final 10-day run of the LP-III program used a fresh batch of the alternate catalyst. The main objective of this run was to demonstrate a simplified procedure to activate the catalyst with dilute syngas in place of dilute hydrogen and without the use of the slurry circulation pump. These process simplifications have the potential to significantly impact commercial capital and operating costs. The activation was followed by a small series of process variable studies designed to evaluate the effectiveness of the activation procedure and further expand the operating experience base of the LPMEOH slurry reactor.

B. In-Situ Catalyst Activation with Syngas

The catalyst activation ER-6 was accomplished using dilute syngas in place of hydrogen and without the use of the slurry pump for recirculation and mixing. The procedure was based on the successful methods developed in the laboratory program under Subtask 3.3. Use of syngas avoids the necessity for having separate hydrogen available for activation purposes.

A batch of 41 wt% (oxide base) slurry using F21/0E75-43 catalyst and Drakeol-10 oil was mixed in the slurry prep tank and pressure-transferred to the reactor. The catalyst oxide slurry was fluidized in the reactor by using a nitrogen purge. The reducing gas was blended from 3.5 mol% CO-Rich gas and 96.5 mol% nitrogen and then fed to the reactor in place of the purge nitrogen. The catalyst activation Run ER-6 procedure began at 1000 on 16 March 1989. The entire activation procedure went smoothly and was completed on schedule at 1600 on 17 March. Run ER-6 was clearly the simplest and most uneventful of any PDU catalyst activation to date. Further details of the catalyst activation are presented in the Run Chronology (Table V-1).

C. Methanol Synthesis Operation

Run E-9 consisted of a series of eight different process conditions or cases. The length of the operating period and the majority of the cases were chosen to evaluate the effectiveness of the activation procedure. In addition to the baseline evaluation runs, four cases (B, D.1, D.2 and F) were included to further expand the operating experience base of the LPMEOH slurry reactor. Case B tested the methanol productivity on a Lurgi type gas feed at a high space velocity and cases D.1 and D.2 examined the effect of water injection on reactor performance. Case F was planned to test the maximum attainable superficial inlet gas velocity to the slurry reactor. The feed gas types tested in Run E-9 were previously defined in Table IV.1. The nominal operating conditions for Run E-9 are shown in Table V.2.

Table V.1

LAPORTE LPMEOH LP-III
CATALYST ACTIVATION RUN ER-06 CHRONOLOGY

Date	Time	Cumulative Time On Reduction Gas (hours)	Notes and Observations
14 Mar 89	1500		Pumped 164 gals (1164 lbs) of oil into the 28.30 Slurry Prep Tank.
	1700		Began loading 822 lbs. of F21-0E75/41 catalyst into the 28.30 to make a 41 wt% catalyst slurry.
	1900		Completed catalyst loading and began stirring the slurry under nitrogen.
16 Mar 89	0830		Slurry sample pulled from 28.30 Slurry Prep Tank.
	0900		Catalyst slurry transferred from the 28.30 Slurry Prep Tank to the 27.10 Reactor. 51 gallons of oil was pumped into the 28.30 and transferred to the 27.10 as a vessel and line flush.
	1000	0.0	Nitrogen feed taken out of reactor. Began feeding reduction gas to the reactor. Side note: the slurry inlet bubble cap was removed from the reactor.
	1100	1.0	Catalyst reduction temperature ramp at a rate of 15°F/hr started. The reactor conditions are: T=200 °F, P=100 psig. Reduction gas flow rate at 16,000 SCFH.
	1400	4.0	The reduction gas uptake by the catalyst looks very good. No trouble maintaining the uptake above the standard curve.
	1745	7.8	Slurry sample pulled from 27.10 Reactor.
	2345	13.8	Reduction ramp ended at 392°F. The reduction gas uptake by the catalyst was 5% above the minimum target value. Begin the 10 hr hold period.
17 Mar 89	0900	23.0	Added 40 gal of oil to 27.14.
	0945	23.8	Slurry sample pulled from 27.10 Reactor.
	1000	24.0	Started temperature ramp to 464°F at a rate of 15°F/hr.
	1450	28.8	Final reduction ramp ended at 464°F. Begin 1 hour temperature hold.
	1530	29.5	Slurry sample pulled from 27.10 Reactor.
	1600	30.0	Catalyst reduction complete. Reduction gas flow to reactor stopped. Reactor fluidized with low flow of high pressure N_2. Activation appears completely successful.

TABLE V.2

NOMINAL TARGET RUN CONDITIONS FOR RUN E-9

Run No.	Gas Type	Pres. psig	Temp. °C	Space Vel. L/hrkg	Gas Vel. ft/sec	Slurry Conc. wt. %	Slurry Height %	Comment
A	CO-Rich	750	250	13000	0.5	35	100	
B	G. Plains	750	250	13000	0.5	35	100	
C.1	CO-Rich	750	250	5800	0.2	35	93	
C.2	CO-Rich	750	250	5000	0.2	35	93	
D.1	CO-Rich*	900	250	5100	0.2	35	91	Water Inject.
D.2	CO-Rich*	750	250	10200	0.4	35	100	Water Inject.
E	CO-Rich	750	250	10100	0.4	35	100	
F	CO-Rich	750	250	17500	0.7	35	100	Max Gas Vel.

Note: * CO-Rich gas feed with water injection

The transition from reduction gas (ER-6) to synthesis gas (E-9) was troublesome but manageable. The initial low reactor feed flow rates resulted in nonuniform temperature and gas holdup profiles within the reactor. When the feed flow was increased to 40,000 SCFH, both the temperature and gas holdup became uniform and the catalyst activity increased substantially. At this higher feed flow, however, the liquid/vapor interface at the top of the slurry level became indiscernible with the nuclear density gauge, although this feed rate was only 20% of the maximum feed rates which had been previously achieved successfully.

The feed rate was continually increased to the target rate of 148,900 SCFH without the appearance of a vapor/liquid slurry interface. The gas holdup at these flowrates was approximately 50+ vol%. Samples from the 27.17 Intermediate Oil Separator showed that there was substantial slurry carryover from the reactor. Methanol samples, however, were clear, indicating that the apparent frothing behavior in the reactor was not occurring in the 27.14 separator. At this point the feed rate was reduced to 30,000 SCFH, which resulted in the formation of a distinct vapor/liquid interface while maintaining uniform temperature and gas holdup profiles within the reactor.

A subsequent reactor shutdown test indicated that only 605 lbs of the original 822 lb catalyst charge were still in the reactor. The catalyst concentration in the slurry had dropped to 28 wt% oxide. A decision was made to slowly bring the reactor feed flowrate back to the target level, while maintaining liquid level and a clear vapor/liquid interface in the reactor. Pumping the oil/slurry mixture back to the reactor, to maintain liquid level as the process oil normally evaporated in the reactor, would allow the solids carried over into the 27.14 separator to be returned to the reactor.

Oil samples from the 27.14 separator were clear of catalyst within 24 hours of beginning to return oil to the reactor. A shutdown test showed the catalyst inventory in the reactor was 667 lbs (82% of the expected amount) and that 150 lbs of catalyst had been lost, either in this frothing period or during the catalyst activation procedure. The stable operating conditions were 34.6 wt% catalyst oxide at a gas holdup of 42.6 vol%. Post run inspections were able to account for approximately 120 lbs of the displaced catalyst.

The remainder of the operations were uneventful and executed according to plan. The water injection tests were accomplished by injecting preheated deionized water directly into the reactor feed gas. The water was pumped to reactor pressure using the 10.56 utility pumps and was preheated in a portable heat exchanger using 600 psig steam. The PDU accumulated 330 hours of methanol synthesis operation during the in- situ catalyst activation run E-9. Table V-3 lists the Run Chronology for the operating period of the run.

