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

Topical Report

Task 2.0: Run E-5, Gas Hold-up and Equipment Evaluation Studies

Contractor

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and

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2 January 1991

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ABSTRACT

Liquid-entrained operations at the LaPorte LPMEOH Process Development Unit (PDU) continued during June and July 1988 under Tasks 2.1 and 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 an optimized and simplified process. Several new design options had been identified and thoroughly evaluated in a detailed process engineering study completed under the LPMEOH Part-II contract (DE-AC22-85PC80007), which then became the basis for the current PDU modification/operating program.

The focus of the Process Engineering Design was to optimize and simplify the LPMEOH process. The proposed process simplifications focused on the slurry loop, which consists of the reactor, vapor/liquid separator, slurry heat exchanger, and slurry circulation pump. Three key conclusions were reached as a result of the detailed process engineering design evaluation: 1) there should be sufficient liquid circulation and turbulence induced by the high synthesis gas velocities to suspend the catalyst particles homogeneously within the slurry, 2) the required internal heat transfer surface should be relatively small so that sufficient heat exchanger area could be installed with little effect on reactor bubble column hydrodynamics, and 3) adequate vapor/liquid disengagement can potentially be achieved by incorporating a reactor freeboard section with a small internal or external demisting device. A new process design capable of operating with one or all of the process simplifications was developed. Fortunately, the PDU process flowsheet modifications were achieved without major reconstruction of existing piping.

Two-Phase Gas Holdup tests began at LaPorte in June 1988 with nitrogen/oil and CO-rich gas/oil systems. The purpose of these tests was to study the hydrodynamics of the reactor, detect metal carbonyl catalyst poisons, and train operating personnel. Any effect of the new gas sparger and the internal heat exchanger would be revealed by comparing the hydrodynamic data with previous PDU hydrodynamic data.

The results of the test showed that, under external slurry loop circulation process conditions, the presence of the new gas sparger and internal heat exchanger provided essentially equivalent gas holdup in the reactor. However, when the external liquid circulation was eliminated, gas holdup increased. Also, from available laboratory and literature data, the low carbonyl levels detected were considered satisfactory for subsequent methanol production.

The "Equipment Evaluation" Run E-5 was conducted at the LaPorte LPMEOH PDU in July, 1988. 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 system, and attempt to run the reactor in an internal-only mode. In addition, a successful catalyst activation with a concentrated (45 wt% oxide) slurry was sought.

The performance of the simplified reactor system was excellent for the entire Run E-5 with only one minor setback. The first attempt at an in-situ catalyst

activation in the new reactor system resulted in only 85% catalyst activation. The activation was considered within the acceptable range and attributed to operating procedures. The remainder of the operating program was exemplary. The presence of an oil phase in the product methanol, seen in previous runs, was eliminated due to repiping of the feed/product heat exchanger and the weight percent oil in the methanol was reduced from 1.3 to 0.6%. Methanol productivity and gas holdup were higher than previous runs at high catalyst loadings. This demonstrated improvement was attributable to the new gas sparger. A higher methanol productivity was achieved without external slurry circulation in comparison to methanol productivity under the same conditions with external slurry circulation. Clearly, in the external loop configuration the catalyst did not contribute significantly to the methanol production while circulating through the slurry loop. Methanol productivity in the new simplified process was greater than autoclave performance, indicating that the design of the new system had eliminated mixing and mass transfer limitations. Also demonstrated was the resilience of the process to unscheduled shutdowns.

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	Producicitivity units: Gram moles of methanol per hour per kilograms of catalyst oxide.
gpm	Gallons per minute
hr	Hours
in	Inches
kg	Kilograms
l	Liters
lb	Pounds
m^2	Square meters
min	Minutes
mol%	Mole percent
ppb	Parts per billion by volume for gas by weight for liquid
psi	Pounds per square inch
psig	Pounds per square inch gauge
psia	Pounds per square inch absolute
scf	Standard cubic feet
SCFH	Standard cubic feet per hour
sec	Seconds
Sl/hr Kg	Space Velocity Units: Standard liters of feed gas per hour per kilograms of catalyst oxide
SV	Gas hourly space velocity Standard liters per hour per kilogram catalyst oxide
TPD	Tons per day
tons	Short tons (2000 lb)
wt%	Weight percent

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I. EXECUTIVE SUMMARY

Since 1981, Air Products and Chemicals, Inc. has been providing research and development work to prove the feasibility of the LPMEOH process at the PDU scale as part of the U.S. Department of Energy's (DOE) indirect coal liquefaction program. Chem Systems Inc. (CSI), the inventor of the process, has been the key subcontractor in the program. Air Products has been joined by the Electric Power Research Institute (EPRI) as a private cost sharing participant. This work has been funded under the DOE contracts DE-AC22-81PC30019, DE-AC22-85PC80007, and the current contract DE-AC22-87PC90005.

The primary focus of this PDU operating program was to prepare for a confident move to the next scale of operation with an optimized and simplified process. Although the PDU had been very reliable in prior operations, several new design options had been identified and thoroughly evaluated in a detailed process engineering study which was completed under the LPMEOH Part-II contract (DE-AC22-85PC80007) and became the basis for the current PDU modification and operating programs.

Process Engineering Design

The focus of the Process Engineering Design was to evaluate options for simplifying and optimizing the LPMEOH process studied under the previous contract. Simplifying the process had the potential to greatly improve the process economics by reducing capital costs and downtime due to equipment failure. The proposed process simplifications focused on the slurry loop, which consists of the reactor, vapor/liquid separator, slurry heat exchanger, and slurry circulation pump. The desired process change was the elimination of the entire slurry loop outside the reactor, which could be achieved if vapor/slurry separation and heat exchange were performed in the reactor vessel. This modification would be a significant process improvement since it eliminated two large high-pressure vessels (the vapor/slurry separator and the heat exchanger shell) and the slurry circulation pump. The 250 gpm centrifugal slurry pump proved to be a highly reliable piece of equipment, however, it required a great deal of preventive maintenance.

Three key conclusions were reached as a result of a detailed process engineering design evaluation: 1) there should be sufficient liquid circulation and turbulence induced by the high synthesis gas velocities to suspend the catalyst particles homogeneously within the slurry, 2) the required internal heat transfer surface should be relatively small so that sufficient heat exchanger area could be installed with little effect on reactor bubble column hydrodynamics, and 3) adequate vapor/liquid disengagement can be achieved by incorporating a reactor freeboard section with a small internal or external demisting device. A new process design capable of operating with one or all of the process simplifications was developed. Fortunately, the PDU process flowsheet modifications were achieved without major reconstruction of existing piping.

Two-Phase Gas Holdup Test

Two-Phase Gas Holdup tests began at LaPorte in June 1988 with nitrogen/oil and CO-rich gas/oil systems. The purpose of these tests was to study the hydrodynamics of the reactor, detect metal carbonyl catalyst poisons, and train operating personnel. Any effect of the newly installed gas sparger and the internal heat exchanger would be revealed by comparing the hydrodynamic data with previous PDU hydrodynamic data. Hydrodynamic information was measured with a nuclear density gauge. The density gauge was mounted on a track which allows measurements along the axis of the reactor. Gas and liquid holdup were calculated from the absorbance of gamma radiation using Beer's law and adsorption coefficients based on calibration experiments.

Under external slurry loop circulation process conditions, the presence of the new gas sparger and internal heat exchanger provided essentially equivalent gas holdup within the reactor. However, when liquid circulation was in use, gas holdup was suppressed and when external liquid circulation was eliminated, gas holdup was higher. In addition, gas holdup profiles were uniform over the height of the reactor.

Two-phase CO-rich gas studies also served to monitor the production of catalyst poisons, particularly iron and nickel carbonyls. Initial levels of carbonyls, determined by gas chromatography and atomic absorption, were below 70 ppb. After an on-stream time of 20 hours, carbonyl levels dropped to 19 ppb of $Fe(CO)5$ and 4 ppb of $Ni(CO)4$. From available laboratory and literature data, these low carbonyl levels were considered satisfactory for subsequent methanol production.

Equipment Evaluation Run E-5

The "Equipment Evaluation" Run E-5 was conducted at the LaPorte PDU in July, 1988. A commercially available catalyst powder (F21/0E75-44) was used. This was a new batch of the same brand and type of catalyst which was used in Runs E-2, E-3, and E-4. The oil used in the catalyst slurry was Drakeol-10 in place of the Freezene-100 oil that was used in previous runs. This was viewed as a means to qualify an alternate supplier for the white mineral oil used in the catalyst slurry. 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 system, and to operate the reactor in an internal-only mode. In addition, a successful catalyst activation with a concentrated (45 wt% oxide) slurry was attempted.

The first attempt at an in-situ catalyst activation in the new reactor system resulted in only 85% catalyst activation. The level of activation was considered within the acceptable range and attributed to operating procedures and the run was continued. The Drakeol-10 oil appeared to perform as an acceptable substitute for the Freezene-100 oil previously used.

Production of methanol was stable in Run E-5A after only 18 hours on-stream with syngas. The presence of an oil phase in the methanol seen in previous runs was eliminated due to repiping of the feed/product heat exchanger. The weight percent oil in the methanol was reduced from 1.3 to 0.6%. Methanol productivity and gas holdup were higher than previous runs at high catalyst loadings. This demonstrated improvement was attributed to the new gas sparger; however, methanol productivity was still slightly below the autoclave curve for high loadings.

The new internal heat exchanger was evaluated in Runs E-5B and E-5C. Again, the reactor performed close to the autoclave results. The overall heat transfer coefficient of the heat exchanger was 74 Btu/hr-ft^2-°F, close to the design value of 94 Btu/hr-ft^2-°F. Operation at high space velocities was not possible with the internal heat exchanger because its area was consciously under-designed to achieve measurable temperature differences with a 35 wt% catalyst slurry where a lower temperature differential existed between slurry and heat transfer oil. There was a concern that large temperature differences at 45 wt% slurry and high gas velocities could produce excessive thermal stresses. Therefore, both internal and external heat exchangers were used in Run E-5C to remove the heat of reaction. Daily methanol production ranged from 8 to 9 TPD for the 45 wt% runs, which exceeded the previous production rates of 5 to 7 TPD at 47 wt% slurry.

Run E-5D was the first test of the LaPorte reactor without external circulation. A higher methanol productivity resulted without external slurry circulation compared to the exact same conditions with external slurry circulation in Run E-5B. Clearly, the catalyst in the external loop configuration did not contribute significantly to the methanol production while circulating in the loop external to the reactor. The internal slurry/gas disengagement and demister performed well.

Runs E-5E and E-5F were completed at the end of July with 34 wt% catalyst slurry. Methanol productivity was apparently greater than autoclave performance, indicating that the design of the new system must have eliminated mixing and mass transfer limitations. The overall heat transfer coefficient for the 34 wt% slurry was 95 Btu/hr-ft^2-°F. Productivity levels achieved in Run E-5F demonstrated that the process was resilient in handling deliberate shutdowns of 1 hour and 24 hour durations. Four unplanned power outages during the month of July also demonstrated the reliability of this process after unscheduled shutdowns.

In summary, the performance of the simplified reactor system was excellent for the entire Run E-5. Additional process changes resulted in reducing slurry oil losses by 75% and substantial improvements in methanol quality. This overall design represents the state-of-the-art for the LPMEOH Process and will be used as the baseline to judge potential performance improvements in the future.

II. INTRODUCTION AND BACKGROUND

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

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

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
1981-1988	300 cc/1 Liter laboratory scale stirred autoclave Method to Activate Conc. Slurries Developed Catalyst Poisons Studied Feed Gas Composition Effects Determined
1983	4.5 in ID x 7 ft tall Lab. PDU (up to 0.14 TPD MeOH) Reactor Productivity Defined Hydrodynamic Behavior Identified Reactor Modeling Begun
1984 - 1985	2 in ID x 18 ft tall LaPorte PDU (up to 8 TPD MeOH) Reactor Performance Demonstrated Catalyst Life Demonstrated Materials of Construction Defined Operating Experience Base

A. Process Development Scale Experience

The primary function of the LaPorte PDU is to acquire data using a small, yet 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 H_2 and CO concentrations were not stoichiometrically balanced, but were representative of synthesis gas directly from a modern Texaco coal gasifier. This gas is typical of that for once-through methanol synthesis in a CGCC plant configured to make electric power and coproduct methanol.

- Balanced Type, representative of CO-Rich gas which has undergone shift and CO_2 rejection so that the H_2 and CO concentrations were approximately stoichiometrically balanced (2/1) in order to achieve an "all-methanol" product.

- H2-Rich Type, in which the H_2 and CO concentrations were not stoichiometrically balanced, but were 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 were blended from H_2, CO, N_2, and CH4 supplied by Air Products' adjacent syngas facility at LaPorte. Carbon dioxide is trucked into the plant as a liquid and stored on-site. Since only a portion of the reactor feed is converted per pass, the unconverted synthesis gas is recycled and mixed with fresh makeup gas. The makeup gas is blended so that the reactor feed (makeup plus recycle) simulates either the balanced or CO-rich gas type in once-through operation. Recycling the unconverted synthesis gas reduces gas consumption by 70% for cost-effective operation at LaPorte.

TABLE II.2

GAS TYPES TESTED AT THE LAPORTE PDU

Component (mol%)	CO-Rich Gas	Balanced Gas	H2-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 the Electric Power Research Institute (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 that 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 a 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. The improved performance and catalyst activity maintenance of Run E-3 versus Run E-1 is shown in Figure II.1.

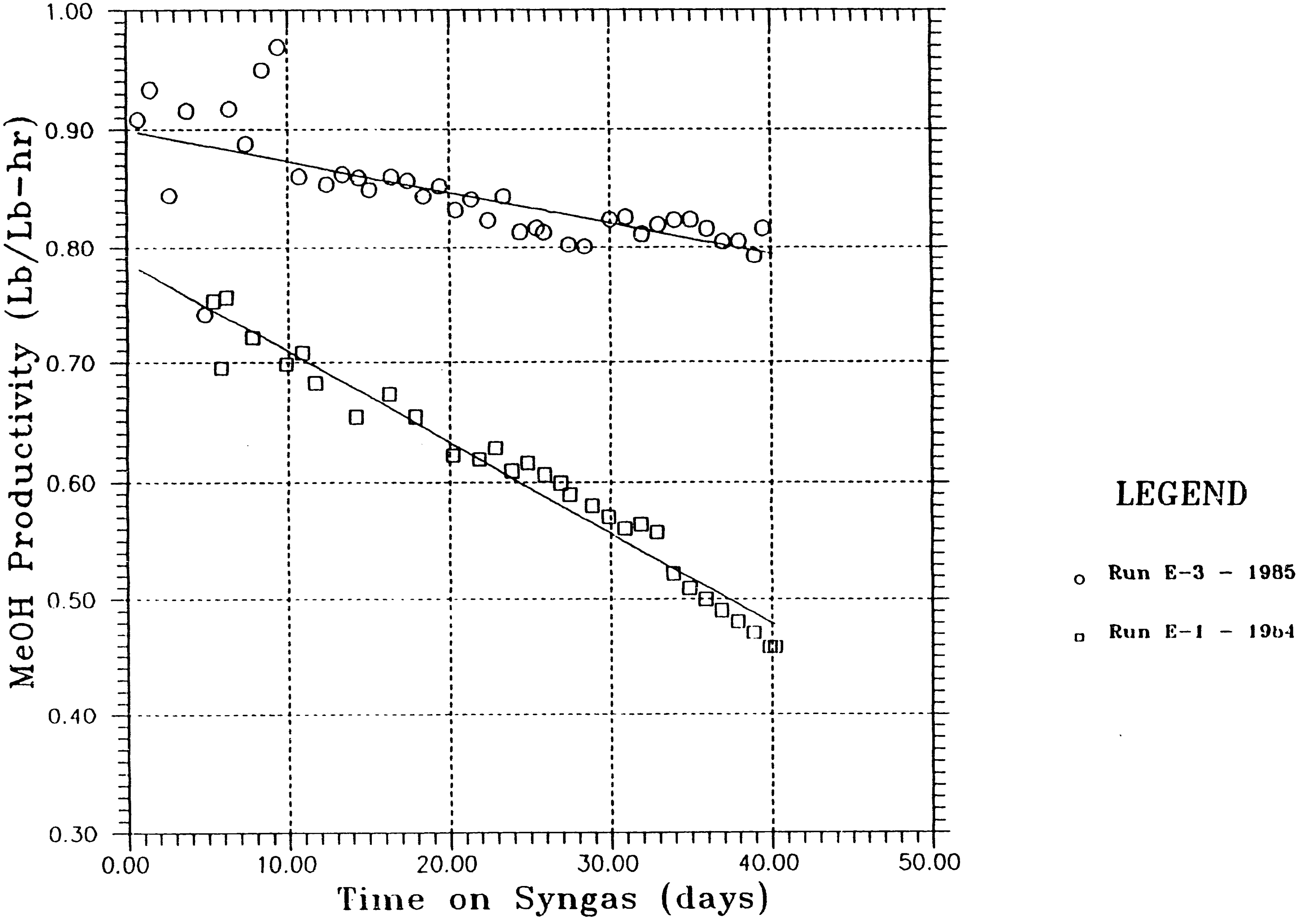
A second operation of the LaPorte PDU at elevated slurry concentrations (again up to 45 wt%) was subsequently performed. A successful catalyst activation was achieved. High operability was again maintained during this 10-day test; the reactor performance exceeded the previous run at these conditions (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.

LaPorte PDU operations successfully demonstrated LPMEOH technology at a representative engineering scale. The PDU accumulated over 2500 hours of methanol synthesis operation with an on-stream factor of 96-100%. Low catalyst deactivation while operating the liquid-entrained system with a 25 wt% catalyst slurry for an extended period of time on CO-rich synthesis gas

Figure II.1

LAPORTE LPMEOH PDU REACTOR PERFORMANCE

Runs E-1&3: CO-Rich Gas, 750 psig, 482°F



was a notable achievement. The ability to activate methanol synthesis catalyst powders in an inert liquid at high concentrations was also noteworthy. Methanol production levels as high as 8 TPD for balanced gas feed and 7 TPD for CO-rich gas feed were achieved; the purity of the methanol product from CO-rich gas was consistently higher than 96% wt%, a good fuel-grade quality.

III. LAPORTE LPMEOH PDU

A. Existing PDU Process Description

A simplified process flowsheet for the LaPorte PDU 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 inert hydrocarbon liquid or slurry that circulates through the reactor is separated from the unconverted synthesis gas and methanol product vapor in the primary V/L separator, and recirculated to the reactor through the slurry heat exchanger. The circulating liquid or slurry can be heated or cooled in the slurry exchanger to maintain a constant reactor temperature, depending upon the level of conversion, system heat losses, and the rate of cold seal flush required by the slurry pump. A utility oil system provides the heating or cooling duty to the slurry exchanger.

The unconverted synthesis gas/product methanol stream leaving the primary V/L separator 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 and additional condensed oil before being piped to product storage. A small purge stream is sent to flare. The bulk of the unconverted synthesis gas is compressed and returned to the front end of the PDU. Additional systems are present to activate the catalyst, provide seal flush to the slurry pump, and mix the catalyst slurry.

A schematic of the LaPorte reactor showing key dimensions and the location of temperature sensors is given in Figure III.2. Both the feed gas and the recirculated slurry enter a plenum chamber in the bottom of the reactor. This mixture then enters the reaction zone through a bubble cap tray distributor. The three-phase slurry flows concurrently through the reactor and exits to a separate vapor/liquid disengagement vessel.

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

B. New PDU Process Design

Although the PDU was very reliable in prior campaigns, several new design options were identified and thoroughly evaluated in a detailed process engineering study completed under the LP-II contract (DE-AC22-85PC80007), which became the basis for the current PDU modification/operating program.

