1. Balanced Type - representative of synthesis gas from a modern, thermally-efficient coal gasifier with shift and CO_2 removal, suitable for total conversion to methanol via recycle of unreacted gases. This is the so-called "all-methanol" application.

2. CO-Rich (Unbalanced) Type - representative of synthesis gas from a modern, thermally-efficient gasifier without shift and CO_2 removal, suitable for single-pass methanol production with a resulting CO-rich fuel gas. This is "single pass, coproduct" application which is synergistic with the Integrated Gasification Combined Cycle (IGCC) process to make electric power.

These different makeup feed compositions are blended from hydrogen, carbon monoxide, nitrogen, and methane supplied by the adjacent Air Products' syngas facility. Carbon dioxide is trucked into the plant as liquid and stored onsite. Since only a portion of the reactor feed is converted per pass, the unconverted synthesis gas is recycled and mixed with fresh makeup feed. The makeup feed is blended according to recycle flow and composition so that the reactor feed (makeup plus recycle) simulates either the balanced or CO-rich gas type. Recycling the unconverted synthesis gas reduces gas consumption by about 70%.

C. Process Description

A simplified process flowsheet for the LaPorte LPMEOH PDU is shown in Figure III-1. The makeup synthesis gas is compressed from 1,030 kPa (150 psia) to the reactor pressure (between 3,550 and 6,310 kPa, 515-915 psia) by the 01.10 feed compressor. The compressed feed is mixed with recycle gas from the 01.20 compressor, and the combined flow is heated through the 21.10 feed/product exchanger.