In addition to the eight process conditions, Run E-9 included a reactor mixing study operating period using a radioactive Mn_2O_3 liquid tracer. The details and results of that work have been previously published as a DOE Topical Report entitled "Task 2.3: Tracer Studies in the LaPorte LPMEOH PDU" and are not discussed here.

D. Discussion of Results

1. Catalyst Activation

The cumulative reduction gas uptake for syngas catalyst activation Run ER-6 is shown in Figure V-1. Both the reduction gas uptake versus time and cumulative reduction gas uptake were excellent for this run. The targeted uptake value (2.58 SCF/lb cat) being obtained after only 10 1/2 hours.

The increased rate of reduction gas uptake at temperature is best illustrated by comparison with the previous hydrogen activation, ER-5, done in August 1988. Figure V.2 shows how the nature of the reduction improved dramatically for this run. This simplified reduction procedure, without the use of the slurry pump, was very successful as demonstrated in subsequent production tests.

Initial startup data, however, indicated the possibility of catalyst carryover during the activation. The reduction gas vent circuit was therefore examined for slurry carryover following the PDU shutdown at the end of Run E-9. Catalyst slurry was found both in the reduction gas vent lines and in the 15.91 Flare Header Knockout Pot. Approximately 100 lbs of catalyst are estimated to have been lost during the course of the activation procedure. This would not significantly effect the reduction gas uptake calculation, however, since it is expected that the majority of this loss occurred later in the activation, near the end of the procedure. It is recommended that the reduction gas superficial velocity be reduced and that slurry carryover be closely monitored for future activations.

2. Process Conditions

The cause of the initial 48-hour period of unstable operations is not known, however, two possible explanations are 1) the feed gas rates were increased too rapidly, and 2) there was a typical unstable operating (or conditioning) period at the beginning of the methanol synthesis operation. The feed rates were increased fairly quickly to the reactor in spite of the lack of a clear liquid level. This was done initially to stabilize the reactor temperature and gas holdup profile. In retrospect, since the temperature profile could have been easily managed below 482°F, it may have been better to operate longer in the nonuniform reactor mode and only slowly introduce the feed gas as the top of the liquid level stabilized.

The second possibility of a short initial conditioning period is consistent with the observations at the beginning of Runs E-6 and E-7 in August and September 1988. A gradual change in slurry properties occurred over the first

TABLE V.3

RUN E-9 CHRONOLOGY

Date	Time	Cumulative Time On Production Gas (hours)	Notes and Observations
17 Mar 89	1650	0	Syngas started to reactor. Feed gas once through to purge nitrogen. Raising reactor pressure. Start of Run E-9.
	1715	.4	Methanol detected in reactor effluent.
	1725	.6	Target reactor pressure and temperature obtained at P=750 psig, T=483°F. Syngas flow rate at 25,000 SCFH.
	1825	1.6	Nitrogen in fresh feed down to 1 mol%. Recycle started. Began increasing feed to reactor.
	1830	1.7	High level alarm in 27.14 Intermediate Oil Separator and reactor level high (213 inches). No oil return flow to reactor. 46.5 gallons of oil drained from 27.14. Oil is clear.
	1935	2.8	Reactor effluent sample shows 13.8 mol% methanol.
	1945	2.9	Feed gas flow rate to reactor at 36,064 SCFH. Temperature and gas holdup profiles are non-uniform across reactor. Average slurry temperature is 470°F. No clear interface designating a slurry level can be detected. Gas holdup in the freeboard region appears to be 50+ vol%.
	2015	3.4	Reactor feed rates are raised from 40,000 SCFH to 100,000 SCFH. The temperature profile became uniform across the reactor (480 °F). The PDU pressure collapsed from 750 psig to 700 psig.
	2030	3.8	Reactor feed rate reduced to 50,000 SCFH to regain reactor pressure. Reactor pressure back to 750 psig.
	2150	5.0	Reactor feed rate at 148,900 SCFH. Gas holdup approximately 50 vol%. A slurry level can not be found in the reactor as the NDG readings show frothing in the entire reactor. It is suspected that slurry is being carried over into the 27.14. Gas holdup across the reactor is non-uniform
	2230	5.7	Product Methanol flowing to 28.10 Storage Tank.

TABLE V.3

RUN E-9 CHRONOLOGY

Date	Time	Cumulative Time On Production Gas (hours)	Notes and Observations
18 Mar 89	0030	7.7	Samples pulled from the 27.14 and 27.12 are loaded with catalyst, confirming catalyst carryover. Methanol samples from the 22.10 Product Separator are clear. The slurry carryover has stopped at the 27.14.
	0045	7.9	Reactor feed rate is dropped to 30,000 SCFH in an attempt to find a clearly defined slurry height. A hi[illegible] slurry level is indicated by the te[illegible]erature profile in the reactor. Sl[illegible]y temperature profile remaine[illegible]niform with height.
	0600	13.2	Slurry level is at design height of 211 inches. Began returning oil to reactor from 27.14 to maintain level. Reactor under normal operating conditions. Both gas holdup profile and temperature profile are uniform across the reactor height.
	1000	17.2	Slurry sample pulled from 27.10 reactor.
	1100	18.2	Began bringing reactor feed rates up to 75,000 SCFH.
	1700	24.2	Reactor feed rates at 75,000 SCFH.
	2400	31.1	27.14 return oil sample is clearing up.
19 Mar 89	1130	42.7	Began bringing up reactor feed rates to 148,900 SCFH.
	1600	47.2	All flow (148,900 SCFH) into reactor. Reactor is stable. Oil sample from 27.14 is clear. Reactor Conditions: 750 psig, 482 °F.
	1815	49.4	27.10 Reactor shutdown test shows 667 lb of catalyst in reactor. Down from 822 lb in the initial charge.
	2030	51.3	Inspected 15.91 Flare Knockout Vessel. Approximately 20 gallons of thick slurry is drained from the vessel. It is determined that approximately 105 lb of the 155 lb of lost catalyst can be attributed to carryover into the 15.91 Flare Gas Knockout circuit during reduction. The balance of catalyst (50 lb) is determined to be credited to dropout in the oil circuit and loss in the slurry samples.

TABLE V.3

RUN E-9 CHRONOLOGY

Date	Time	Cumulative Time On Production Gas (hours)	Notes and Observations
20 Mar 89	1100	65.8	Slurry sample is pulled from 27.10 Reactor.
	1700	71.8	Sample from 27.14 shows 7.9 wt% methanol in the condensed oil. Methanol product is 0.12 wt% oil. The inlet temperature to the 27.14 Intermediate Separator is moved up to 280°F from 270°F to avoid methanol knockout.
21 Mar 89	0930	88.3	27.10 Reactor shutdown test verifies 3/19/89 shutdown test results. The catalyst inventory is stable.
	1235	91.1	Methanol product is rerouted to 22.16 Day Tank from Storage Tank.
22 Mar 89	0300	105.5	Product flow returned to the Storage Tank. 2112 gallons of methanol is isolated in the 22.16 Day Tank for future testing.
	0900	111.5	27.14 oil samples still show high methanol concentration. The inlet temperature to the intermediate separator is moved up to 300°F from 280°F to reduce methanol in the condensed oil.
	0930	112.0	27.14 Intermediate Oil Separator temperature increased to 300°F.
23 Mar 89	0600	132.5	Plant has very stable operations.
24 Mar 89	0740	158.2	Changed feed composition to Great Plains gas in preparation for Case B. Stable operation.
	1900	169.5	Begin Case B. Nominal conditions are Great Plains gas, 13000 Sl/hr kg, 482°F, 750 psig, 35 wt% cat ox.
25 Mar 89	1600	190.5	End of Case B. Switched feed composition back to CO-rich gas at 50,000 SCFH.
	1800	192.5	Slurry allowed to thicken to increase catalyst concentration. Feed gas flow at 70,000 SCFH.
	2300	197.5	Begin Case C.1. Nominal conditions are CO-Rich gas, 6000 Sl/hr kg, 482°F, 750 psig, 35 wt% cat ox.

