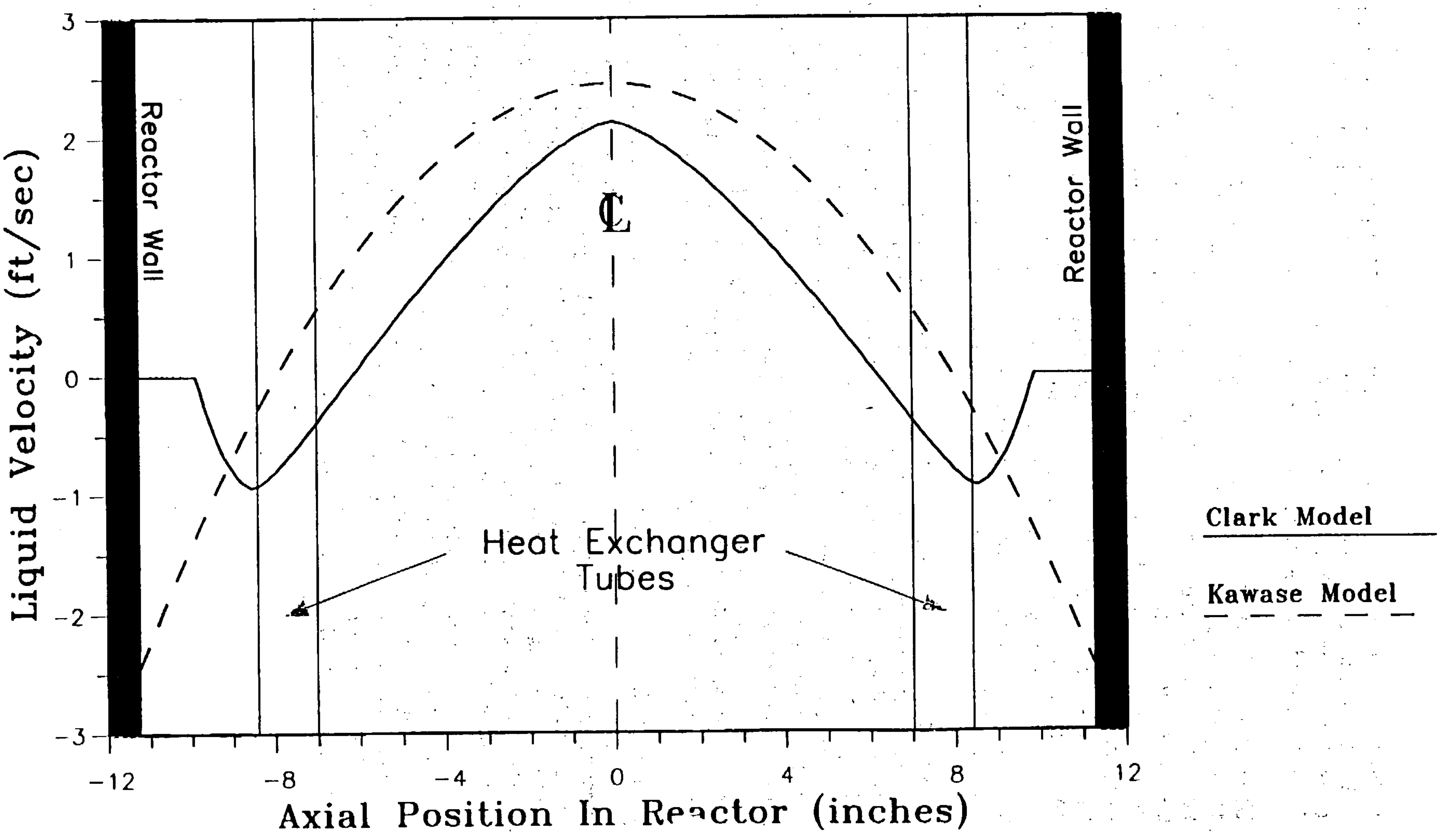
Figure III.3

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

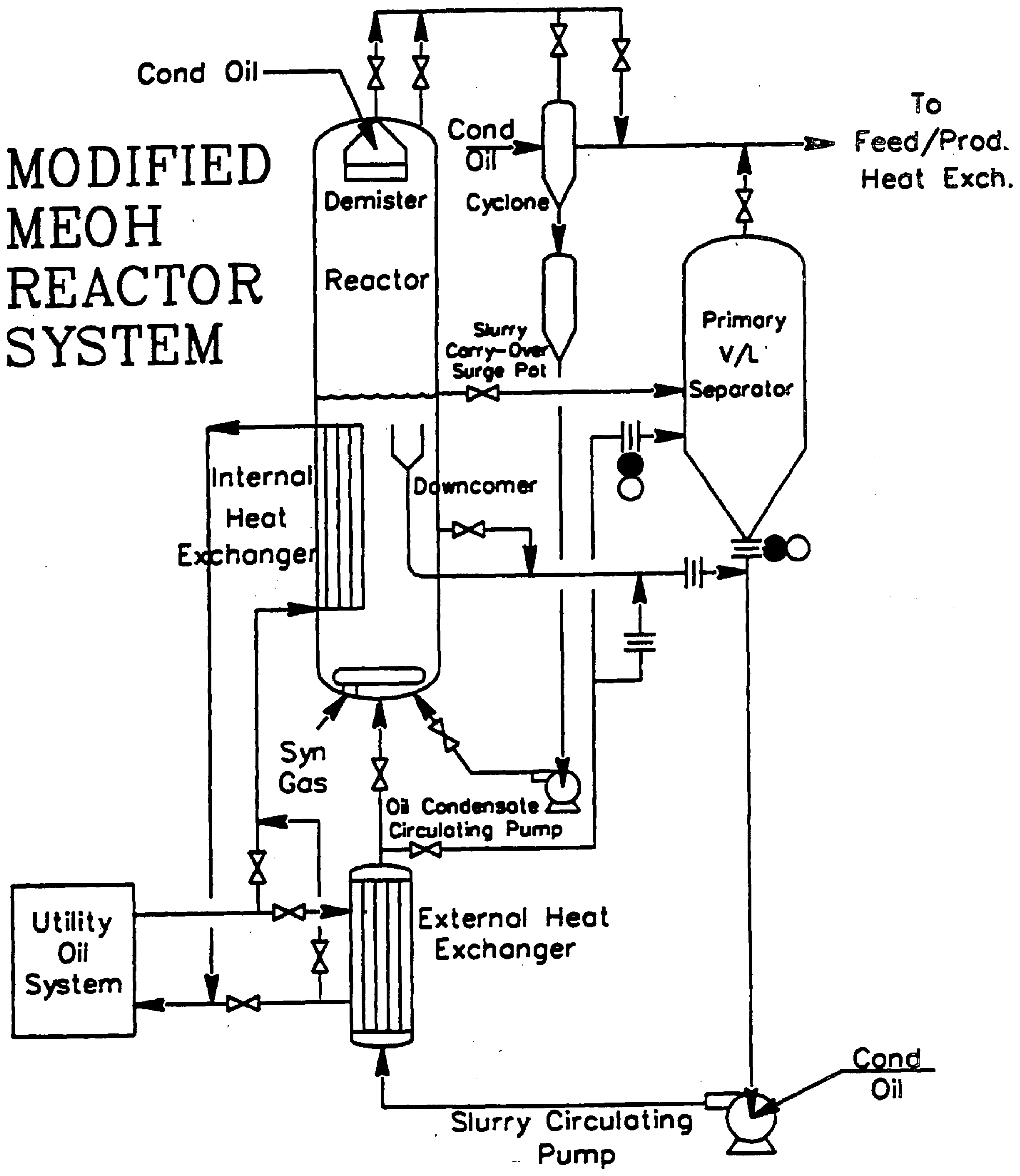
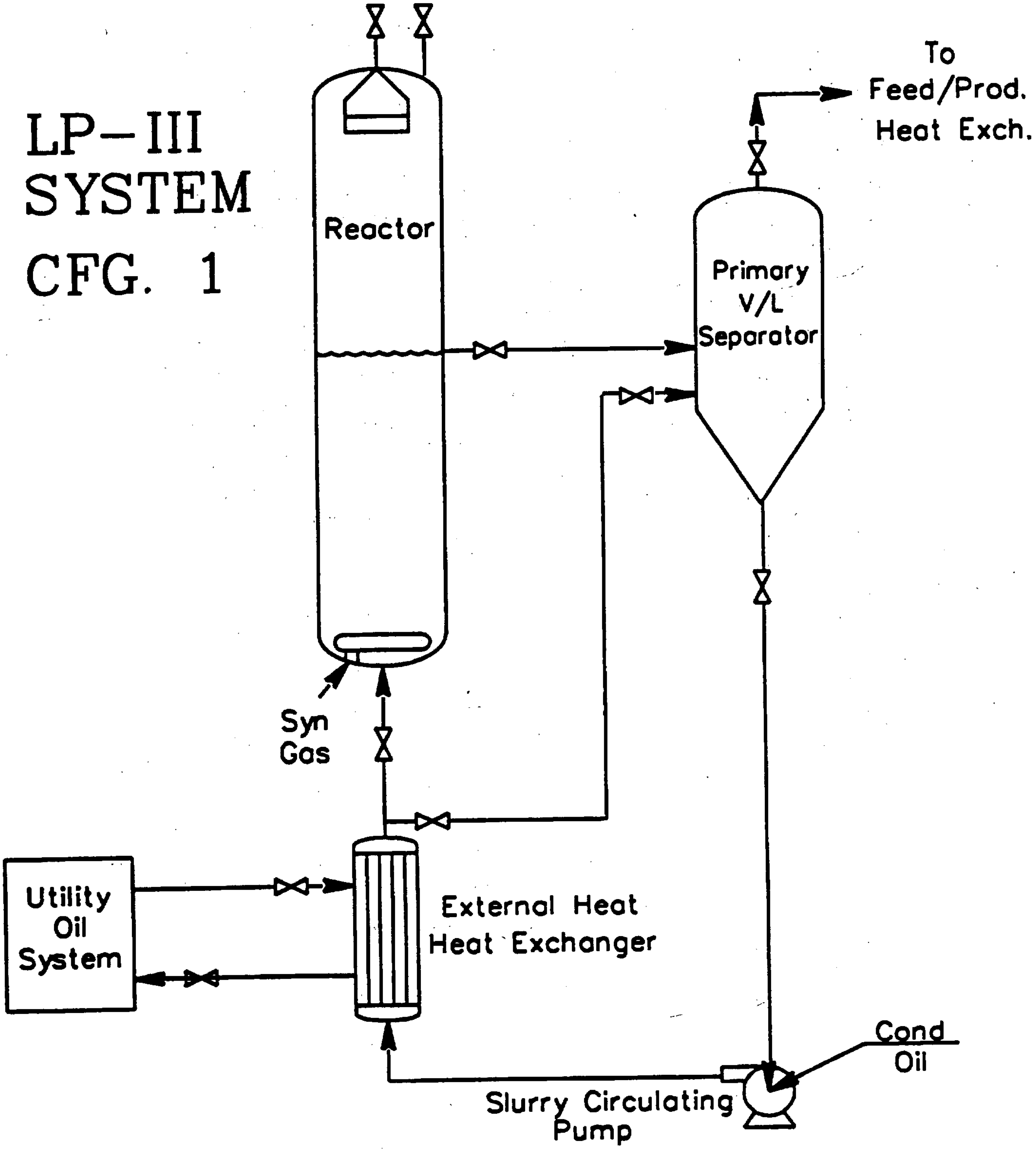

MODIFIED MEOH REACTOR SYSTEM
Cond Oil
Demister
Reactor
Cond Oil
Cyclone
To Feed/Prod. Heat Exch.
Slurry Carry-Over Surge Pot
Primary V/L Separator
Internal Heat Exchanger
Downcomer
Syn Gas
Oil Condensate Circulating Pump
Utility Oil System
External Heat Exchanger
Slurry Circulating Pump
Cond Oil

