IV. COMMISSIONING HIGHLIGHTS

A. General

Construction work at the LaPorte site began in September 1982 and was completed on schedule in November 1983.

As part of the plant commissioning procedure, a formal Operational Readiness Inspection/Safety Audit was performed at the site upon completion of construction work. This involved bringing in members of several engineering disciplines, including Process, Project, Start-up, Operations, and Safety Engineering, to compare the as-built condition of the PDU with the specifications of the hazards analysis performed during the PDU design phase. Checks were made on both process and facility safety to ensure personnel safety and proper compliance with applicable regulations. Each individual system was function-checked to ensure operability. For example, pressure relief devices were inspected for proper installation, pressure rating, and relief flow area; alarms and switches were tested to prove that they performed the correct function at the desired set point. At the same time, signals to the PDU microcomputer were checked for both integrity and proper transmitter calibration.

Upon completion of the above checks, a final leak check with nitrogen was performed on the PDU at the maximum supply pressure. The PDU reactor was then run under cold conditions using water in the reactor loop and nitrogen circulating at normal operating pressure. This run-in period was used to check plant flowmeters by doing plant mass balances. Operation of the slurry pump and compressor was closely monitored to ensure proper working order. Sample lines to the gas chromatographs were checked to ensure that tubing connections were tight and that lines were not plugged or crimped. The PDU was then heat-cycled under nitrogen to check flange connections, especially in the areas of high process-oil

temperature, to ensure that they were tight. Upon completion of this checkout, the water was replaced by process oil, and the heat cycling was repeated. The PDU was then taken to its maximum operating temperature and pressure using a mixture of hydrogen in nitrogen as the final leak check.

With the PDU secure, test runs under synthesis gas and process oil without catalyst were performed. These permitted checkouts of the on-line process analyzers, gas chromatographs, feed gas paymeters, and the flare system.

B. Exotherm Problem and Solution

During the run-in phase, a particular problem was encountered with exotherm events in the front end preheat train. The problem is believed to have been residual nickel catalyst from the old Chicago LPM unit. Some nickel fines remained in several vessels despite earlier cleaning and inspection. These fines catalyzed the formation of nickel carbonyl and are conjectured to have triggered an observed methanation reaction. There were two exothermic events in the front end carbonyl removal system which originally included an economizer, electric heater, and guard beds. The PDU was subsequently cleaned with a specific chemical wash which removed nearly all traces of nickel. In addition, front end high temperature preheat of the feed gas was eliminated. The PDU was modified to eliminate the economizer and electric heater, and the alumina was removed from the guard beds. These actions solved the exotherm problem. A subsequent carbonyl survey showed an iron carbonyl concentration of less than 10 ppbv in the reactor feed. This low iron carbonyl concentration was judged to be acceptable for the initial, short-term PDU operations. A detailed description of the problem and solution is provided in Appendix A.

C. Nuclear Density Gauge Calibration

The nuclear density gauge (NDG), as described in Part III, Section D, was calibrated with a known density of Freezene-100 oil at various temperatures. Figure IV-1 is a plot of the voltage reading of the NDG versus the specific gravity of Freezene-100 oil. A reading of -11.1 volts is obtained when the calibration line is extrapolated to zero density. This number agrees very well with the actual voltage readings of the empty reactor taken before the 10-day shakedown operation at a position 54 in. (137 cm) above the tray and shown in Table IV-1. The equation for this fundamental calibration line for Freezene-100 oil is

$$\rho_L = 0.22 \ln \frac{-11.1}{V - V_o} \qquad \text{(Eq. IV-1)}$$

where ρ_L = specific gravity of Freezene-100 oil, g/cm^3,
V = NDG output, volts, and
V_o = "zero" NDG output with the source shutter closed.

During the March 1984 10-day shakedown operation, measurements of the voltage output with the source shutter closed, V_o, indicated frequent small changes in the "zero" reading. Therefore, this measurement was repeated frequently for precise density measurements. Table IV-2 lists the "zero" readings obtained in March 1984.

Table IV-3 lists all of the elevations for which "calibration ratios" were measured during PDU commissioning. The only significant deviations from unity were for the positions below 26 in. (66 cm), at which the reactor wall is 1/8 in. (0.32 cm) thicker than at the higher elevations. It should also be noted that the NDG traversing mechanism operates only between 15-3/4 (40 cm) and 176 in. (447 cm) above the tray due to physical obstructions at the ends of the reactor.