TABLE V.3

RUN E-9 CHRONOLOGY

Date	Time	Cumulative Time On Production Gas (hours)	Notes and Observations
26 Mar 89	1300	211.5	End of Case C.1.
	1330	212.0	Feed gas flow dropped to 57,500 SCFH for Case C.2.
	1600	214.5	Reactor lined out for Case C.2.
27 Mar 89	1100	233.5	End of Case C.2.
	1110	233.7	Began water injection test at 1.5 gph (0.5 mol%). Feed target is 1.5 mol% H_2O. CO concentration in reactor outlet immediately begins to drop.
	1150	234.4	Raising water flow to 3.6 gph (1.0 mol%).
	1230	235.0	Water injection increased to 6.5 gph. Visible drop in CO in reactor outlet with H2O addition steps.
	1350	236.3	Operating temperature for the 27.14 Intermediate Oil Separator decreased to 280°F.
	1800	240.5	Begin Case D.1. Nominal conditions are CO-Rich gas with 1.5 mol% water injection, 5000 Sl/hr kg, 482°F, 750 psig, 35 wt% cat ox.
	1830	241.0	Injection of water has lowered gas holdup approximately 1 vol%.
	2230	245.0	Raising fresh feed rate to lowe CO_2 in recycle.
28 Mar 89	1200	258.5	Water injection Case D.1 ended. Bypass installed on steam trap to increase injection temperature.
	1330	260.0	Plant back on line with 2 mol% H_2O injection.
	1450	261.3	Water injection increased to 11 gph.
	1800	264.5	No corresponding improvement in production with water injection increase. Feed flow changed to 115,000 SCFH. Begin Case D.2. Nominal conditions are CO-Rich gas with 2 mol% water injection, 10,000 Sl/hr kg, 482°F, 750 psig, 35 wt% cat ox.
29 Mar 89	1540	286.2	Isolated a slurry sample.
	1600	286.5	Water injection Case D.2 ended.

TABLE V.3

RUN E-9 CHRONOLOGY

Date	Time	Cumulative Time On Production Gas (hours)	Notes and Observations
	1605	286.6	Water flow stopped. Constant reactor conditions maintained to observe production changes.
	1900	289.5	Begin Case E. Nominal conditions are CO-Rich gas, 10,000 Sl/hr kg, 482°F, 750 psig, 35 wt% cat ox.
30 Mar 89	1200	306.5	Baseline Case E ended. Feed flow increased to 146,000 SCFH.
	2230	317.0	Beginning to bring feed up for maximum superficial gas velocity case.
	2315	317.8	Gas velocity peaks at 0.72 ft/sec, which corresponds to a feed rate of 205,000 SCFH. Methanol production will be roughly 12.5 TPD.
31 Mar 89	0000	318.5	Start of Case F. Nominal conditions are CO-Rich gas, 17,500 Sl/hr kg, 482°F, 750 psig, 35 wt% cat ox.
	1200	330.5	Baseline Case F ended.
	1215	331.4	Reactor being shutdown. The end of run E-9 and of PDU operations for the LP-III contract. Shutdown procedures begun.

FIGURE V.1

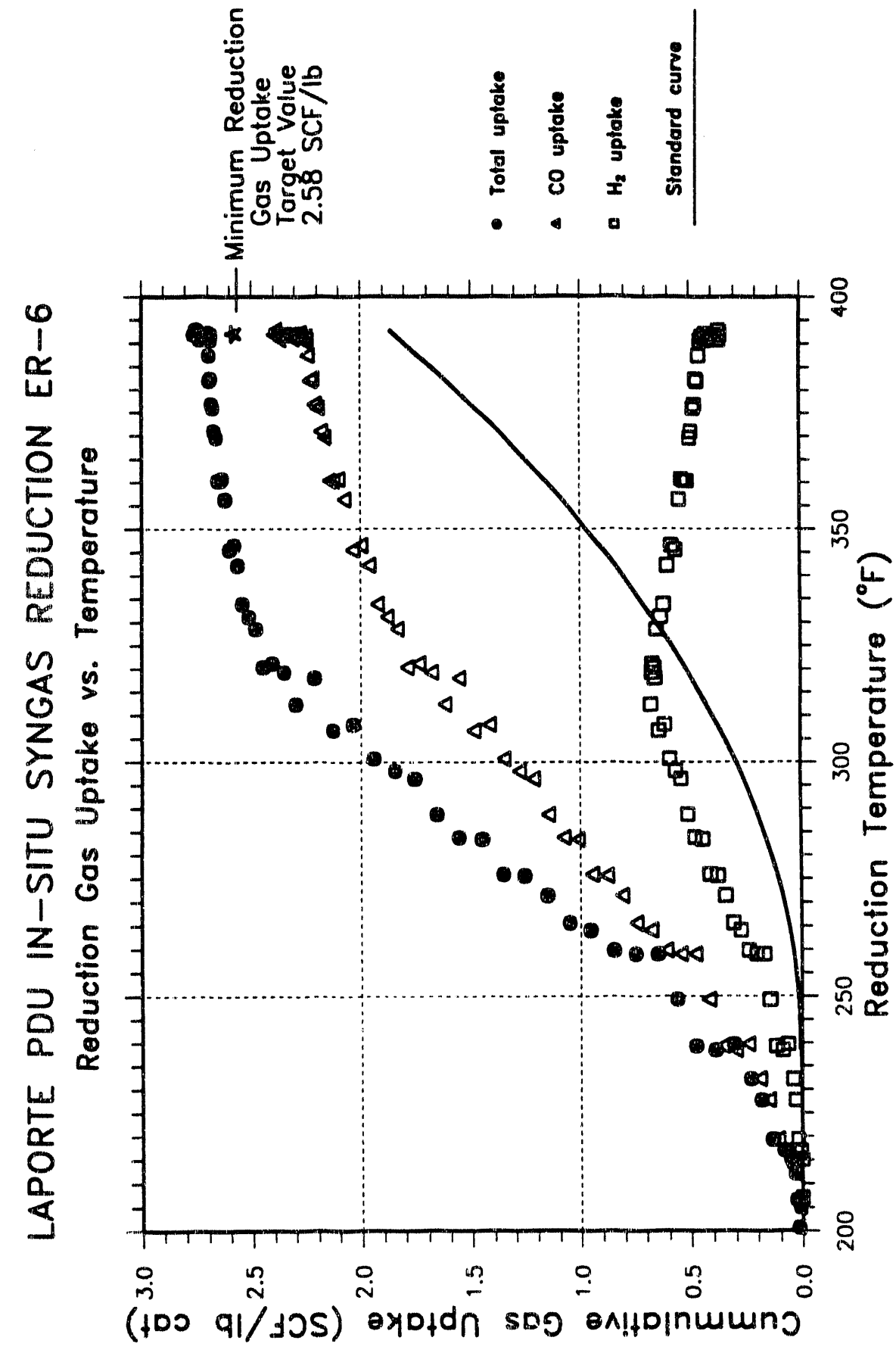
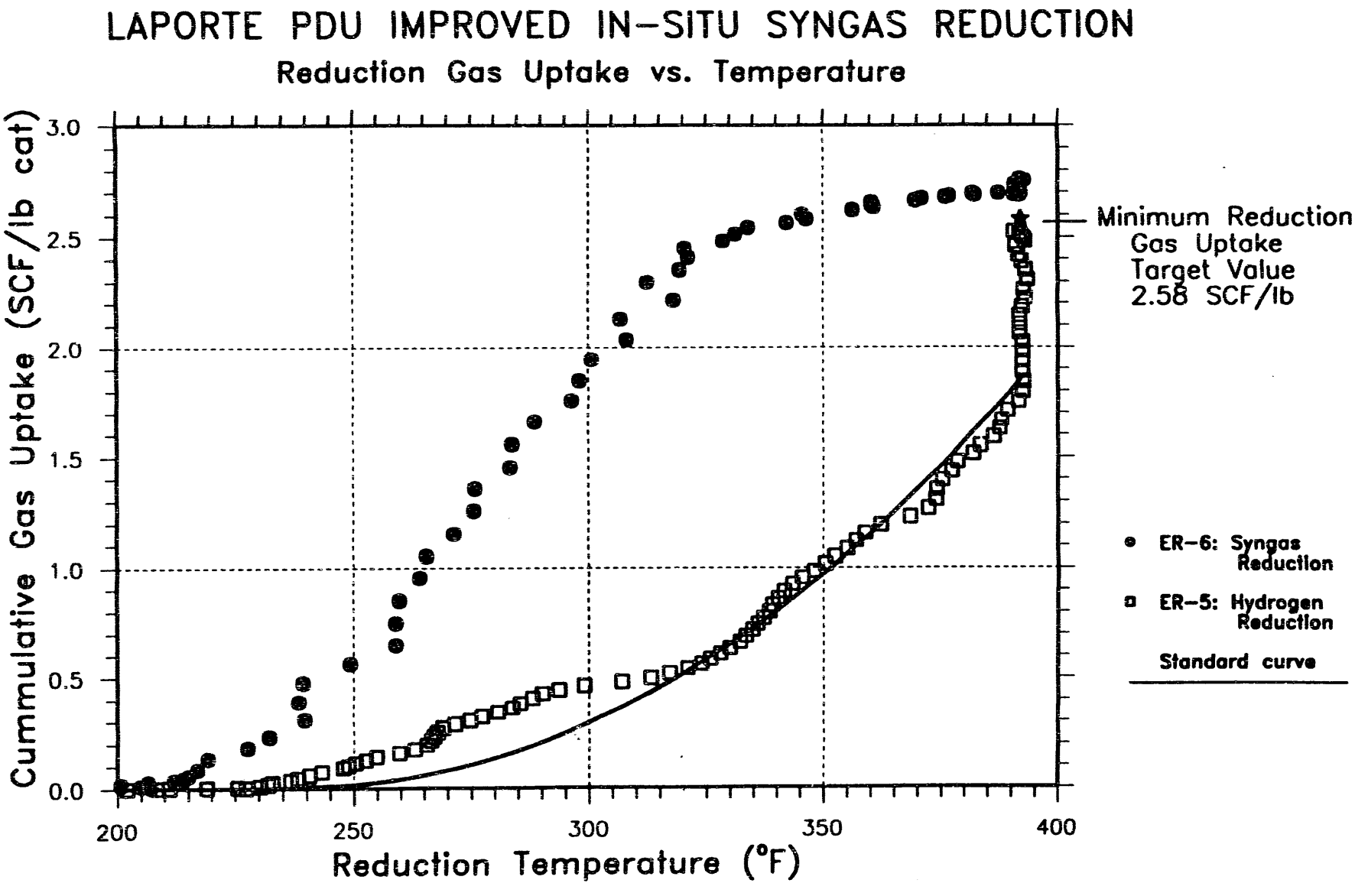