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

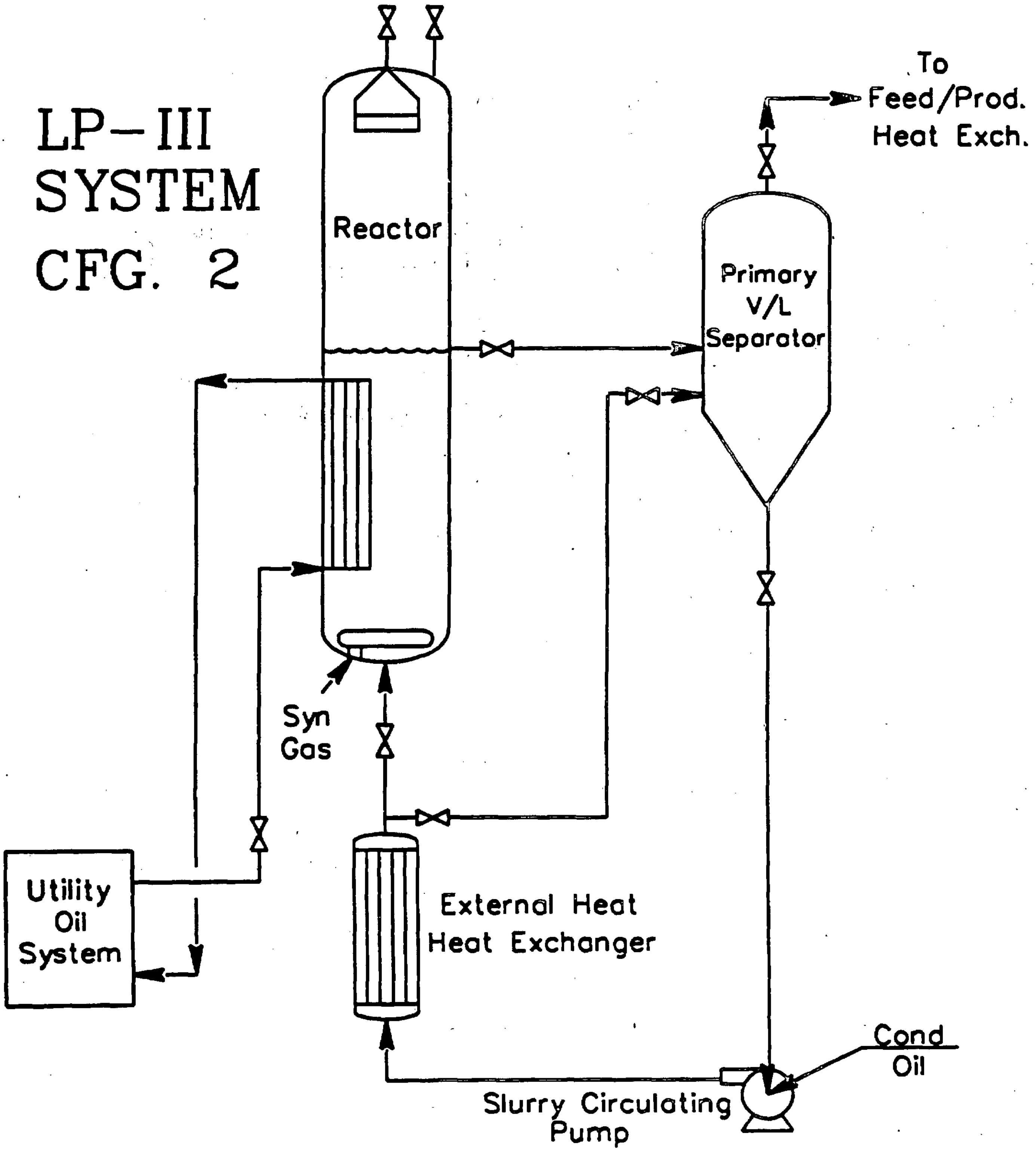

LP-III
SYSTEM
CFG. 2
Reactor
To
Feed/Prod.
Heat Exch.
Primary
V/L
Separator
Syn
Gas
Utility
Oil
System
External Heat
Heat Exchanger
Cond
Oil
Slurry Circulating
Pump