FIGURE IV-1
LAPORTE LPMEOH PDU
NUCLEAR DENSITY GAUGE
VOLTAGE/DENSITY CALIBRATION

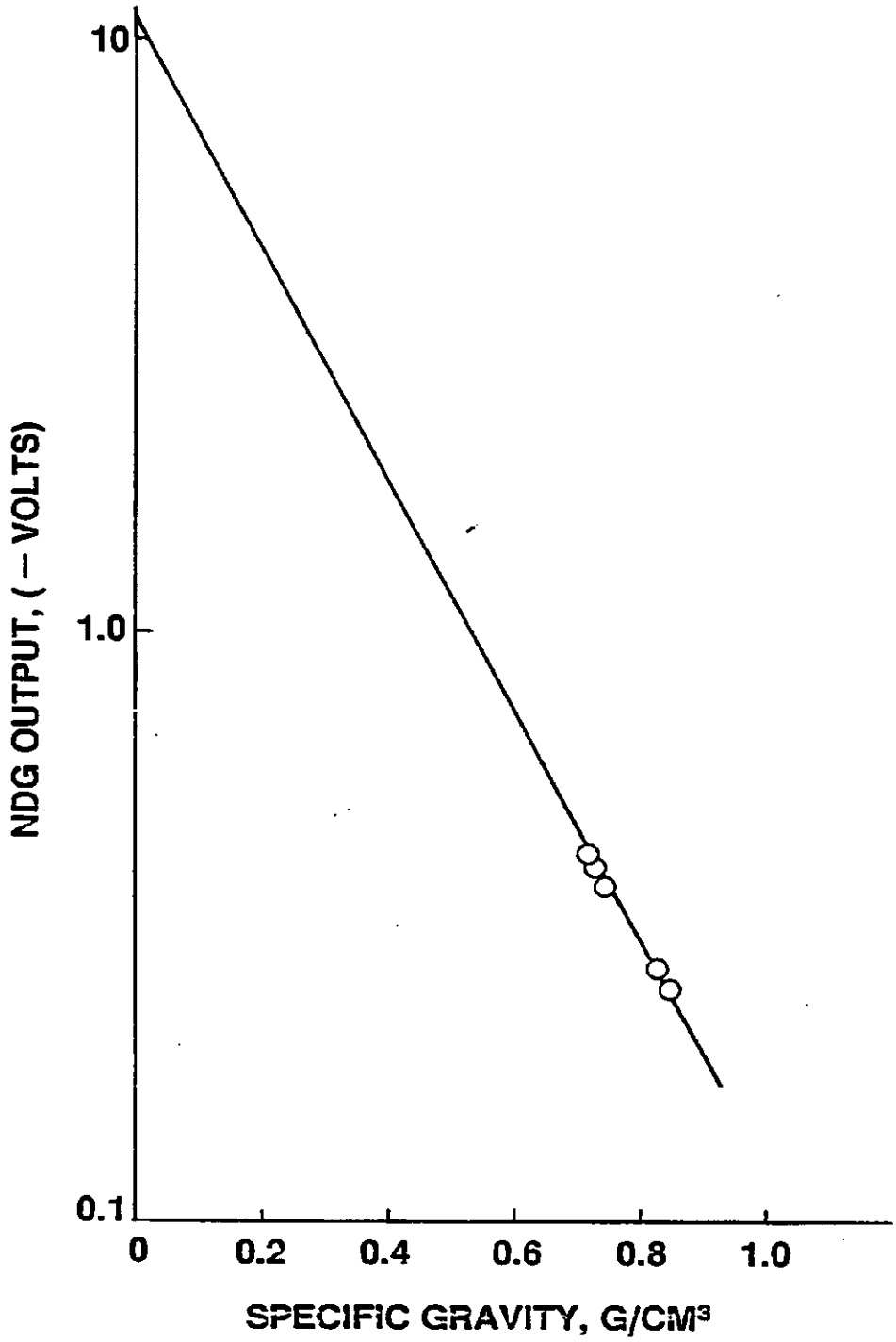

TABLE IV-1

NUCLEAR DENSITY GAUGE READINGS OF EMPTY REACTOR

Position, in. above tray	Reading, volts (March) with standard block	Reading, volts (March) shutter open	Reading, volts (1 Feb.) with standard block
16 (bottom, 41 cm)	-2.19	-7.5	-2.17
22 (56 cm)	-2.24	-7.69	-2.25
54 (137 cm)	-3.24±.01	-11.14	-3.26
96 (244 cm)	-3.15±.01	-11.0	-3.20
136 (345 cm)	-3.20	NA	-3.25
174 (top, 442 cm)	-3.22	NA	-3.15