LAPORTE PDU IN-SITU SYNGAS REDUCTION ER-6
Reduction Gas Uptake vs. Temperature
Minimum Reduction Gas Uptake Target Value 2.58 SCF/lb
Total uptake
CO uptake
H_2 uptake
Standard curve
Cummulative Gas Uptake (SCF/lb cat)
Reduction Temperature (°F)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
200
250
300
350
400

FIGURE V.2


LAPORTE PDU IMPROVED IN-SITU SYNGAS REDUCTION
Reduction Gas Uptake vs. Temperature
Cummulative Gas Uptake (SCF/lb cat)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
200
250
300
350
400
Reduction Temperature (°F)
Minimum Reduction Gas Uptake Target Value 2.58 SCF/lb
ER-6: Syngas Reduction
ER-5: Hydrogen Reduction
Standard curve

seven days of Run E-6 and the gas holdup continued to change for 20 days into Run E-7. This variation in properties could be caused by a physical change in the catalyst particles (eg. particle size degradation; catalyst surface chemistry; surface or pore wetting) or a change in the process oil composition (eg. increase in average molecular weight; increase in dissolved methanol). In either case, it appears to be only an initial startup phenomenon since this behavior was not observed when over half of the catalyst inventory was replaced in the addition/withdrawal tests at the end of Run E-7. The reason for the increased impact at the start of this run, versus Run E-6, may be due to some or all of the changes in the activation procedure prior to each of the runs. Those are: 1) activation using dilute syngas versus dilute hydrogen, 2) internal circulation only versus use of the slurry pump, and 3) a 35 wt% target slurry concentration versus 45 wt%.

No further work was done to investigate these events. The possible causes are listed above so that these parameters can be closely monitored (or tested) during future PDU runs or during the initial startup of commercial facilities.

The PDU performed well following the 48-hour startup, and all of the proposed test cases were completed. Maintenance to the 01.20 compressor prior to the start of Run E-9 resulted in an increase in the output capacity which allowed a superficial gas velocity of 0.72 ft/sec to be tested as Case F. This was accomplished successfully and extended the tested range of inlet gas velocities by 12%. The complete run summary is provided in Table V.4 and the detailed data acquisition sheets are included as Appendix B.

Figure V.3 shows the methanol productivity performance as a function of space velocity. Although the distribution of the data is consistent with the behavior predicted from autoclave experience, this was the first time that the PDU results exceeded the laboratory results by over 20%. This is attributed primarily to the enhanced performance of the partially back-mixed bubble column reactor as compared to a well mixed autoclave reactor. This observed behavior is believed real and not an artifact of measurement errors since the measured catalyst inventory or methanol production rate would have to be in error by 100% in order for the PDU data to be in agreement with CSTR autoclave predictions.

Laboratory autoclave results for water injection tests, performed under Subtask 3.3, predicted that a 15-20% enhancement in catalyst productivity was possible using water injection in the reactor feed gas. Two water injection cases were completed as part of Run E-9 to verify this result at the PDU scale. The first case, D1, was done with 1.82 mol% water in the reactor feed gas at a dry space velocity of 5032 Sl/hr kg ox. The second, D2, was done with 1.33 mol% water in the feed at a dry space velocity of 10,084. Nominal CO-Rich gas conditions were maintained at 482°C and 750 psig.

The PDU and the slurry performed well for this study. The gas holdup was stable and uniform within the reactor and equivalent to the previous case without water injection. The reactor feed contained 1.33 to 1.82 mol% water but no water was detected in the reactor effluent. This loss of water was matched by a corresponding increase in CO_2 and H_2, and decrease in CO. Essentially, the water was being completely shifted to CO_2.