The Process Engineering studies done under the LP-II contract examined the feasibility of several proposed modifications to the LaPorte PDU reactor section. These modifications included a continuous catalyst addition/withdrawal system to maintain catalyst activity, replacement of the existing external loop with an internal heat exchanger, use of an agitator for mass

Figure III.1

SIMPLIFIED PROCESS FLOWSHEET FOR LAPORTE PDU

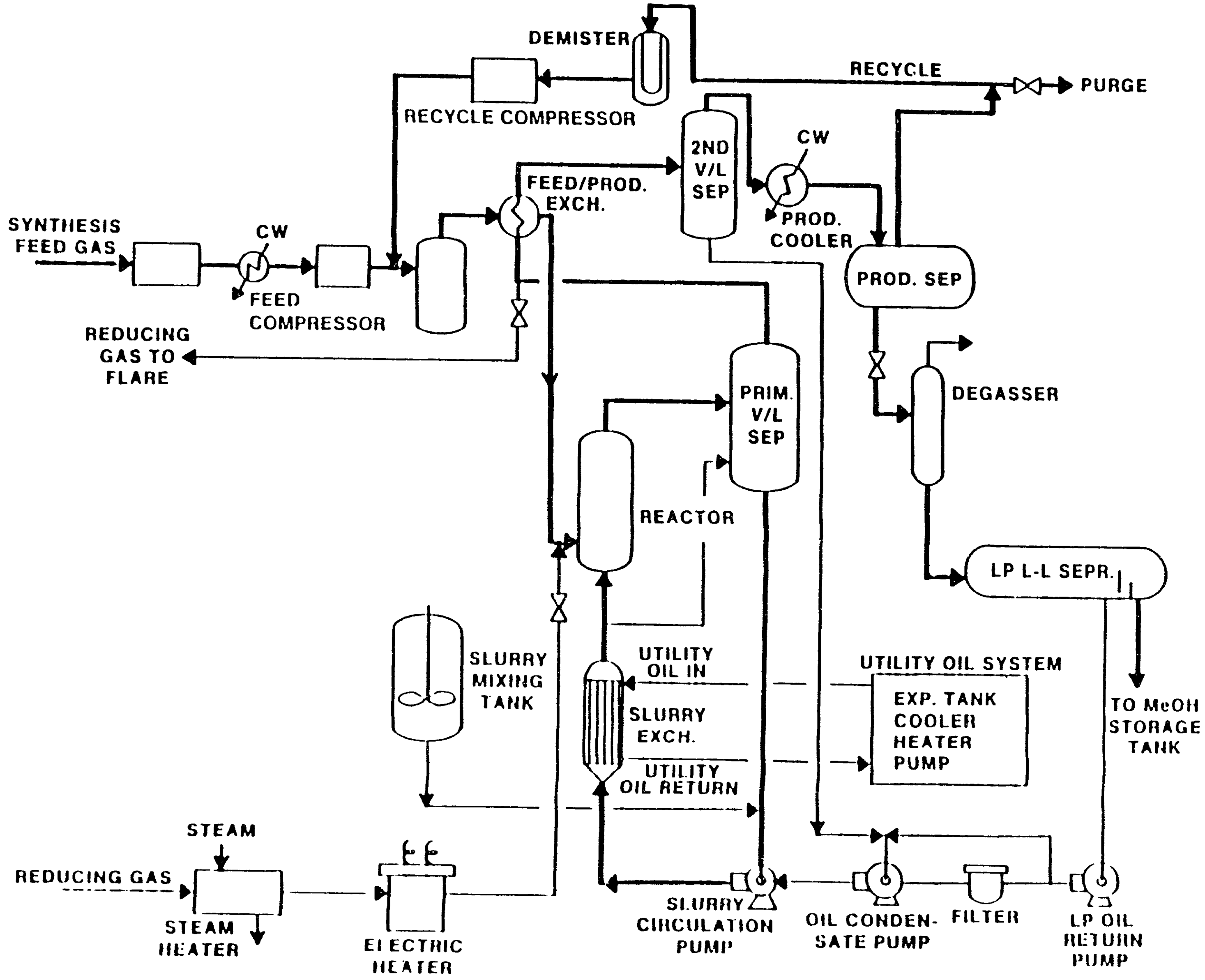
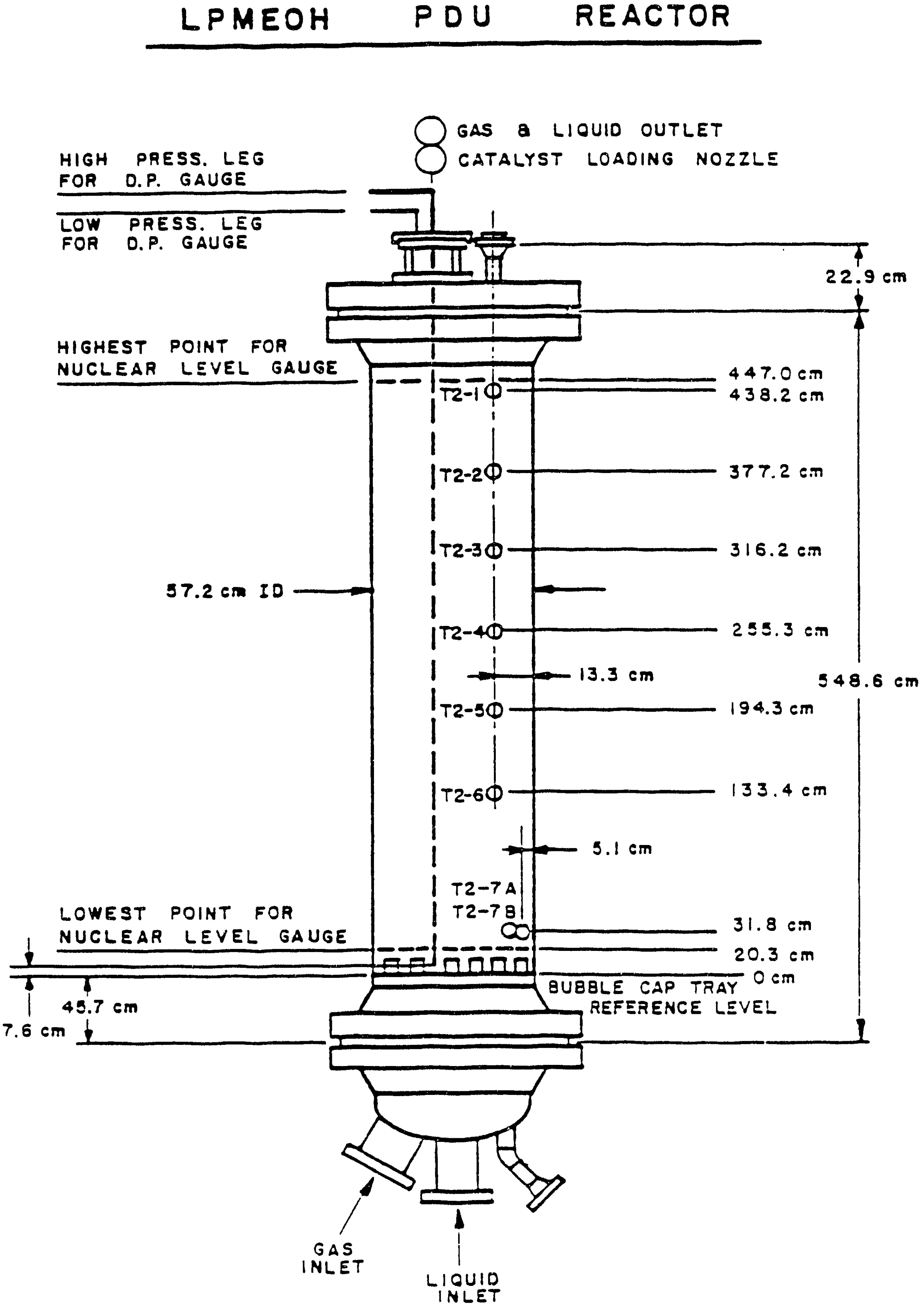


Figure III.2


LPMEOH PDU REACTOR
GAS & LIQUID OUTLET
CATALYST LOADING NOZZLE
HIGH PRESS. LEG FOR D.P. GAUGE
LOW PRESS. LEG FOR D.P. GAUGE
22.9 cm
HIGHEST POINT FOR NUCLEAR LEVEL GAUGE
447.0 cm
438.2 cm
T2-1
T2-2
377.2 cm
T2-3
316.2 cm
57.2 cm ID
T2-4
255.3 cm
13.3 cm
548.6 cm
T2-5
194.3 cm
T2-6
133.4 cm
5.1 cm
T2-7A
T2-7B
31.8 cm
LOWEST POINT FOR NUCLEAR LEVEL GAUGE
20.3 cm
0 cm
BUBBLE CAP TRAY REFERENCE LEVEL
45.7 cm
7.6 cm
GAS INLET
LIQUID INLET

transfer enhancement with concentrated slurries, extension of the reactor height to achieve vapor/liquid disengagement, and installation of either a cyclone or demister to minimize slurry carry-over from the reactor. (See Final Report of DE-AC22-85PC80007 for details of Process Engineering Studies.) The key conclusions reached as a result of the detailed process engineering evaluation were:

1) A catalyst addition/withdrawal system has good merit and is worthy of consideration in the continuing PDU operating program.

2) The required internal heat transfer surface should be relatively small so that sufficient heat exchanger area could be installed with little effect on reactor bubble column hydrodynamics.

3) While an agitator would probably yield the desired enhanced mixing and mass transfer effects, the high cost of testing the unit at the LaPorte PDU and the risk associated with the mechanical seal operating at the severe LPMEOH reactor conditions cannot be justified.

4) Adequate vapor/liquid disengagement can potentially be achieved by incorporating a reactor freeboard section.

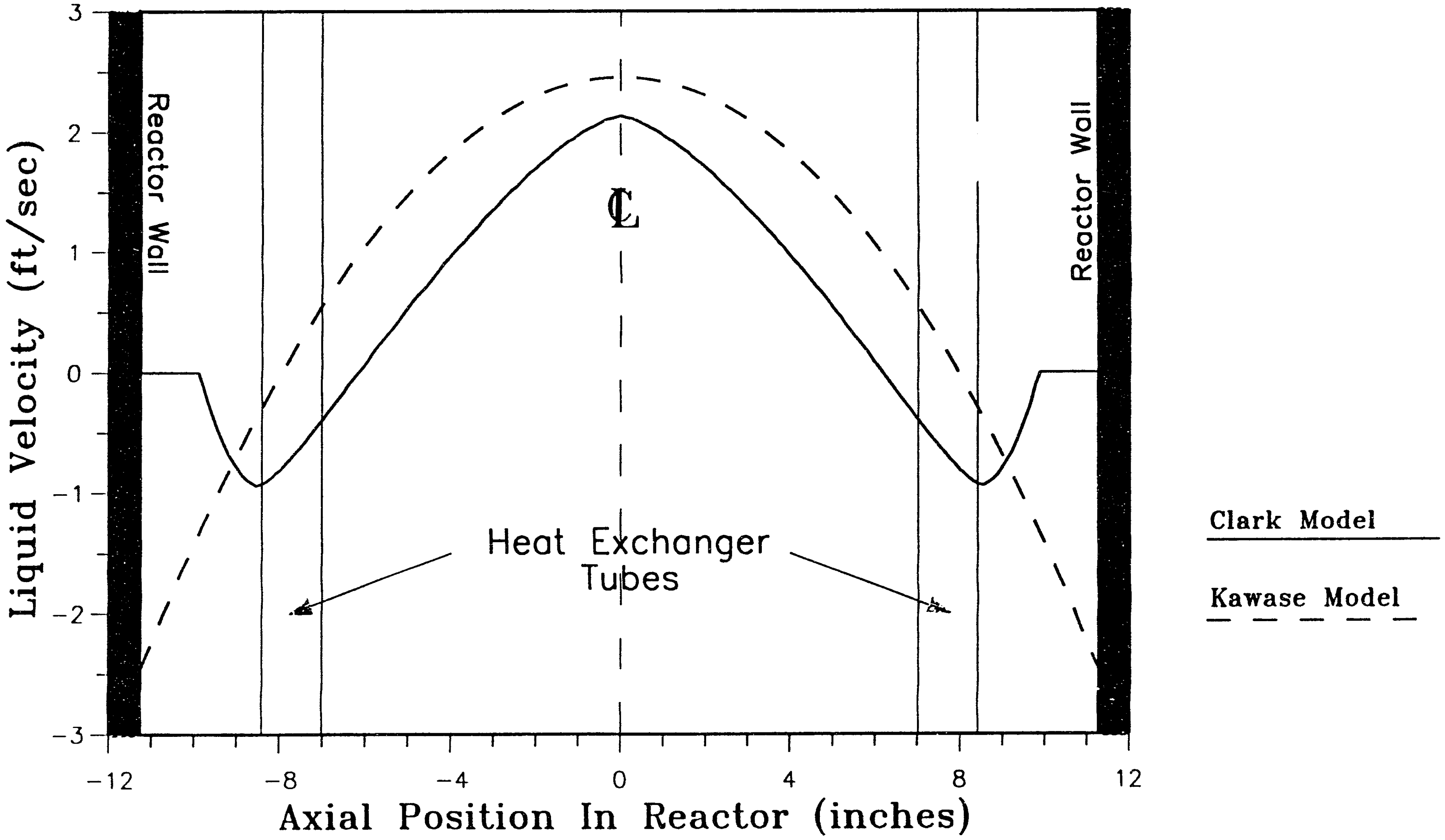
5) An external cyclone and a reactor internal demister should be installed and examined separately in providing extra gas/slurry separation in conjunction with the primary separation step.

Simplifying the process had the potential to greatly improve the process economics by reducing capital costs and the amount of downtime due to equipment failure. The proposed process simplifications were evaluated along with the idea that sufficient liquid circulation and turbulence should be induced by the high synthesis gas velocities to suspend the catalyst particles homogeneously within the slurry without using the external slurry pump. The desired process simplification was the elimination of the entire loop outside the reactor, which could be achieved if vapor/slurry separation and heat exchange were performed in the reactor vessel. This modification would be a significant process improvement since it eliminated two large high-pressure vessels (the vapor/slurry separator and the heat exchanger shell) and the slurry circulation pump. The 250 gpm centrifugal slurry pump proved to be a highly reliable piece of equipment, however, it required a great deal of preventive maintenance.

The slurry pump influences liquid mixing in the reactor by providing a net upward slurry circulation rate through the reactor. This net flow is in addition to the internal circulation within the reactor, which is induced by the high superficial gas velocity through the reactor. In order to determine the impact of elimination of the slurry pump on the liquid mixing, the internal slurry circulation was estimated using bubble column models developed by Clark, et al. (1987) and Kawase, et al. (1986). The predictions from each of these models are shown in Figure III.3. Although the quantitative results from each of the models vary, the conclusions reached are the same for both. The gas induced net liquid velocity is 0 ft/sec, but the upward velocity at the centerline of the reactor is 2.0 to 2.5 ft/sec, and near the walls the downward velocity is -1.0 to -2.0 ft/sec. By comparison, the pump induced

Figure III.3

AXIAL VELOCITY PROFILE FOR 27.10 SLURRY REACTOR
CIRCULATION INDUCED BY GAS FLOW ONLY



superficial liquid velocity is 0.06 to 0.15 ft/sec, approximately 20 times less than the gas induced velocity. Since the pump induced liquid velocity contributes only about 5% to the overall slurry velocities within the reactor, it was judged to be nonessential to the reactor mixing.

Upon the evaluation of a continuous addition/withdrawal system it was decided this system was not worthy of testing at the LaPorte PDU. The main purpose was to demonstrate that catalyst addition/withdrawal would be successful in maintaining a constant methanol production rate. The expense of the complex mechanical equipment and the lack of its translation to a commercial scale were major deciding factors. Also, the type of data needed to make a decision as to whether catalyst addition/withdrawal would be successful in maintaining methanol production rate, could be obtained to a better accuracy with a batch catalyst addition/withdrawal at a much lower cost. Therefore, a batch catalyst addition/withdrawal was recommended to be tested at the end of the "Catalyst Life" run of the current operating program.

In addition to the reactor system there was also a focus on improving oil recovery and product quality. The existing design limited the temperature of syngas preheat to the reactor to approximately 350°F. This was done as a safety precaution to avoid methanation side reactions in the feed gas line to the reactor. However, a literature review which indicated that nickel catalyzed methanation reactions require temperatures in excess of 500°F and previous experience during LPMEOH Part-II operations, indicated that 350°F was an overly conservative temperature constraint. For example, the 27.13 vapor/liquid separator outlet and product gas feed line to the 21.10 feed/product heat exchanger operated routinely at 482°F without incident.

Relaxing this limitation allowed repiping of the feed/product heat exchanger from concurrent to countercurrent service, thus lowering the oil condensation temperature. Thermodynamic modeling indicated that reducing the oil condensation temperature from 310°F to 250°F would result in a threefold decrease in the oil impurity concentration in the product methanol and eliminate the additional oil phase which separated from the methanol phase (see Table III.1). This would improve both product methanol quality and oil recovery. An additional benefit would be the elimination of a difficult liquid/liquid separation in the 22.15 liquid/liquid separator. The feed/product heat exchanger was, therefore, repiped from concurrent to countercurrent to allow the intermediate oil separator to be operated at 250°F, versus the 350°F operating temperature used in the previous runs, thus allowing more oil to be removed from the reactor effluent gas stream.

TABLE III.1

COMPARISON OF EFFLUENT GAS COOLING ON OIL KNOCKOUT AND PRODUCT COMPOSITION

21.10 Outlet Temperature = 310°F

Component (mol%)	Reactor Outlet	27.14 Vapor	MeOH Phase	Oil Phase	
H_2	2.25	2.34	----	----	
CO	59.31	61.47	0.01	----	
CO_2	23.44	24.29	0.44	0.03	
N_2	1.66	1.73	----	----	
H_2O	0.07	0.07	0.76	----	
MeOH	9.56	9.90	97.35	0.04	
Witco-40	3.71	0.20	1.43	99.93	(5.1% oil loss)
Total	100.0	100.0	100.0	100.0	
Total Flow	4,996	4,817	432.2	3.20	lbmol/hr

21.10 Outlet Temperature = 250°F

Component (mol%)	Reactor Outlet	27.14 Vapor	MeOH Phase	Oil Phase	
H_2	2.25	2.34	----	----	
CO	59.31	61.56	0.01	----	
CO_2	23.44	24.33	0.44	----	
N_2	1.66	1.73	----	----	
H_2O	0.07	0.07	0.76	----	
MeOH	9.56	9.92	98.24	----	
Witco-40	3.71	0.05	0.55	----	(1.3% oil loss)
Total	100.0	100.0	100.0		
Total Flow	4,996	4,811	428.3		lbmol/hr

While the goal of eliminating all three of the major equipment items (external separator, slurry pump, and external heat exchanger) is a valuable one, eliminating any of the three would be a worthwhile accomplishment. Therefore, a new process design capable of operating with one or all of the process simplifications, and capable of testing either an internal demister or external cyclone to minimize slurry carry-over was developed and is schematically shown in Figure III.4.

Fortunately, the PDU process flowsheet modifications were achieved without major reconstruction of existing piping. The PDU was modified to be able to run in one of the following modes:

- An external slurry circulation mode with external heat exchange and a separate vapor/liquid separation vessel similar to the original LP-II System mode. (See Figure III.5.)

Figure III.4

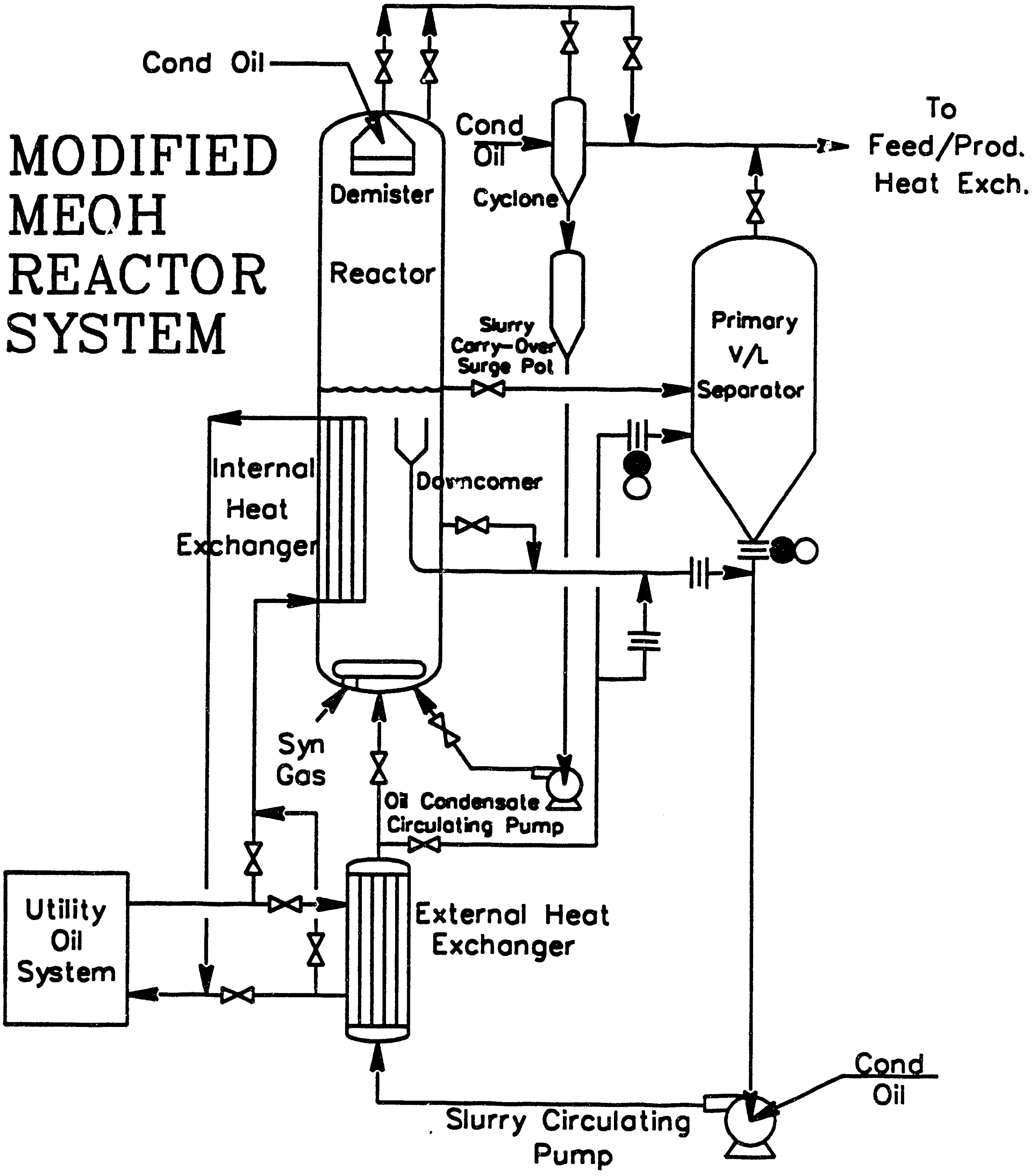
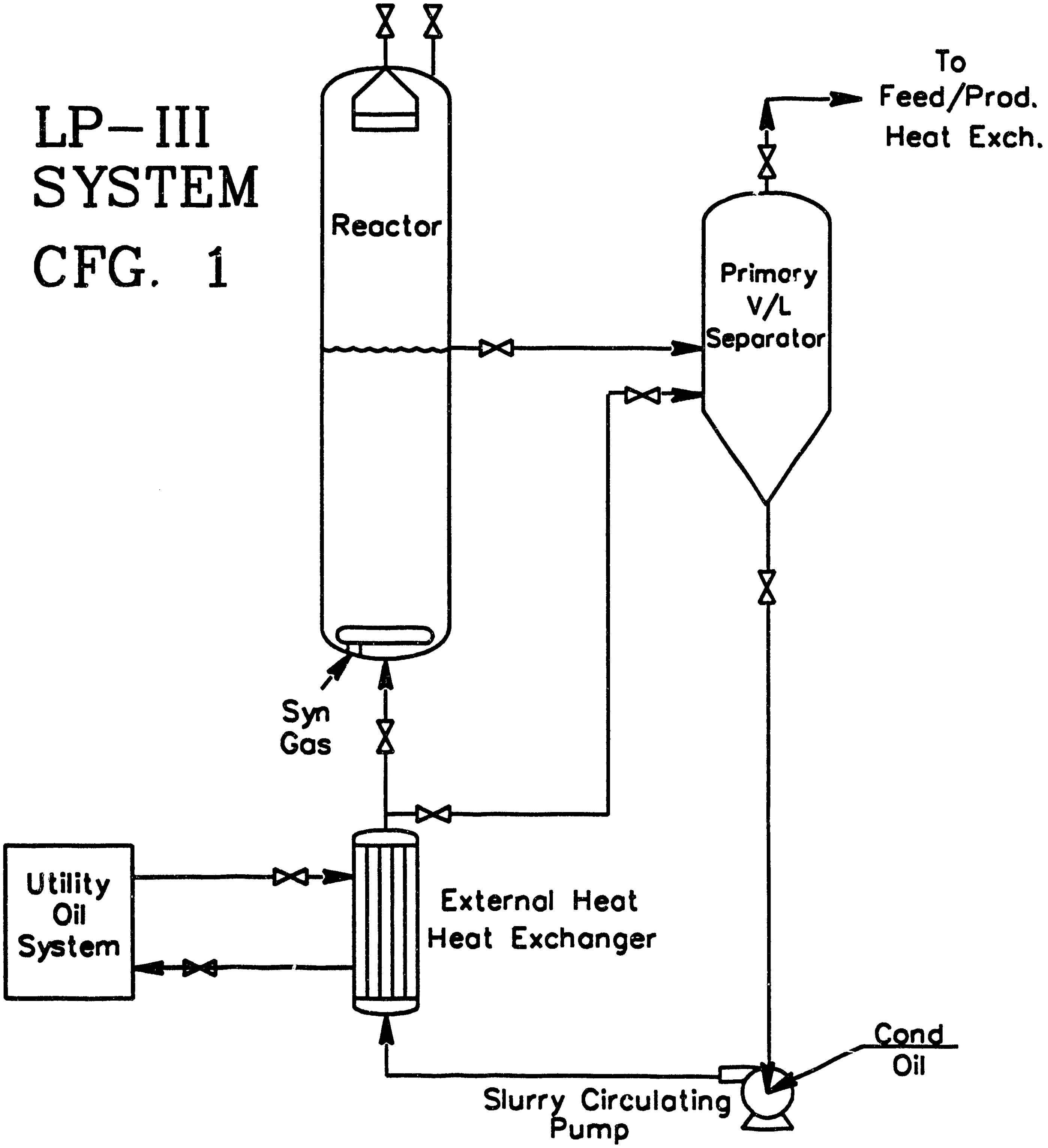

MODIFIED MEOH REACTOR SYSTEM
Cond Oil
Demister
Reactor
Cond Oil
Cyclone
To Feed/Prod. Heat Exch.
Slurry Carry-Over Surge Pot
Primary V/L Separator
Internal Heat Exchanger
Downcomer
Syn Gas
Oil Condensate Circulating Pump
Utility Oil System
External Heat Exchanger
Cond Oil
Slurry Circulating Pump

Figure III.5


LP-III SYSTEM CFG. 1
Reactor
To Feed/Prod. Heat Exch.
Primary V/L Separator
Syn Gas
Utility Oil System
External Heat Heat Exchanger
Cond Oil
Slurry Circulating Pump

- An external slurry circulation mode with internal heat removal and a separate vapor/liquid separation vessel. (See Figure III.6.)