Figure III.7

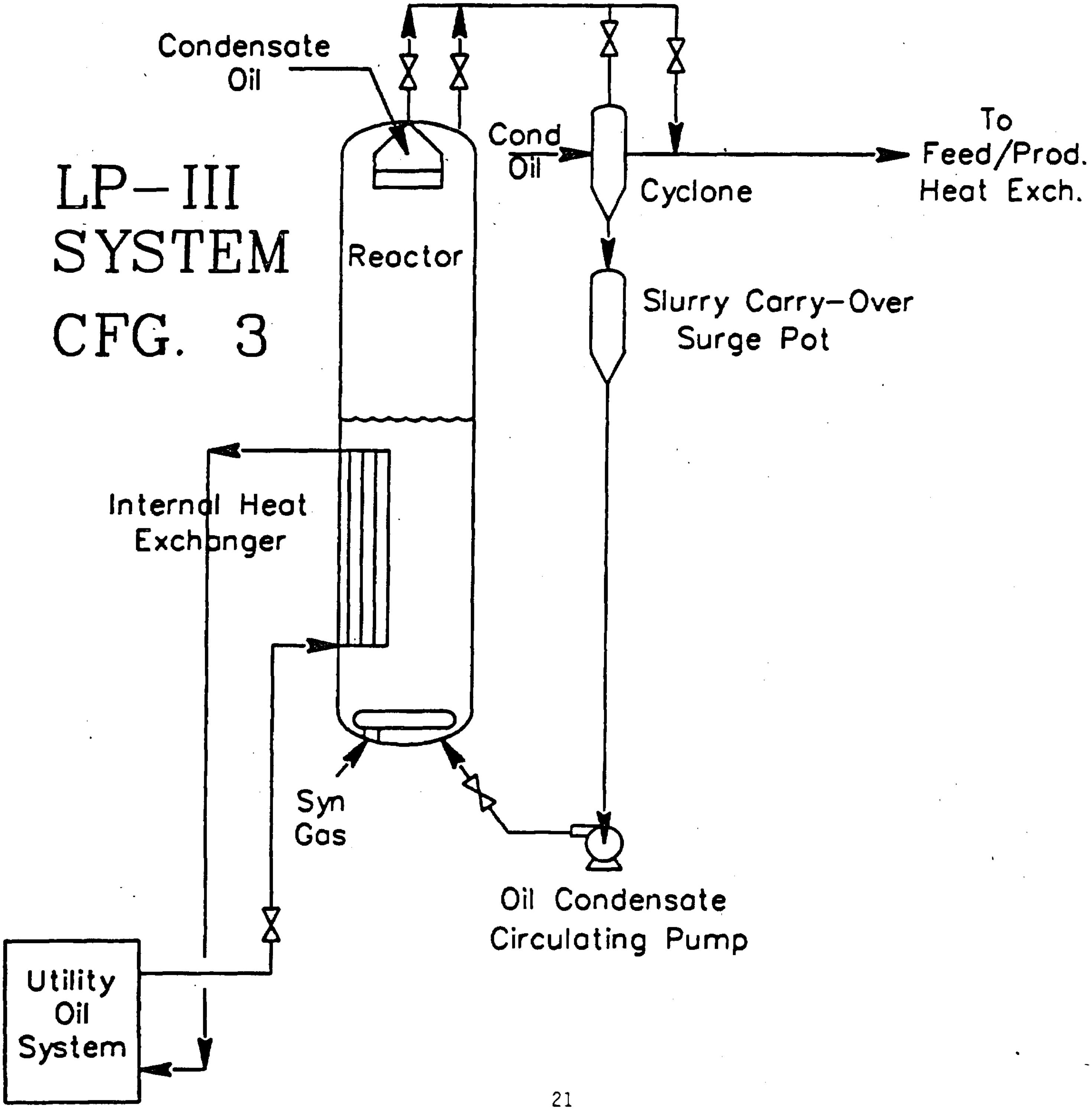

Condensate Oil
LP-III SYSTEM CFG. 3
Reactor
Cond Oil
Cyclone
To Feed/Prod. Heat Exch.
Slurry Carry-Over Surge Pot