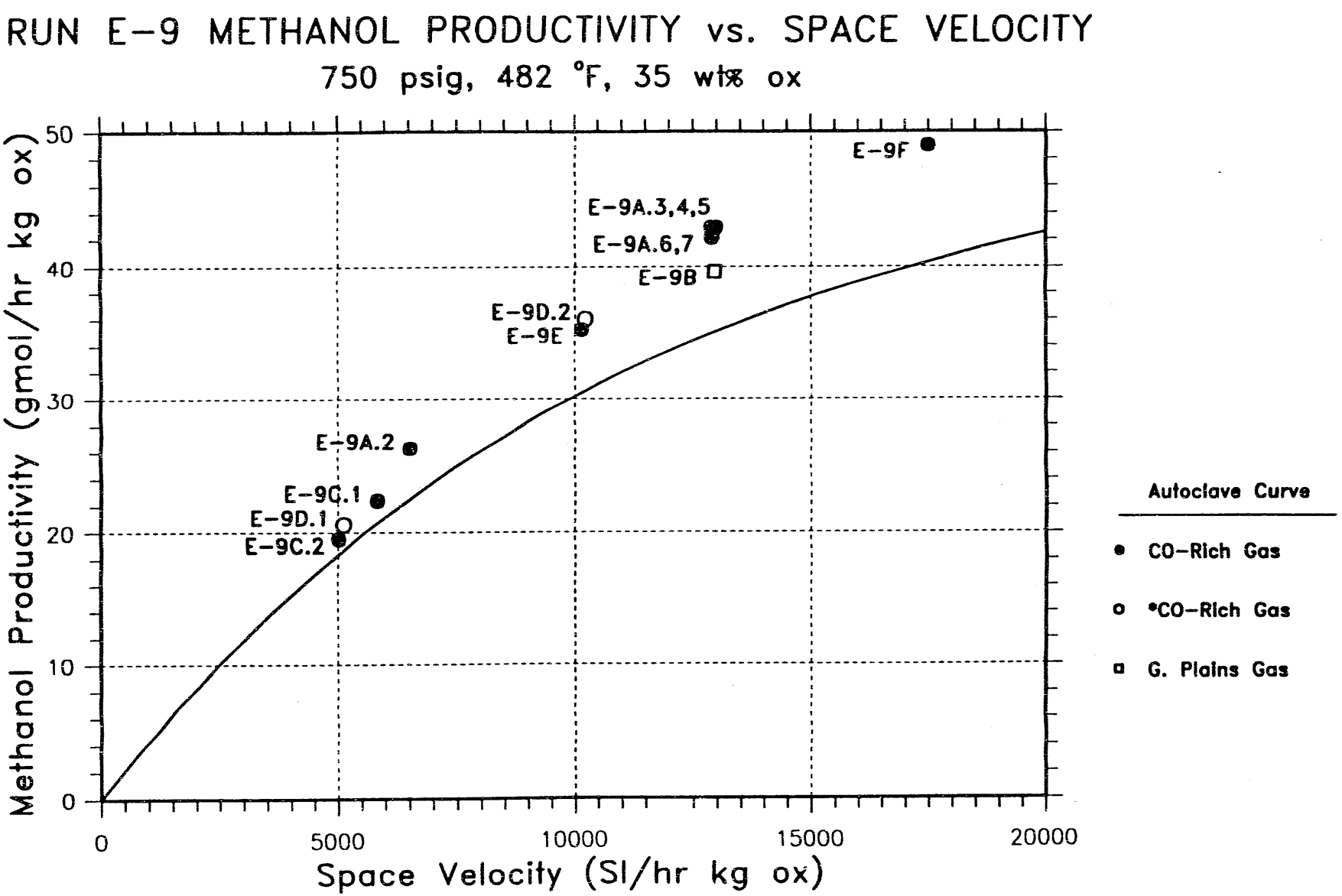
TABLE V.4

DATA SUMMARY FOR LAPORTE LPMEOH PDU RUN E-9

Case	Balance Period Date & Time	Gas Type	Days On Syngas	Temp (deg C)	Pres. (psig)	Inlet Gas Velocity (ft/sec)	Space Velocity (l/hr-kg)	Slurry Conc. (wt% ox.)	Gas Holdup (vol%)	Slurry Height (%)	Catalyst Inventory (kg)	CO Conv. (%)	MeOH Productivity (gmol/hr-kg)	Pct. of Autocl. (%)	Net MeOH Production (TPD)
E-9A.1	18 MAR 0100 -18 MAR 1000	CO-Rich	0.72	249.6	753.0	0.11	3067	28.0	30.3	100	274	26.5	17.6	152	4.28
E-9A.2	19 MAR 0000 -19 MAR 1100	CO-Rich	1.76	250.9	753.5	0.26	6514	32.8	38.4	100	303	18.6	26.3	120	7.08
E-9A.3	19 MAR 1500 -20 MAR 0600	CO-Rich	2.54	250.3	753.0	0.52	12880	34.6	42.6	100	303	14.8	42.9	124	11.25
E-9A.4	20 MAR 0600 -21 MAR 0600	CO-Rich	3.54	250.1	753.2	0.52	12968	34.6	42.8	100	303	14.7	42.8	123	11.23
E-9A.5	21 MAR 0600 -22 MAR 0600	CO-Rich	4.52	250.1	751.9	0.52	12986	34.8	43.2	100	302	14.8	42.9	123	11.26
E-9A.6	22 MAR 0600 -23 MAR 0600	CO-Rich	5.52	249.9	752.4	0.52	12893	34.9	43.6	100	302	14.6	42.1	121	11.04
E-9A.7	23 MAR 0600 -24 MAR 0800	CO-Rich	6.60	249.9	752.6	0.52	12914	34.9	43.4	100	302	14.6	42.2	122	11.05
E-9B	24 MAR 1900 -25 MAR 1600	G. Plains	7.94	250.0	753.0	0.52	12953	33.1	39.0	100	302	32.5	39.6	--	10.17
E-9C.1	25 MAR 2300 -26 MAR 1300	CO-Rich	8.81	249.8	753.0	0.23	5833	35.2	39.9	93	302	17.5	22.4	112	5.93
E-9C.2	26 MAR 1600 -27 MAR 1100	CO-Rich	5.56	249.8	753.0	0.20	5018	35.0	39.4	93	302	17.7	19.5	110	5.18
E-9D.1	27 MAR 1800 -28 MAR 1200	CO-Rich*	10.77	250.1	753.0	0.20	5126	35.4	38.5	91	302	18.7	20.6	114	5.47
E-9D.2	28 MAR 1800 -29 MAR 1600	CO-Rich*	11.94	250.0	753.0	0.40	10220	34.4	42.4	100	302	16.0	36.0	120	9.39
E-9E	29 MAR 1900 -30 MAR 1200	CO-Rich	12.77	250.1	753.0	0.40	10148	34.4	42.3	100	301	15.6	35.2	118	9.22
E-9F	31 MAR 0000 -31 MAR 1200	CO-Rich	13.77	250.2	742.8	0.72	17483	34.4	42.5	100	301	12.6	49.0	118	12.79

*CO-Rich gas matrix with approx. 1.5 mol% water injection in the reactor feed

Figure V.3


RUN E-9 METHANOL PRODUCTIVITY vs. SPACE VELOCITY
750 psig, 482 °F, 35 wt% ox
Methanol Productivity (gmol/hr kg ox)
Space Velocity (Sl/hr kg ox)
0
10
20
30
40
50
0
5000
10000
15000
20000
E-9F
E-9A.3,4,5
E-9A.6,7
E-9B
E-9D.2
E-9E
E-9A.2
E-9C.1
E-9D.1
E-9C.2
Autoclave Curve
CO-Rich Gas
*CO-Rich Gas
G. Plains Gas

The catalyst productivities for these two cases (on a normalized dry space velocity basis) are 2.9% higher than the identical conditions without water injection (see Table V.5). This is significantly lower than the 15-20% productivity enhancement that had been observed in the laboratory autoclave study. This 2.9% increase in productivity can be predicted simply on the basis of hydrogen enrichment in the reactor feed caused by the fast water-gas shift reaction.