- A non-circulating slurry mode with internal heat removal and a reactor freeboard zone with demister option in combination with an external cyclone for effluent vapor/liquid separation. This is the optimum desired configuration with the incorporation of all three process engineering study results. (See Figure III.7.)

- An external slurry circulation mode with external heat removal and an internal downcommer for circulating slurry vapor/liquid separation and reactor freeboard zone with demister option in combination with an external cyclone for effluent vapor/liquid separation. (See Figure III.8.)

- An external slurry circulation mode with internal heat removal and an internal downcommer for circulating slurry vapor/liquid separation and reactor freeboard zone with demister option in combination with an external cyclone for effluent gas vapor/liquid separation. (See Figure III.9.)

Vapor/liquid disengagement was accomplished in a new, longer, all stainless steel reactor by incorporating a freeboard section followed by a demisting mesh pad. If desired, the demisting pad could be bypassed to use a small-diameter external cyclone to knock out small slurry droplets. Recovered slurry droplets were returned to the reactor via a positive displacement pump.

The internal heat exchanger consisted of parallel 1-inch-diameter tubes manifolded at each end by a 16-inch-diameter heater ring. The heat exchanger occupied only 3.5% of the reactor cross-sectional area and was not expected to interfere with the reactor hydrodynamics.

Feed synthesis gas was introduced to the reactor using a circular gas sparger. The estimated slurry circulation rate resulting from the feed gas flow was an order of magnitude higher than the superficial velocity resulting from the slurry pump and was sufficient to suspend the catalyst particles.

Process economics were also improved by increasing the reactor productivity as a result of higher catalyst loading. The newly designed gas sparger was developed to suspend a high concentration catalyst slurry while providing intimate gas/slurry mixing and suitable mass transfer. We are currently preparing the paperwork to patent the sparger design.

The remainder of the reactor design (diameter, liquid height, instrumentation, etc.) was unchanged from the original PDU reactor design (see Figure III.10). Figure III.11 is a schematic illustration of the LaPorte PDU flowsheet incorporating the reactor internal slurry configuration.

Figure III.6

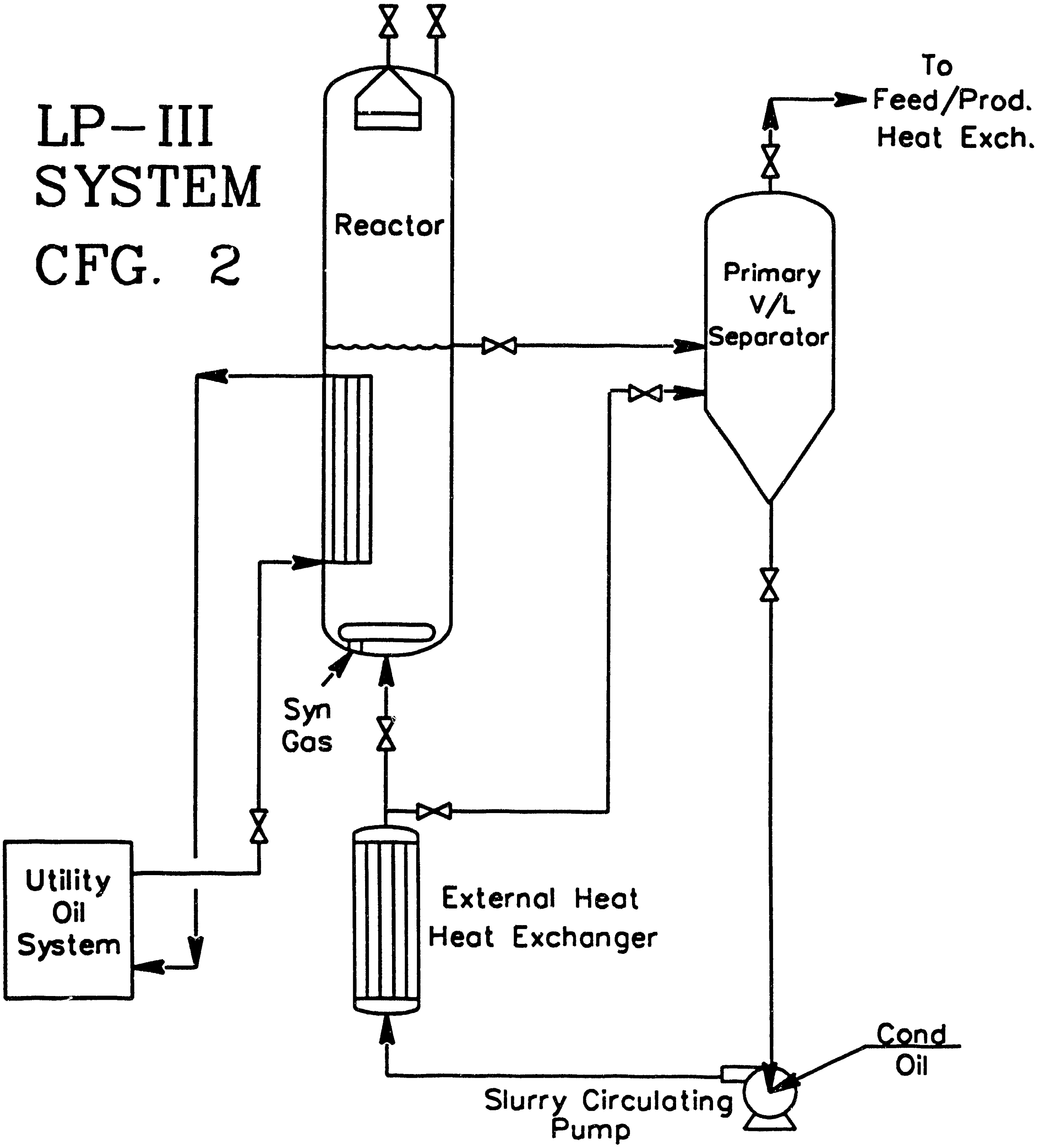

LP-III
SYSTEM
CFG. 2
Reactor
To
Feed/Prod.
Heat Exch.
Primary
V/L
Separator
Syn
Gas
Utility
Oil
System
External Heat
Heat Exchanger
Cond
Oil
Slurry Circulating
Pump

Figure III.7

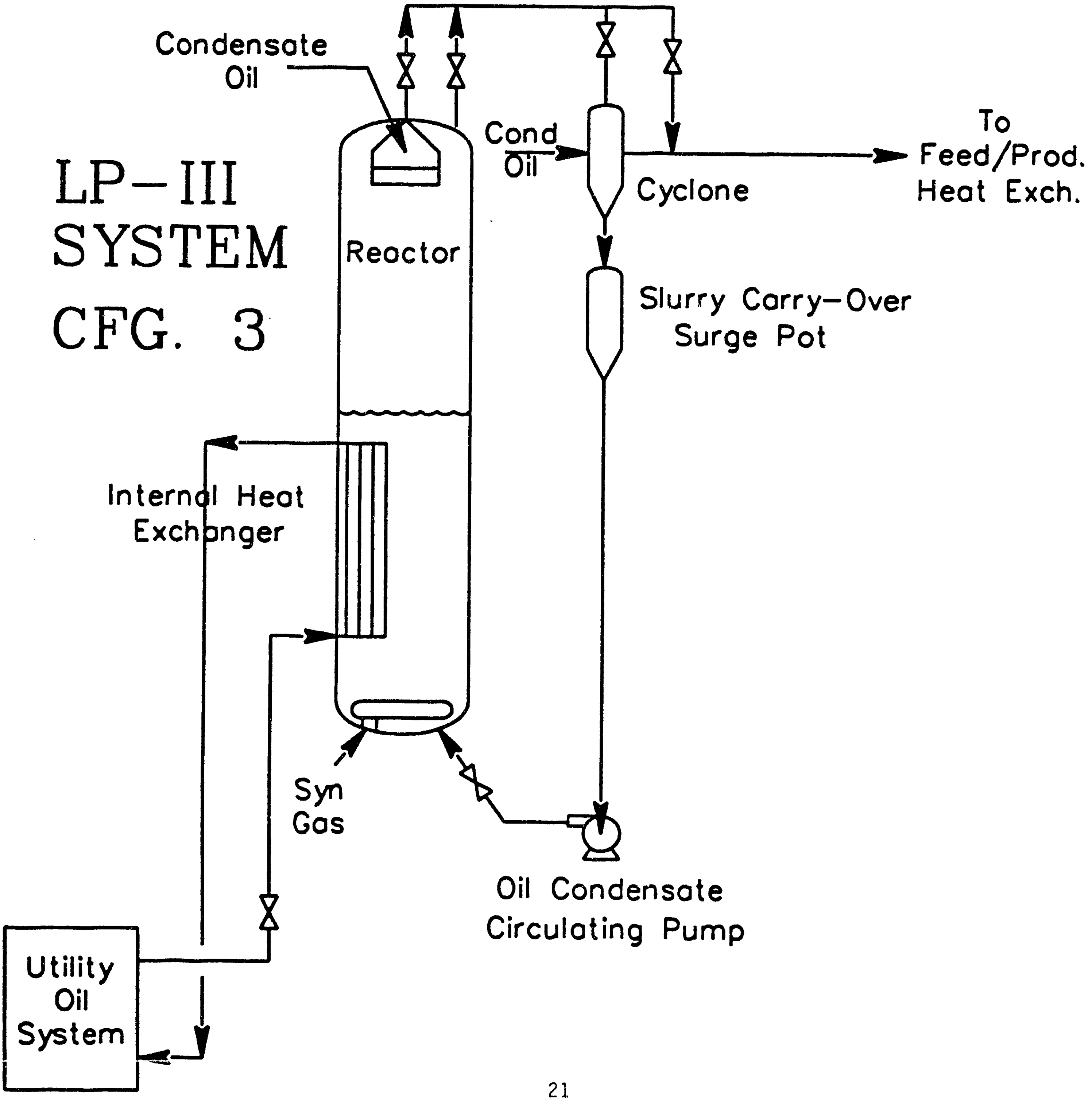

LP-III
SYSTEM
CFG. 3
Condensate
Oil
Reactor
Cond
Oil
Cyclone
To
Feed/Prod.
Heat Exch.
Slurry Carry-Over
Surge Pot
Internal Heat
Exchanger
Syn
Gas
Oil Condensate
Circulating Pump
Utility
Oil
System

Figure III.8

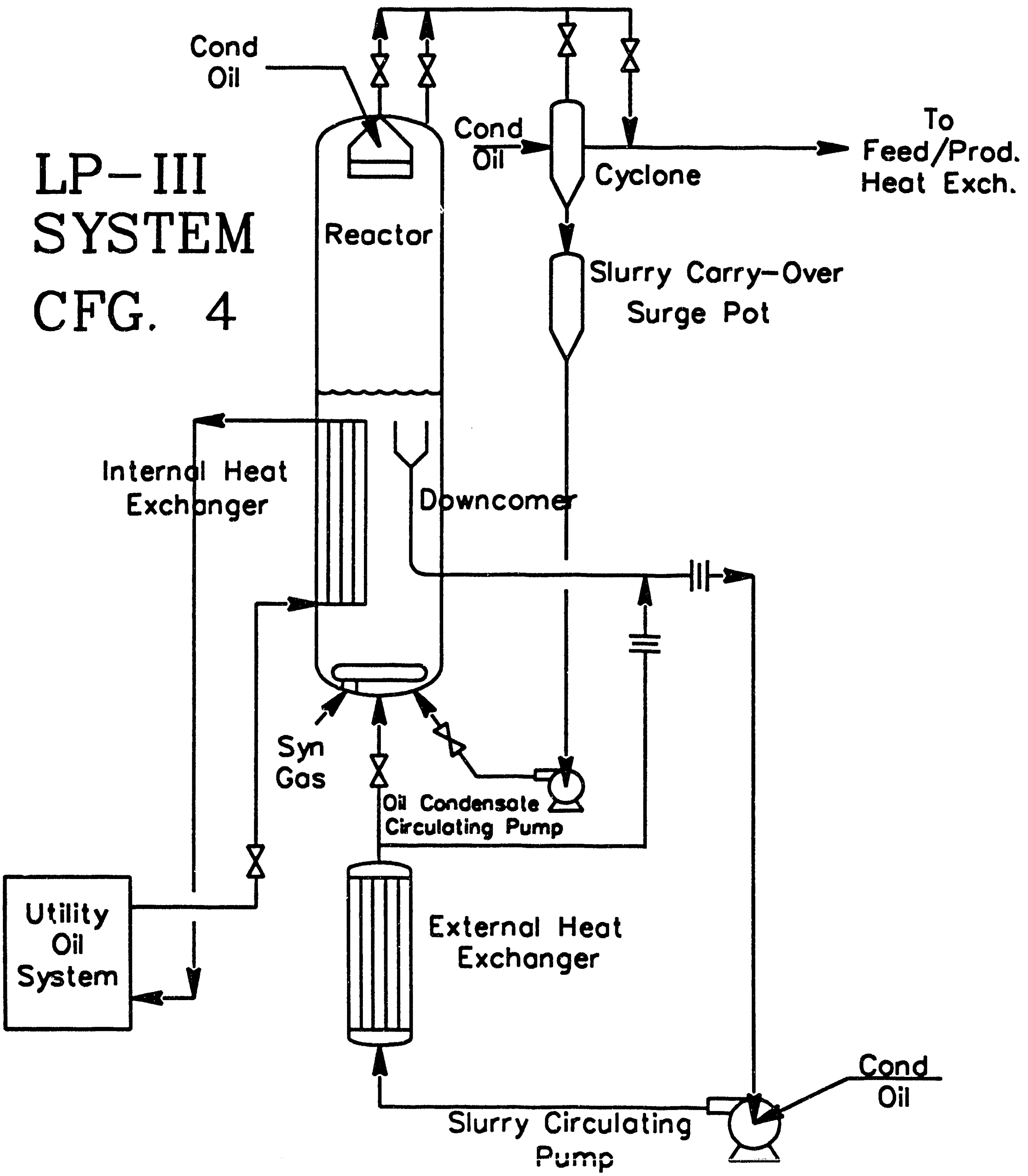
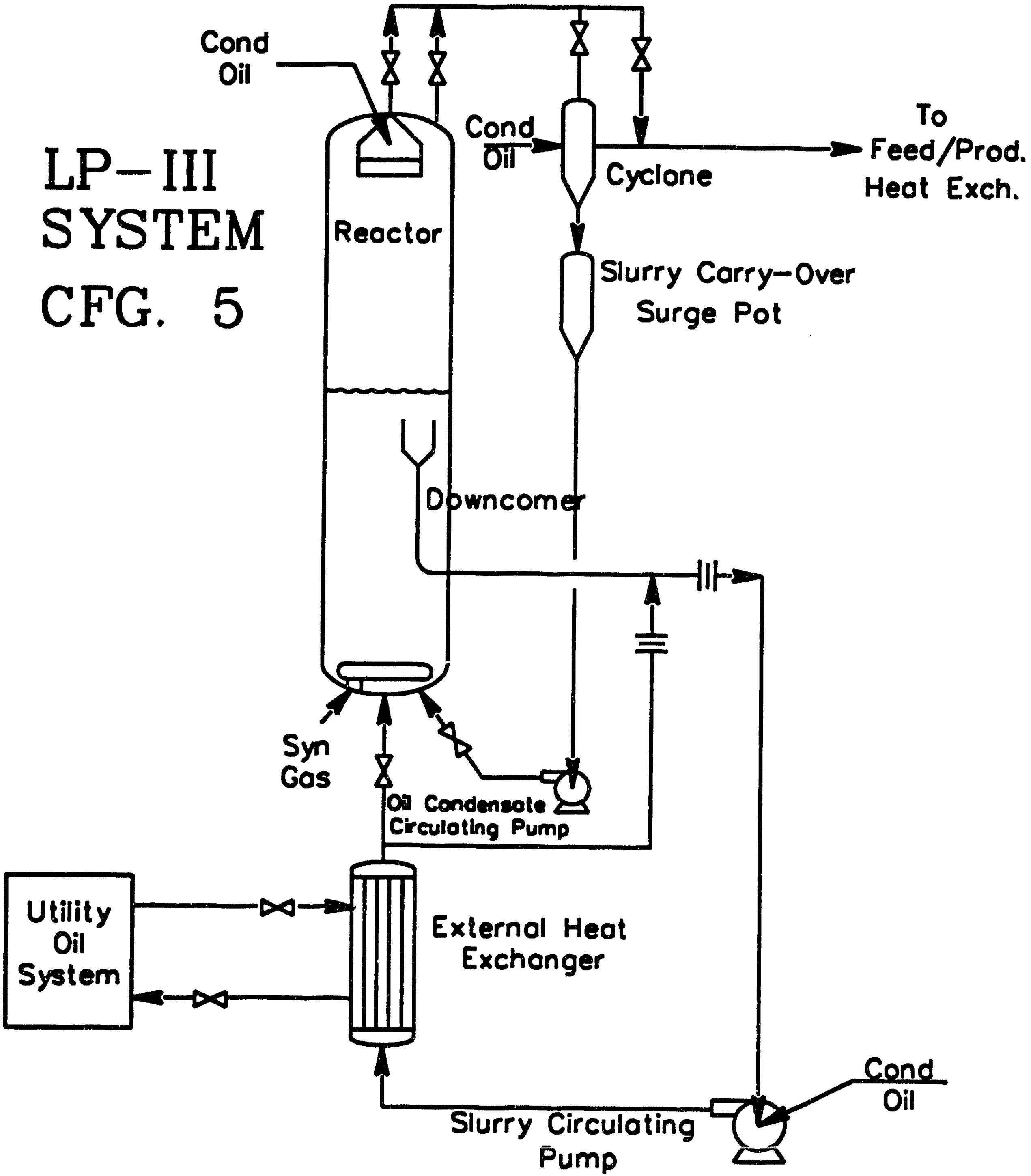
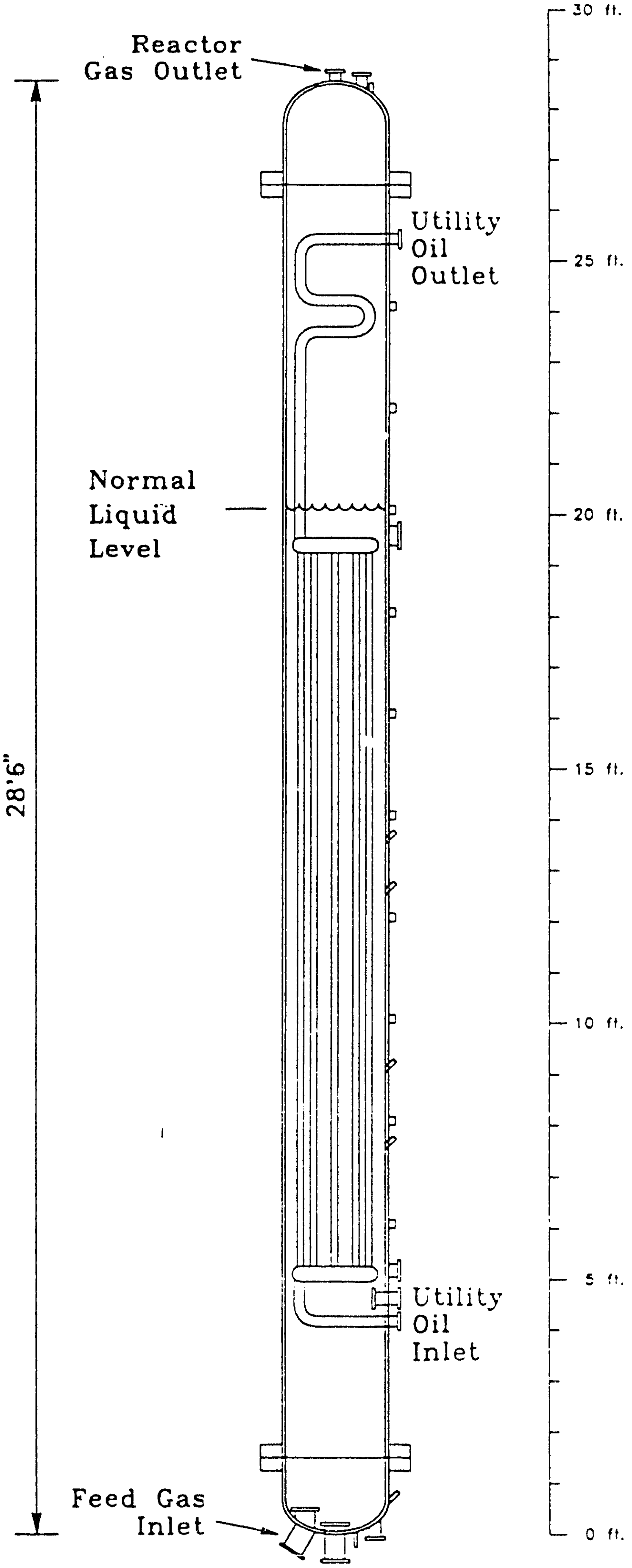