Internal Heat Exchanger
Syn Gas
Oil Condensate Circulating Pump
Utility Oil System

Figure III.8

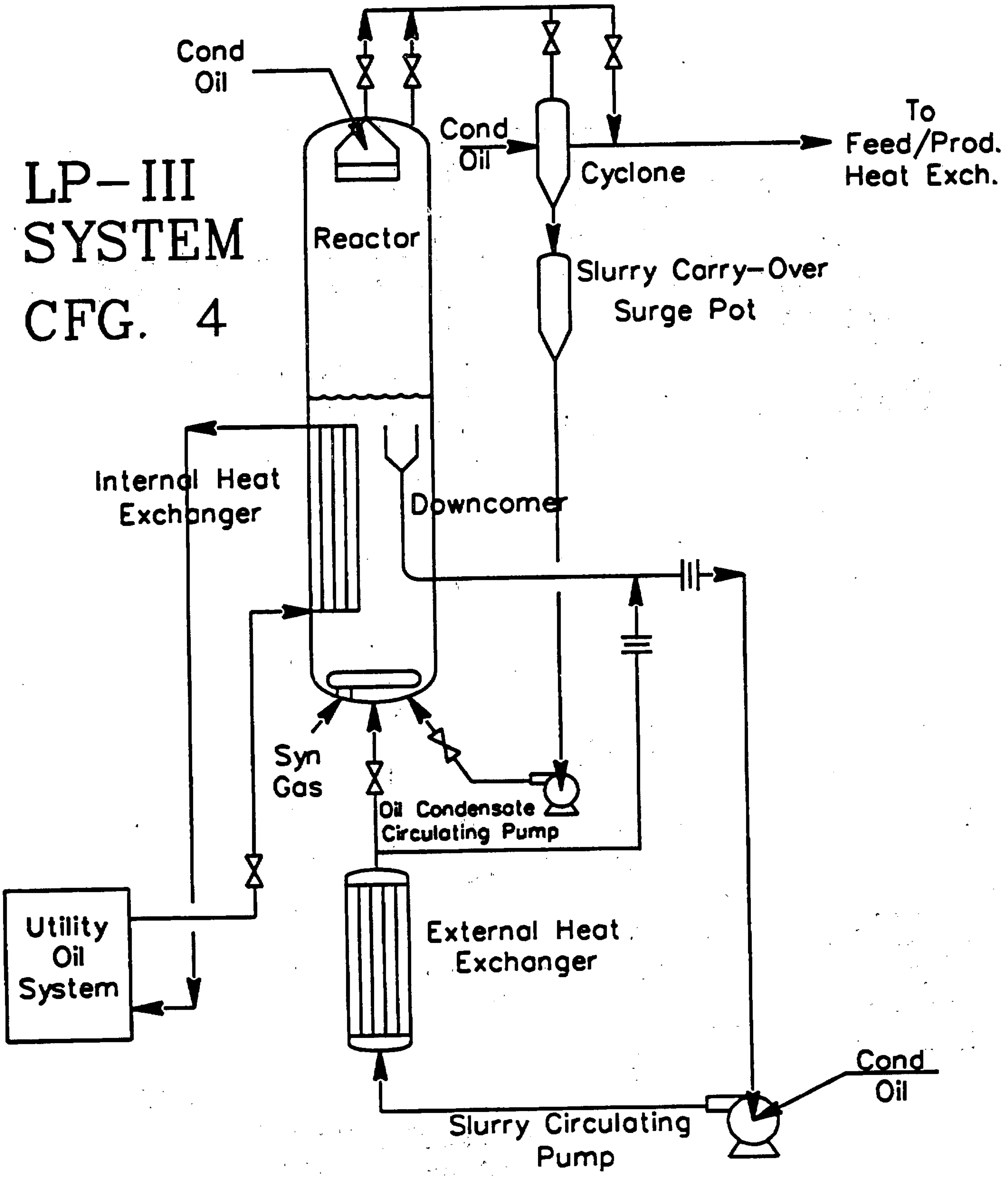
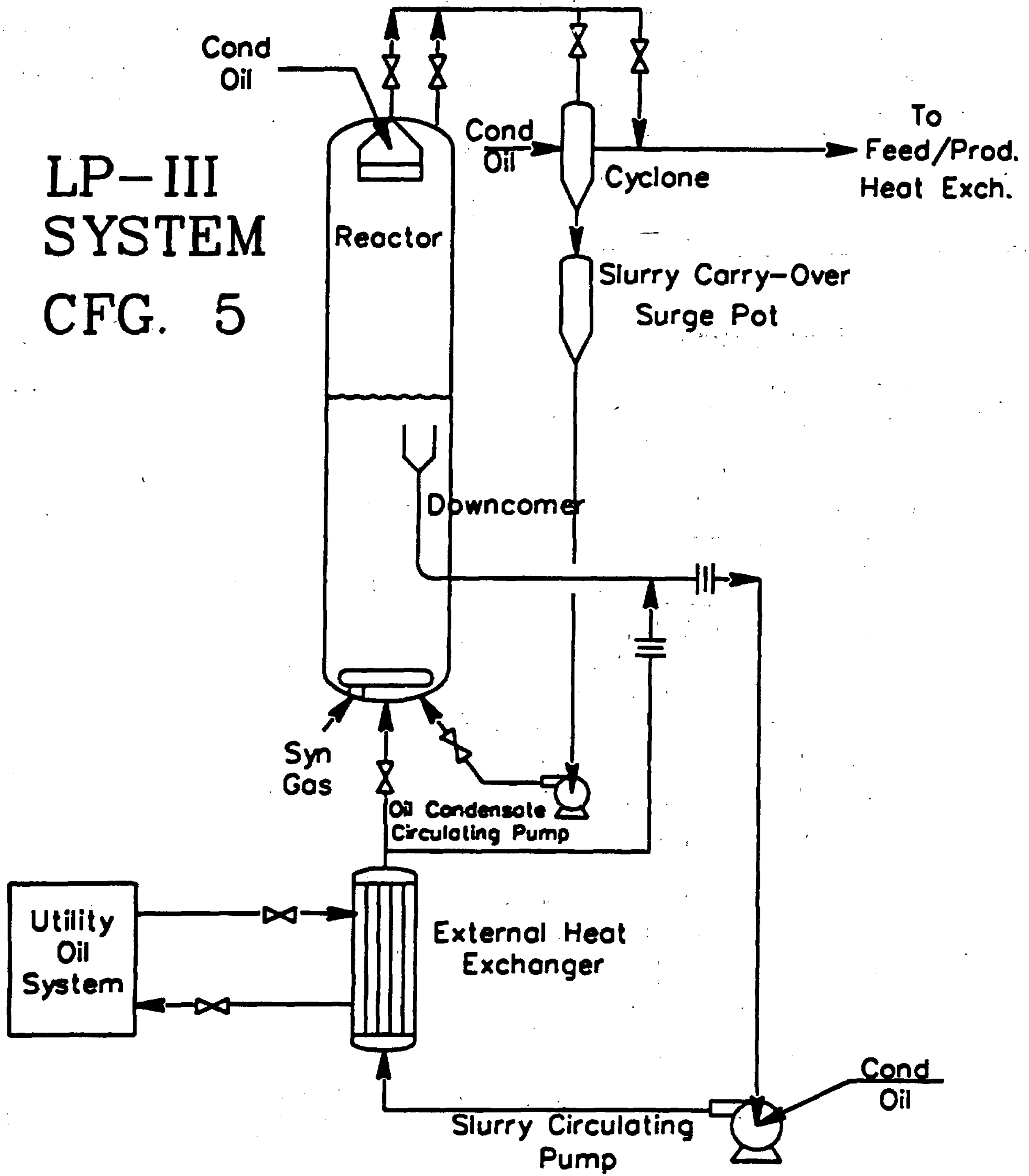