TABLE V.5

RESULTS OF WATER ADDITION TEST CASES

Case E-9:	C.2	D.1	E	D.2
Space Vel. (Sl/hr-kg ox.)	5,018	5,126	10,148	10,220
Temperature (°F)	482	482	482	482
Pressure (psig)	753	753	753	753
Water in Feed (mol %)	0.0	1.82	0.0	1.33
Meas. Productivity (gmol/hr-kg)	19.48	20.64	35.18	35.95
Normalized Prod. (gmol/hr-kg)	19.48	20.05	34.95	35.95
Change in Productivity vs. Dry Feed Gas		2.9 %		2.9 %
Lab Data Prediction of Change vs. Dry Feed Gas		19 %		- 5 %

Two possible causes for the apparent discrepancy between the laboratory and PDU results are: 1) The lab study used a low copper catalyst, F21/0E75-44, and a high copper catalyst, F21/0E75-43, was used at the PDU. The two catalysts could respond differently to water. 2) At a 5,000 space velocity, the PDU bubble column behavior is equivalent to three stirred reactors in series versus the laboratory CSTR configuration, which results in a higher conversion at similar conditions. This tight approach to equilibrium might be masking an enhancement which would be significant on an older or less active catalyst.

3. Product Methanol Composition

The product methanol compositions for all of the cases in Run E-9 are shown in Table V.6. Once stabilized, the methanol purity varied from 95.03 to 98.59 wt% and averaged 96.48 wt%. The average impurities were 0.52 wt% water, 0.33 wt% oil, 0.75 wt % ethanol, 0.67 wt% higher alcohols and 1.24 wt% other oxygenates. The concentration of mineral oil in the product varied from 0.12 to 0.57 wt%.

As in Run E-8, the concentration of higher molecular weight byproducts in the methanol product increased with longer reactor residence times. The higher alcohol and other oxygenates concentrations decreases from 2.3 to 1.2 wt% and 1.9 to 0.8 wt% respectively as the space velocity increased (residence time decreased) from 5,000 to 17,500 Sl/hr kg-ox.

TABLE V.6

Methanol Product Compositions for LaPorte PDU Run E-9

Case No.	E-9A.1	E-9A.2	E-9A.3	E-9A.4	E-9A.5	E-9A.6	E-9A.7	E-9B
Balance Period:								
Start Date	03/18/89	03/18/89	03/19/89	03/20/89	03/21/89	03/22/89	03/23/89	03/24/89
Start Time	01:00	24:00	16:00	06:00	06:00	06:00	06:00	19:00
End Date	03/18/89	03/19/89	03/20/89	03/21/89	03/22/89	03/23/89	03/24/89	03/25/89
End Time	10:00	11:00	06:00	06:00	06:00	06:00	08:00	16:00
Gas Type	CO-Rich	CO-Rich	CO-Rich	CO-Rich	CO-Rich	CO-Rich	CO-Rich	G Plains
Temperature (deg F)	481.3	483.6	482.5	482.2	482.2	481.8	481.8	482.0
Pressure (psig)	753.0	753.5	753.0	753.2	751.9	752.4	752.6	753.0
Space Vel. (Sl/hr kg-cat-ox)	3067	6514	12880	12968	12986	12893	12914	12953
Slurry Conc. (wt% oxide)	28.0	32.9	34.6	34.6	34.8	34.9	34.9	33.1
METHANOL PRODUCT COMPOSITION (wt%)								
Methanol	94.003	94.003	96.783	96.713	96.733	96.678	96.757	98.588
Water	0.374	0.374	0.525	0.523	0.562	0.579	0.578	0.470
Dimethyl ether	0.061	0.061	0.019	0.016	0.015	0.015	0.014	0.018
Methyl formate	1.485	1.485	1.035	1.048	1.048	1.020	0.938	0.152
Methyl acetate	0.701	0.701	0.187	0.179	0.170	0.162	0.159	0.000
Ethanol	1.476	1.476	0.715	0.698	0.672	0.645	0.662	0.278
Iso-propanol	0.023	0.023	0.000	0.000	0.000	0.000	0.000	0.000
N-propanol	0.632	0.632	0.276	0.269	0.257	0.247	0.254	0.092
Sec-butanol	0.052	0.052	0.033	0.021	0.031	0.030	0.031	0.022
Isobutanol	0.134	0.134	0.040	0.038	0.036	0.035	0.036	0.000
N-butanol	0.303	0.303	0.143	0.150	0.134	0.127	0.133	0.044
T-amyl alcohol	0.023	0.023	0.000	0.000	0.000	0.000	0.000	0.000
2&3-Pentanol	0.058	0.058	0.000	0.000	0.000	0.000	0.000	0.000
Isopentanol	0.110	0.110	0.040	0.040	0.036	0.035	0.035	0.000
1-Pentanol	0.177	0.177	0.083	0.084	0.079	0.078	0.081	0.027
Oil	0.388	0.388	0.121	0.221	0.227	0.349	0.322	0.309
Molecular wt of product	32.84	32.84	32.26	32.34	32.32	32.34	32.22	32.10

Methanol Product Compositions for LaPorte PDU Run E-9

Case No.	E-9C.1	E-9C.2	E-9D.1	E-9D.2	E-9E	E-9F
Balance Period:						
Start Date	03/25/89	03/26/89	03/27/89	03/28/89	03/29/89	03/31/89
Start Time	23:00	13:00	18:00	12:00	19:00	00:00
End Date	03/26/89	03/27/89	03/28/89	03/29/89	03/30/89	03/31/89
End Time	13:00	11:00	12:00	16:00	12:00	12:00
Gas Type	CO-Rich	CO-Rich	CO-Rich*	CO-Rich*	CO-Rich	CO-Rich
Temperature (deg F)	481.6	481.6	482.2	482.0	482.2	466.9
Pressure (psig)	753.0	753.0	753.0	753.0	753.0	728.1
Space Vel. (Sl/hr kg-cat-ox)	5833	5018	5126	10220	10148	17483
Slurry Conc. (wt% oxide)	35.2	35.0	35.4	34.4	34.4	34.4
METHANOL PRODUCT COMPOSITION (wt%)						
Methanol	95.360	95.025	95.095	96.744	96.533	96.789
Water	0.421	0.398	0.431	0.628	0.540	0.643
Dimethyl ether	0.024	0.027	0.023	0.013	0.015	0.012
Methyl formate	1.336	1.411	1.327	0.950	0.983	0.702
Methyl acetate	0.396	0.469	0.423	0.166	0.205	0.132
Ethanol	1.054	1.166	1.078	0.649	0.775	0.650
Iso-propanol	0.000	0.019	0.019	0.000	0.000	0.000
N-propanol	0.425	0.479	0.445	0.253	0.304	0.252
Sec-butanol	0.038	0.044	0.048	0.030	0.032	0.034
Isobutanol	0.071	0.082	0.077	0.036	0.043	0.033
N-butanol	0.213	0.239	0.213	0.128	0.157	0.133
T-amyl alcohol	0.000	0.000	0.000	0.000	0.000	0.000
2&3-Pentanol	0.025	0.048	0.051	0.000	0.000	0.000
Isopentanol	0.066	0.073	0.068	0.037	0.043	0.037
1-Pentanol	0.124	0.141	0.134	0.079	0.094	0.081
Oil	0.448	0.379	0.568	0.287	0.276	0.502
Molecular wt of product	32.35	32.67	32.68	32.31	32.37	32.32

*CO-Rich gas matrix with approx. 1.5 mol% water injection in the reactor feed

4. Reactor Internal Heat Exchanger

The overall heat transfer coefficient for the internal heat exchanger was calculated from the Run E-9 utility oil data. No fouling factor was used for the heat transfer coefficient calculations since the reactor internals had been cleaned immediately prior to the start of the run. A comparison of the predicted and measured overall coefficients indicated that the average absolute error was 6.4% for the 12 stable operating cases of Run E-9. None of the errors exceeded 13% (see Table V.7).