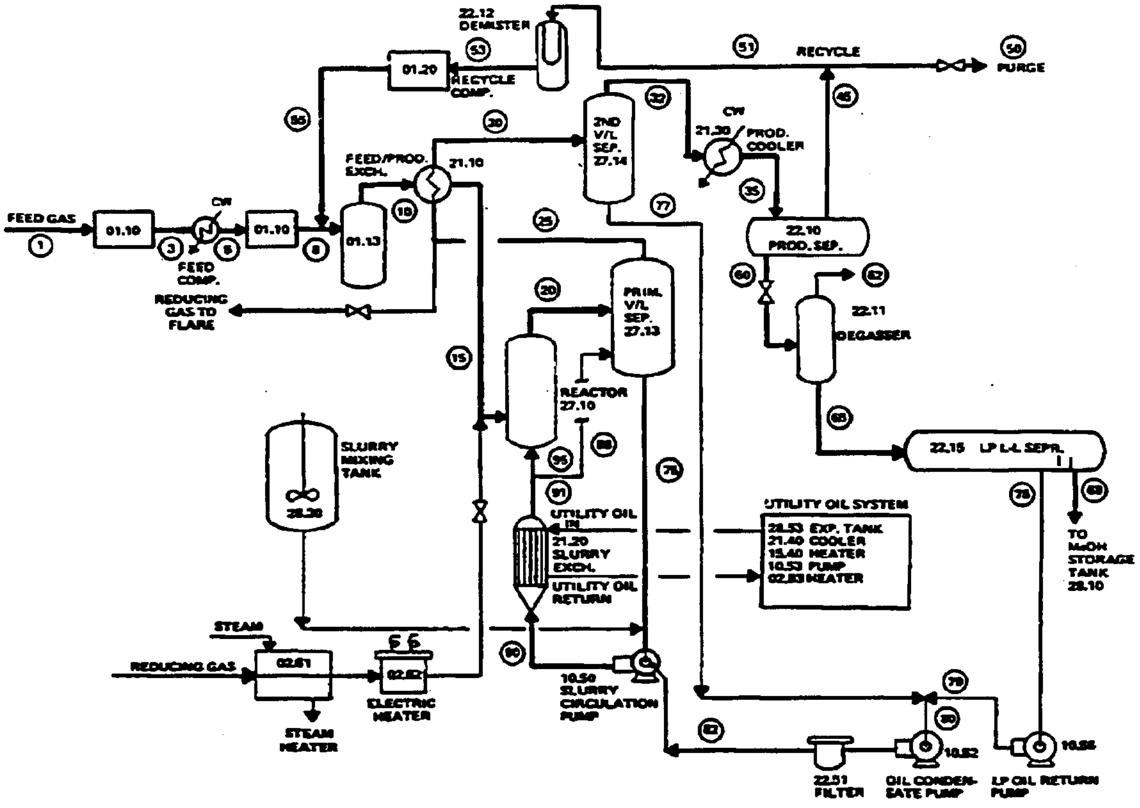


Figure III-1. LaPorte LPMEOH PDU Simplified Process Flowsheet

The heated feed gas is introduced in the reactor bottom and mixed with the incoming catalyst/oil slurry in a distributor/plenum zone. The distributor system includes a bubble cap tray and gas and liquid spargers. The slurry that circulates through the reactor is separated from the methanol product and unconverted synthesis gas in the 27.13 primary V/L separator. The slurry is recirculated by the 10.50 slurry circulation pump to the bottom of the reactor via the 21.20 slurry heat exchanger. The circulating slurry can be heated or cooled in the slurry heat exchanger to maintain a constant reactor temperature, depending on the operating conditions. A utility oil system, which includes a utility oil expansion tank (28.53), utility oil circulation pumps (10.53), a utility oil cooler (21.40), and utility oil heaters (02.83, 15.40), is designed to provide indirect heating or cooling of the circulating slurry. The slurry circulation pump is a centrifugal pump driven by a variable speed electric motor. A specially designed double mechanical seal is provided with an inboard flush and a circulating barrier fluid to provide a secure isolation of the slurry from the atmosphere.

The methanol product and unconverted synthesis gas exiting the top of the primary V/L separator are cooled against the incoming feed gas in the feed/product exchanger to 150°C (302°F), condensing most of the small amount of vaporized hydrocarbon liquid (oil component of the slurry) into the 27.14 intermediate V/L separator. This liquid is returned to the process as seal flush for the slurry circulation pump via the 10.52 oil condensate pumps. The uncondensed vapor is further cooled to about 40°C (104°F) by cooling water in the 21.30 product gas cooler. Condensed methanol product and a small quantity of inert hydrocarbons, flow from the 22.10 product separator, are reduced in pressure and the flashed gas is vented at the top of the 22.11 degasser to the flare header. The methanol-hydrocarbon liquid passes through the 22.15 low-pressure liquid-liquid separator, where the hydrocarbon oil separates and is returned to the process via the 10.56 oil return pump. The methanol product is sent to the 28.10 product storage tank.

The unconverted synthesis gas leaving the product separator is compressed and recycled to the front end of the PDU. A small purge stream is withdrawn to prevent the buildup of inerts in the reactor feed gas.

The oxide form of the catalyst is reduced (i.e., activated) with a mixture of hydrogen in nitrogen. This gas mixture is heated by the 02.61 reduction steam heater and the 02.62 reduction electric heater before it enters the reactor. In the liquid-fluidized operating mode, the catalyst bed is reduced in the reactor before introduction of the synthesis gas and hot hydrocarbon liquid. In the liquid-entrained mode, the catalyst reduction takes place with slurry circulation through the reactor and slurry loop, also before the synthesis gas is introduced. The latter reduction method is referred to as liquid phase, in-situ reduction.

D. LaPorte LPMEOH PDU Modifications

Material Change-out (November 1984 - February 1985)

Analysis of the data from the first activity maintenance run at LaPorte (Run E-1) (Reference 2) revealed a higher rate of decline in methanol productivity than predicted from laboratory results. Associated with the productivity decline, increasing iron and nickel concentrations were detected on the catalyst. It is believed that the buildup of these poisons contributed to the high rate of activity decline seen during Run E-1. As a result, an investigation was performed to determine the metallurgical changes necessary to minimize carbonyl formation.

The source of the iron on the catalyst was determined to be iron carbonyl generated from contact of high CO partial pressure at elevated temperatures with the carbon steel and low alloy steel materials used for piping and vessels at the LaPorte LPMEOH PDU. It was decided to upgrade carbon steel surfaces with type 304-stainless steel in all feed and recycle gas areas where operating temperatures were greater than 93°C (200°F). A new 304-stainless steel feed/product exchanger was purchased and installed. The reactor, primary vapor/liquid separator, feed surge tank (01.13), and intermediate oil separator were fitted with stainless steel liners and reinstalled in the PDU. In addition, the carbon steel pulsation bottles on the discharge of the feed and recycle compressors were replaced with 304-stainless steel bottles. These modifications were performed between November 1984 and February 1985. A complete listing of the metallurgical change-out for the affected process piping and equipment is given in Table III-3.

Reactivation of LaPorte LPMEOH PDU for Run E-3 (February - April 1985)

During the commissioning of the LaPorte LPMEOH PDU, the presence of a nickel contaminant in miscellaneous piping and vessels was identified (Reference 1), and found to be a source of nickel carbonyl under synthesis gas conditions. A subsequent cleaning program employing a nickel stripping solution (Metex) selectively removed the contamination without attacking the PDU materials of construction. However, analysis of the carbonyl survey results from Run E-1 indicated that sources of nickel were still present in the feed compressor area, which had not been treated with Metex. Further chemical cleaning was prescribed in order to remove this nickel material from the LaPorte PDU. Additional cleaning requirements were also identified in order to reduce concerns over the possible introduction of debris and other contamination. A summary of the wash solutions is given in Table III-4, and further details of the cleaning procedures are provided in Appendix A.