LP-III
SYSTEM
CFG. 4
Cond
Oil
Reactor
Cond
Oil
Cyclone
To
Feed/Prod.
Heat Exch.
Slurry Carry-Over
Surge Pot
Internal Heat
Exchanger
Downcomer
Syn
Gas
Oil Condensate
Circulating Pump
Utility
Oil
System
External Heat
Exchanger
Slurry Circulating
Pump
Cond
Oil

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

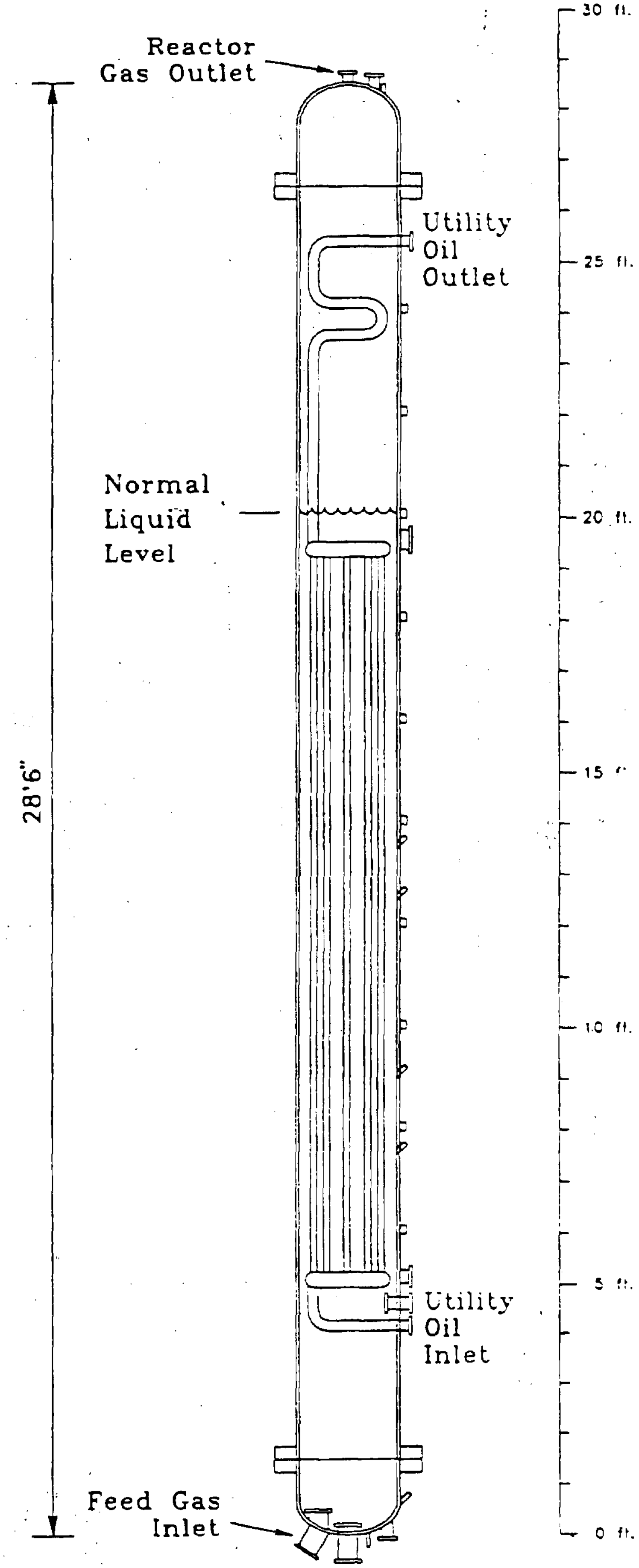
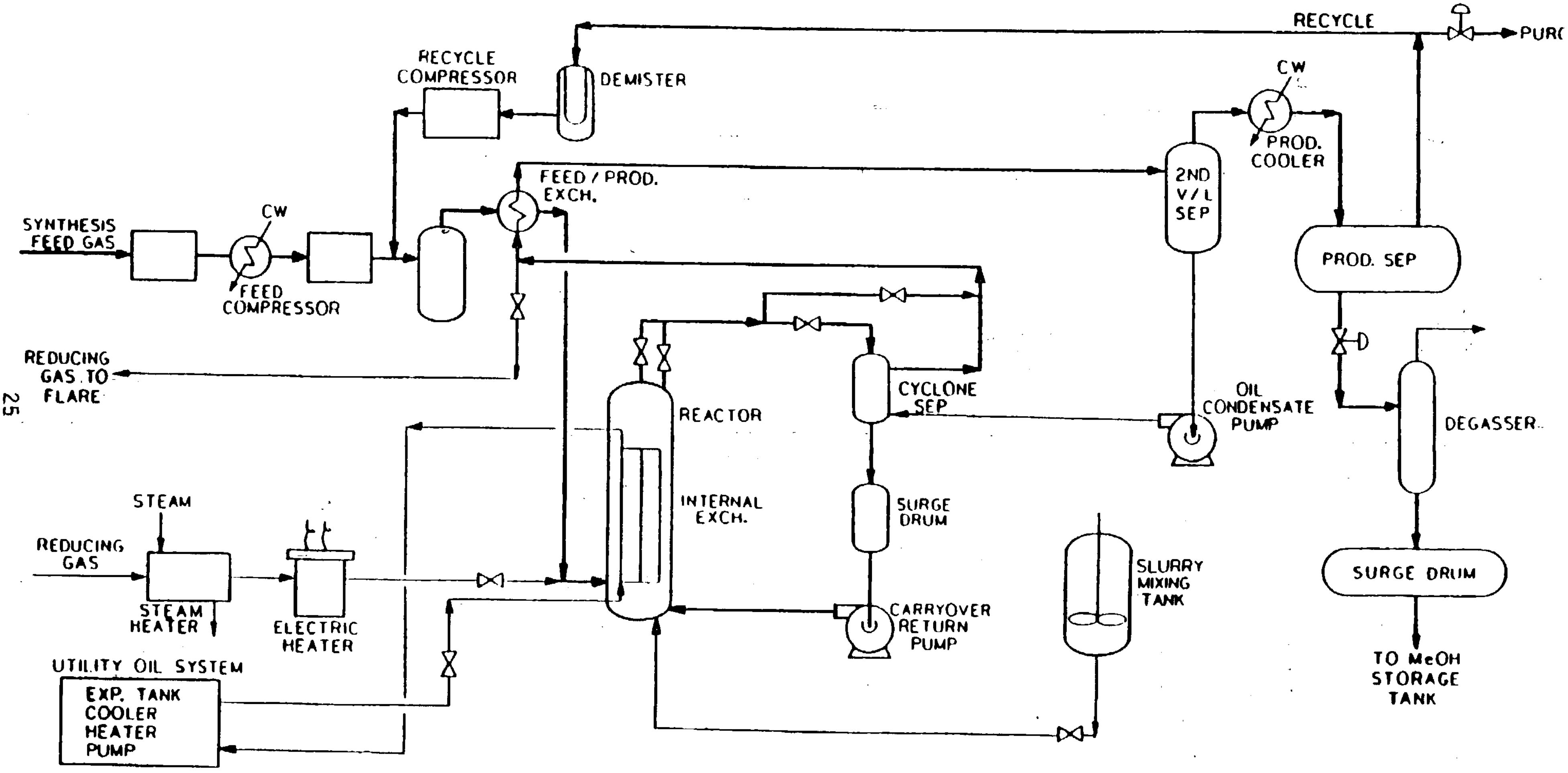