LP-III SYSTEM CFG. 4
Cond Oil
Cond Oil
Cyclone
To Feed/Prod. Heat Exch.
Reactor
Slurry Carry-Over Surge Pot
Internal Heat Exchanger
Downcomer
Syn Gas
Oil Condensate Circulating Pump
Utility Oil System
External Heat Exchanger
Cond Oil
Slurry Circulating Pump

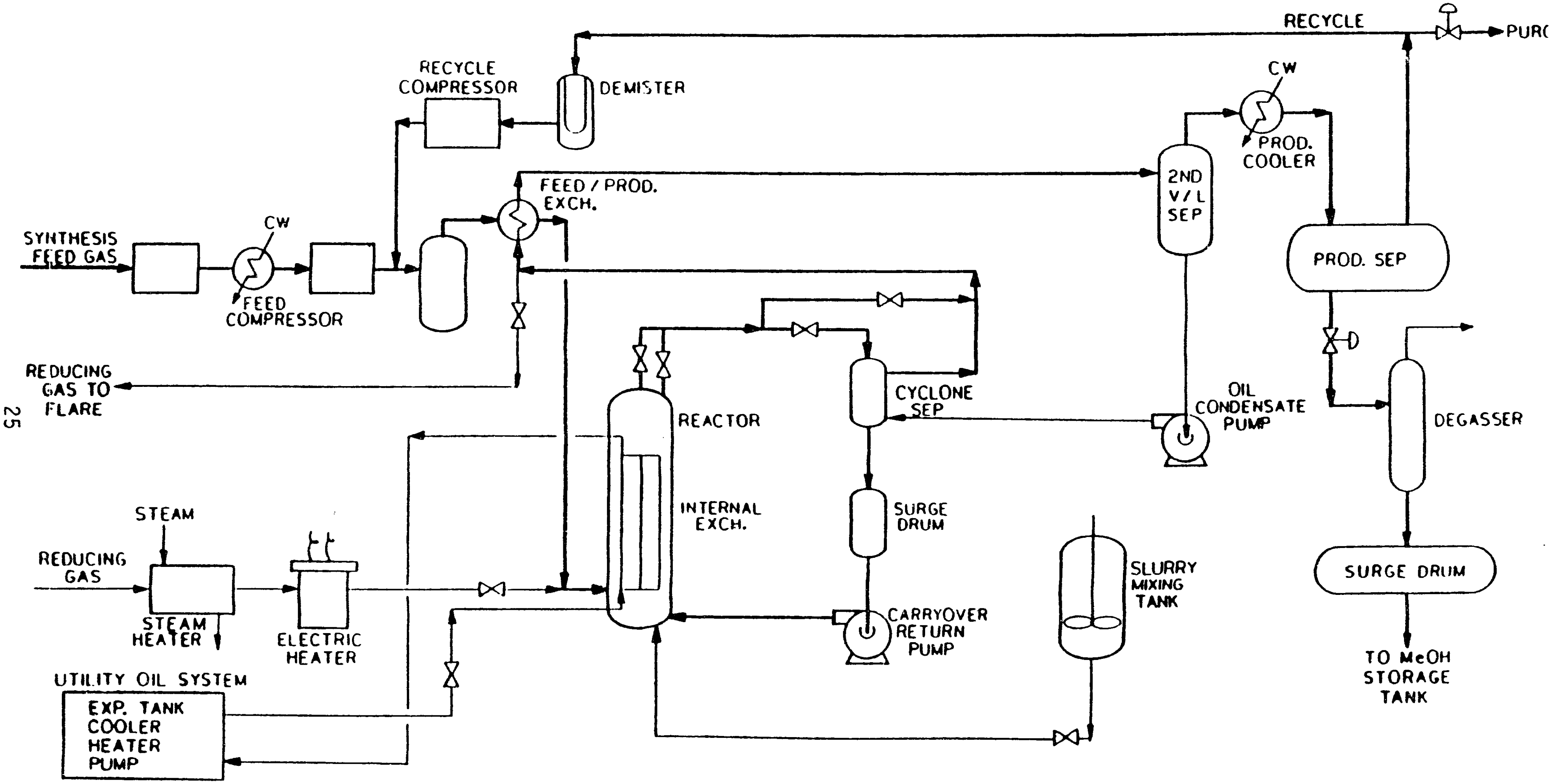
Figure III.9


LP-III
SYSTEM
CFG. 5
Cond
Oil
Reactor
Cond
Oil
Cyclone
To
Feed/Prod.
Heat Exch.
Slurry Carry-Over
Surge Pot
Downcomer
Syn
Gas
Oil Condensate
Circulating Pump
Utility
Oil
System
External Heat
Exchanger
Slurry Circulating
Pump
Cond
Oil

LPMEOH REACTOR AT LAPORTE PDU



SIMPLIFIED PROCESS FLOWSHEET FOR LAPORTE PDU



IV. GAS HOLDUP STUDY

Two-phase gas holdup studies were conducted at the LaPorte Liquid Phase Methanol Process Development Unit during June and July 1988. Gas holdup was measured with a nuclear density gauge (NDG) which had been calibrated prior to the gas holdup studies. Appendix A contains a detailed report on the calibration of the NDG.

The gas holdup studies were necessary to determine if the hydrodynamics of the modified reactor system were acceptable relative to the hydrodynamics of the original reactor system. In the modified reactor system, the goal was to eliminate the external liquid circulation loop. The new reactor contains an internal heat exchanger. In addition, the new gas and liquid sparger designs were used. It was suspected that these changes would affect the liquid circulation patterns, but the subsequent effect on gas holdup could not be predicted.

Two-phase gas holdup studies were performed as a function of pressure, temperature, gas velocity, external liquid circulation rate (liquid velocity), and reactor height with nitrogen and CO-Rich gas in Drakeol-10 oil.

Results

Two-phase gas holdup studies were conducted to study reactor hydrodynamics, train operating personnel, test for metal carbonyls, and test new equipment. The strategy of the tests was to measure gas holdup while operating over a range of operating conditions. In addition, the reactor was to be operated with and without the internal heat exchanger in place to quantify its effect on gas holdup performance. However, initial gas holdup tests with the internal heat exchanger in place were successful so the heat exchanger was left in for all subsequent tests.

Nominal conditions for the gas holdup studies are listed in Table IV.1. For each case, nominal superficial gas velocities of .03, 0.1, 0.2, 0.4, and 0.6 ft/s were studied and designated as GH-03-C1, GH-03-C2, etc. Superficial gas velocity is defined as the volumetric flow rate of gas at reactor conditions divided by the reactor cross-sectional area. For each condition, eight gas holdup measurements were taken at different reactor heights.

TABLE IV.1

NOMINAL CONDITIONS FOR TWO-PHASE GAS HOLDUP STUDY

Case	Gas	Pressure psig	Temp. °F	Liquid Flow gpm
C *	N2	80	170	198
D	N2	80	170	0
E	N2	300	170	0
F	N2	750	170	0
G	N2	750	170	198
I	N2	750	482	198
J	N2	750	482	75
S	CO-Rich	750	482	0
T	CO-Rich	750	482	75
U	CO-Rich	750	482	198
V	CO-Rich	900	482	198
W	CO-Rich	900	482	0

*Cases A and B were part of the NDG calibration. (See Appendix A)

Gas holdup as a function of superficial gas velocity is shown in Figures IV.1, IV.2, and IV.3 and Table IV.2. As superficial gas velocity increased, the gas holdup increased, following a relationship which is widely reported and accepted in the literature.

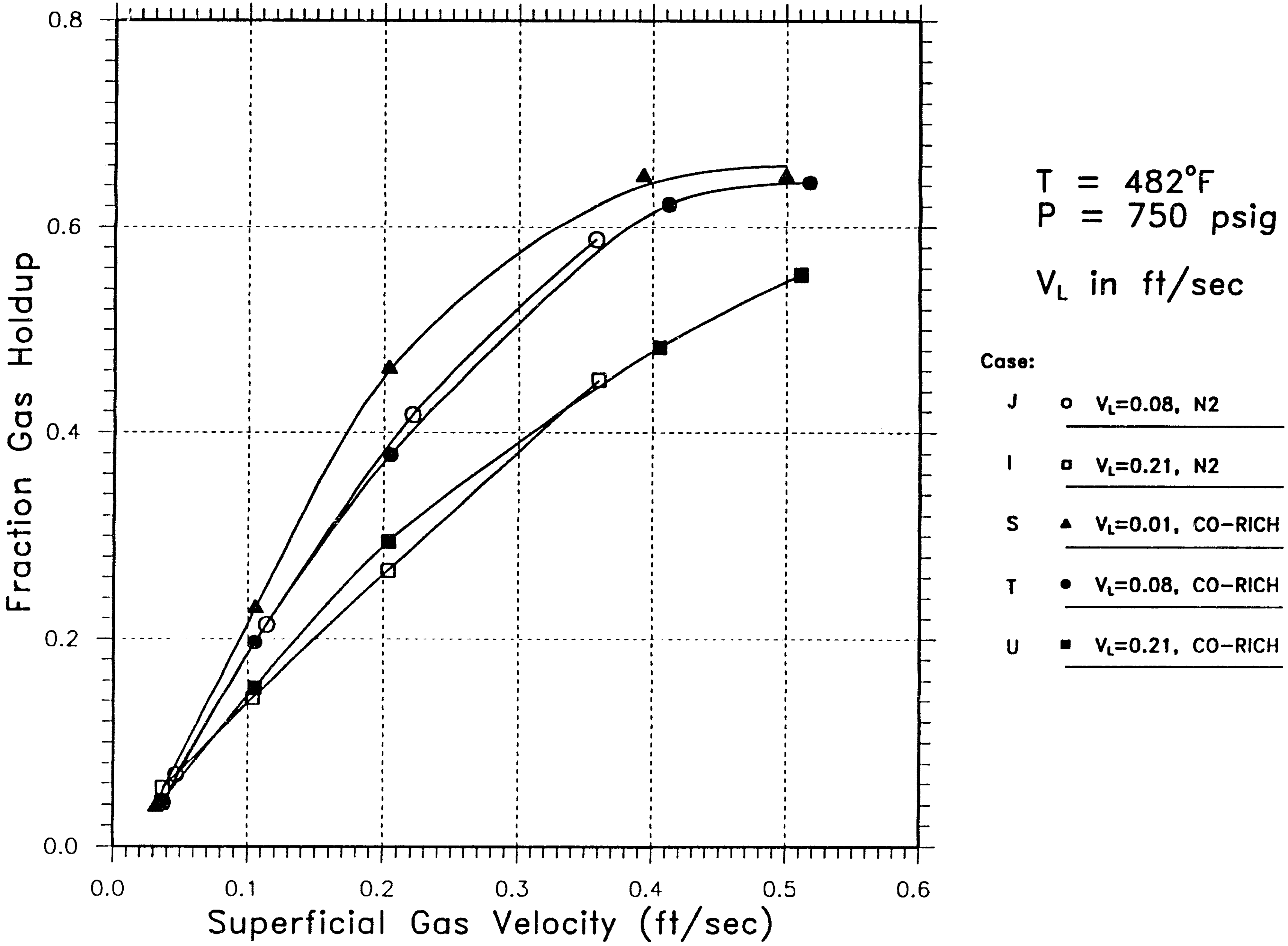
The effect of the type of gas used is shown in Figure IV.1. At 482°F and 750 psig, there is little difference between the gas holdup generated with nitrogen, and the gas holdup generated with CO-rich gas over a range of gas superficial velocities between 0 and .6 ft/sec and superficial liquid velocities between .08 and .21 ft/sec. This implies that the small density difference between N_2 and CO-rich gas and/or the difference in solubility of N_2 and CO-rich gas has little effect on gas holdup. The CO-rich gas composition contains 51 mol% CO, 35 mol% H_2, 13 mol% CO_2, and 1 mol% N_2.

Figure IV.1 also illustrates the effect of external liquid circulation on gas holdup. There is no observable impact of liquid superficial velocity on gas holdup at superficial gas velocities of 0.04 ft/sec. However, above superficial gas velocities of .1 ft/sec, the gas holdup decreases as the superficial liquid velocity increases. At high gas superficial velocities above 0.5 ft/sec the relative impact of liquid velocity on gas holdup is less pronounced. If the gas velocity is considered relative to the liquid velocity, then the observed decrease in gas holdup with increasing liquid velocity is analogous (at least qualitatively) to the typical observation of lower gas holdup at lower gas velocities. Sangnimnuan, et.al. (1984) and deBruijn (1988), who did not see a liquid velocity effect, operated at very low liquid superficial velocities below .01 ft/sec.

Figure IV.1

EFFECT OF GAS TYPE ON TWO PHASE GAS HOLDUP

NITROGEN AND CO-RICH GAS DATA



The effect of pressure on gas holdup is shown in Figure IV.2. At both high and low liquid velocities, gas holdup increases with an increase in pressure at gas velocities greater than .1 ft/sec. Unlike the tests comparing CO-rich gas and N_2 gas effect on holdup, an increase in pressure greatly increases the density of the gas and the solubility of the gas in the oil.

Tarmy, et al. (1984) also observed this same pressure dependence and attributed it to smaller bubble formation due to an increased gas momentum because of higher gas densities. Idozawa, et al. (1987) observed the pressure dependence on gas holdup but they also performed experiments showing that a decrease in surface tension increases gas holdup. In the liquid phase methanol system, we estimate that the oil/gas surface tension decreased by approximately 20% when the pressure was raised from 15 psig to 750 psig. It is unclear from the LaPorte data whether the pressure effect on gas holdup was caused by the change in gas density or the change in the physical properties of the oil.

Both Idogawa, et al. (1987) and Sangnimnuan, et al. (1984) see no effect of pressure on gas holdup above 750 psig. This is also confirmed in the liquid phase methanol reactor by comparing Case S with Case W in Table IV.2.

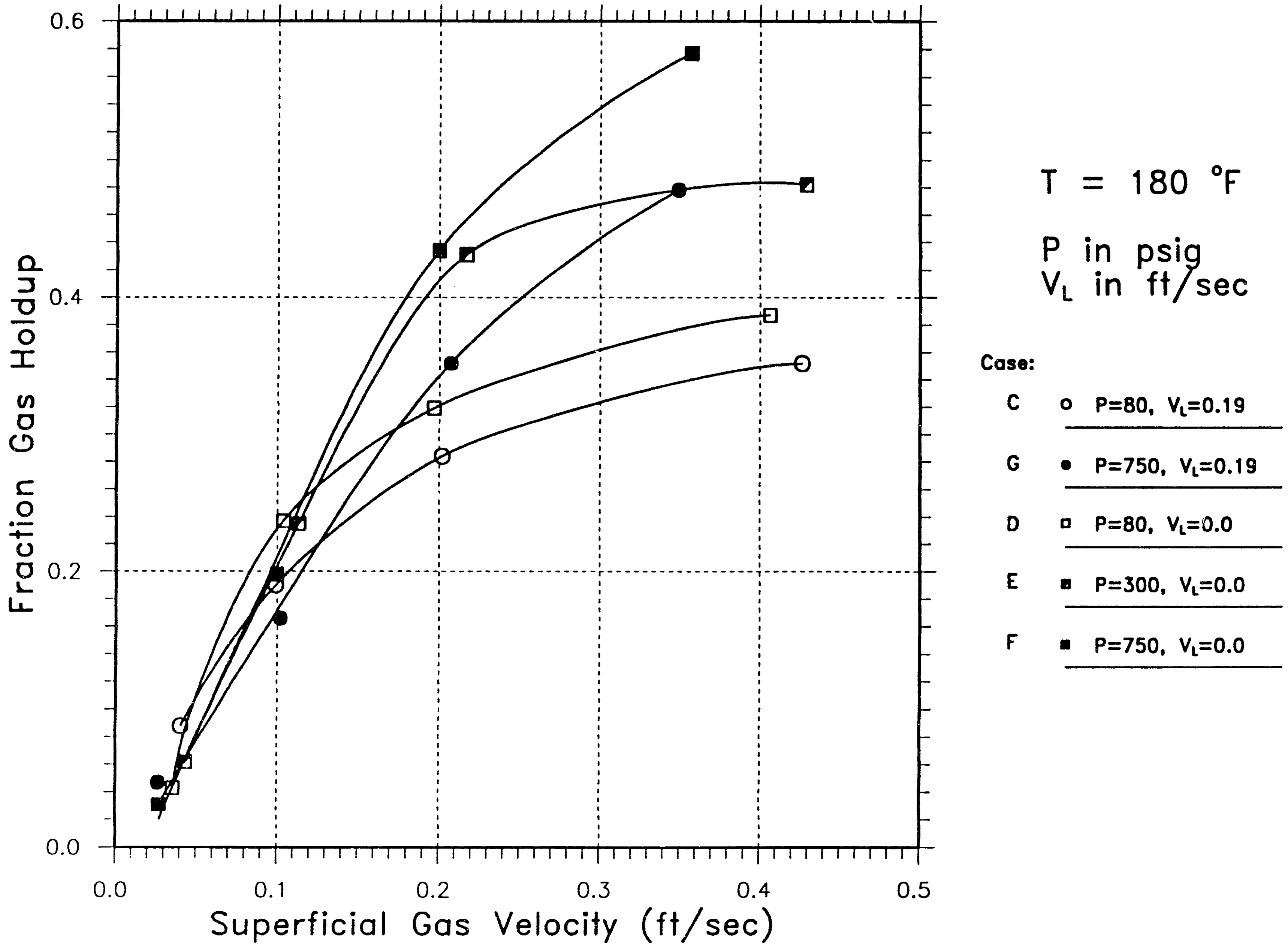
The effect of temperature on gas holdup, shown in Figure IV.3, does not follow any expected trend. Assuming gas composition has no effect on gas holdup (see Figure IV.1), then at zero net liquid flow increase in temperature increases gas holdup. At a net liquid flow of 0.2 ft/sec the opposite appears to be true. These are not clearly defined trends, however, and could simply be due to scatter in the data.

Gas holdup as a function of reactor height (from the bottom head) is shown in Figure IV.4 for a liquid velocity of zero. The gas holdup profiles are more uniform over the reactor height at low gas velocities than at high gas velocities. This is probably due to the bubble reaching an equilibrium size at a lower point in the column at the low gas velocities. Similar profile uniformity is observed over a range of superficial liquid velocities.

A comparison of gas holdup profiles with height for the new and old reactor is shown in Figure IV.5. The uniformity in the axial gas holdup distribution of the new reactor is comparable to that for the old reactor. Figure IV.6 illustrates that the average gas holdup in the new reactor is equal to or greater than the holdup in the old reactor over a range of superficial gas velocities.

Two-phase CO-rich gas studies also served to monitor the production of catalyst poisons, particularly iron and nickel carbonyls. Initial levels of carbonyls, determined by gas chromatography and atomic absorption, were below 70 ppb. As shown in Figure IV.7, after approximately 20 hours on stream the carbonyl levels dropped to 20 ppb of $Fe(CO)_5$ and 5 ppb of $Ni(CO)_4$. From available laboratory and literature data, these low carbonyl levels were considered satisfactory for subsequent methanol production.