TABLE IV-2

NUCLEAR DENSITY GAUGE "ZERO" READINGS

Date	Time, hrs	Readings, millivolts
5 March 1984	--	-67
5 March 1984	--	-65
7 March 1984	1645	-43
7 March 1984	1850	-46
8 March 1984	0630	-43
8 March 1984	1515	-40
9 March 1984	1000	-39
9 March 1984	1730	-44
10 March 1984	1100	-41
11 March 1984	1600	-46
12 March 1984	1500	-44
12 March 1984	2330	-47
13 March 1984	2230	-48
14 March 1984	1600	-47
15 March 1984	1700	-48
16 March 1984	1430	-45
17 March 1984	1500	-47
18 March 1984	1600	-48
19 March 1984	1900	-50

TABLE IV-3

NUCLEAR DENSITY GAUGE CALIBRATION RATIOS

Position, inches above reactor tray	Calibration ratio C_R
15-3/4 (bottom of traverse, 40 cm)	0.67
22 (56 cm)	0.68
24 (61 cm)	0.69
36 (91 cm)	1.00
48 (122 cm)	1.00
54 (137 cm)	1.00
60 (~~152 cm~~)	0.99
72 (183 cm)	0.99
94 (239 cm)	0.97
136 (345 cm)	1.00
174 (top, 442 cm)	0.96

Nuclear Density Gauge Calibration for Three-Phase System

When the reactor contains a significant mass of material other than Freezene-100 oil (i.e., methanol synthesis catalyst), the differences in the specific absorbances of the components must be considered. Specific absorbances of the common elements for gamma radiation from Cs-130 were provided by Texas Nuclear Corporation. Tables IV-4 and IV-5 list the absolute and relative specific absorbances for the materials of interest.

In terms of voltage output from the NDG, the relationship between the reading and the density of the reactor's contents is

$$\frac{(V - V_o)}{C_R \cdot (V(o) - V_o)} = \exp\left(-\Sigma_1\, \varepsilon_1 a_1 \rho_1 L\right) \qquad \text{(Eq. IV-2)}$$

where V = voltage output, volts,

$V(o)$ = voltage output for empty vessel, volts,

V_o = voltage output with shutter closed (background reading), volts,

ε_1 = volume fraction of component 1,

a_1 = specific absorbance, cm^2/g,

ρ_1 = specific gravity, g/cm^3,

L = effective path length, cm, and

C_R = calibration ratio (Table IV-3).

Earlier calibration tests with Freezene-100 oil had shown that the value of $a_L L$ is about 4.5 cm^3/g for the LaPorte PDU reactor. The $a_L L$ for Freezene-100 oil is known only to about 1% due to uncertainty in both the density of the oil and the value for the effective path length.

For the general case of a three-phase (solid/liquid/gas) system Equation (IV-2) becomes

TABLE IV-4

SPECIFIC ABSORBANCES OF LPMEOH PROCESS MATERIALS

	wt%	Specific Absorbance, a_1 cm^2/g
1. Freezene-100 Oil		
C	85.2	0.0775
H	14.8	0.1537
Total	100.0	0.0888
2. Methanol Catalyst (Oxide)		
Cu	*	0.0728
Zn	*	0.0734
Al	*	0.0750
O	*	0.0775
Total	100.0	0.0742
3. Methanol Catalyst (Reduced)		
Cu	*	0.0728
Zn	*	0.0734
Al	*	0.0750
O	*	0.0775
Total	100.0	0.0740
4. Nitrogen		
N	100.0	0.0775
5. Balanced Gas**		
C	19.9	0.0775
H	7.6	0.1537
O	32.0	0.0775
N	40.5	0.0775
Total	100.0	0.0833
6. CO-rich Gas***		
C	36.6	0.0775
H	3.3	0.1537
O	58.8	0.0775
N	1.3	0.0775
Total	100.0	0.0800

* Proprietary Information

** Volume %: 19% CO, 55% H_2, 5% CO_2, 21% N_2, MW=14.5

*** Volume %: 51% CO, 35% H_2, 13% CO_2, 1% N_2, MW=21

TABLE IV-5

RELATIVE SPECIFIC ABSORBANCES

	Relative Specific Absorbances	$(a_1L)^{-1}$, g/cm^3	a_1L, cm^3/g
Freezene-100 Oil	1.00	0.22	4.546
Methanol Catalyst (Oxide)	0.836	0.263	3.802
Methanol Catalyst (Reduced)	0.833	0.264	3.788
Nitrogen	0.873	0.252	3.968
Balanced Gas	0.938	0.235	4.255
CO-rich Gas	0.901	0.244	4.098

$$\epsilon_S a_S \rho_S L + \epsilon_L a_L \rho_L L + \epsilon_G a_G \rho_G L = \ln \frac{C_R\,[V(o) - V_o]}{(V - V_o)} \qquad \text{(Eq. IV-3)}$$

Since $\epsilon_G \rho_G \ll \epsilon_L \rho_L$ for most cases, the differences between a_G and a_L (or between a_G and a_S in the gas/solid case) can usually be ignored. However, because $\epsilon_S \rho_S$ is comparable in magnitude to $\epsilon_L \rho_L$ in an ebullated bed, the difference between a_L and a_S (about 20%) must be included in the calibration.