Figure III.

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.

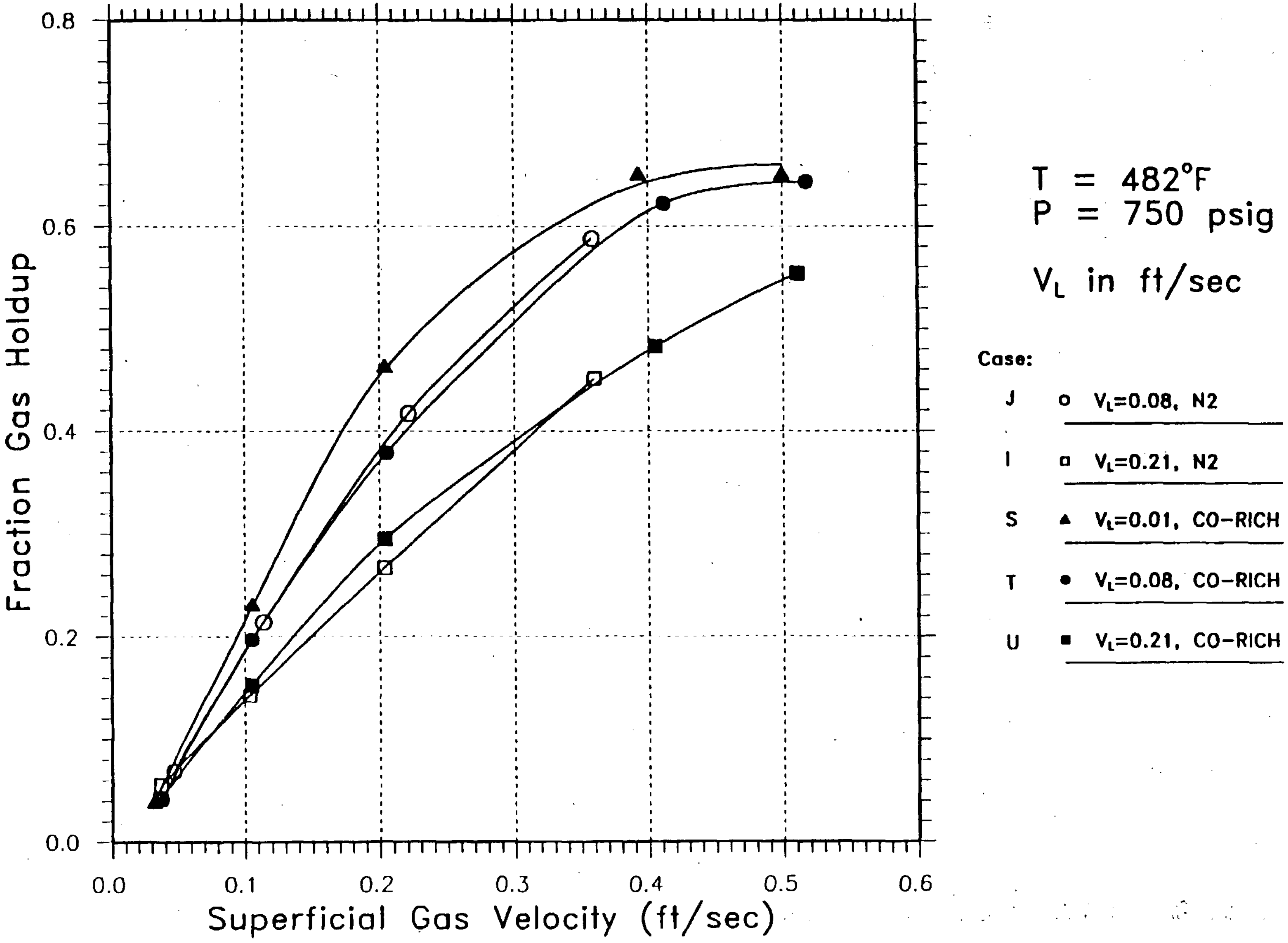
The effect of the type of gas used is shown in Figure IV.1. At 482°F and 750 psig, there is little difference between the gas holdup generated with nitrogen, and the gas holdup generated with CO-rich gas over a range of gas superficial velocities between 0 and .6 ft/sec and superficial liquid velocities 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