Following the chemical cleaning operations, an extensive series of carbonyl surveys was performed on the LaPorte LPMEOH PDU. The results of the surveys indicated that iron carbonyl concentrations were above an acceptable level for start-up and operation of the unit. (Further information on the poison survey results are

TABLE III-3

LAPORTE LPMEOH PDU

METALLURGICAL CHANGE-OUT

(November 1984 - February 1985)

Component	Old Material	New Material
21.10 Feed/Product Exchanger	Carbon - 1/2% Moly(S)/304SS(T)	304-SS (S and T)
27.10 Reactor	Carbon - 1/2% Moly	304-SS Lined
27.14 Intermediate Separator	Carbon - 1/2% Moly	304-SS Lined
27.13 Primary Separator	1-1/4% Chrome - 1/2% Moly	304-SS Lined
Piping, 21.10(S) to 27.10*	1-1/4% Chrome - 1/2% Moly	304-SS
Piping, 27.10 to 27.13	1-1/4% Chrome - 1/2% Moly	304-SS
Piping, 27.13 to 21.10(T)	1-1/4% Chrome - 1/2% Moly	304-SS
Piping, 21.10 to 27.14	Carbon Steel	304-SS
Piping, 27.14 to 21.30	Carbon Steel	304-SS
01.13 Feed Surge Tank	Carbon Steel	304-SS Lined
Piping, 01.10 to 01.13	Carbon Steel	304-SS
01.10 Discharge Bottles	Carbon Steel	304-SS
Piping, 01.10 Interstage	Carbon Steel	304-SS
Piping, PV-129 to 01.14	Carbon Steel	304-SS
Piping, 01.13 to 21.10(S)	Carbon Steel	304-SS
01.20 Discharge Bottle	Carbon Steel	304-SS
Piping, 01.20 Recycle	Carbon Steel	304-SS

*Old carbonyl guard beds bypassed.

TABLE III-4

LAPORTE LPMEOH PDU
CHEMICAL WASH SOLUTIONS

Detergent Wash (Oil/Catalyst Removal)

3 wt% Caustic, 1 wt% Trisodium Phosphate,
1 wt% Sodium Metasilicate, 0.1 wt% Triton X-100
Non-ionic Detergent in Demineralized Water
(6 hr. circulation)
Demineralized Water Flush

Citric Acid Wash (Rust Removal)

Acid Step - 3 wt% Citric Acid with Inhibitor
pH Adjusted to 3.0-3.5 with Ammonia
(4 hr. minimum circulation at 150°F)

Chelating Step - 0.5 wt% Citric Acid Addition
pH Adjusted to 8.5-9.5 with Ammonia
0.5 wt% Sodium Nitrite Addition
(4 hr. minimum circulation at 150°F)
Demineralized Water Flush

Metex Wash (Nickel Removal)

Demineralized Water with Metex Solid and Liquid Component
pH Adjusted with Caustic
(1/2 hr. circulation)
Demineralized Water Flush

Passivation Flush

1 wt% Caustic, 0.5 wt% Sodium Nitrite (2 hr. circulation)

provided in Section IV-B). Since the vessels in the slurry loop had previously been lined with stainless steel, the source of the iron carbonyl was believed to be the other components of the loop. (The slurry loop includes the 10.50 slurry pump, 21.20 slurry exchanger, 27.10 reactor, 27.13 primary V/L separator, and associated piping and valves.) As a result, the remaining surfaces in the slurry loop were replaced or coated with materials that would not readily form metal carbonyls. A complete summary of the changes is given in Table III-5. Detailed information on the material upgrade can be found in Appendix B.

E. Process Equipment Additions to LaPorte LPMEOH PDU

In-Line Nuclear Density Gauge

An in-line nuclear density gauge (NDG) was installed downstream of the 10.50 slurry pump. The in-line NDG provides another indicator of changes in the rheological properties of the slurry, and allows a redundant check of the slurry concentration as determined by oil/catalyst inventory and slurry sample analysis. Appendix C contains more detail on the usage of the in-line nuclear density gauge.

22.16 Product Day Tank

A product day tank was installed downstream of the 22.15 liquid-liquid separator (stream 68 of Figure III-1). As the methanol level in the product day tank nears capacity, the methanol is transferred to the product storage tank. The use of the day tank allows closer monitoring of the methanol production rate, thus improving the closure of material balances around the PDU. With improved monitoring capability, performance parameters (e.g., productivity and conversion) can be determined with greater certainty.