Figure IV.2



PRESSURE EFFECT ON TWO PHASE GAS HOLDUP

NITROGEN GAS DATA

Table IV.2

LPMEOH LaPORTE PDU
TWO-PHASE GAS HOLDUP RESULTS

(Gas Holdup Averaged Over Reactor Height)

Run #:	Gas Type	Temp: {Deg F}	Pres: {psig}	Liq Vel: {ft/s}	Gas Vel: {ft/s}	Fractional Gas Holdup
GH-03-C1	Nitrogen	177.7	80.5	0.191	0.040	0.088
GH-03-C2	Nitrogen	179.0	80.5	0.193	0.099	0.190
GH-03-C3	Nitrogen	181.1	81.0	0.190	0.202	0.284
GH-03-C4	Nitrogen	182.9	81.0	0.193	0.426	0.352
GH-03-D1	Nitrogen	180.8	80.0	0.000	0.036	0.047
GH-03-D2	Nitrogen	188.9	80.0	0.000	0.104	0.237
GH-03-D3	Nitrogen	178.3	80.0	0.000	0.196	0.319
GH-03-D4	Nitrogen	174.9	80.0	0.000	0.406	0.387
GH-03-E1	Nitrogen	185.5	289.6	0.019	0.043	0.062
GH-03-E2	Nitrogen	183.7	303.7	0.019	0.113	0.235
GH-03-E3	Nitrogen	177.3	316.9	0.014	0.217	0.431
GH-03-E4	Nitrogen	175.6	314.6	0.018	0.429	0.482
GH-03-F1	Nitrogen	179.5	794.0	0.000	0.027	0.039
GH-03-F2	Nitrogen	178.9	786.0	0.008	0.100	0.198
GH-03-F3	Nitrogen	177.6	780.1	0.015	0.200	0.434
GH-03-F4	Nitrogen	175.6	777.6	0.019	0.357	0.577
GH-03-G1	Nitrogen	178.1	729.6	0.191	0.026	0.047
GH-03-G2	Nitrogen	177.1	743.4	0.192	0.102	0.166
GH-03-G3	Nitrogen	175.9	758.0	0.192	0.207	0.352
GH-03-G4	Nitrogen	174.6	773.6	0.191	0.349	0.478
GH-03-I1	Nitrogen	481.5	746.5	0.205	0.037	0.056
GH-03-I2	Nitrogen	481.5	750.6	0.202	0.104	0.143
GH-03-I3	Nitrogen	479.0	759.3	0.209	0.203	0.451
GH-03-I4	Nitrogen	477.5	770.7	0.205	0.360	0.451
GH-03-J1	Nitrogen	479.9	745.4	0.078	0.047	0.069
GH-03-J2	Nitrogen	480.3	738.3	0.079	0.114	0.214
GH-03-J3	Nitrogen	483.3	752.7	0.078	0.221	0.417
GH-03-J4	Nitrogen	480.8	763.9	0.077	0.358	0.588
GH-03-S1	CO-Rich	480.0	750.5	0.010	0.032	0.040
GH-03-S2	CO-Rich	484.5	751.5	0.009	0.106	0.232
GH-03-S3	CO-Rich	485.0	750.5	0.000	0.204	0.464
GH-03-S4	CO-Rich	485.5	751.0	0.009	0.393	0.651
GH-03-S5	CO-Rich	479.0	751.5	0.005	0.500	0.651
GH-03-T1	CO-Rich	475.0	751.0	0.078	0.038	0.042
GH-03-T2	CO-Rich	483.0	751.0	0.078	0.105	0.197
GH-03-T3	CO-Rich	482.0	750.5	0.079	0.205	0.379
GH-03-T4	CO-Rich	477.0	751.0	0.078	0.412	0.622
GH-03-T5	CO-Rich	480.5	751.5	0.078	0.518	0.643
GH-03-U1	CO-Rich	479.0	751.0	0.205	0.036	0.042
GH-03-U2	CO-Rich	482.0	752.0	0.204	0.105	0.153
GH-03-U3	CO-Rich	478.5	751.0	0.205	0.204	0.295
GH-03-U4	CO-Rich	478.0	751.5	0.206	0.405	0.483
GH-03-U5	CO-Rich	476.5	751.0	0.204	0.511	0.554
GH-03-V1	CO-Rich	477.5	869.0	0.206	0.033	0.038
GH-03-V2	CO-Rich	481.0	892.5	0.206	0.103	0.154
GH-03-V3	CO-Rich	478.5	891.5	0.204	0.198	0.290
GH-03-V4	CO-Rich	479.0	895.0	0.205	0.336	0.427
GH-03-W1	CO-Rich	478.5	868.0	0.010	0.030	0.042
GH-03-W2	CO-Rich	479.0	876.0	0.010	0.103	0.233
GH-03-W3	CO-Rich	481.5	877.0	0.011	0.206	0.466
GH-03-W4	CO-Rich	484.0	895.0	0.009	0.313	0.651

Figure IV.3

TEMPERATURE EFFECT ON TWO PHASE GAS HOLDUP

NITROGEN AND CO-RICH GAS DATA

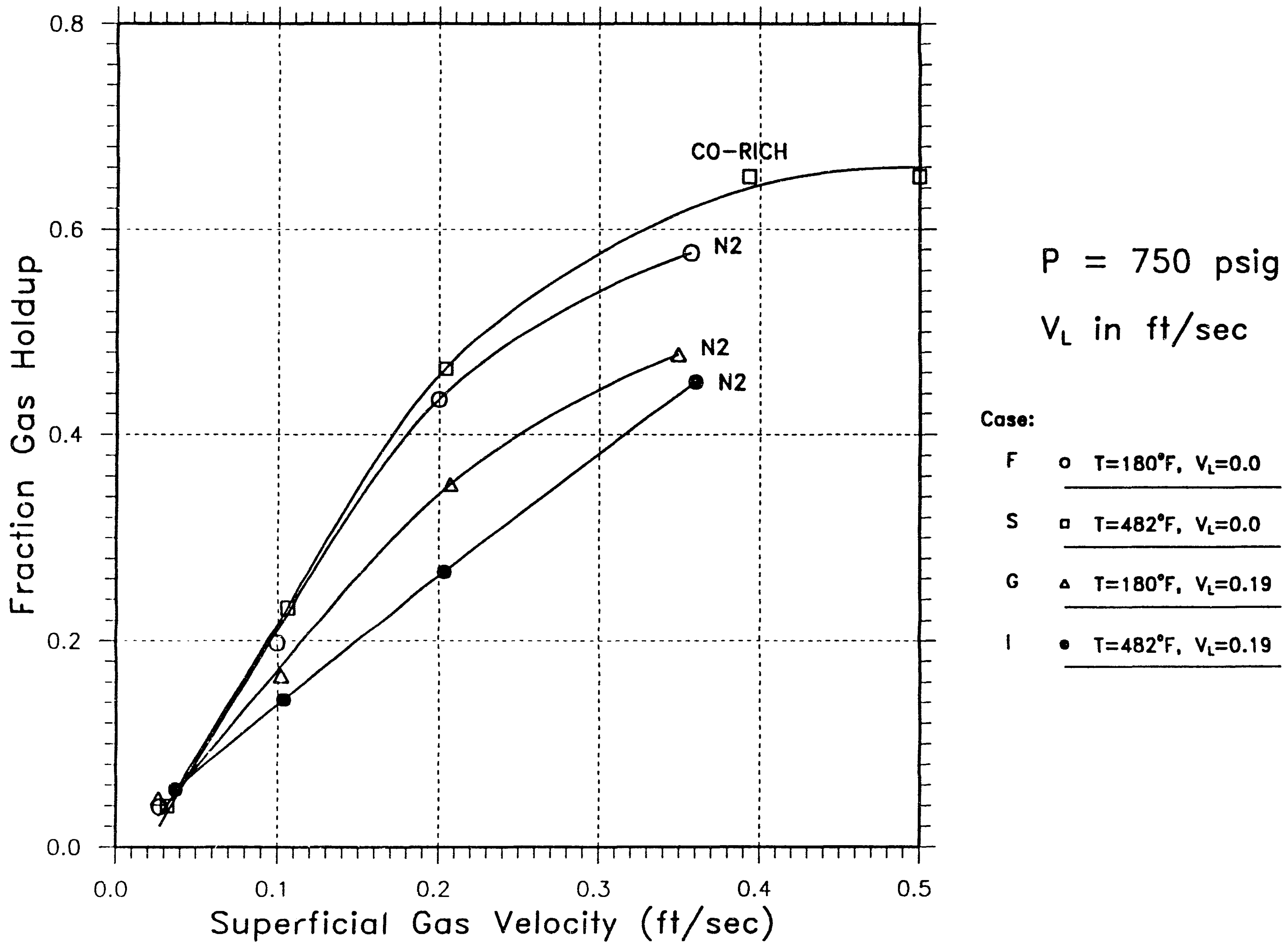


Figure IV.4

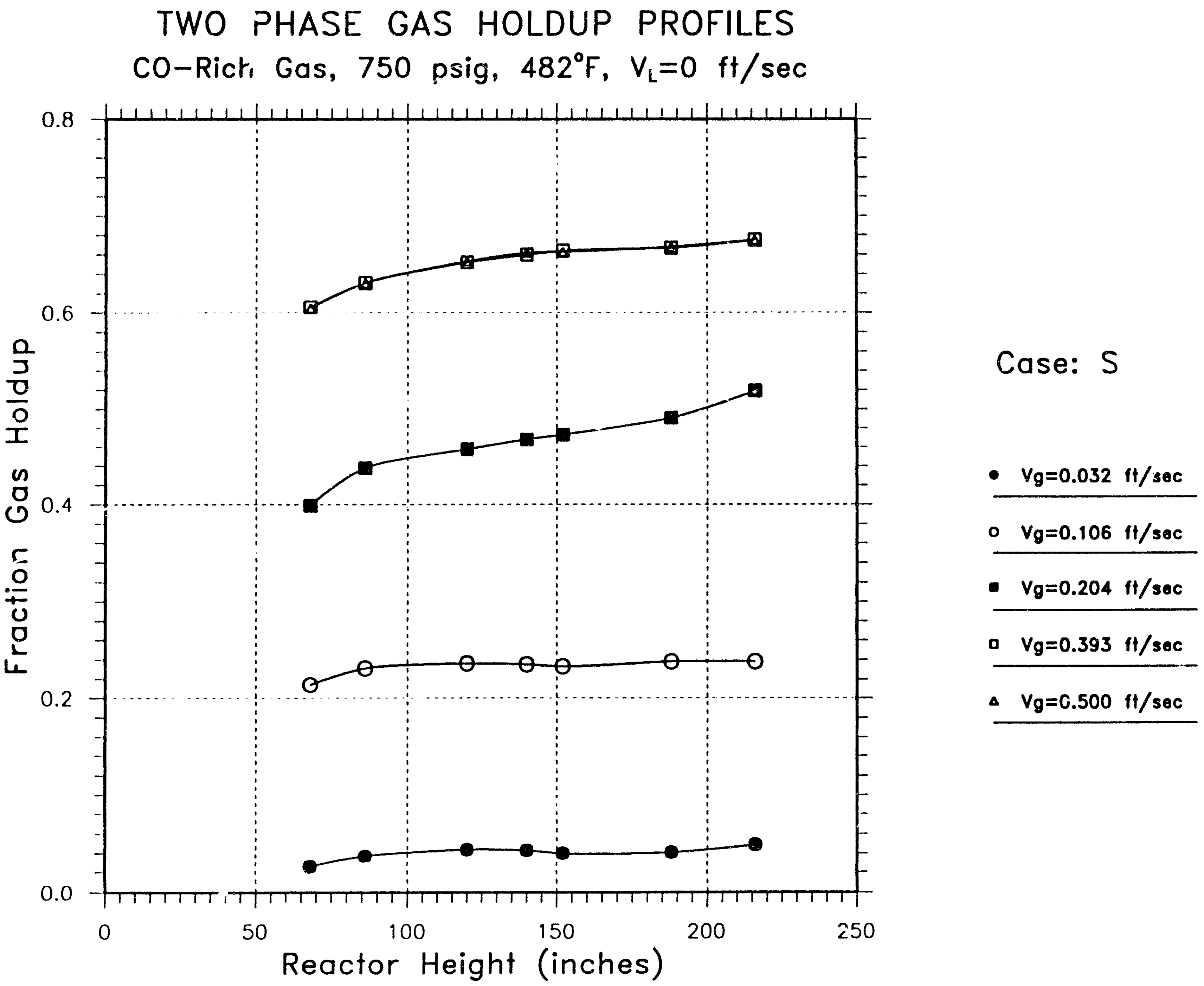

TWO PHASE GAS HOLDUP PROFILES
CO-Rich Gas, 750 psig, 482°F, V_L=0 ft/sec
Fraction Gas Holdup
0.0
0.2
0.4
0.6
0.8
Reactor Height (inches)
0
50
100
150
200
250
Case: S
● Vg=0.032 ft/sec
○ Vg=0.106 ft/sec
■ Vg=0.204 ft/sec
□ Vg=0.393 ft/sec
△ Vg=0.500 ft/sec

Figure IV.5

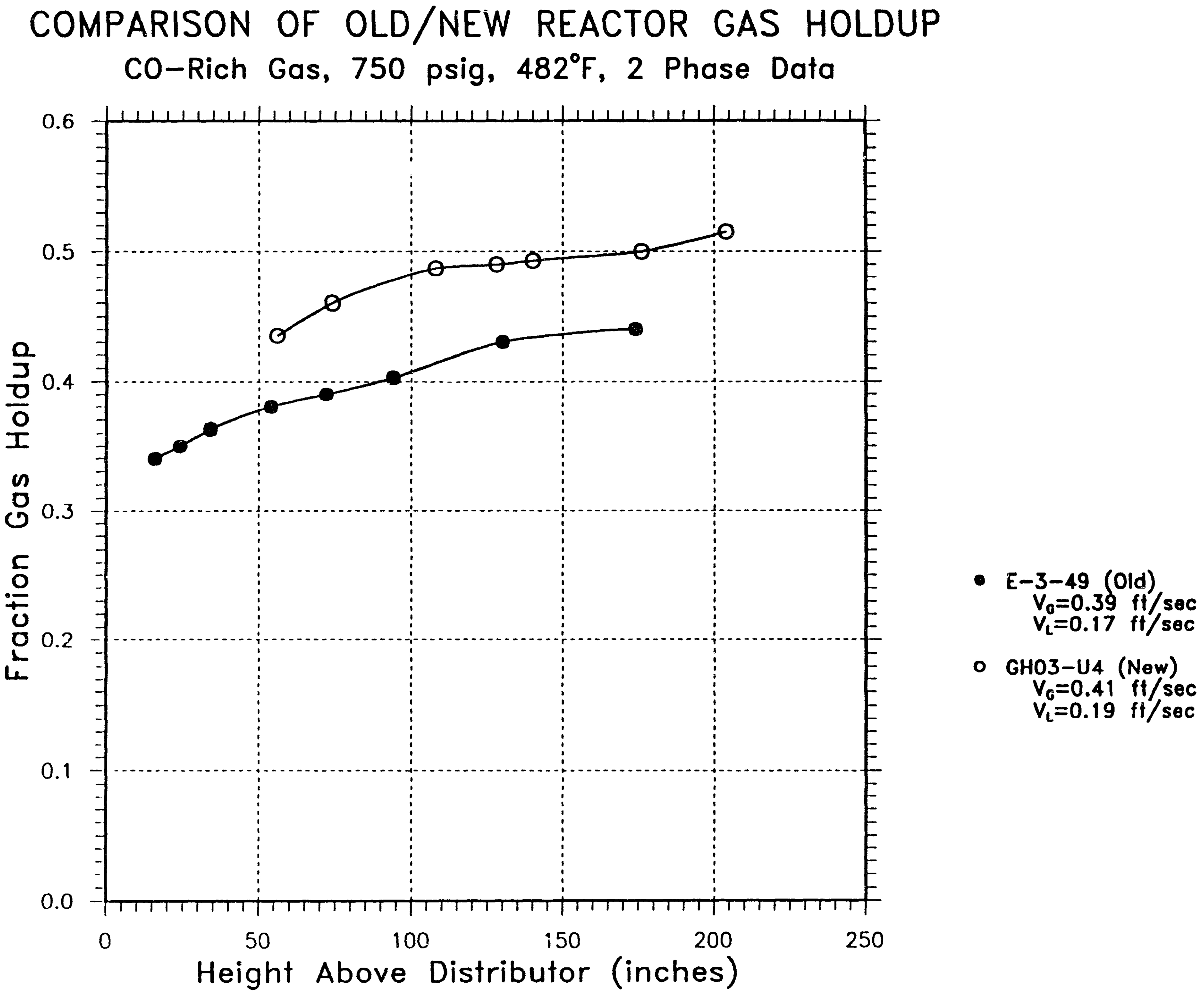

COMPARISON OF OLD/NEW REACTOR GAS HOLDUP
CO–Rich Gas, 750 psig, 482°F, 2 Phase Data
Fraction Gas Holdup
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0
50
100
150
200
250
Height Above Distributor (inches)
● E–3–49 (Old) V_G=0.39 ft/sec V_L=0.17 ft/sec
○ GH03–U4 (New) V_G=0.41 ft/sec V_L=0.19 ft/sec

Figure 11.0

COMPARISON OF OLD/NEW REACTOR GAS HOLDUP

CO-Rich Gas, 750 psig, 482°F, 2 Phase Data

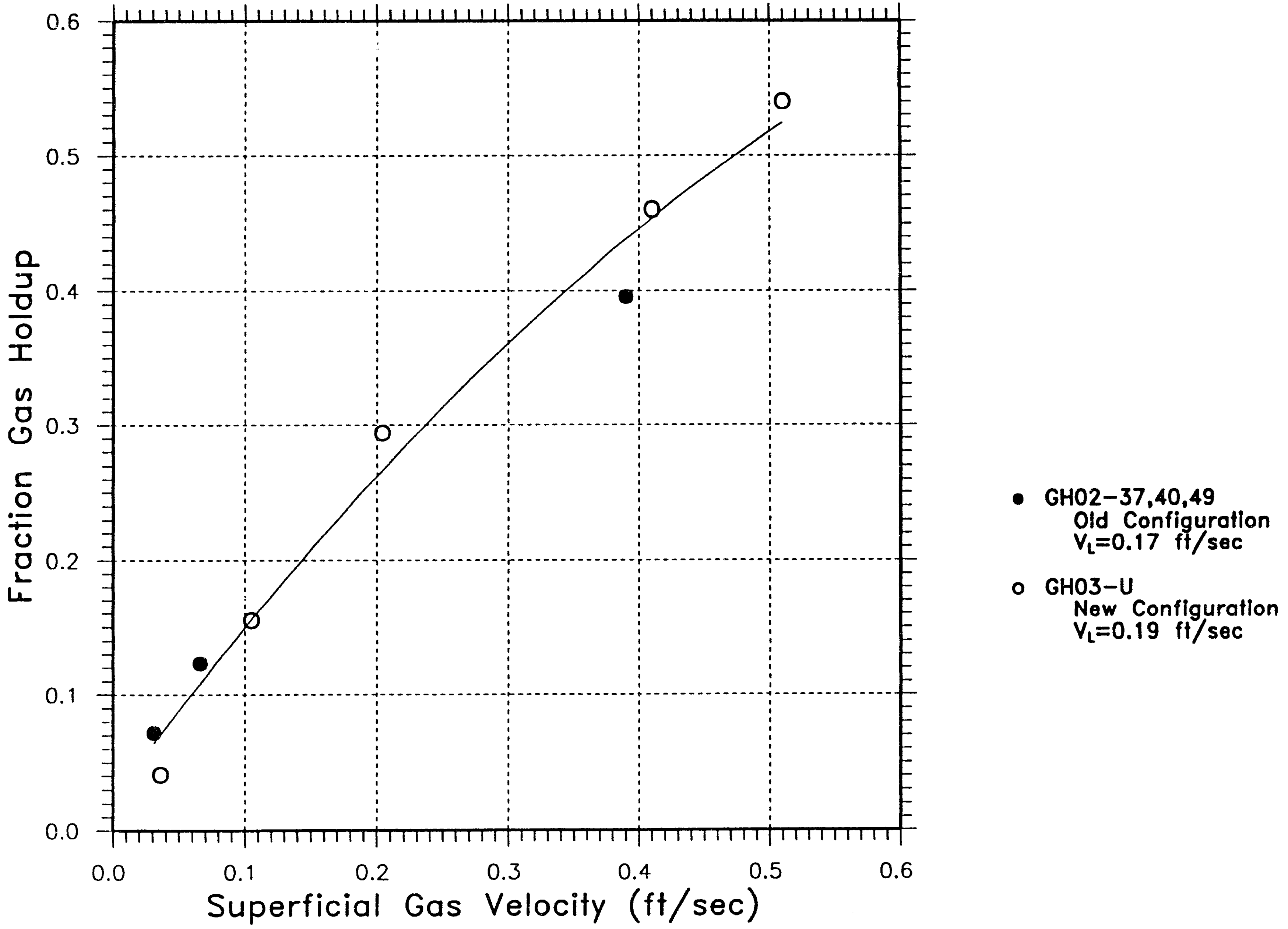
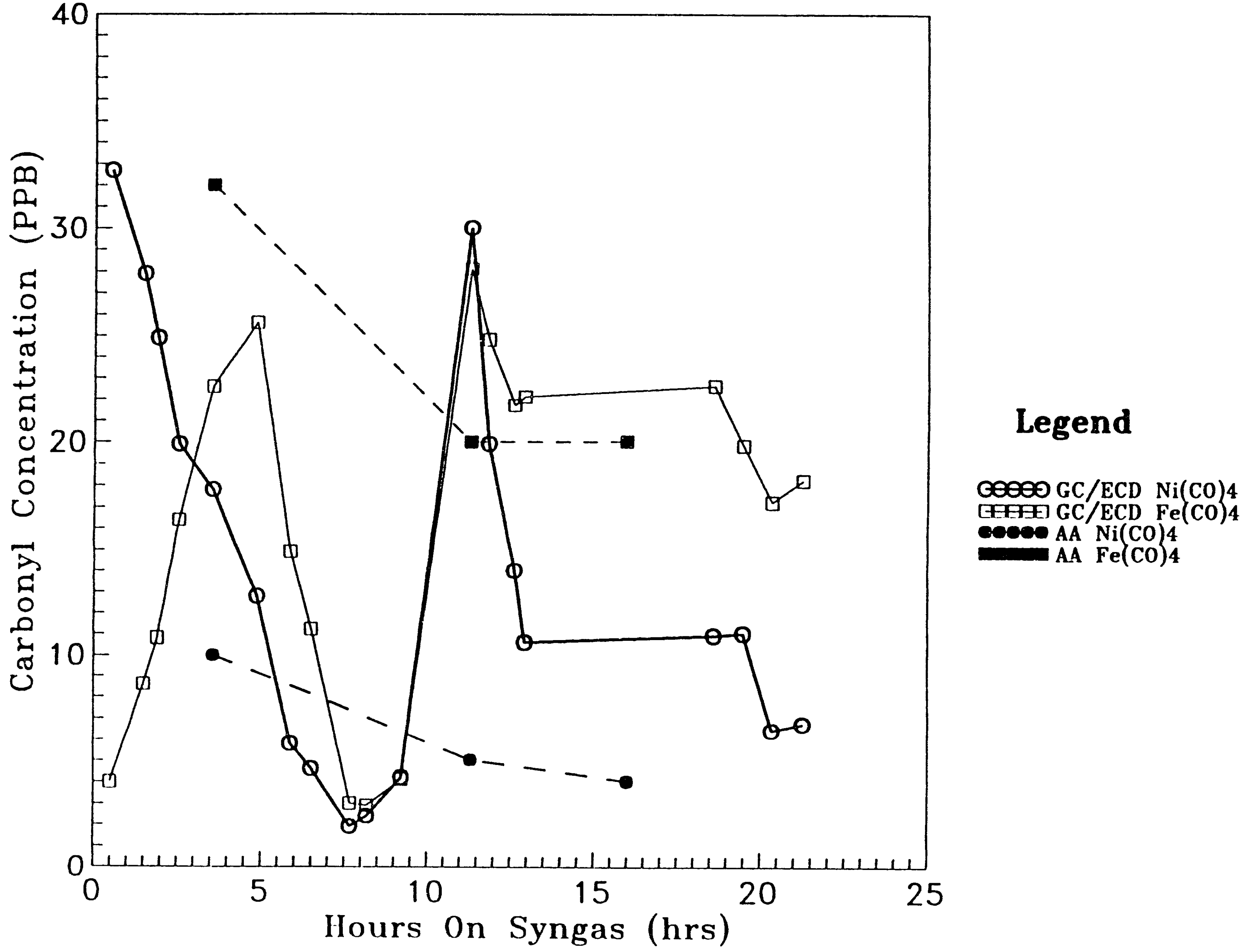


Figure IV.7



LaPorte PDU Carbonyl Burnout Prior to Run E-5

V. EQUIPMENT EVALUATION RUN (RUN E-5)

A. Introduction

Run E-5 was conducted at the LaPorte LPMEOH PDU in July, 1988. A commercially available catalyst powder (F21/OE75-44) was used. This was a new batch of the same catalyst which was used in Runs E-2, E-3, and E-4. The objective of Run E-5 was to systematically evaluate each new piece of equipment which had been added to the system: spargers, internal heat exchanger, vapor/liquid disengagement zone, demister, and cyclone. In addition, a catalyst activation with a concentrated (45 wt% oxide) slurry was conducted.