D. Two-Phase Gas Holdup Data

Prior to the beginning of the 10-day shakedown run with synthesis gas and catalyst, a series of two-phase gas holdup measurements was performed. The density of the two-phase fluid in the reactor was determined by both nuclear density gauge and differential pressure measurements.

Table IV-6 lists the gas holdup data which were obtained with the N_2/Freezene-100 system. For the high-pressure cases, the holdups calculated from the nuclear density gauge measurements ($\epsilon_{G,NGD}$) and the pressure drop measurements ($\epsilon_{G,\Delta P}$) are in very good agreement. The ΔP measurements for the lower pressure data (tests #I1 to I4) consistently yield gas holdups much lower than those indicated by the nuclear density gauge. The nuclear density gauge is thought to yield the more reliable results.

Two-phase density was calculated using the voltage data measured by the NDG and Equation (IV-2). The occasional failure of the measured density to match the pure liquid density at zero superficial gas velocity is probably due to the entrainment of some gas bubbles through the liquid circulation system.

TABLE IV-6

TWO-PHASE GAS HOLDUP DATA ON N_2/FREEZENE-100 OIL

NDG Survey No.	T °C (°F)	P kPa (psia)	u_G cm/s	$\bar{\rho}$ g/cm^3 by NDG	ΔP kPa (psia)	ρ_L g/cm^3	ρ_G g/cm^3	ϵ_G, NDG %	ϵ_G, ΔP %
A1P	185 (366)	5210 (755)	12.8	0.415	17.9 (2.60)	0.739	0.038	46.2	48.3
A2P	186 (368)	5310 (770)	9.5	0.449	19.7 (2.85)	0.737	0.038	41.3	43.2
A3P	185 (366)	5310 (770)	7.4	0.489	21.4 (3.11)	0.739	0.038	35.7	38.2
A4P	185 (365)	5380 (780)	3.7	0.559	25.5 (3.70)	0.739	0.040	25.7	26.4
A5P	184 (363)	5240 (760)	1.2	0.697	31.8 (4.61)	0.739	0.038	5.9	7.8
A6P	182 (360)	5410 (785)	0.0	0.739	34.3 (4.98)	0.740	0.040	0.0	1.1
A7P	182 (359)	5310 (770)	0.0	0.739	34.5 (5.00)	0.740	0.040	0.0	0.6
A8P	181 (358)	5310 (770)	0.0	0.740	34.5 (5.00)	0.740	0.040	0.0	0.6
A9P	204 (400)	5270 (765)	0.0	0.723	35.8 (5.19)	0.724	0.037	0.0	(5.1)*
A10P	204 (400)	5340 (775)	0.0	0.728	35.8 (5.19)	0.724	0.038	0.0	(5.1)*
A1	251 (484)	5240 (760)	14.0	0.393	16.5 (2.40)	0.692	0.034	45.5	49.3
A2	252 (485)	5340 (775)	10.4	0.446	22.1 (3.20)	0.692	0.034	37.5	32.3
A3	250 (482)	5340 (775)	8.3	0.476	21.4 (3.10)	0.692	0.034	32.8	34.5
A4	248 (479)	5380 (780)	7.2	0.495	23.1 (3.35)	0.694	0.035	30.2	29.2
A5	247 (477)	5310 (770)	4.8	0.538	25.6 (3.71)	0.696	0.034	23.7	22.0
A6	247 (476)	5310 (770)	3.4	0.577	26.9 (3.90)	0.696	0.034	17.9	17.5
A7	247 (476)	5170 (750)	0.0	0.649	31.1 (4.51)	0.696	0.034	(7.0)*	(4.7)*
A8	246 (475)	5070 (735)	0.0	0.675	31.0 (4.50)	0.696	0.034	(3.1)*	(4.9)*
B1	251 (483)	6310 (915)	8.3	0.466	20.6 (2.99)	0.692	0.040	34.6	36.2
B2	248 (479)	6310 (915)	7.2	0.489	22.0 (3.19)	0.694	0.040	31.4	32.1
B3	249 (481)	6380 (925)	5.0	0.530	24.2 (3.51)	0.692	0.042	24.9	25.0
B4	250 (482)	6310 (915)	3.2	0.567	25.9 (3.75)	0.692	0.040	19.2	20.0
B5	249 (480)	6100 (885)	0.0	0.620	28.3 (4.11)	0.694	0.040	(11.3)*	(12.5)*
I1	69 (157)	630 (91)	12.2	0.623	34.5 (5.00)	0.816	0.006	23.8	14.1
I2	69 (157)	635 (92)	6.7	0.671	37.9 (5.50)	0.816	0.006	17.8	5.5
I3	69 (156)	795 (115)	2.3	0.724	37.2 (5.40)	0.816	0.008	11.3	6.9
I4	69 (156)	655 (95)	0.0	0.784	41.4 (6.00)	0.816	0.006	(4.0)*	(3.2)*

* The high gas holdup measured at zero gas velocity is probably due to the entrainment of gas bubbles through the liquid circulation system.