TABLE III-5

LAPORTE LPMEOH PDU
METALLURGICAL CHANGE-OUT (APRIL 1985)

	Old Material	New Material
Piping	1-1/4% Chrome - 1/2% Moly	304-SS
Mogas Valves	1-1/4% Chrome - 1/2% Moly	Existing body coated with 310-SS, new 316-SS ball
Rockwell Valves	Carbon Steel*	Replaced or isolated from process with stellited 316-SS gate or globe valves
Expansion Joints	304/321-SS	Same
Slurry Heat Exchanger		
Tubes	304-SS	Same
Heads	1-1/4% Chrome - 1/2% Moly	310-SS Coated
Tube Sheet	Carbon - 1/2% Moly	310-SS Coated
Valve 340-S	Carbon Steel	Replaced with Stellited 316-SS gate valve
FE-174	316-SS	Same
Slurry Pump		
Liner	HC-250	Same
Casing	Carbon - 1% Moly	310-SS Coated

*Rockwell valve plugs had been coated with a 70% nickel - 10% chrome hard facing.

IV. GAS HOLDUP TEST AND POISONS SURVEY

A. Two-Phase Gas Holdup Studies

During the PDU reactivation following the first set of metallurgical upgrades (March/April 1985), a series of two-phase gas holdup measurements was taken to study the effect of temperature, pressure, and superficial gas velocity on the gas holdup in the bubble column reactor at LaPorte. The data show no apparent effect of temperature on gas holdup at 6,310 kPa (915 psia), although pressure was found to have a marked effect on gas holdup at 76°C (169°F). The studies also revealed a trend toward increased gas holdup with increasing reactor height, especially when the gas holdup was high. Increasing the liquid velocity suppressed the gas holdup modestly and perhaps tended to flatten the axial profiles. Table IV-1 lists the range of conditions covered in the study. Most of the data were obtained at a liquid velocity of 2 cm/s, as compared to a liquid velocity of 5 cm/s for the data gathered during 1983 and 1984 (Reference 1). A nuclear density gauge (NDG), which traverses the height of the reactor, was used to determine the gas holdup in the reactor. To ensure accurate density measurements, the NDG requires frequent recalibration to check the parameters required for density calculation. Calibrations for the reactor and slurry line NDG's performed for Runs E-2 and E-3 are documented in Appendix C for reference. The gas holdup data obtained during March and April 1985 are presented and discussed below. A significant result of this test series was the discovery of detectable variations in gas holdup as a function of axial position. The data show a consistent trend of increasing gas holdup with increasing elevation. This variation becomes more pronounced when the gas holdup exceeds 30%.

The 1983/1984 data at LaPorte indicated that gas holdup as measured by the NDG at an elevation of 54 in. (137 cm) above the distributor tray agreed with the average gas holdup across the entire reactor

TABLE IV-1

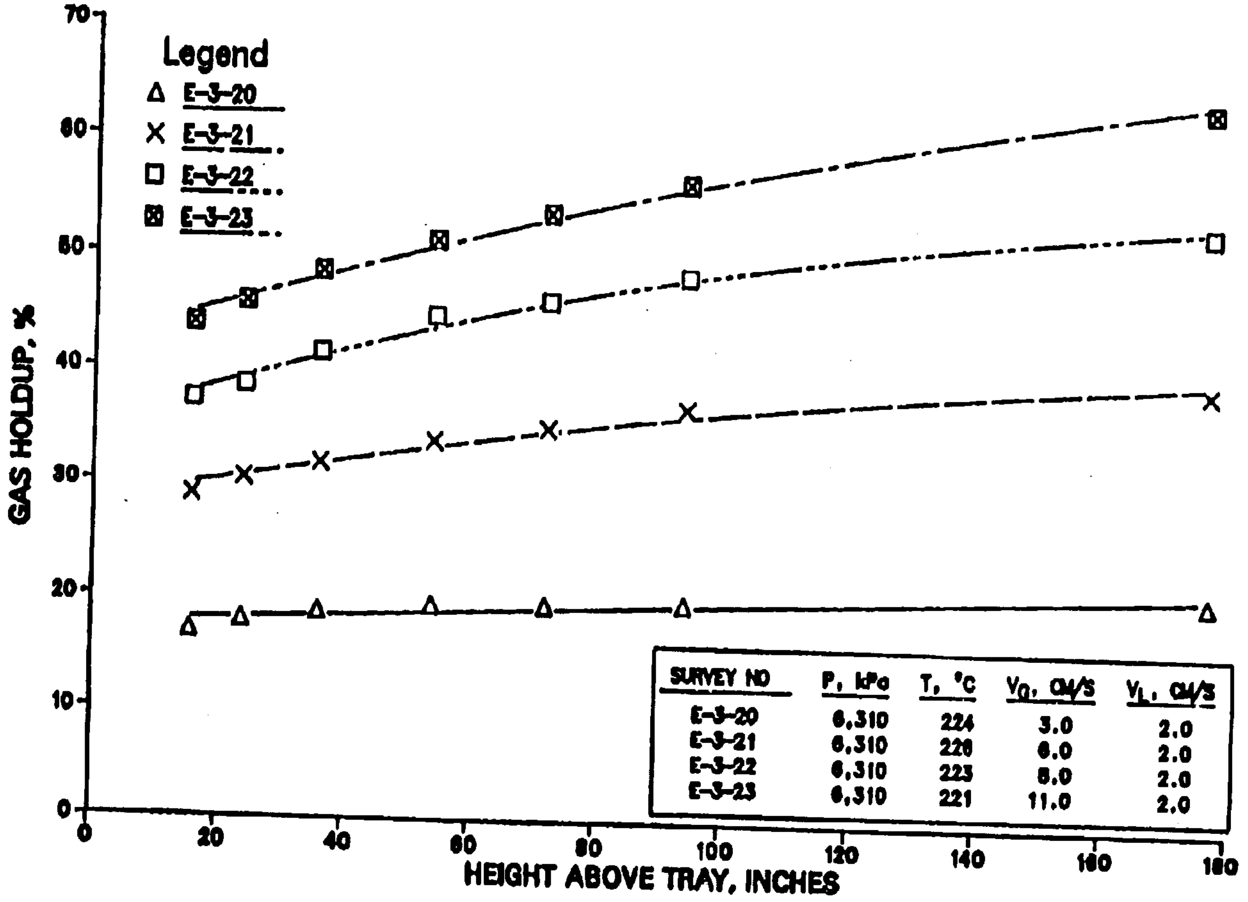
RANGE OF PARAMETERS IN TWO-PHASE GAS HOLDUP STUDIES (MARCH 1985)