The plan to systematically evaluate each new piece of equipment was set up in four stages as shown in Figure V.1. The possible operating modes, which were identified from the previous process engineering study and resulting PDU modifications, were to be evaluated in the following order: 1) sparger gas distribution, 2) internal heat exchanger, 3) no bulk liquid circulation, and 4) shutdown test. While these operating modes were being tested, the V/L disengagement zone, demister, and cyclone would be individually evaluated.

B. In-Situ Activation

A batch of 40 wt% (oxide basis) slurry using F21/OE75-44 catalyst powder and Drakeol-10 oil was mixed in the 28.30 slurry prep tank under a nitrogen blanket and pressure-transferred to the slurry loop. The reducing gas was blended, the composition was verified (4 mol% H_2, 96 mol% N_2), and it was introduced to the reactor. The reduction gas leaving the reactor was sent to the flare. The temperature of the slurry was slowly increased during the activation process along a predefined temperature ramp using utility oil in the 21.20 external slurry heat exchanger. The inventory of oil in the slurry decreased over the course of the reduction as oil vapors were stripped from the reactor by the reduction gas. As a result, the slurry concentration increased to 45 wt% (as oxide) during the activation. Further details of the catalyst activation for Run E-5 are presented in the Catalyst Activation Chronology (see Table V-1).

The reactor slurry temperature was calculated by averaging readings from a series of thermocouples installed at various heights in the reactor. In the initial phase of the activation procedure it was discovered that the reported average slurry temperature was artificially low since the temperature calculation included a thermocouple which was not fully immersed in the liquid phase of the reactor. When this was corrected the actual activation temperature ramp rate exceeded the maximum recommended ramp rate. The reduction in temperature, reported in the chronology at 0530 on 7/15/88, was a result of cooling the slurry temperature to coincide with the predefined temperature program. There were no other major operational problems, and the NDG readings indicated a flat axial solids profile throughout the activation procedure.

However, the analytical data presented in the Results and Discussion section, indicated that the catalyst was not fully reduced during this activation procedure. The amount of hydrogen that reacted with the copper oxide to convert it to copper metal (zero valence state) was 1.37 scf of hydrogen per pound of catalyst (scf/lb) This is 15% short of the theoretical hydrogen

Figure V.1 NEW EQUIPMENT EVALUATION – SIMPLIFIED FLOWSHEET

Individually verify the performance of each new equipment item over 3–4 weeks.

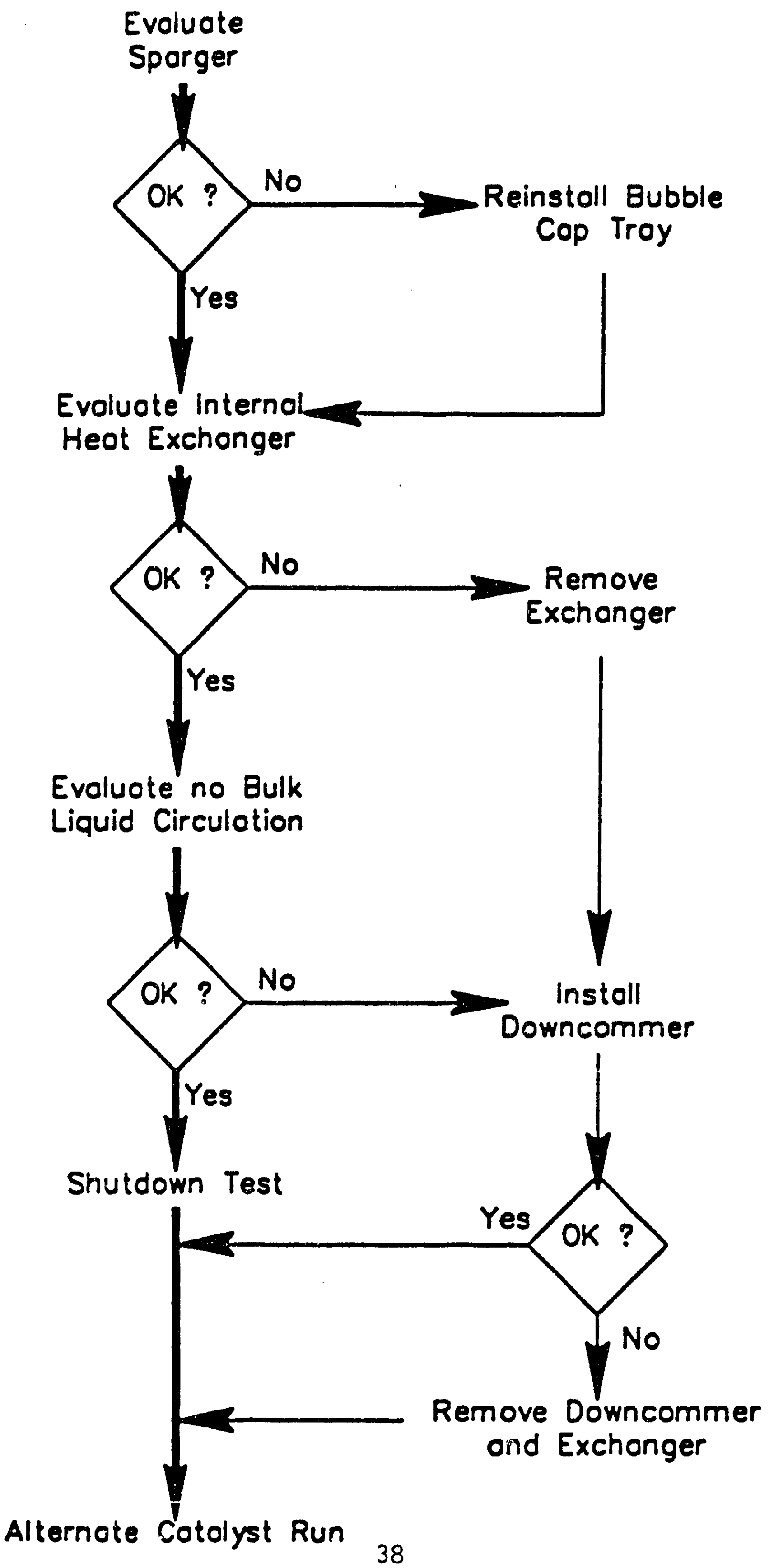


TABLE V.1

CATALYST ACTIVATION RUN ER-04 CHRONOLOGY WITH CATALYST F21/0E75-44

Date	Time	Cumulative Time On Reduction Gas (Hours)	Notes and Observations
7/14/88	0400		Charged 3990 lb of Drakeol-10 to slurry prep tank.
	0620		Pressure-transferred slurry prep tank contents to slurry loop in order to preheat oil to 250°F at a 75°F/hr maximum rate.
	1200		Oil temperature at 250°F. Transferred oil back to slurry prep tank in order to begin catalyst loading.
	1320		Oil in slurry prep tank reduced to 200°F. Loaded 2678 lb of catalyst powder (F21/0E75-44) to slurry prep tank.
	1430		Transfer final 787 lb of Drakeol-10 oil left in 27.10 reactor to slurry prep tank.
	2050		Transferred slurry from slurry prep tank to primary separator. Slurry pump started.
	2340		Reduction gas flow started to reactor.
7/15/88	0200	2 1/3	Conditions for reduction flow steady at 28,000 SCFH with the reactor at 165 psig. Began heating up the slurry from 204°F at an initial rate of 15°F/hr.
	0244	3.07	Hydrogen consumption first detected on gas chromatograph at a slurry temperature of 220°F.
7/15/88	0530	5 5/6	Temperature reduced from 262°F to 248°F to maintain maximum temperature ramp rate.
	1610	16 1/2	Temperature at 391°F. Power loss results in GC shutdown, reactor flow maintained and stable. Beginning of bulk reduction period.
7/16/88	0900	33 1/3	Bulk reduction completed; 27.10 temperature ramped down to 473 F in preparation to introducing syngas.

uptake of 1.62 scf/lb, indicating that the copper catalyst was not fully reduced during this procedure.

C. Methanol Synthesis Operation

After completion of the catalyst activation, the CO-Rich synthesis gas supplies were brought on-line and the PDU began operating under the first condition for Run E-5. The process parameters for the 6 cases of Run E-5 are summarized in Table V-2 and the detailed run chronology is listed in Table V.3. The purpose of the first case was to directly compare the performance of the new reactor in the slurry circulation mode to that of the old reactor system. In the second case, the effect of using the internal heat exchanger for heat removal was examined. The third case was a maximum flow rate test which was originally planned for the internal heat exchanger only. Because of an intentional under-design of the area in order to provide accurate heat transfer data with a 35 wt% slurry, however, it was necessary to use the external heat exchanger as a trim to remove the excessive heat load created by running at maximum rates with a 45 wt% slurry. The final three cases of this run examined the performance of the slurry reactor without the use of the external slurry loop. Overall the PDU accumulated 259.4 hours of methanol synthesis operation during this equipment evaluation Run E-5.

D. Discussion of Results

Figure V.2 shows a comparison of the results of the in-situ catalyst activation Runs ER-3 (prior to Run E-4) and ER-4 (prior to Run E-5). Runs ER-3 and ER-4 were done at nearly identical slurry catalyst concentrations and reduction gas flows. As noted previously, the sharp reduction in temperature which occurred in Run ER-4 at approximately 270°F was due to a miscalculation of the slurry temperature. The most significant difference between the two activation curves is in the total H_2 uptake, which matched autoclave predictions for Run ER-3 but fell short by 15% in Run ER-4. One possible cause for this difference is that the rapid temperature swing at the beginning of activation caused an irreversible change in the catalyst properties which prevented complete activation. A second possibility is that the reduction gas flow was marginally too low and was insufficient to remove the CO_2 and H_2O byproducts from the slurry that were generated during catalyst activation. Avoiding thermal swings and increasing the reduction gas flow while maintaining the H_2 partial pressure is recommended for future activations.

Table V.2 lists the conditions and results for the equipment evaluation Run E-5. Production of methanol was stable in Run E-5A after only 18 hours on-stream with syngas. Methanol productivity, as illustrated in Figure V.3, and gas holdup were higher than previous runs (Run E-4) at high catalyst loadings. The improvement in catalyst methanol productivity over the previous Run E-4, in spite of the poor activation, is a significant result. This demonstrated improvement is attributable to the new gas sparger. However, as expected from the poor activation, methanol productivity was still slightly below the laboratory autoclave curve. Mass transfer limitations may also have been present during this run. Catalyst productivities at these conditions indicated that the performance of the new reactor, with the gas sparger and the internal heat exchanger installed, exceeded that of the old reactor system.

TABLE V.2

CONDITIONS AND RESULTS FOR EQUIPMENT EVALUATION
(RUN E-5)

CO-Rich Feed Gas

Catalyst: F21/0E75-44; Oil: Drakeol-10

CASE:	A	B	C	D	E	F
Balance Period:						
Start Date	18 July	20 July	21 July	23 July	25 July	27 July
Start Time	1400	0100	0600	1100	0500	1600
End Date	19 July	21 July	23 July	25 July	26 July	28 July
End Time	1400	0100	0600	0000	0500	0800
Bal. Hours on Syngas	24	24	33	37	20	16
Cumm. Hours on Syngas	74.0	110.0	147.0	189.0	218.0	236.0
Configuration:						
Heat Exchanger	External	Internal	Ext/Int	Internal	Internal	Internal
Slurry Loop	External	External	External	None	None	None
Reactor Conditions:						
Temperature (/C)	250.4	250.1	250.2	250.2	250.1	250.5
Pressure (psig)	752.8	753.1	752.1	751.6	752.8	754.8
Space Velocity (Sl/hr-kg)	5297	5313	7084	5445	11356	11444
Inlet Gas Velocity (ft/sec)	0.41	0.41	0.55	0.41	0.51	0.51
Gas Holdup (vol%)	23.1	23.3	26.7	27.6	34.0	33.8
Slurry Conc. (wt% ox.)	45.0	44.9	45.9	45.0	34.1	33.9
Catalyst Inventory (kg ox.)	595	592	589	571	339	338
Conversion/Production Results:						
CO Conversion (%)	12.8	12.8	11.6	13.6	11.8	11.2
Methanol in Effluent (mol %)	8.12	8.04	6.79	8.79	7.70	7.37
Methanol Productivity (gmol/hr-kg cat ox)	14.7	15.0	18.0	16.8	30.3	29.6
Productivity as % of Autoclave	81	83	81	91	105	103
Production (TPD)	7.65	7.81	9.19	8.29	8.87	8.61

TABLE V.3

CHRONOLOGY RUN E-5 WITH CATALYST F21/0E75-44

Date	Time	Cumulative Time On Production Gas (Hours)	Notes and Observations
7/16/88	1138	0	Start syngas flow to the 27.10. Begin Run E-05.
	1145	1/6	MeOH concentration in the reactor effluent at 0.058%. First MeOH production of LPIII.
	1205	1/2	Utility oil used to cool the 27.10. Significant reaction had begun.
	1530	3 5/6	Sample from the 22.15 product/oil separator shows 1 small drop of oil in methanol product.
	1600	4 1/3	Slurry sample taken from external slurry loop. TIC-188 set at 270 F to attempt to lower the amount of oil in the product MeOH.
	2130	9 5/6	Slurry sample taken from the external circulating slurry loop.
	2330	11 5/6	TIC-188 set at 260 F to determine how much less oil will make it into the product at the lower temperatures.
7/17/88	0930	21 5/6	The slurry circulation flow was discovered to be running at higher than 300 gpm rates since beginning of run E-05. The circulation rate was lowered to 225 gpm. High liquid circulation rates gave artificially low gas holdup; after lowering flow, saw increase in gas holdup.
	1245	25 1/6	Drained 150 lb oil from 22.16 prior to transferring product methanol from the day tank.
	1400	26 1/3	Pulled a slurry sample from the external slurry loop.
	1505	27 2/5	Power outage to the control room and the computer.
	1700	29 1/3	Power restored to control room and computer restarted. Good data again.
	2300	35 1/3	Draining of the 22.16 revealed no evidence of oil in the product methanol.

TABLE V.3

CHRONOLOGY RUN E-5 WITH CATALYST F21/0E75-44

(continued)

Date	Time	Cumulative Time On Production Gas (Hours)	Notes and Observations
7/18/88	0019	36 2/3	Total power failure for about 2 minutes. HYCO flaring. 10.50 circulation pump not running and feed gas to 27.10 off.
	0027	36 5/6	10.50 circulation pump restarted and flowing at 190 gpm.
	0039	37	Gas flow to the 27.10 restarted.
	0125	37 5/6	HYCO line pressure low having trouble maintaining reactor feed flow.
	0220	38 5/6	HYCO pressure restored flow returning to normal.
	1200	48 3/6	Brief power outage taken to move control room to its own individual circuit.
	1300	49 3/6	10.50 circulation pump has developed a seal oil leak which leaks at a rate of 5 lb/hr.
	1400	50 3/6	Beginning of Case E-5A. Nominal conditions for this case are CO-Rich feed gas, 5,300 Sl/hr-kg cat space velocity, 250 °C, 750 psig, and 45 wt% catalyst. The purpose of this run is to evaluate the new gas sparger.
7/19/88	1400	74 3/6	End of case E-5A. Made 7.65 TPD MeOH and a productivity of 14.7 g-mole/hr-kg or 81% of autoclave.
	1600	76 3/6	Opened the 28.30 and accounted for 1036 pounds of slurry not in the slurry system.
	1500	77 3/6	Switching from external heat exchanger to internal heat exchanger revealed that the utility oil temperature to reactor temperature was approaching design limits at the high weight percent and low space velocity.
7/20/88	0100	87 3/6	Beginning of Case E-5B. Nominal conditions for this case are CO-Rich feed gas, 5,300 Sl/hr-kg cat, 250 °C, 750 psig, and 45 wt% catalyst. The purpose of this run is to study the performance of heat transfer using the internal heat exchanger.

TABLE V.3

CHRONOLOGY RUN E-5 WITH CATALYST F21/0E75-44

(continued)

Date	Time	Cumulative Time On Production Gas (Hours)	Notes and Observations
	1200	98 3/6	27.13 vessel was x-rayed to determine the exact liquid level in the vessel. Found level at 18.7% and LR-203 read 20-21%.
	1400	100 3/6	Heavy rains caused instability in reactor temperature and effluent methanol concentrations. Temperatures were stabilized by 1600 hours.
7/21/88	0100	111 3/6	End of Case E-5B. Production of 7.81 TPD MeOH and a productivity of 15.0 g-mole/hr-kg which is 83 % of autoclave.
	0600	116 3/6	Beginning of E-5C. Nominal conditions for this case are CO-Rich feed gas, 7,000 Sl/hr-kg cat, 250 °C, 750 psig, and 46 wt % catalyst. High space velocity (7000 l/hr-kg) and because of the safety factor on the internal heat exchanger, both internal and external heat exchangers are in service.
	1138	120	Slurry sample taken for determination of catalyst activity.
	1700	127 3/6	Line pressure from HYCO fluctuating wildly, thus feed rate to 27.10 is unstable. The line pressure did not stabilize until 1945, so approximately 3 hours of data does not reflect the actual performance of the PDU at the higher space velocities.
7/22/88	0025	134 5/6	Complete power outage. No flow to the 27.10 of either gas or slurry. GC's down.
	0032	134 7/8	Restarted 10.50 and flow of slurry resumed.
	0040	135	Gas flow restored to 27.10 but MeOH PDU running off HYCO line pressure, decided to back flow rates down to 120,000 SCFH until pressure is restored.
	0515	139 5/6	HYCO still off line and 01.10 suction pressure getting critically low. Started bringing in nitrogen to maintain suction pressure.

TABLE V.3

CHRONOLOGY RUN E-5 WITH CATALYST F21/0E75-44

(continued)

Date	Time	Cumulative Time On Production Gas (Hours)	Notes and Observations
	0600	140 3/6	HYCO reports they are up and running and pressure returning to feed hydrogen and CO. Start of ramping to high space velocity case and backing out nitrogen.
	1330	147 5/6	Restart high flow case E-5C.
7/23/88	0600	164 3/6	End of Case E-5C with a record MeOH production rate of 9.19 TPD and a productivity of 18.0 g-mole/hr-kg which is 79% of autoclave performance.
	0740	166	Begin reactor isolation; 10.50 pump speed slowed down; begin bypassing gas flow through the 27.11 demister and the 27.10 cyclone.
	0845	167	Reactor isolation complete and the level holding at 207 1/2".
	1100	169 3/6	Beginning of Case E-5D, nominal conditions of 5000 space velocity, isolated reactor, 482 F and 750 psig.
	1630	175	First slurry sample taken using the new reactor side arm slurry sampling system. Estimate that we loose approximately 5 lb of slurry in this sampling procedure.
	1740	176	The 27.10 demister pressure drop is trending upward.
7/24/88	0800	190 3/6	Noted a cyclic pattern to the %MeOH in the reactor effluent. Problem was the steam tracing on the sample line was not turned on and at night the line would cool and the MeOH would drop out.
	1230	195	The 27.10 Demister DP up to 4.25 psi. 27.12 liquid examined for solids, found to be fairly clear. Does not appear that catalyst is carrying over.
	1245	195 1/6	The 27.10 demister was back flushed with oil and the DP dropped to 1.9 psi. Cyclone DP dropped from 7.3 to 7.0 psi at the same time.
	1600	199 1/3	Since the demister wash at 1245 hours, the demister DP has climbed to 2.52 psi.

TABLE V.3

CHRONOLOGY RUN E-5 WITH CATALYST F21/0E75-44

(continued)

Date	Time	Cumulative Time On Production Gas (Hours)	Notes and Observations
	2200	203 1/3	DP on the demister dropped quickly from almost 4 psi to 1.9 psi. May have some sort of a break through.
7/25/88	0000	205 1/3	End of Case E-5D, with a MeOH production of 8.3 TPD and a productivity of 16.8 g-mole/hr-kg which is 91% of autoclave.
	0000	205 1/3	Begin dilution of reactor slurry concentration by slowly adding oil from the 27.14 to the 27.10 and allowing the slurry to spill over to the 27.13 through the cracked open V-1493s valve.
	0300	208 1/3	Dilution complete with the final slurry concentration of 33.8 weight percent solids.
	0400	209 1/3	Beginning of run E-5E, with nominal conditions of 10,000 space velocity, 35 weight percent catalyst, isolated reactor, 482 F and 750 psig.
	1000	215 1/3	Lab is seeing free oil in the MeOH sample for the first time since the high flow case. May be entrainment.
7/26/88	0500	234 1/3	Slurry sample taken from the reactor side arm slurry sampling system.
	0500	234 1/3	End of Case E-5E with a production rate of 8.9 TPD and a productivity of 30.3 g-mole/hr-kg which is 105% of autoclave.
	0750	236 1/6	Beginning of 1 hour shutdown period. HV-150-2 closed, no flow to the reactor. NDG scans taken to watch profile and estimate weight percent solids and catalyst loading.
	0850	237 1/6	HV-150-2 opened and flow restored to the reactor.
	1200	241 1/3	Gas holdup and the reactor profile have returned to the pre-shutdown conditions.
	1230	241 5/6	HV-150-2 closed for the 24 hour shut down period. No gas flow to the reactor.