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Figure IV-2 shows the gas holdups derived from the NDG data plotted as a function of superficial gas velocity. The data at 5,270 kPa (765 psia) and 6,310 kPa (915 psia) agree very well with the CSI correlation, based on the Chem Systems Lab PDU data (Reference 1). As expected, the low-temperature, medium-pressure gas holdups are lower and are closer to commonly used gas holdup correlations such as that of Akita and Yoshida (Reference 2):

$$\frac{\epsilon_G}{(1-\epsilon_G)^4} = 0.2 \left(\frac{\rho_L u_G}{g_c g \sigma}\right)^{4\ 1/8} \left(\frac{\rho_L u_G}{g \mu_L}\right)^{3\ 1/6} \qquad \text{(Eq. IV-4)}$$

where ϵ_G: Gas holdup, volume fraction,
ρ_L: Liquid density, lb/ft^3 (kg/m^3),
u_G: Superficial gas velocity, ft/s (m/s),
g: Acceleration of free fall, 32.174 ft/s^2 (9.8067 m/s^2),
g_c: Proportionality factor, 32.174 ft-lb/lb_f-s^2 (1 kg-m/N-s^2),
σ: Liquid surface tension, lb_f/ft (N/m), and
μ_L: Liquid viscosity, lb/ft-s (kg/m-s).

Figure IV-3 compares the same data with the more recent Hikita/Asai correlation (Reference 3):

$$\epsilon_G = 0.672 \left(\frac{u_G \mu_L}{g_c \sigma}\right)^{0.578} \left(\frac{\mu_L^4 g}{\rho_L g_c^3 \sigma^3}\right)^{-0.131} \left(\frac{\rho_G}{\rho_L}\right)^{0.062} \left(\frac{\mu_G}{\mu_L}\right)^{0.107} \qquad \text{(Eq. IV-5)}$$

where μ_G: Gas viscosity, lb/ft-s (kg/m-s), and
ρ_G: Gas density, lb/ft^3 (kg/m^3).

Equation (IV-5) is one of the few general correlations that incorporates a significant gas density effect; these predictions are much better than those of the Akita/Yoshida correlation, but much improvement is still needed, especially in correlating the high-pressure data.