Nominal Pressure kPa (psia)	Nominal Temperature °C (°F)	Range of Superficial Gas Velocity cm/s (ft/s)	Range of Superficial Liquid Velocity cm/s (ft/s)
170 (25)	76 (169)	4-20 (0.13-0.66)	2 (0.07)
660 (95)	76 (169)	3-19 (0.10-0.62)	2 (0.07)
6,310 (915)	76 (169)	3-8 (0.10-0.26)	2 (0.07)
6,310 (915)	150 (302)	3-12 (0.10-0.39)	2-5 (0.07-0.16)
6,310 (915)	225 (437)	3-11 (0.10-0.36)	2 (0.07)

as measured by pressure drop. Only a few axial NDG surveys were made during the late 1983/early 1984 studies because the NDG traverse was not functioning through most of that period. The traverse was operational by February 1984, and subsequent measurement of two-phase gas holdup for the N_2/Freezene-100 system showed little effect of elevation on the gas holdup in the reactor. The gas holdup increased only slightly with elevation, but the differences were often within the apparent scatter of the data. The general conclusion from these earlier measurements was that elevation probably had little effect on gas holdup.

The data from the more recent two-phase studies, which exhibit axial profiles for higher gas holdups, show that the trend toward higher void volume at higher elevations is real. Some of these profiles are shown on Figure IV-1. Changes of 30% or more in gas holdup between the top and bottom of the reactor are observed under some conditions. However, measurements at the 54-in. (137-cm) elevation still represent a reasonable average value across the reactor and should provide a reasonable basis for comparison to other data obtained from the LaPorte LPMEOH reactor.

During the two-phase studies, liquid velocity was changed from 2 cm/sec to 5 cm/sec to determine whether there would be any effect on the gas holdup. The complete profiles are shown in Figure IV-2. Increasing the liquid velocity tended to flatten the axial profile, but did not significantly change the gas holdup at the 54-in. (137-cm) position. The small decrease in gas holdup between surveys E-3-35 and E-3-36 can be largely explained by the slight decrease in gas velocity that occurred between the two test periods.



SURVEY NO	P, kPa	T, °C	V_G, CM/S	V_L, CM/S
E-3-20	6,310	224	3.0	2.0
E-3-21	6,310	226	6.0	2.0
E-3-22	6,310	223	8.0	2.0
E-3-23	6,310	221	11.0	2.0

Figure IV-1. LaPorte LPMEOH PDU Axial Gas Holdup Profile for N_2/ Freezene-100 System