TABLE V.3

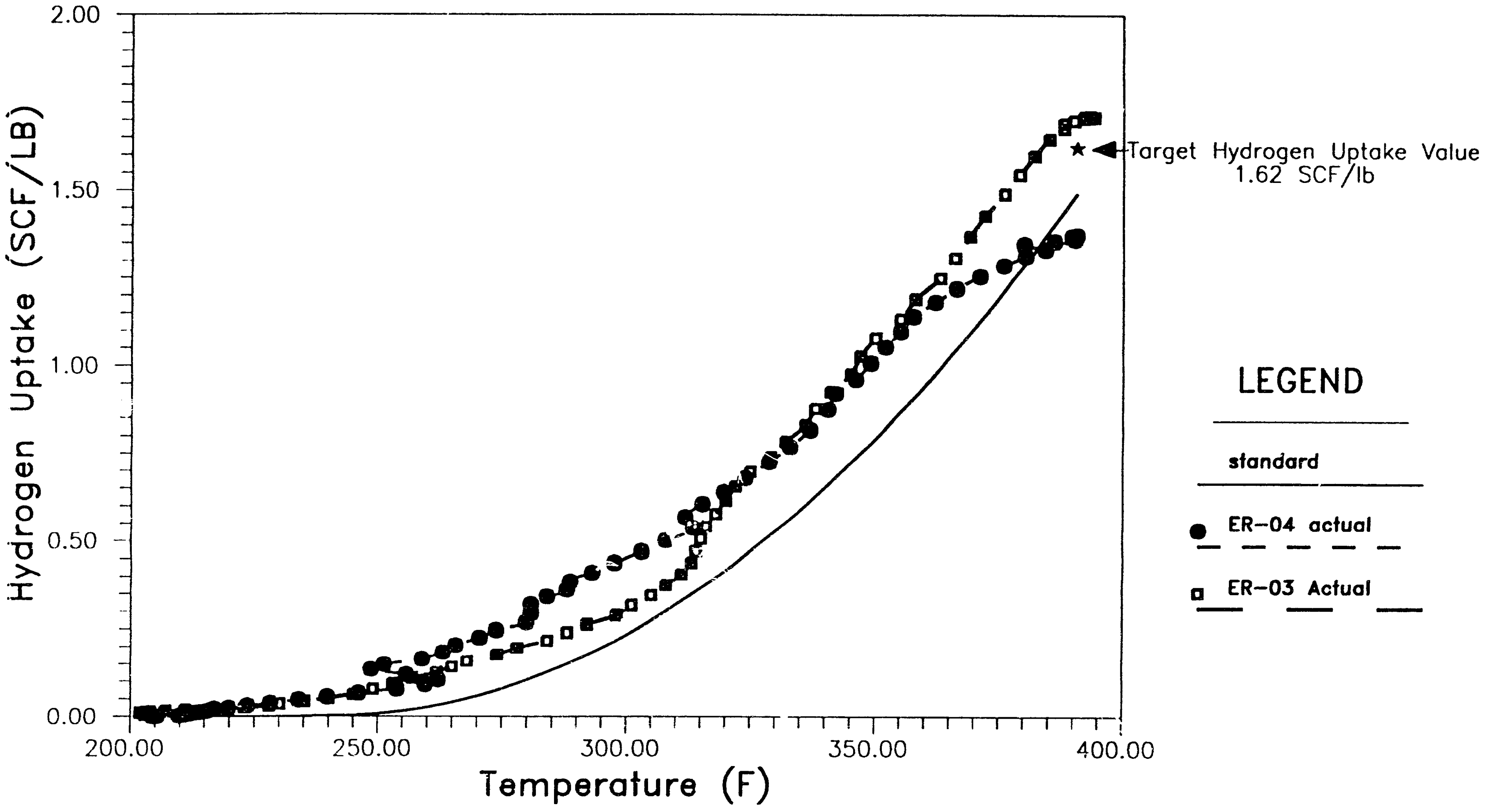
CHRONOLOGY RUN E-5 WITH CATALYST F21/0E75-44

(continued)

Date	Time	Cumulative Time On Production Gas (Hours)	Notes and Observations
7/27/88	1245	266 1/6	Utility oil temperature raised in an attempt to heat up the slurry in the 27.10.
	1308	267 1/2	HV-150-2 opened and flow to the 27.10 resumed. Flow ramped up slowly. Temperature profile in the reactor became uniform almost instantly after the gas flow was resumed.
	1540	270	Lined out in temperature and flow at 482 F and 145,000 SCFH.
	1600	270 1/3	Start recovery case E-6F with the nominal conditions of 34 weight percent solids, 10,000 space velocity, 482 F and 750 psig.
	1800	272 1/3	Severe thunderstorm that lasted until 1930 hours. Reactor temperature unstable thus performance will not be representative during this period of time.
7/28/88	0800	286 1/3	End of recovery case E-6F with a production rate of 8.6 TPD and a productivity of 29.6 g-mole/hr-kg which is 103% of autoclave. Recovery from the 24 hour shut down considered successful.
	1015	288 1/2	Beginning of final shutdown. Total correct on stream time was 259.4 hours. This on stream time excludes power outages and shutdown test where no feed gas was fed to the reactor.

Figure V.2

Reduction Comparison
Hydrogen Uptake VS Temperature



The new internal heat exchanger was evaluated in Runs E-5B and E-5C. As shown in Figure V.3, removing the exothermic heat of reaction with either the external or internal heat exchanger had no observable effect on reactor performance. Again, the reactor was performing closer to the autoclave prediction than in the previous E-4 run. Operation at high space velocities and high methanol production rates was not possible using the internal heat exchanger alone. This was because the exchanger surface area was consciously designed to be low in order to achieve a measurable and accurate temperature difference between the utility oil and the reacting catalyst slurry at low production rates. The performance with high catalyst slurry loadings exceeded expectations, resulting in a high heat load on the internal heat exchanger and a large temperature differential between the slurry and heat transfer oil. Operating with large temperature differences would produce excessive thermal stresses and would exceed the design limits of the internal heat exchanger. Therefore, both the internal and external heat exchangers were used in Run E-5C to remove the heat of reaction. The new reactor system performed well in this mode of operation and daily methanol production ranged from 7.8 to 9.2 TPD, exceeding the previous production rates of 5.4 to 6.4 TPD at equivalent conditions and slurry loadings.

Run E-5D was the first test of the LaPorte reactor system operating without external slurry circulation. A higher methanol productivity was achieved in Run E-5D than in the equivalent Runs E-5A or E-5B using the external slurry loop (see Figure V.3). The increased productivity could be due to higher gas/liquid interfacial area or reduced backmixing in the absence of external liquid circulation. Clearly, in the external loop configuration the catalyst did not contribute significantly to the methanol production while circulating through the slurry loop external to the reactor. Thus, Run E-5D demonstrated that the use of the external slurry loop was not required or desirable for future PDU runs.

Runs E-5E and E-5F were completed at the end of July with a 34 wt% slurry. As shown in Figure V.3, the methanol productivity for Run E-5E improved relative to the previous cases and was slightly greater than autoclave performance. This indicated either improved mixing (reduced backmixing) and/or reduced mass transfer limitations at the more dilute slurry concentration.

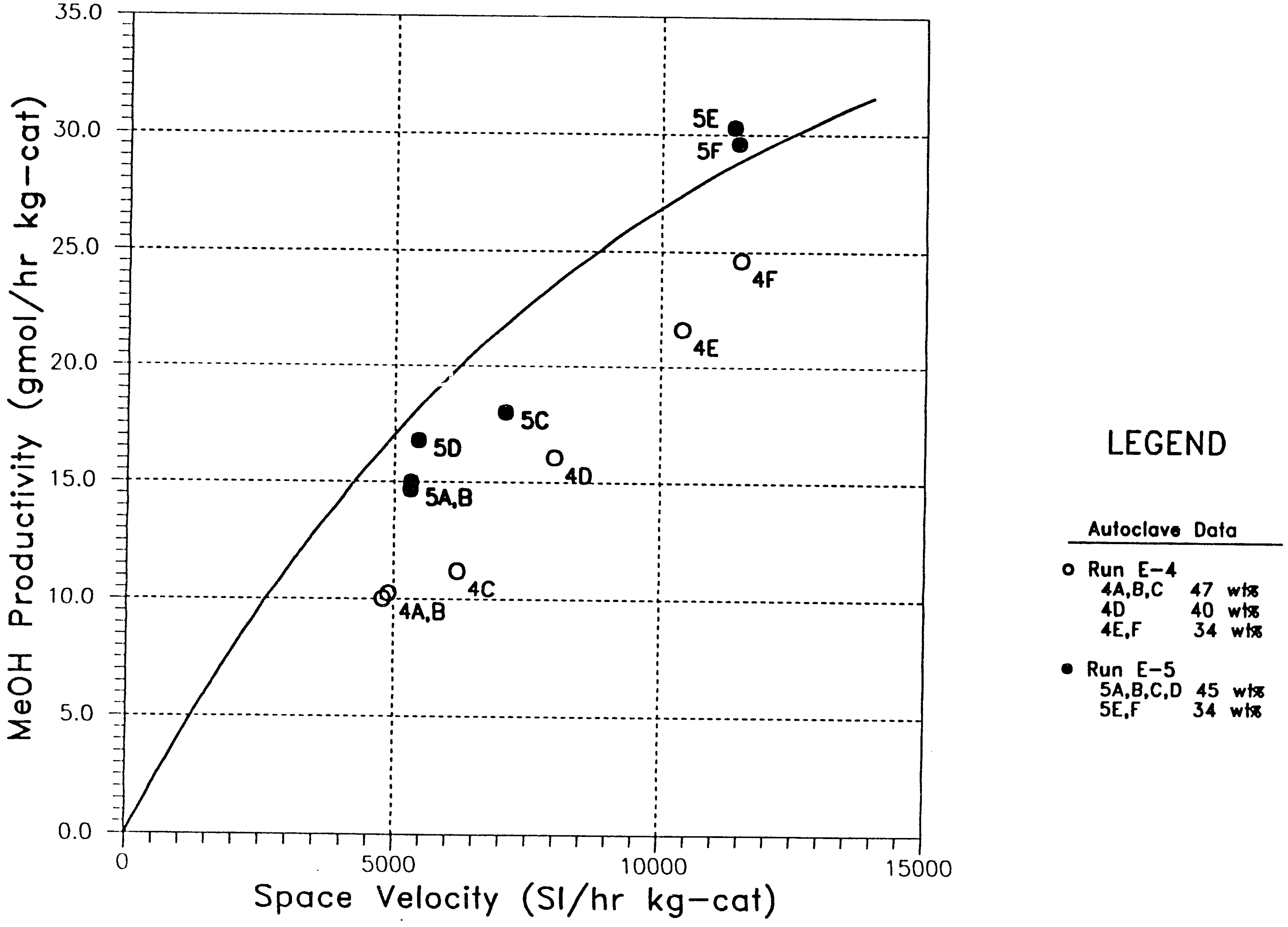
The next objective of the test program was to evaluate the ability of the new reactor system to maintain performance after either a planned or unplanned shutdown. With the elimination of the external circulation the catalyst suspension in the slurry phase is dependant solely on the agitation provided by the upward vapor phase velocity. It was possible that a temporary loss of feed gas would result in the catalyst forming a packed layer in the lower section of the reactor which would plug the inlet gas sparger and/or not refluidize. The test to evaluate this was carried out in two stages. In the first stage the reactor feed was stopped for one hour and then restarted. In the second stage the reactor was isolated for 24 hours and then restarted.

The first one-hour shutdown test was done at the completion of Run E-5E. NDG scans of slurry density as a function of reactor height immediately after the reactor feed flow was stopped, were uniform, indicating that the catalyst was evenly distributed in the slurry. Approximately 10-15 minutes into the test there was a significant density gradient, indicating that the catalyst had begun to settle out of the slurry. This density gradient continued to

Figure V.3

LAPORTE LPMEOH PDU REACTOR PERFORMANCE

Run E-5: CO-Rich Gas, 750 psia, 482°F



increase over the course of the shutdown. The feed flow was slowly reintroduced to the reactor after the one hour shutdown period without incident. The reactor temperature and feed flow were back at pre-shutdown levels within 30 minutes. These conditions were held steady for three hours, during which time the volume fraction gas holdup and the reactor effluent methanol concentration also stabilized at pre-shutdown levels.

The 24-hour shutdown test was begun immediately after it was concluded that the reactor performance had fully recovered from the one- hour test. As in the previous test, the reactor feed flow was stopped and the reactor was isolated and maintained at pressure. Shortly after shutdown the reactor slurry was cooled to 425°F using the internal heat exchanger to minimize continued reactions.

The same catalyst settling behavior was observed as seen in the previous test. The final degassed slurry height was 160 inches from the bottom head of the reactor and the nuclear density gauge was able to measure slurry densities in the region from 68 inches from the bottom head to the top liquid height. Figure V.4 illustrates the stable slurry density profile that was observed 15 hours after the feed gas to the reactor was stopped. There were two distinct regions within the settled slurry, a dense catalyst layer in the bottom 65% of the slurry with a clear oil layer on top. The dense catalyst layer varied from 42 to 45 wt% catalyst as oxide, within the observable region.

The feed flow was reintroduced to the reactor 24 1/2 hours after start of the shutdown period and the reactor conditions were stable within 2 1/2 hours. Run E-5F was done immediately after the shutdown test at the same conditions as the previous Run E-5E. As shown in Figure V.3 the reactor returned smoothly to pre-shutdown production rates.

Productivity levels achieved in Run E-5F demonstrated that the process was resilient in handling deliberate shutdowns of one hour and 24 hour durations. Four unplanned power outages during the month of July also demonstrated the reliability of this process after unscheduled shutdowns.

The external axial cyclone vapor/liquid separator performed well, with a average pressure drop of 7.6 psi. The internal demister pressure drop initially cycled between 2 and 5 psi between backflushings with clean process oil and appeared to be operating well. However, during Case E-5D the pressure drop across the demister dropped quickly from 4 psi to 1.9 psi. This was assumed to be evidence that the demister had become plugged and dislodged, which was confirmed upon post run inspection.

Internal Heat Exchanger Evaluation

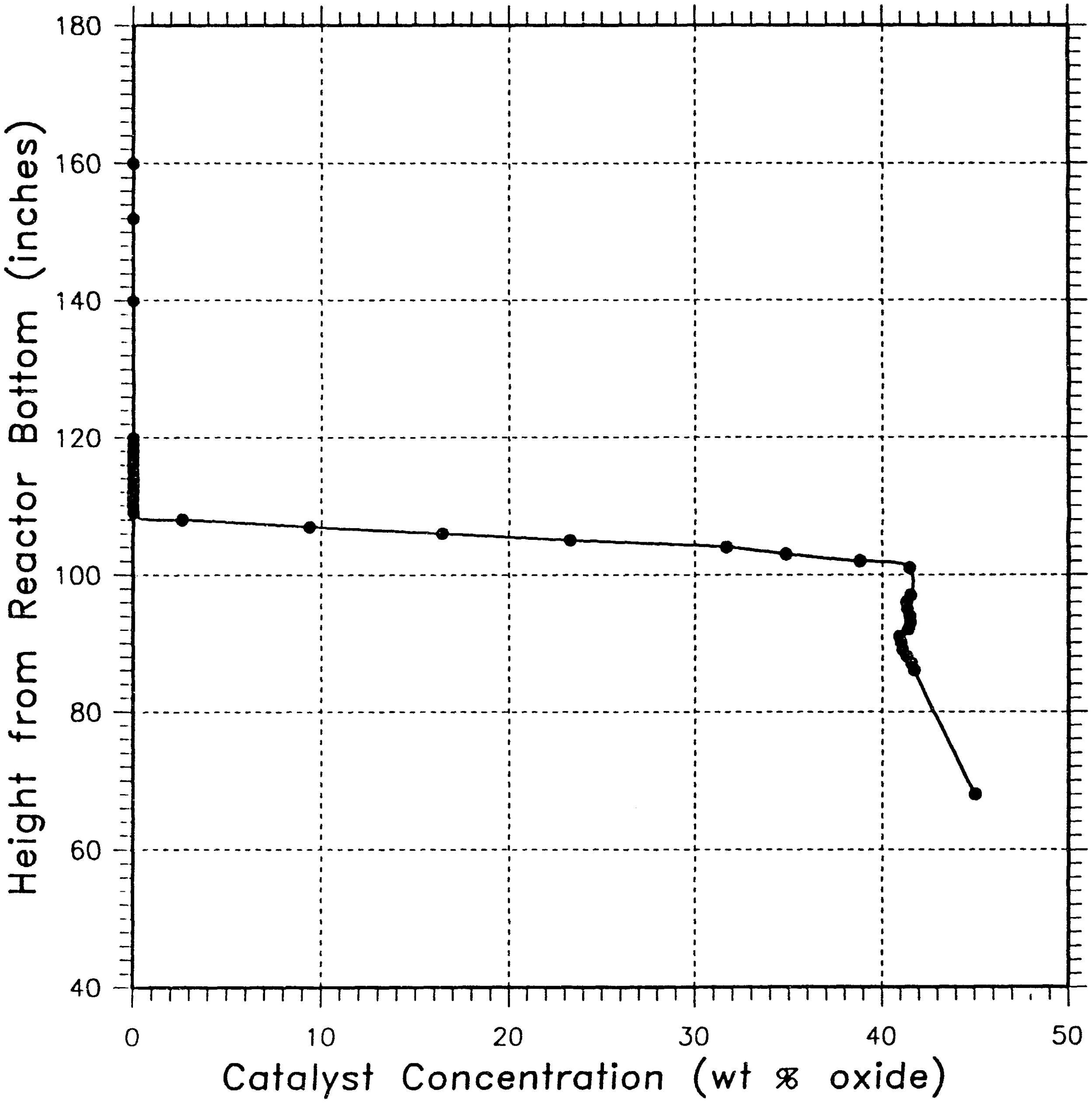
The overall heat transfer coefficient for the internal heat exchanger was calculated from the Run E-5 utility oil data. Hence, the measured overall heat transfer coefficient was based upon the actual utility oil flowrate, temperature rise, the predicted utility oil heat capacity, and the reactor temperature.

A quantitative comparison of the predicted and measured overall coefficients indicated that the average absolute error was 8.6% for the five cases of Run E-5 (see Table V.4). In all cases the uncertainty in the measured

Figure V.4

24 HOUR SHUTDOWN TEST

SETTLED SLURRY SOLIDS DENSITY PROFILE



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

TABLE V.4

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

Case	E5B	E5C	E5D	E5E	E5F
Catalyst Conc. (wt%)	44.9	45.9	45.0	34.1	33.9
Overall Coefficient					
Predicted	94.3	43.8	92.1	95.5	96.3
Measured	74.2	42.0	79.1	93.5	97.8
Percent Error	-21.3	-4.1	-14.1	-2.1	1.6
Slurry Side Coefficients					
Predicted	295.5	320.5	294.8	303.1	303.0
Measured	159.7	245.5	193.3	284.4	317.6
Percent Error	-46.0	-23.4	-34.4	-6.2	4.8

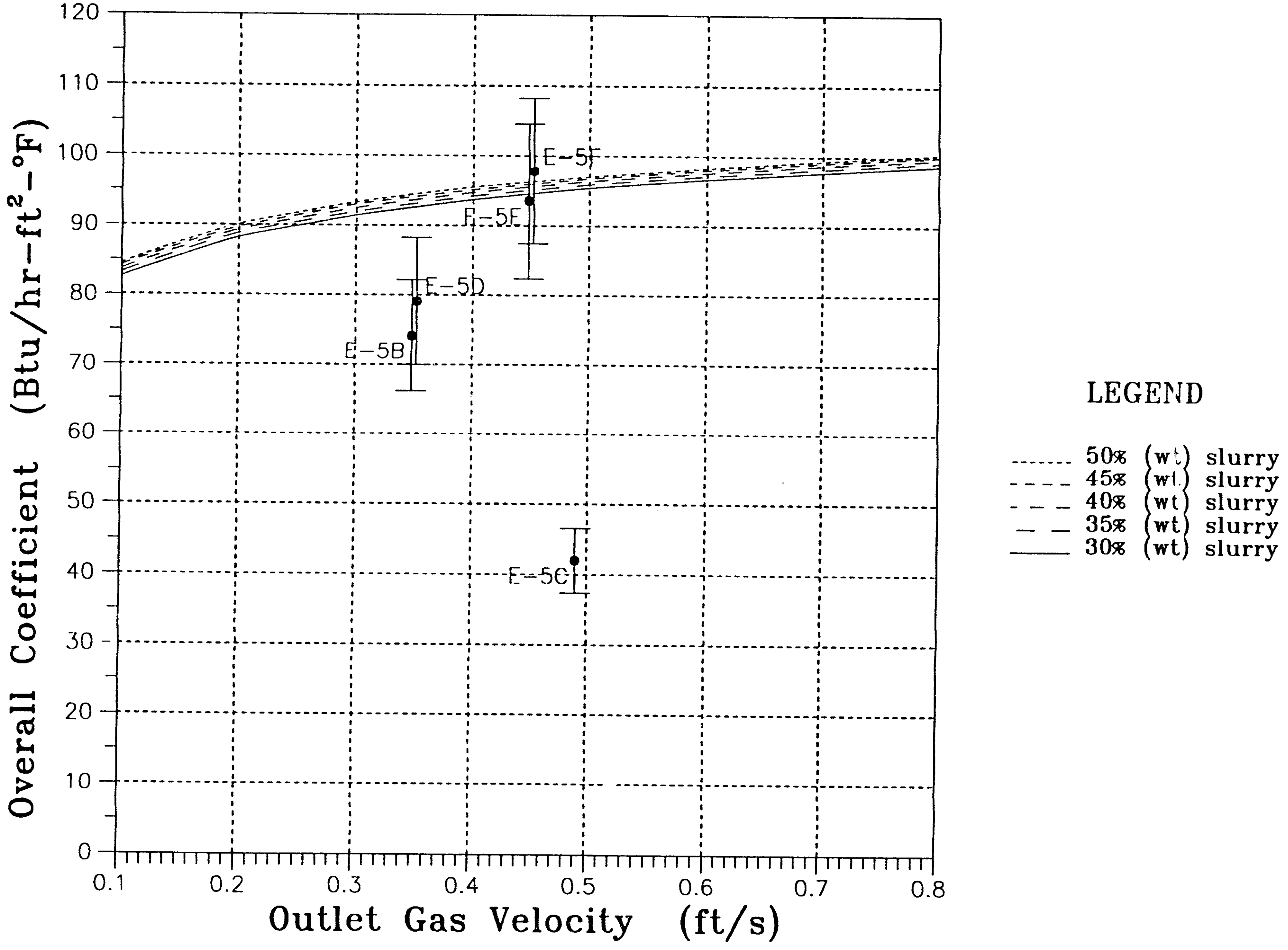
These uncertainties were based on generously assumed uncertainties in the physical readings and properties of 0.5% in the heat exchanger area, 5.0% in the utility oil heat capacity, 10.0% in the utility oil flowrate, 1.0% in both the utility oil temperature change and the log mean temperature across the heat exchanger, and 15.0% in the predicted internal tube-side heat transfer coefficient. The typical oil flowrate averaged 156 gpm and the slurry to utility oil temperature difference averaged 34 to 79°F.