FIGURE IV-2

GAS HOLDUP FOR N_2/FREEZENE-100 LAPORTE LPMEOH REACTOR

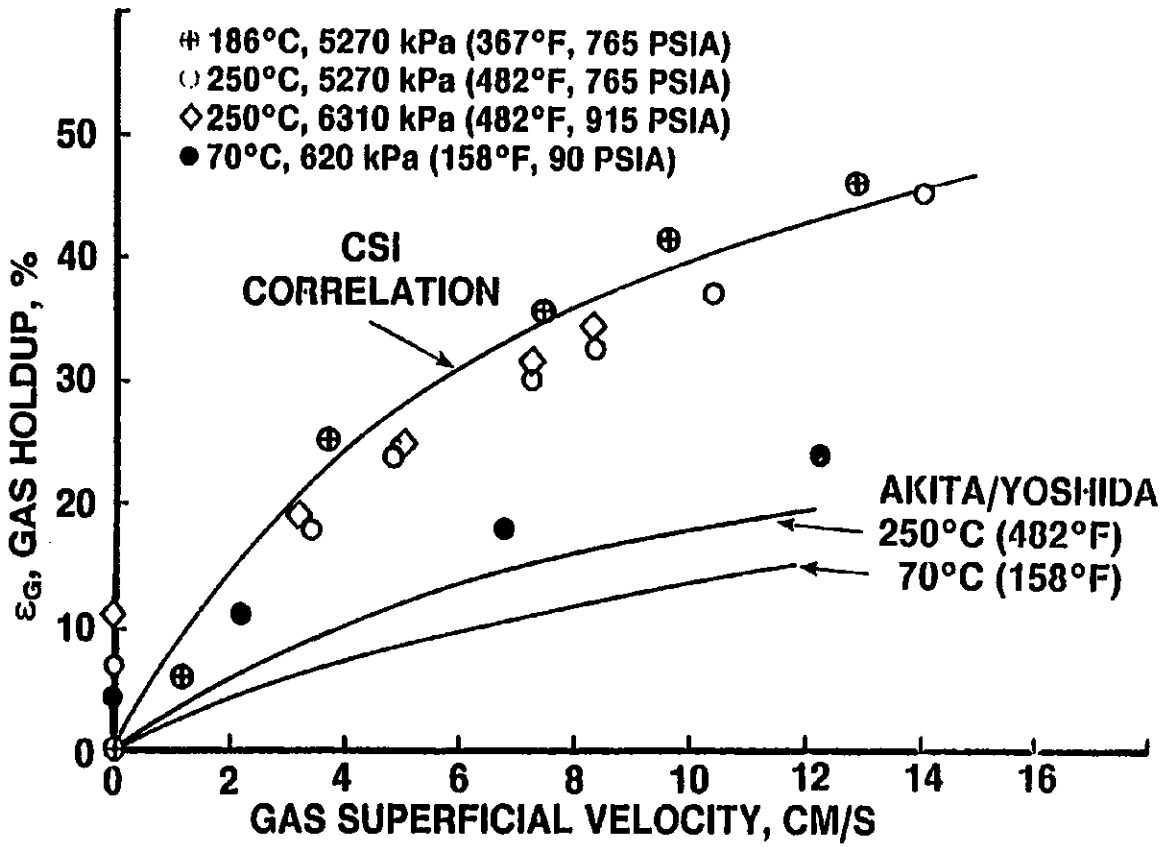

FIGURE IV-3

GAS HOLDUP FOR N_2/FREEZENE-100 COMPARISON WITH HIKITA/ASAI CORRELATION

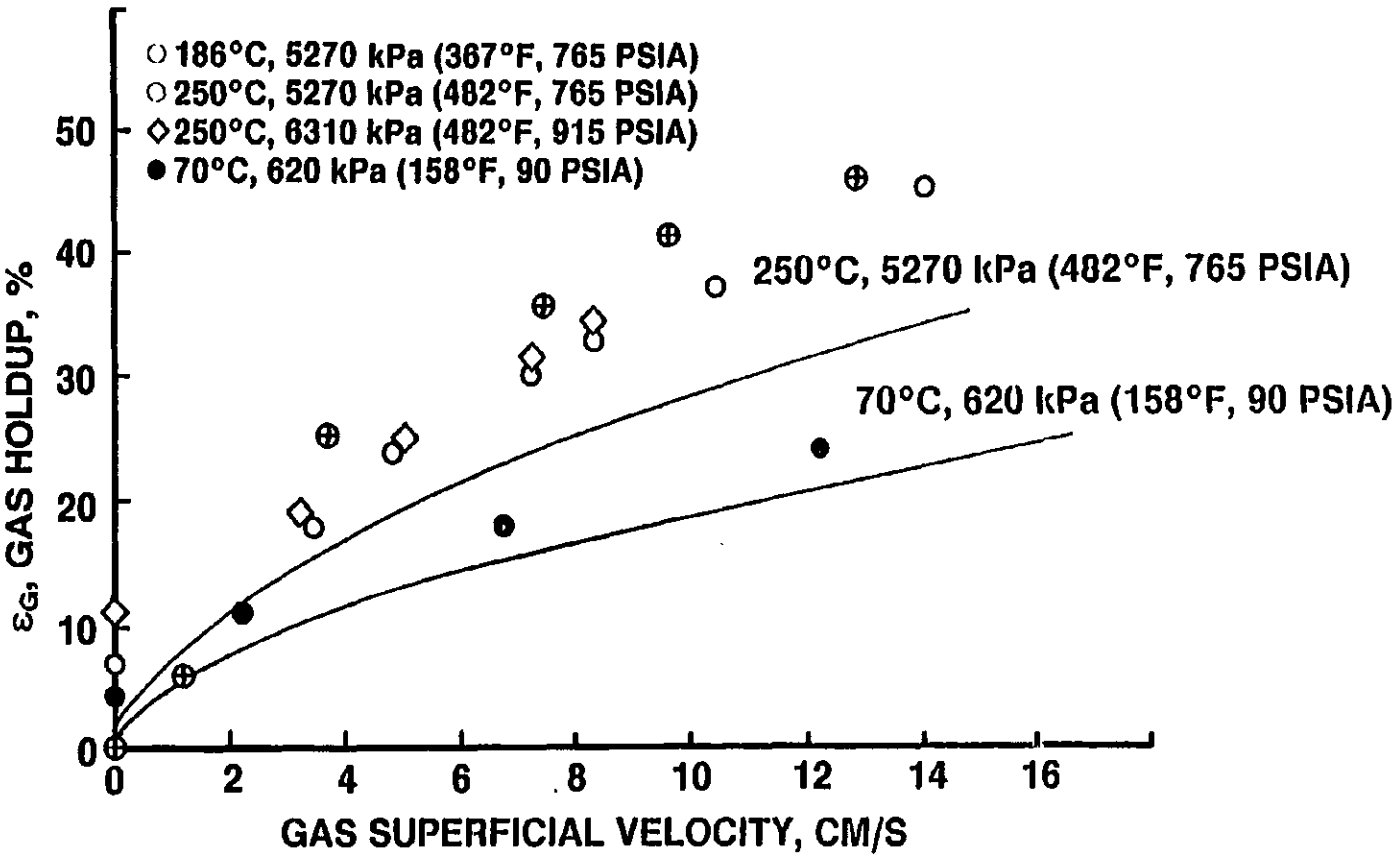

Table IV-7 and Figure IV-4 show the results of the two-phase gas holdup tests made with the balanced gas/Freezene-100 system.

All nuclear density gauge data are for the 54-in. (137 cm) reactor position. Again, the data agree very well with those obtained in the Lab PDU with the N_2/Freezene-100 and the He/Freezene-100 systems. It is evident that the balanced gas results are consistently lower than the nitrogen results, and that the 5,270 kPa (765 psia) results are lower than those for 6,310 kPa (915 psia), although the differences are not significant. The "gas entrainment" problem noted in the earlier N_2/Freezene-100 gas holdup tests was absent, possibly due to the conditioning of the oil by the removal of light ends during heat-up. The apparent density of the oil tended to increase during the test period, which was evident by comparing surveys B5R, C7, and D8. However, measurement of the specific gravity of an oil sample from the 27.13 primary V/L separator at the end of the tests (0.862 g/cm^3 @ 20°C) showed no density increase. A sample of oil from the 27.14 intermediate V/L separator gave a slightly lower density (0.853 g/cm^3 @ 20°C), an indication that light components were lost from the reactor loop.

One test was made of the variation in gas holdup with reactor height. The results, obtained at 6,380 kPa (925 psia) and 251°C (483°F) with N_2 at 3.75 cm/s (0.12 ft/s), are given in Table IV-8. They exhibit no variation in gas holdup with reactor height. The results by differential pressure are in good agreement with the NDG results.