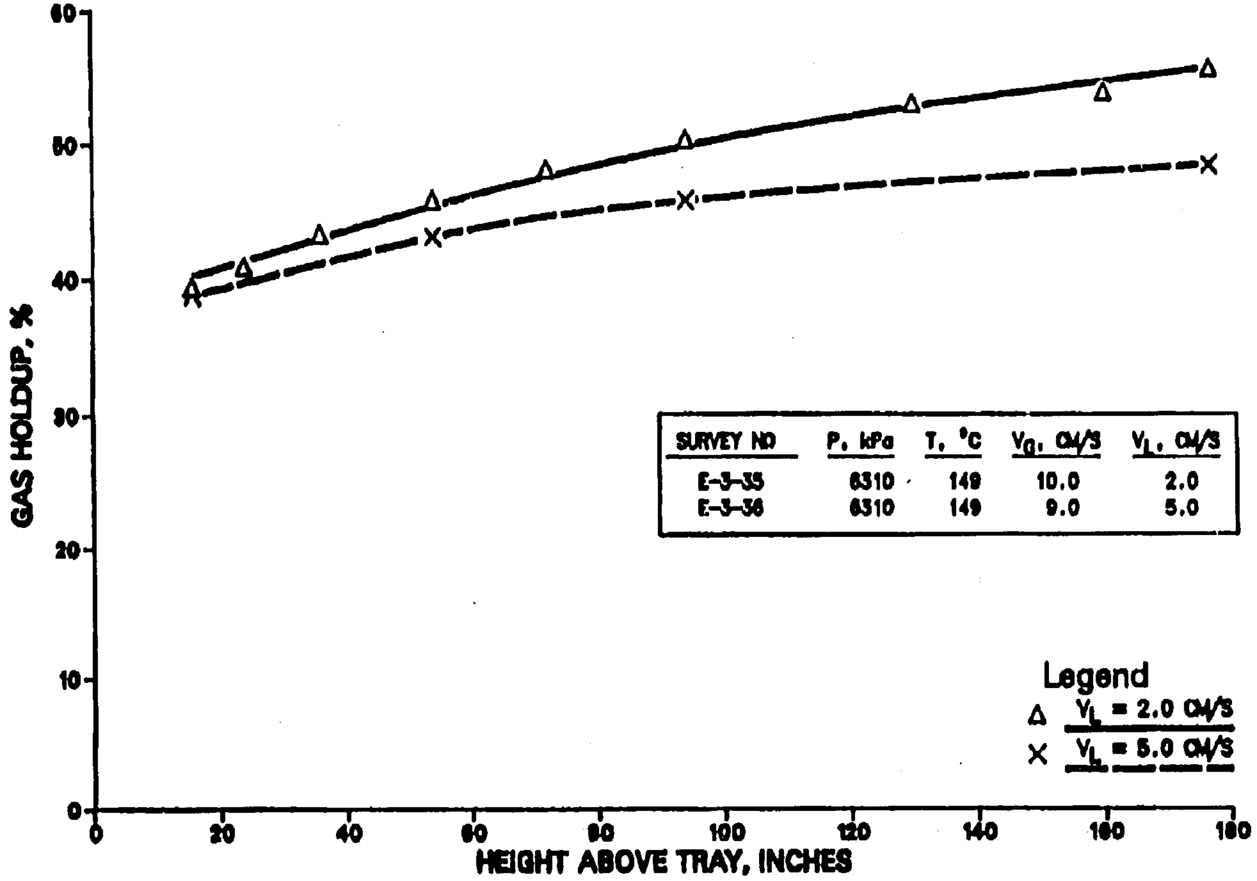


Figure IV-2. LaPorte LPMEOH PDU Effect of Liquid Velocity of Gas Holdup for N_2/Freezene-100 System

All two-phase gas holdup data at the 54-in. (137-cm) elevation obtained during March 1985 for the N_2/Freezene-100 system are listed in Table IV-2. As shown in Figure IV-3, the results are significantly higher than the data obtained in 1983/1984, especially at high superficial gas velocities. A portion of the difference perhaps can be attributed to a lower liquid velocity used in this test series (2 cm/s vs. 5 cm/s). Another possible cause is that heating Freezene-100 oil to 250°C (482°F) changes its bubble-coalescing and foaming properties in some unknown but significant manner, perhaps by volatilizing light components of the oil. The slurry-line NDG readings taken during the period of the carbonyl survey (250°C) did show an apparently steady increase in liquid density, probably as a result of volatilizing the light ends of the oil (Table IV-3).

Figure IV-4 compares the gas holdup data at 6,310 kPa (915 psia) and various temperatures. Although the oil viscosity should change by a factor of 4 over the temperature range investigated, no apparent temperature effect on gas holdup is observed from these data. This is in agreement with the correlation of Akita and Yoshida (Reference 3), which contains only a small inverse dependence of gas holdup on liquid viscosity. The gas holdup data at 76°C (169°F) and various pressures are plotted as a function of the superficial gas velocity in Figure IV-5. The effect of pressure could be the result of changes in gas density. The effect of pressure and superficial gas velocity on the gas holdup for the N_2/Freezene-100 system can be correlated by the equation:

$$\varepsilon_G = 0.128 \left(\frac{P}{915}\right)^{0.2} U_G^{0.578} \qquad \text{(Eq. IV-1)}$$