When the predicted overall heat transfer coefficients were plotted versus the superficial gas velocity, a narrow band of curves was produced (Figure V.5). These curves were based upon the average conditions of the five cases; Case C conditions were much different. Using only slurries of 30 to 50 wt% oxide, the predicted coefficients ranged from 82 to 85 Btu/hr-ft^2-°F at 0.10 ft/sec, to 98 to 101 Btu/hr-ft^2-°F at 0.80 ft/sec. Cases E-5E and E-5F were both just outside the band of predicted values. The predicted band was obviously within the range of uncertainty for these cases. However, Cases B, C, and D were further from the predicted values and were not correct even within their ranges of uncertainty.

Considering the physical setup of the reactor, Cases B and C would be expected to be less accurate due to the effect of the external oil circulation on heat transfer. Additionally, Case C involved the use of both the internal and external slurry heat exchanger, thereby increasing the error, since the utility oil flowrate through the exchanger was much lower. However, Cases D, E, and F should have been accurate since they had no external oil slurry circulation flow and relied entirely on the internal heat exchanger. Cases E and F were both within 3% of predicted, but Case D had an overall coefficient which was 14% low for unknown reasons.

FIGURE V.5

OVERALL COEFFICIENT vs. SUPERFICIAL GAS VELOCITY
Run E-5, 27.10B Internal Heat Exchanger



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

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

$$\text{where } St = h_o/(rho*c_p*u_g)$$

The slope of the line (beta) predicted by the Deckwer correlation was 0.10; however, except for Case E-5F, the data from Run E-5 was beneath this line (Figure V.6). This result indicates that the shell-side coefficient is being overestimated. The scatter of data was greater than that found by Deckwer in his experiments with organic slurries.

Analytical Results and Activity Testing

As stated before, the activation period cumulative H_2 and CO consumption curves indicate that the catalyst was only 85% reduced. Average autoclave performance on samples of freshly reduced catalyst indicated only 87% activation as shown below in Table V.5 and in Figure V.7.

TABLE V.5

AUTOCLAVE TESTS OF POST-REDUCTION CATALYST SAMPLES

Sample #	Space Velocity (Sl/hr-kg cat)	CO Conversion (%)	Methanol Productivity (gmol/hr-kg cat)	Approach to Autoclave Curve (%)
ER-4-EOR-A-1	5,000	13.4	14.5	83.8
ER-4-EOR-A-2	10,200	10.2	24.0	88.0
ER-4-EOR-B-1	5,200	13.2	15.5	87.0
ER-4-EOR-B-2	9,600	11.3	24.0	90.8

Conditions: CO-Rich Gas, 765 psia, 250°C (482°F)

The crystallite size of the catalyst grew only slightly over the course of the run, the change being generally within the accuracy of the measurement techniques. Table V.6 summarizes the crystallite size and surface area data available from Run E-5.

Figure V.6

DECKWER CORRELATION

27.10B Shell-side Heat Transfer Coefficient, Run E-5

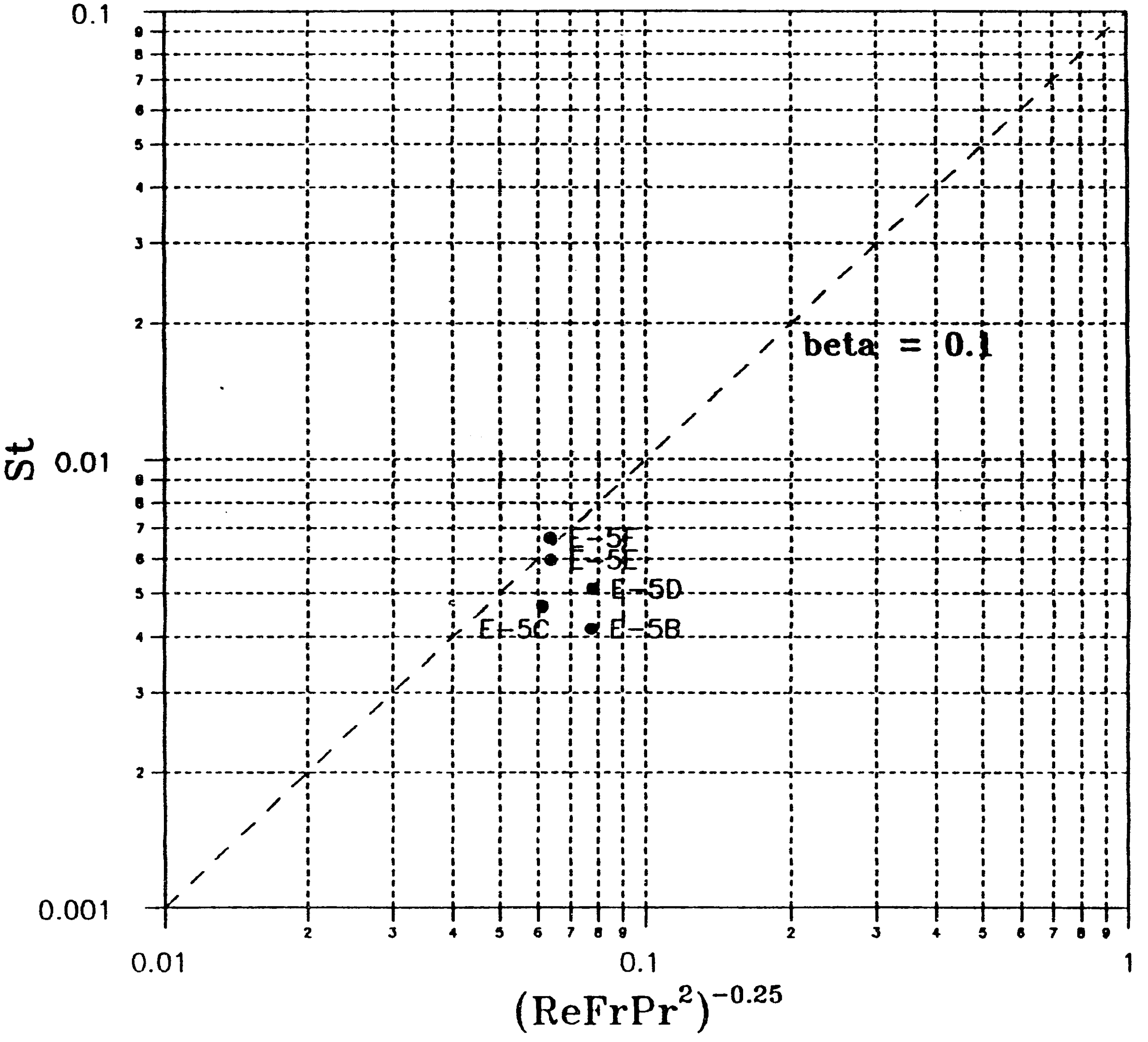


Figure V.7

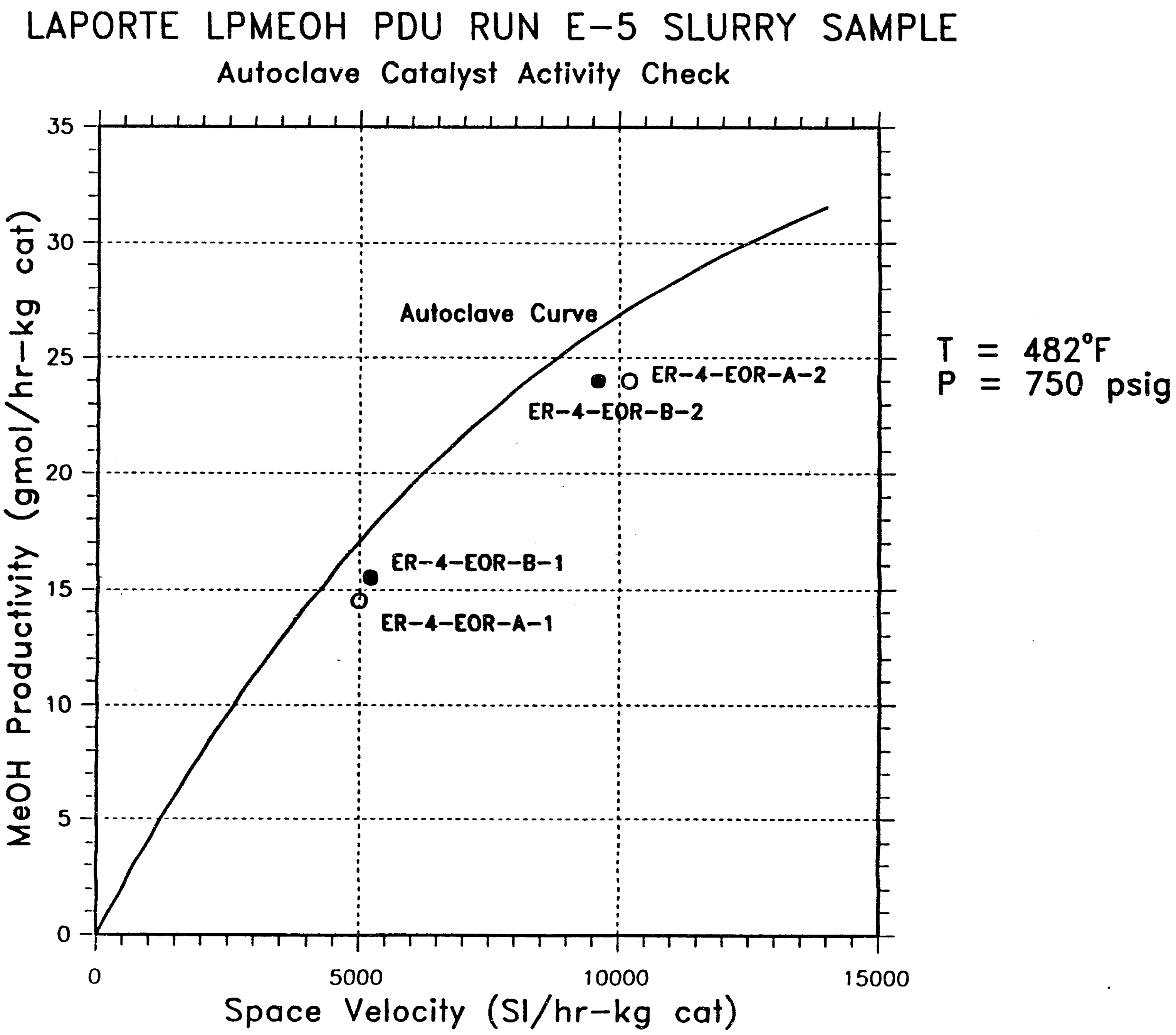

LAPORTE LPMEOH PDU RUN E-5 SLURRY SAMPLE
Autoclave Catalyst Activity Check
MeOH Productivity (gmol/hr-kg cat)
35
30
25
20
15
10
5
0
0
5000
10000
15000
Space Velocity (Sl/hr-kg cat)
Autoclave Curve
ER-4-EOR-A-2
ER-4-EOR-B-2
ER-4-EOR-B-1
ER-4-EOR-A-1
T = 482°F
P = 750 psig

TABLE V.6

CATALYST ANALYSIS FOR RUN E-5

Sample #	Hours on Syngas	Crystallite Size by XRD (angstroms) Cu	ZnO	BET Surface Area (m^2/gm)
ER4-05	0.0	83.1	70.4	
ER4-06B	0.0	105	79.6	102.9
E5-01	4.4	109	79.1	
E5-02	9.9	119	73.0	
E5-03	24.4	109	81.8	
E5-04	120.0	135	83.5	
E5-05	172.9	118	86.2	85.2

Product Methanol Composition

Typical product methanol composition is shown for Run E-5 in Table V.7. Methanol purity averaged 96 wt%. The repiping of the feed/product heat exchanger from concurrent to countercurrent allowed the intermediate oil separator to be operated at 270°F instead of the 350°F used in the previous runs, thus allowing more oil to be removed from the reactor effluent gas stream. The presence of an oil phase seen in the methanol in previous runs was eliminated, and the weight percent of dissolved oil methanol was reduced from the 1.3 wt% to 0.6 wt%.

During Case E of this run free oil was again found in the methanol, even though the oil dissolved in the methanol was only 0.55 wt%. This indicated the possibility of oil droplet carryover from the 27.14 Intermediate Oil Separator. As a result, it was recommended that a demister be installed in the top of the 27.14 vessel to prevent future oil droplet carryover.

Carbonyls

Throughout Run E-5 the production of catalyst poisons, particularly iron and nickel carbonyls, were monitored. Table V.8 shows the levels of $Fe(CO)_5$ and $Ni(CO)_4$ in parts per billion in the reactor feed gas and in the intermediate vapor/liquid separator over the entire Run E-5. From available laboratory and literature data, the low carbonyl levels found indicate that the problem of the formation of catalyst poisons has been eliminated with the changing of the material of construction.

Alternate Oil Evaluation

The observable hydrodynamic performance during the gas holdup tests, the catalyst activation and the methanol synthesis run was nearly identical to the previous results. On this basis, the Drakeol-10 oil appeared to perform as an acceptable substitute for the Freezene-100 oil previously used in the catalyst

TABLE V.7
LaPorte LPMeOH PDU
Typical Methanol Product Compositions for Run E-5

CASE	E-5A	E-5B	E-5C	E-5D	E-5E	E-5F
GAS TYPE	CO-Rich	CO-Rich	CO-Rich	CO-Rich	CO-Rich	CO-Rich
SLURRY CONC. (WT% OX.)	45.0	44.9	45.9	45.0	34.1	33.9
SPACE VELOCITY(Sl/hr-kg)	5,297	5,313	7,084	5,445	11,356	11,444
METHANOL PRODUCT COMPOSITION:						
WT % OIL	0.660	0.670	0.627	0.527	0.550	0.564
WT % WATER	0.702	0.700	0.734	0.446	0.683	0.697
WT % METHANOL	94.540	94.400	95.610	96.350	96.400	96.770
WT % METHYL FORMATE	0.700	0.830	0.680	0.704	0.745	0.786
WT % ETHANOL	1.370	1.425	1.025	0.843	0.455	0.552
WT % ISO-PROPANOL	0.030	0.025	0.020	0.020	0.012	0.015
WT % METHYL ACETATE	0.370	0.417	0.240	0.251	0.083	0.103
WT % N-PROPANOL	0.698	0.596	0.413	0.329	0.163	0.207
WT % SEC-BUTANOL	0.070	0.083	0.070	0.050	0.040	0.042
WT % ETHYL ACETATE	0.024	0.024	0.017	0.020	0.023	0.000
WT % ISOBUTANOL	0.120	0.117	0.080	0.054	0.024	0.040
WT % N-BUTANOL	0.290	0.283	0.200	0.163	0.700	0.110
WT % T-AMYL ALCOHOL	0.030	0.030	0.020	0.016	0.022	0.000
WT % 2&3-PENTANOL	0.040	0.061	0.030	0.024	0.000	0.000
WT % ISOPENTANOL	0.110	0.099	0.066	0.047	0.026	0.030
WT % 1-PENTANOL	0.170	0.170	0.123	0.102	0.052	0.060
WT % ETHYL BUTYRATE	0.080	0.080	0.055	0.045	0.025	0.030
MOL WT OF PRODUCT(lb/mol)	32.990	32.670	32.460	32.580	32.850	32.790

TABLE V.8

RUN E-5 CARBONYL CONCENTRATIONS

Time On Syngas (hr)	27.10 Feed Gas Concentration $Fe(CO)_5$ (ppb)		21.10 Off Gas Concentration $Fe(CO)_5$ (ppb)	
		$Ni(CO)_4$ (ppb)		$Ni(CO)_4$ (ppb)
6.23			0.5	8.4
6.37			0.4	6.3
6.60			0.3	6.1
6.72			0.4	5.6
9.48	2.1	4.9		
9.58	2.0	2.1		
9.67	2.1	3.0		
9.76	1.6	5.1		
20.47			0.3	6.7
20.62			0.3	6.0
21.15			0.3	5.1
21.50	1.8	2.5		
21.92	1.8	2.0		
22.10			0.3	4.1
22.20			0.4	4.4
22.38	1.7	1.3		
22.50	1.7	1.0		
23.08	2.0	4.0		
23.27	1.9	3.8		
23.35			0.5	8.2
23.45			0.5	7.4
31.13			0.5	7.2
31.22			0.5	7.5
31.37	1.4	2.9		
31.45	1.6	2.7		
45.95	1.4	2.4		
46.05	1.5	1.0		
46.18			0.5	6.0
46.28			0.5	7.0
50.82			0.7	5.3
50.92			0.7	4.9
51.37	1.5	2.3		
51.47	1.5	4.1		
51.60	1.5	1.2		
105.23	1.0	7.3		
105.32	0.9	2.6		
105.42			0.9	2.3
105.52			0.6	2.9
105.65	1.1	2.2		
116.65	1.0	8.5		
116.80	0.8	4.6		
116.90			0.5	5.1
116.98			0.4	4.7
117.08	0.9	3.4		

TABLE V.8

RUN E-5 CARBONYL CONCENTRATIONS

(continued)

	27.10 Feed Gas Concentration		21.10 Off Gas Concentration	
Time On Syngas (hr)	$Fe(CO)_5$ (ppb)	$Ni(CO)_4$ (ppb)	$Fe(CO)_5$ (ppb)	$Ni(CO)_4$ (ppb)
127.82	0.8	3.8		
127.98			0.6	
128.07			0.4	3.0
128.19			0.3	3.0
128.32	0.6	0.6		
128.43	0.6	0.9		
128.63	0.9	2.8		
141.57	0.7	3.6		
142.05	1.0	5.3		
142.24	1.2	5.8		
142.48			0.4	3.1
142.63			0.5	4.2
148.30	1.0	11.4		
148.68	0.9	5.7		
148.98			0.5	4.2
149.08			0.5	5.1
149.22	1.0	3.0		
165.08	1.1	7.1		
165.18	0.9	3.2		
165.27	1.0	3.9		
165.37			0.4	3.9
165.92			0.2	2.7
166.02			0.4	3.9
175.28	0.5	0.3		
175.72	0.7	0.4		
175.83			0.1	0.4
175.92			0.1	0.4
195.83	0.9	4.1		
196.03	0.8	2.3		
196.15	0.8	1.6		
196.22		1.4		
196.65			0.4	3.0
196.78			0.5	3.2
197.03			0.4	3.0
197.20			0.4	3.1
213.65	0.7	3.3		
213.77	0.8	4.0		
213.85	0.8	2.8		
213.95	0.7	2.1		
214.05			0.3	2.9
214.13			0.3	2.9
214.25			0.3	3.2
214.35			0.3	4.0
214.92			0.4	2.4

slurry. Either oil would be an acceptable candidate for future commercialization. The physical properties of both the Freezene-100 and Drakeol-10 oils are listed in Table V.9.

Post Run Inspection

Run E-5 was concluded on July 28, 1988 after approximately 12 days of operation. During the post run inspection the process equipment was opened and found to be in good condition. There was no evidence of catalyst blocking or plugging. This was a significant improvement over the previous 45 wt% run which showed a substantial catalyst build-up on the bubble cap tray. All other major pieces of equipment were also found to be much cleaner than in previous runs.

The demister was the only piece of equipment not in good shape. It was dislodged and pushed past the top support bracket. The demister was also plugged with about 25 pounds of slurried catalyst.

During this inspection period, the internal heat exchanger was equipped with an expansion loop to relieve thermal stresses caused by high heat loads experienced during periods of high methanol production. This modification was made so that operation at high catalyst loadings and high gas velocities would be possible. In addition, the 27.14 Oil Separator was retrofit with a demister to eliminate the possibility of oil carryover into the product methanol.

Table V.9

Properties of Oils Used for Catalyst Slurry

	Freezene-100	Drakeol-10
Average Mol. Wt.	340	366
Distillation by ASTM D1160, (°F)		
Initial Boiling Point	505	541
10%	603	667
50%	696	765
90%	802	898
End Point	883	
Hydocarbon Type		
% Paraffinic	100	65
% Naphthenic	0	35
Specific Gravity at 77°F	0.868	0.849
Surface Tension at 77°C, (lb/ft)	0.0021	0.0021
Viscosity at 77°F, (lb/ft-hr)	82	76
Pour Point, °F	-35	19
Flash Point, °F	>230	365

VI. CONCLUSIONS AND RECOMMENDATIONS

A detailed Process Engineering Study, Two-Phase Gas Holdup Study, and Equipment Evaluation Run E-5 were performed under Tasks 2.1 and 2.2 of the new modification/operating program. The process simplifications to the slurry loop, which were identified and examined in the Process Engineering Study, resulted in a new flexible process design of the LaPorte PDU. The aim of the process simplifications was the elimination of the entire loop (vapor/slurry separation vessel, slurry circulating pump, and external heat exchanger) from outside the reactor. The subsequent Two-Phase Gas Holdup studies and Equipment Evaluation Run E-5 demonstrated the improvements to the PDU operation attributable to the implemented process simplifications. The major accomplishments of these tasks are summarized as follows:

- The performance of the new reactor with the new sparger and the new internal heat exchanger exceeds the performance of the old reactor.
- There is sufficient slurry circulation and turbulence induced by the high synthesis gas velocities to suspend the catalyst particles homogeneously within the slurry without bulk slurry circulation.
- The required internal heat transfer area to remove the heat of reaction is small enough such that a sufficient heat exchanger area can be installed with little effect on reactor bubble column hydrodynamics.
- Reactor effluent vapor/liquid disengagement can be achieved with a reactor freeboard section in combination with an external cyclone. The short operating period limited a thorough cyclone evaluation.
- The repiping of the feed/product heat exchanger from cocurrent to countercurrent allowed the intermediate oil separator temperature to be reduced from 350°F to 270°F, thus allowing more oil to be removed from the reactor effluent gas stream. The oil phase seen in the methanol product in previous runs was eliminated and the weight percent oil in the methanol product was reduced from the 1.3 wt% seen in previous runs to 0.6 wt%.
- The new slurrying oil, Drakeol-10, recommended from the laboratory program was acceptable for the PDU operation.
- Catalyst powder was successfully activated with the in-situ activation technique at 45 wt% slurry loading.
- From available laboratory and literature data, the low carbonyl levels found indicate the problem of the formation of these catalyst poisons has been eliminated with the changing of the materials of construction.
- The ability to maintain catalyst activity and the resilience of the newly simplified process after extended shutdown periods in Run E-5 were demonstrated. Four unplanned power outages during the month of July also demonstrated the reliability of this process after unscheduled shutdowns.

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