TABLE IV-7

TWO-PHASE GAS HOLDUP DATA ON BALANCED GAS/FREEZENE-100 OIL

NDG Survey No.	T °C (°F)	P kPa (psia)	u_G cm/s	$\bar{\rho}$ g/cm³ by NDG + / #	ΔP kPa (psia)	ρ_L g/cm³	ρ_G g/cm³	$\epsilon_{G,NDG}$ %	$\epsilon_{G,\Delta P}$ %
B2R*	249 (481)	6310 (915)	6.8	.505 /.501	22.8 (3.30)	0.706	0.040	30.2	31
B4R*	249 (481)	6420 (931)	3.5	.586 /.585	26.5 (3.85)	0.706	0.040	18.0	20
B5R*	252 (486)	6090 (883)	0.0	.699 /.695	33.1 (4.80)	0.703	0.038	0.6	0
C1	250 (482)	6380 (925)	3.4	.593 /.588	28.3 (4.10)	0.705	0.021	16.4	17
C2	250 (482)	6380 (925)	4.5	.561 /.560	27.2 (3.95)	0.705	0.021	21.1	20
C3	246 (475)	6370 (924)	6.7	.516 /.523	24.5 (3.55)	0.708	0.022	28.0	28
C4	244 (471)	6380 (925)	8.5	.492 /.491	22.8 (3.30)	0.710	0.022	31.7	33
C5	237 (458)	6370 (924)	10.9	.449 /.449	20.3 (2.95)	0.715	0.022	38.4	41
C6	228 (443)	6370 (924)	13.0	.421 /.415	18.5 (2.68)	0.720	0.023	42.9	47
C7	233 (452)	5140 (746)	0.0	.727 / --	34.1 (4.95)	0.717	0.018	-1.4	1
D1	249 (481)	5400 (783)	3.2	.606 /.606	28.3 (4.11)	0.706	0.017	14.7	17
D2	249 (481)	5350 (776)	4.6	.564 /.564	26.9 (3.90)	0.706	0.017	20.6	21
D3	253 (487)	5250 (761)	6.9	.518 /.519	23.8 (3.45)	0.702	0.017	26.9	30
D4	253 (487)	5250 (762)	8.3	.486 /.484	22.7 (3.29)	0.702	0.017	31.5	33
D5	249 (480)	5260 (763)	11.1	.443 /.442	20.0 (2.90)	0.706	0.017	38.2	41
D6	244 (472)	5250 (761)	14.7	.399 /.399	17.6 (2.55)	0.709	0.017	44.8	49
D7	239 (462)	5300 (768)	17.7	.374 /.376	16.2 (2.35)	0.712	0.017	48.6	53
D8	243 (469)	5400 (783)	0.0	.724 /.722	33.7 (4.89)	0.711	0.018	-1.9	2

* N_2/Freezene-100 oil data checks.
\+ Based upon linearized output indicated on NDG meter.
\# Based upon direct NDG voltage output.