TABLE IV-2

LAPORTE LPMEOH PDU
TWO-PHASE GAS HOLDUP N_2/FREEZENE-100 SYSTEM
(March 1985)

Survey No.	Pressure, kPa (psia)	Temperature °C (°F)	Superficial Gas Velocity, cm/s	Superficial Liquid Velocity, cm/s	Gas Holdup, (@ 54-in. Elevation) %
E-3-4	170 (25)	76 (169)	4	2	13
E-3-5	170 (25)	76 (169)	7	2	20
E-3-6	170 (25)	76 (169)	13	2	28
E-3-7	170 (25)	76 (169)	20	2	32
E-3-8	660 (95)	76 (169)	3	2	18
E-3-9	660 (95)	76 (169)	7	2	26
E-3-13	6310 (915)	76 (169)	3	2	24
E-3-14	6310 (915)	76 (169)	6	2	38
E-3-15	6310 (915)	76 (169)	8	2	42
E-3-16	6310 (915)	149 (300)	12	2	49
E-3-17	6310 (915)	149 (300)	10	2	44
E-3-18	6250 (905)	153 (307)	4	2	25
E-3-20	6340 (920)	224 (435)	3	2	19
E-3-21	6310 (915)	226 (439)	6	2	34
E-3-22	6310 (915)	223 (438)	8	2	45
E-3-23	6310 (915)	221 (430)	11	2	49
E-3-26	660 (95)	77 (171)	4	2	17
E-3-27	660 (95)	76 (169)	7	2	24
E-3-28	660 (95)	77 (171)	12	2	32
E-3-29	660 (95)	77 (171)	19	2	38
E-3-32	170 (25)	77 (171)	7	2	20
E-3-33	170 (25)	76 (169)	12	2	26
E-3-34	170 (25)	76 (169)	19	2	31
E-3-35	6310 (915)	149 (300)	10	2	46
E-3-36	6310 (915)	149 (300)	9	5	43