The shell-side (slurry-side) heat transfer coefficient was backed out from the overall coefficient using the same technique as described earlier for Run E-8. A comparison of the predicted and measured slurry side coefficients are also shown in Table V.7. The average absolute error was 25% with the maximum error being 57%. The predicted and measured shell side heat transfer coefficients are plotted versus the superficial gas velocity in Figure V.4.

TABLE V.7

RUN E-9
27.10B INTERNAL HEAT EXCHANGER COEFFICIENTS
(Btu/hr ft^2 °F)

Case	Slurry Conc. (wt% ox)	Overall Coefficient			Slurry Side Coefficient		
		Predicted	Measured	% Error	Predicted	Measured	% Error
E-9A.3	34.6	91.3	91.8	0.5	297.7	302.2	1.5
E-9A.4	34.6	91.3	91.8	0.5	298.4	303.3	1.7
E-9A.5	34.8	93.0	103.8	11.7	298.6	449.4	50.5
E-9A.6	34.9	93.3	103.8	11.3	298.5	442.0	48.1
E-9A.7	34.9	92.6	102.8	11.1	298.3	439.6	47.3
E-9B	33.1	94.6	107.1	13.1	297.8	469.1	57.5
E-9C.1	35.2	89.0	87.8	-1.3	242.8	234.3	-3.5
E-9C.2	35.0	88.2	87.1	-1.2	233.1	225.7	-3.2
E-9D.1	35.4	87.6	85.6	-2.3	233.0	219.4	-5.8
E-9D.2	34.4	91.0	99.8	9.6	279.7	383.3	37.1
E-9E	34.4	91.2	100.0	9.6	279.6	383.0	37.0
E-9F	34.4	93.9	90.0	-4.2	325.3	282.1	-13.3
Average Error				6.4			25.5

Figure V.5 is a parity plot of the measured shell-side coefficients of the reactor internal heat exchanger from Runs E-5 through E-9 for the Deckwer correlation. The measured results are well correlated by the Deckwer equation even though the data are generally out of the stated correlated range. These PDU results confirm that, with an appropriate uncertainty factor, the Deckwer equation can be successfully used to predict the slurry heat transfer coefficients for large scale LPMEOH reactors.

Figure V.4

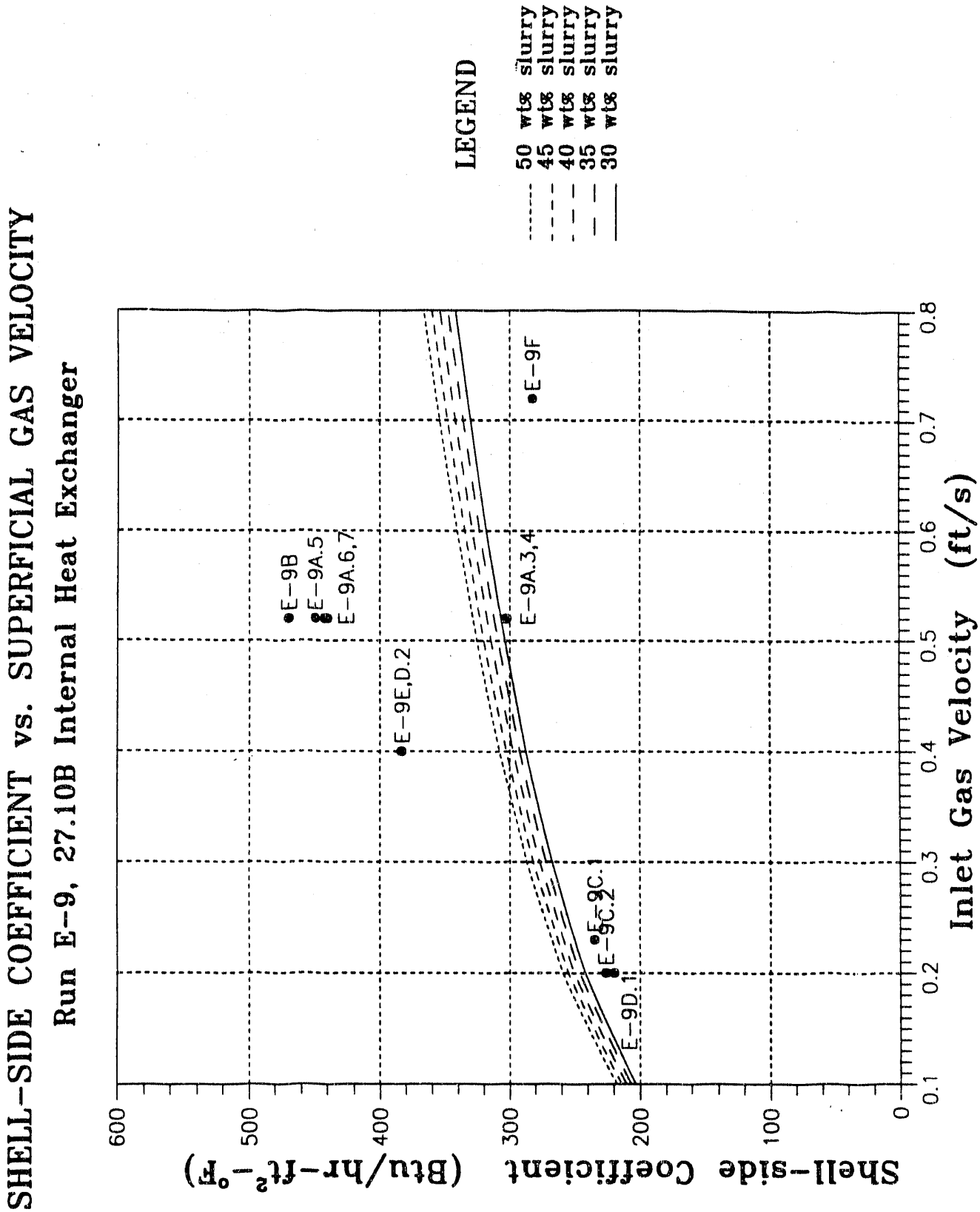
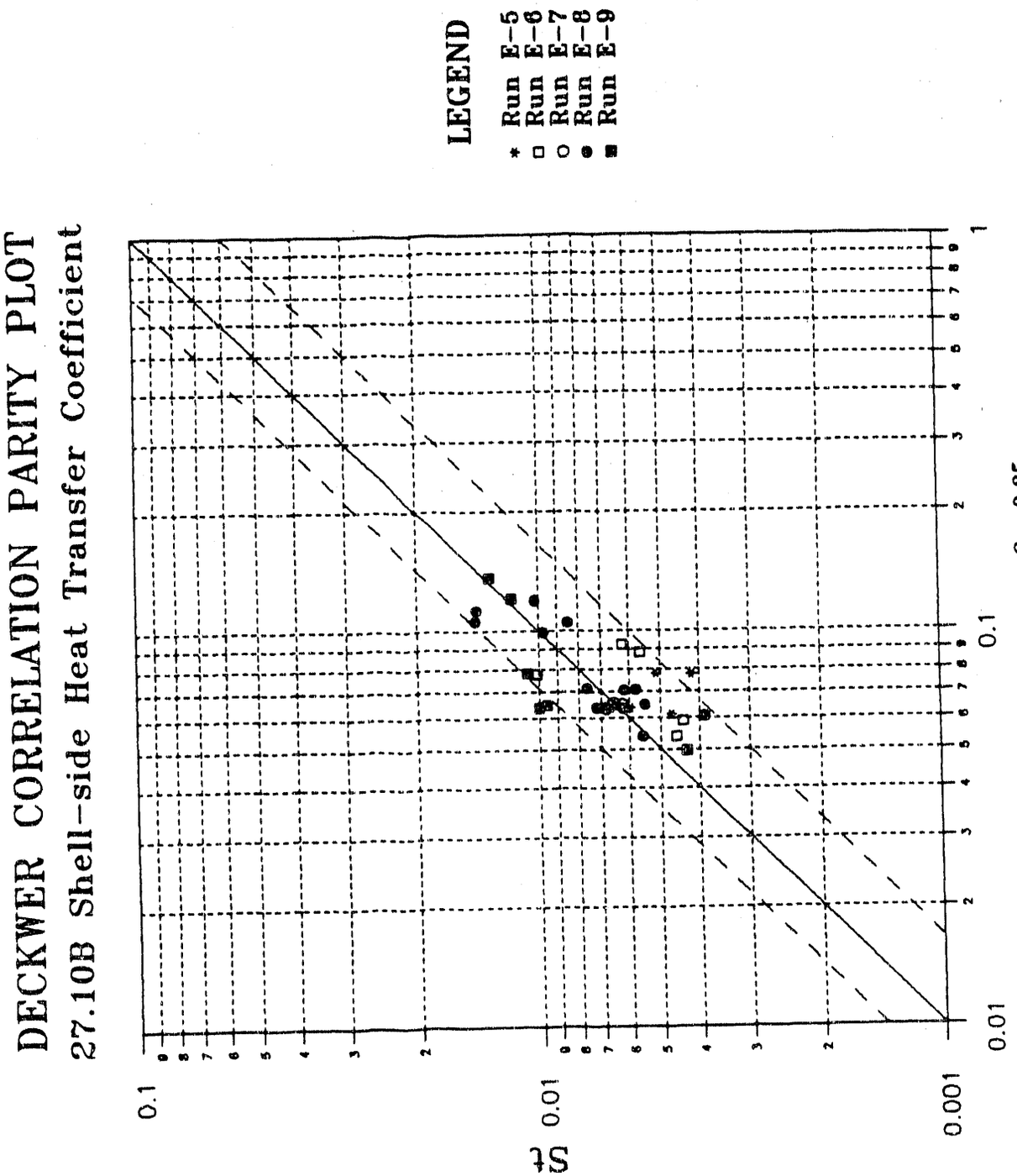