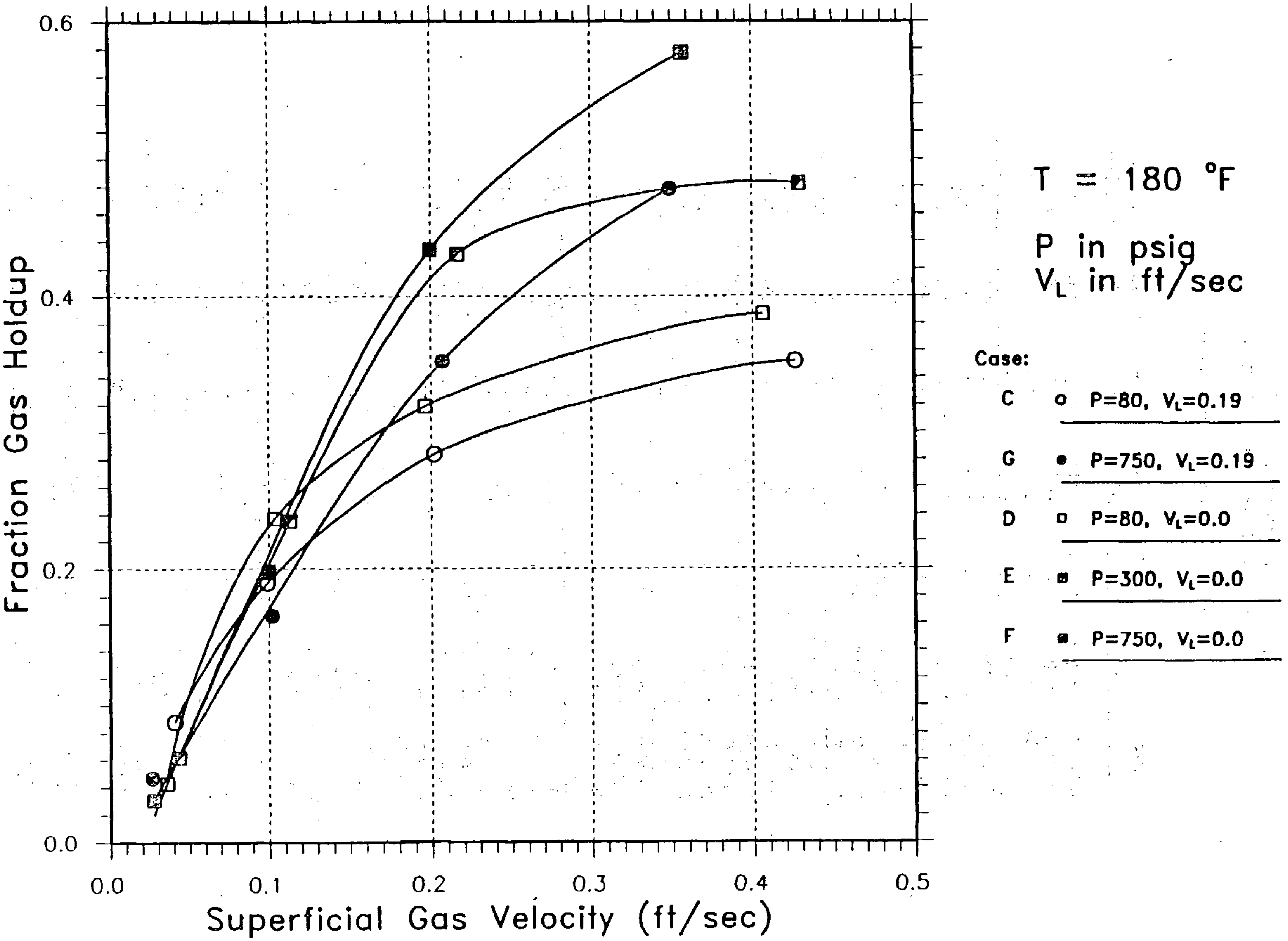


Table IV.2

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

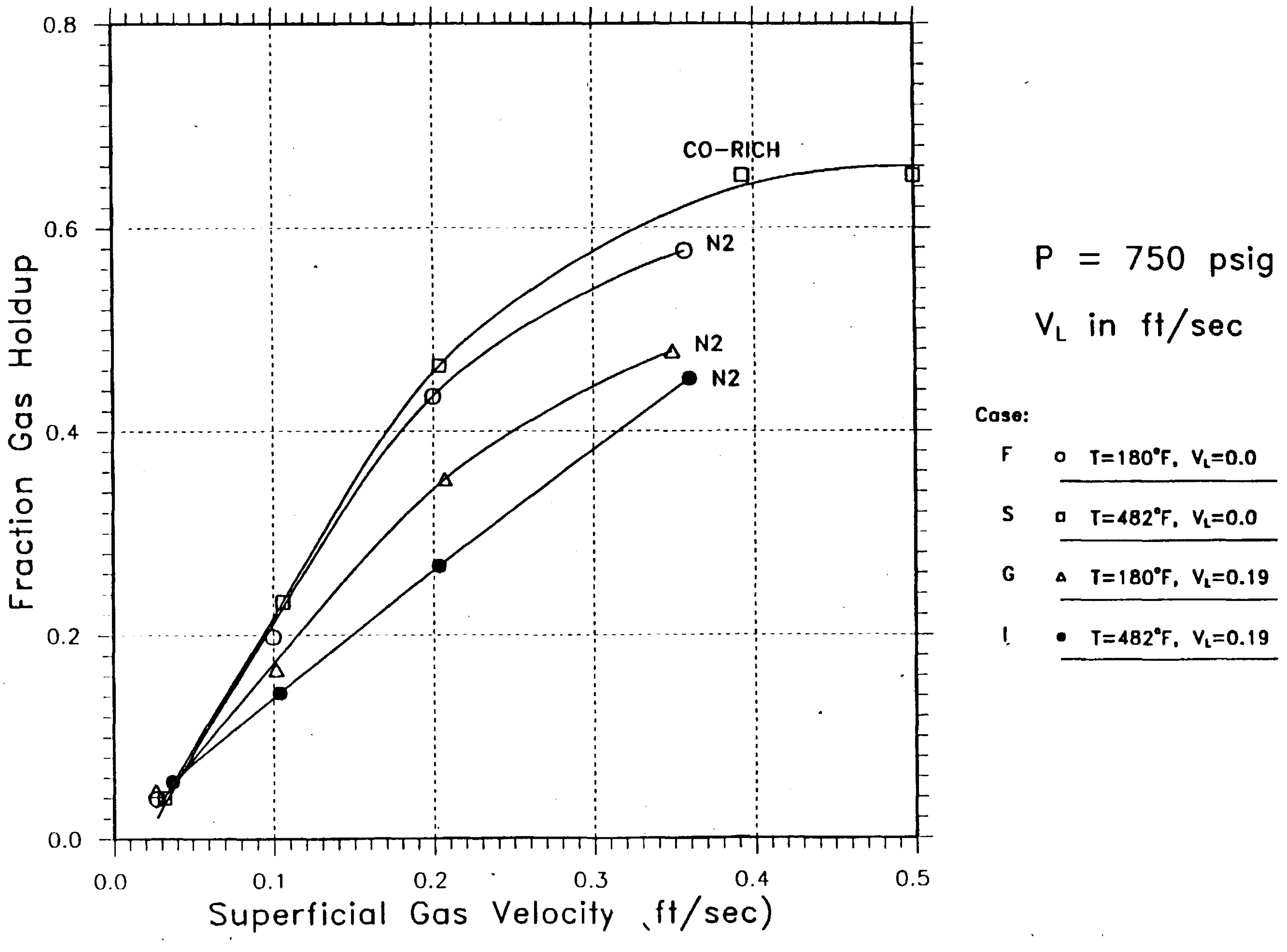
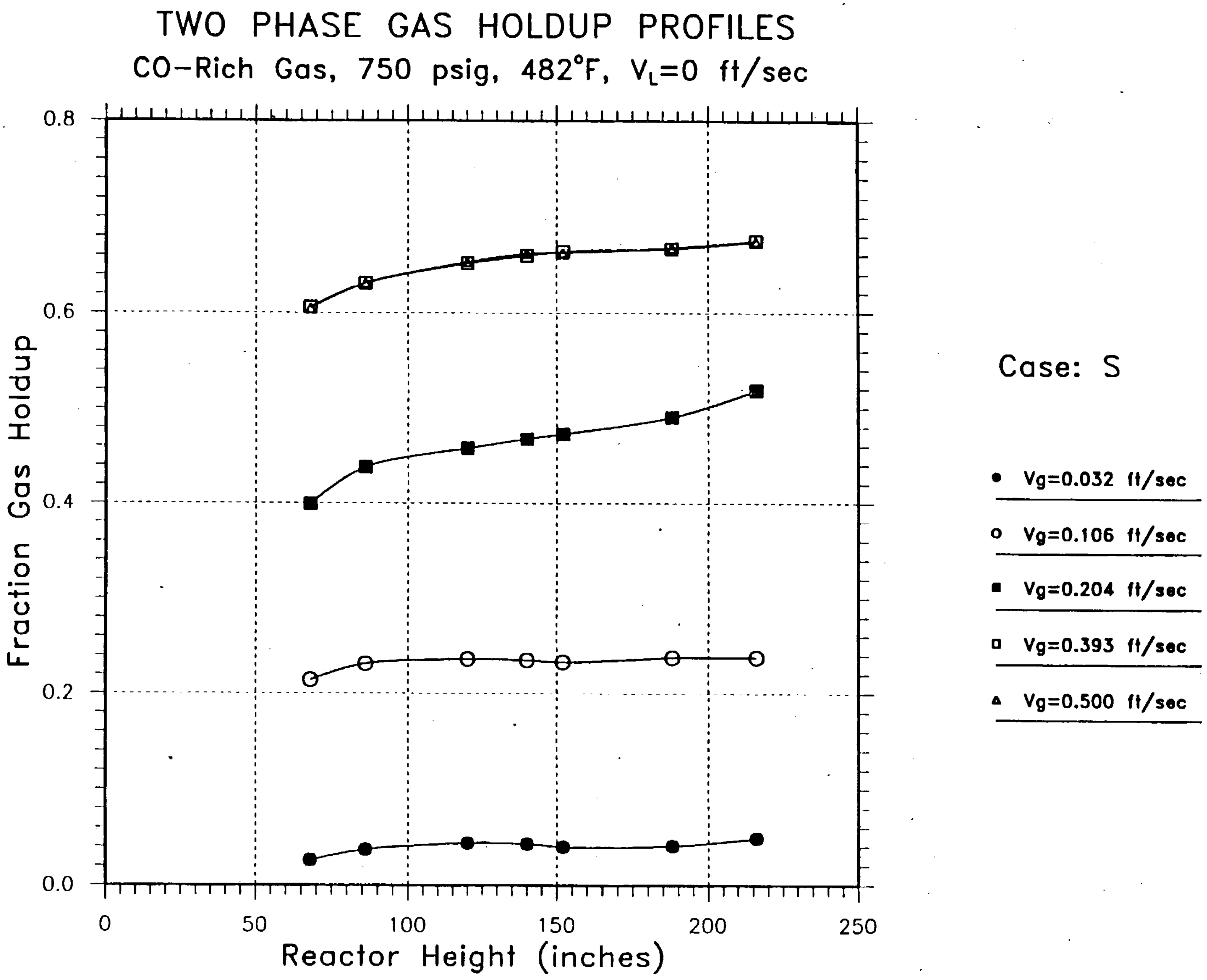


Figure IV.4


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