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FIGURE IV-4
TWO-PHASE GAS HOLDUPS FROM LAPORTE LPMEOH PDU

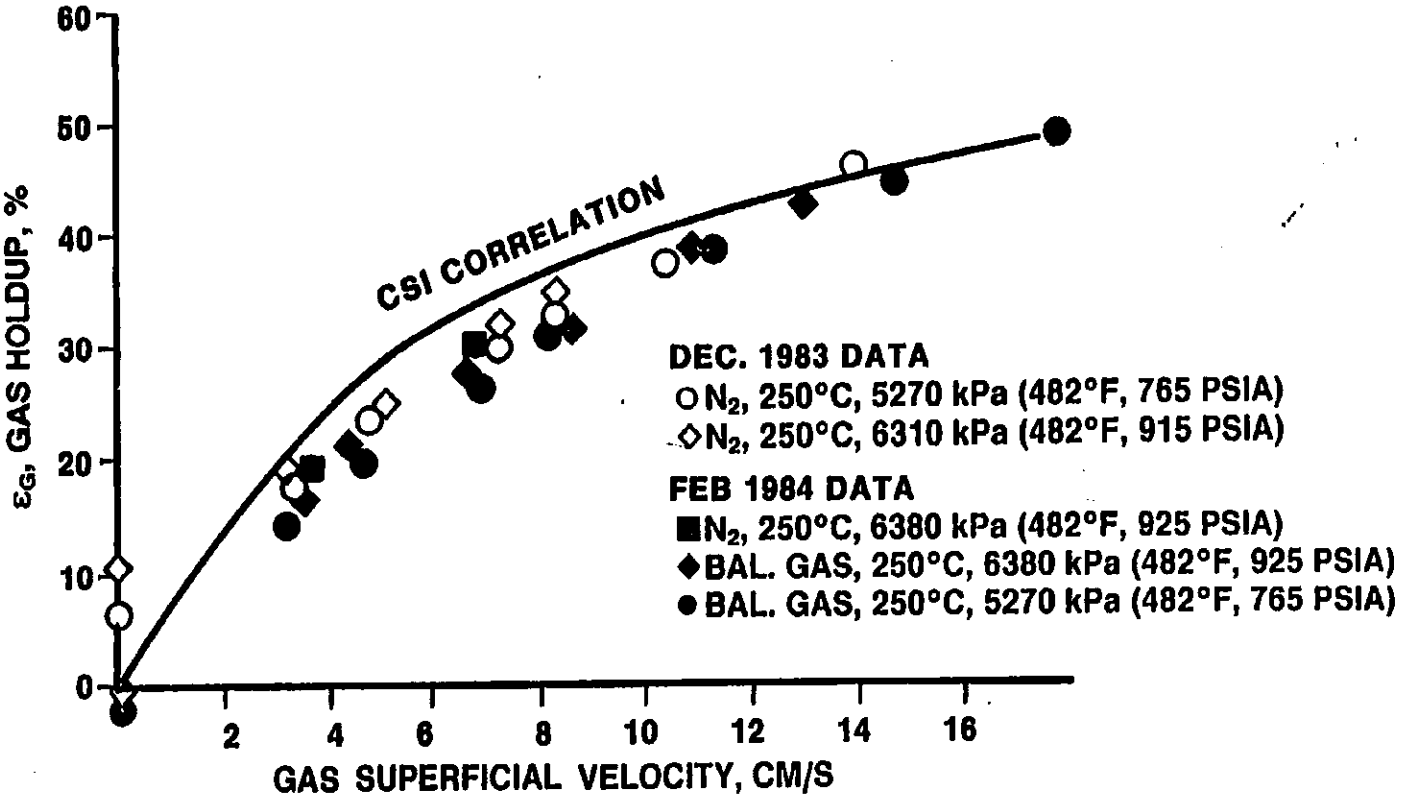

TABLE IV-8

VARIATION OF GAS HOLDUP WITH REACTOR HEIGHT

(4 February 1984)

NDG Position Above Tray in.	NDG Reading (inside scale) %	NDG Reading (corrected per Table IV-10) %	U_G cm/s	$\epsilon_{G,NDG}$ %
16 (41 cm)	62.5	47.5	3.75	19
54 (137 cm)	47.5	47.5	3.75	19
94 (239 cm)	48	47	3.75	19
136 (345 cm)	49	49	3.75	19
174 (442 cm)	49	48	3.75	19