SHELL-SIDE COEFFICIENT vs. SUPERFICIAL GAS VELOCITY
Run E-9, 27.10B Internal Heat Exchanger
LEGEND
50 wt% slurry
45 wt% slurry
40 wt% slurry
35 wt% slurry
30 wt% slurry
E-9B
E-9A.5
E-9A.6,7
E-9E,D.2
E-9A.3,4
E-9F
E-9C.1
E-9C.2
E-9D.1
Shell-side Coefficient (Btu/hr-ft²-°F)
Inlet Gas Velocity (ft/s)
0
100
200
300
400
500
600
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8

Figure V.5


DECKWER CORRELATION PARITY PLOT
27.10B Shell-side Heat Transfer Coefficient
LEGEND
Run E-5
Run E-6
Run E-7
Run E-8
Run E-9
St
0.1
0.01
0.001
0.01
0.1
1
$(ReFrPr^2)^{-0.25}$

5. Post Run Inspection

Run E-9 ended on 31 March 1989 after 14 days on synthesis gas. At the conclusion of Run E-9 the reactor, oil separation section, and flare header circuit were opened and inspected. In contrast to the previous run the reactor was flushed with clean oil prior to vessel inspection to expedite the cleanup. Overall, the PDU was very clean, as would be expected for such a short run.

The top head of the reactor was removed on 3 April after the reactor was drained, flushed with clean oil and purged with nitrogen. The top head, walls and internals of the reactor were fairly clean with an approximate 1/16 inch coating of dilute slurry. The only locations where there was any significant buildup of catalyst was on horizontal surfaces.

The 27.14 Secondary Vapor Liquid Separator had no significant catalyst buildup. The 27.14 demister appeared black but open confirming that some slurry had carried over to this vessel and had impinged on the demister. The inlet to the downstream 21.30 product condenser was clean, however, indicating the effectiveness of the demister.

The 15.91 Flare Header Knockout Pot and the flare header circuit was disassembled and as expected contained a large amount of catalyst slurry which had carried over during the catalyst activation ER-6. Approximately 50 lbs of catalyst were drained from the 15.91 and an unmeasured quantity was found in the flare piping. All of the other equipment items were essentially free of catalyst slurry. Overall, 30 lbs of catalyst were unaccounted for at the end post run inspection.

VI. CONCLUSIONS AND RECOMMENDATIONS

Run E-9 was the completion of PDU operations under the DOE LP-III contract (DE-AC22-87PC90005). Overall, this was a tremendously successful series of runs producing over 1/2 million gallons of methanol (1677 tons) during 212 operating days. The average production rate of 8 TPD exceed the PDU design nameplate capacity of 5 TPD by 60%. As a result of these tests, the LPMEOH technology is ready to be economically demonstrated at a commercial scale.

The PDU performed very well over the wide range of process conditions listed below in Table V.8 for the 64 operating days of Runs E-8 and E-9. Worthy of special note are successful operations at slurry concentrations of 50 wt% oxide, operation at inlet superficial gas velocities of 0.72 ft/sec and a sustained production rate of 12.8 TPD. Five hundred and four tons of methanol were produced with an average product purity of 97.0 wt% methanol and 98.0 wt% total alcohols. Total lost time was 21 out of 1546 hours for an overall 98.6% on-stream factor.

TABLE V.8

RANGE OF OPERATING VARIABLES FOR RUNS E-8 & 9

	Minimum	Maximum
Reactor Pressure, psig	500	900
Reactor Temperature, °C	235	285
°F	455	545
Space Velocity, liter/hr-kg cat	2,100	17,500
Superficial Gas Velocity, ft/sec	0.13	0.72
Catalyst Loading, wt% ox.	32	50
Slurry Level, %	64	100
, L/D	6.8	10.6
Feed Gas Composition		
H_2/CO Ratio	0.49	3.94
CO_2 Concentration (mol %)	0.94	18.09
H_2O Concentration (mol %)	--	1.82
Methanol Production Rate (TPD)	1.4	12.8

Slurry heat transfer coefficients for the reactor internal heat exchanger were measured for a the range of process conditions described in Table V.8 above.

A catalyst activation using dilute synthesis gas and without the use of the slurry pump was accomplished and resulted in fully activated catalyst slurry.

The PDU equipment and vessels were in good condition following over six months of continuous operations. Catalyst buildup was minimal on most surfaces and heat exchanger fouling was very limited.

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

- Future catalyst activations should be done with dilute synthesis gas and without external circulation using a slurry pump. The superficial gas velocity should be minimized and the catalyst carryover should be carefully monitored. Recirculation of reduction gas with water removal should also be investigated. The synthesis gas should be introduced very slowly to the reactor immediately following catalyst activation. Samples of the slurry should be obtained at this time, if possible, in order to help identify the cause of the reactor startup conditioning period.

- The Deckwer correlation is adequate to predict the shell-side heat transfer coefficient in the reactor internal heat exchanger with a shell-side fouling factor of 0.0015 hr-ft^2-°F/Btu.

- Water injection does not substantially increase the methanol production rate for fresh catalyst and CO-Rich feed gas conditions. The potential for water injection to enhance the performance for CO_2 lean gas feeds (eg. Shell type gas) should be verified in future runs.

- A demister with clean oil backflushing is inadequate to eliminate residual slurry carryover from the LPMEOH reactor and should not be used in any future programs. The demister works very well however to eliminate oil mist carryover from the 27.14 Oil Knockout Pot and should be included in future design work.

VII. REFERENCES

Deckwer, W. D., "Hydrodynamic Properties of the Fischer-Tropsch Slurry Process," Ind. Eng. Process Des. Dev. 19 (1980), 699-708.

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