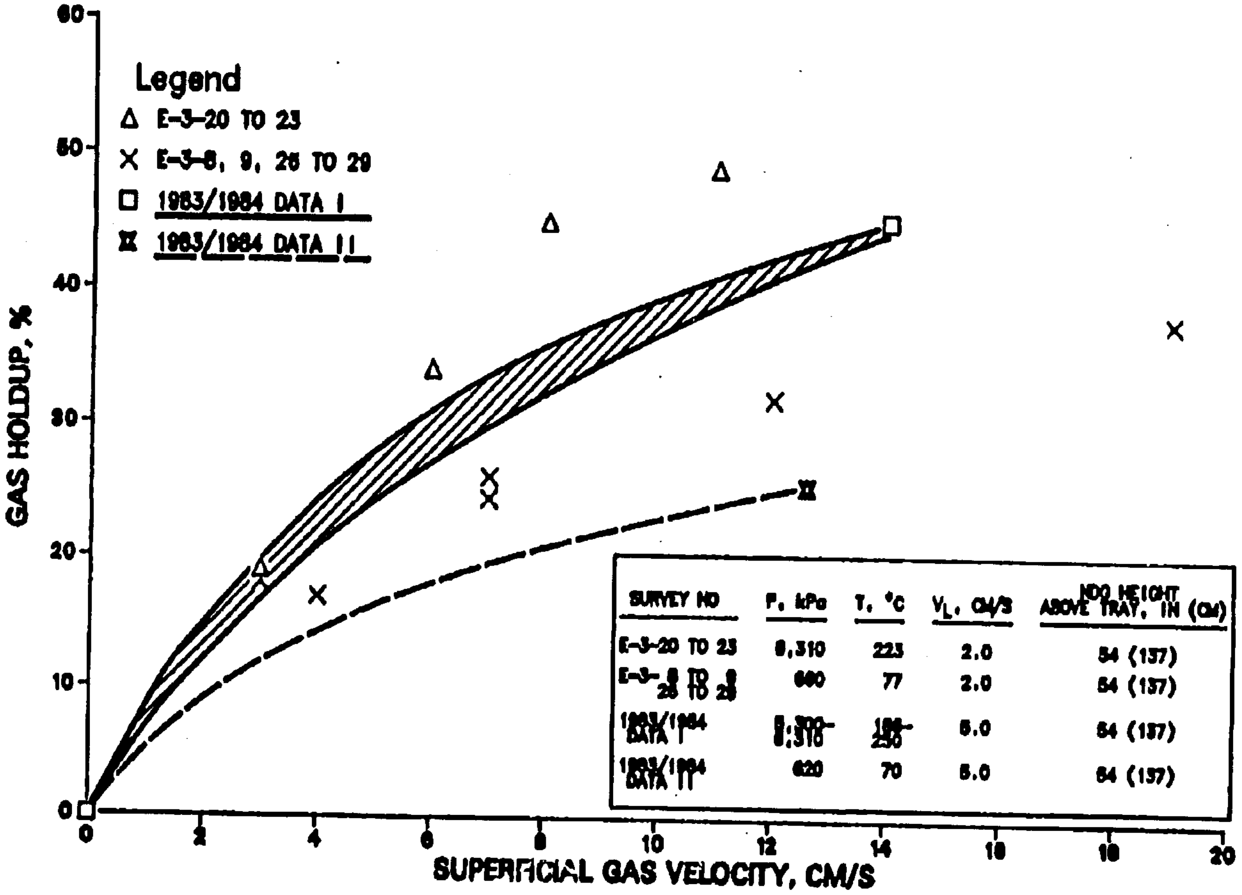


Figure IV-3. LaPorte LPMEOH PDU Comparison of Gas Holdup Data for N_2/Freezene-100 System

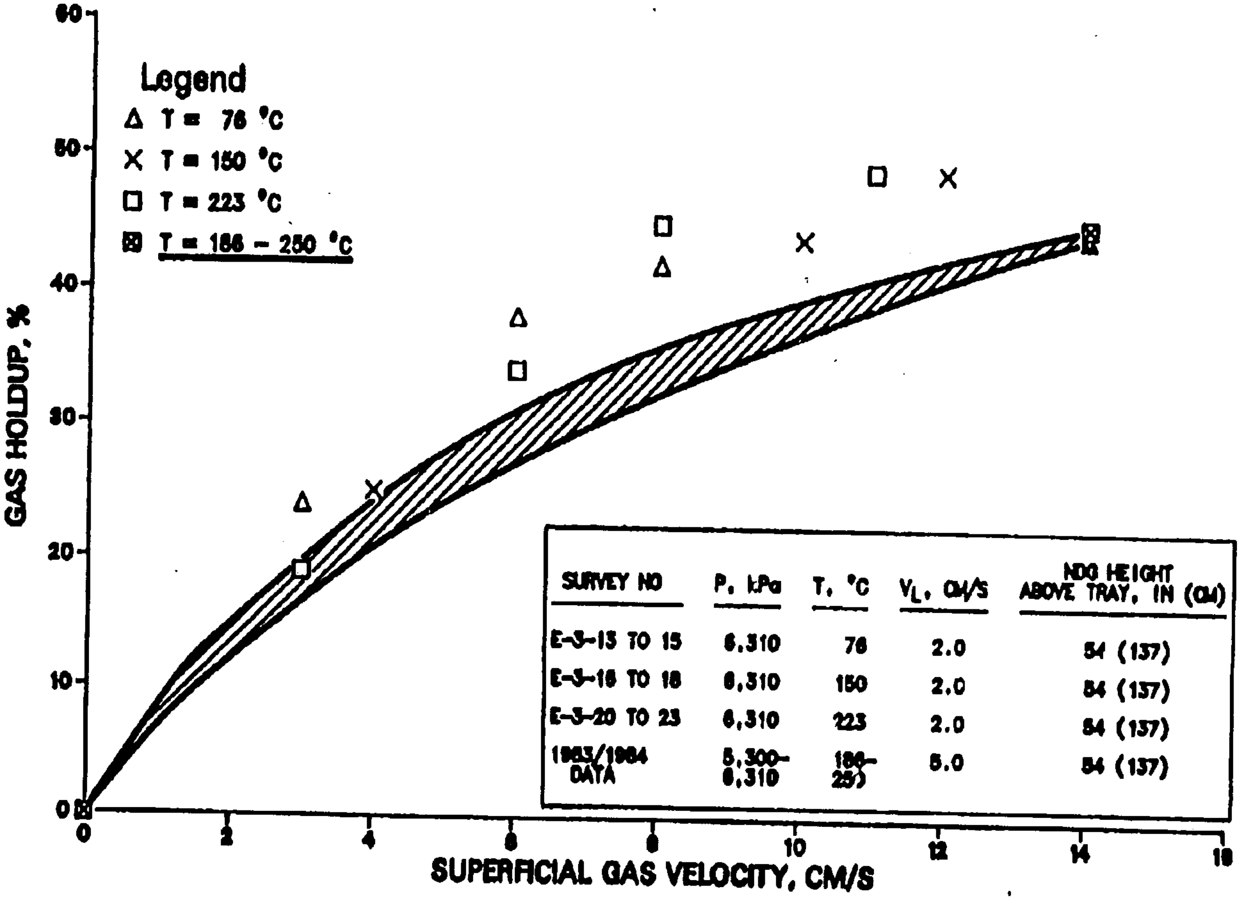
TABLE IV-3

LAPORTE LPMEOH PDU

APPARENT DENSITY INCREASE OF CIRCULATING LIQUID

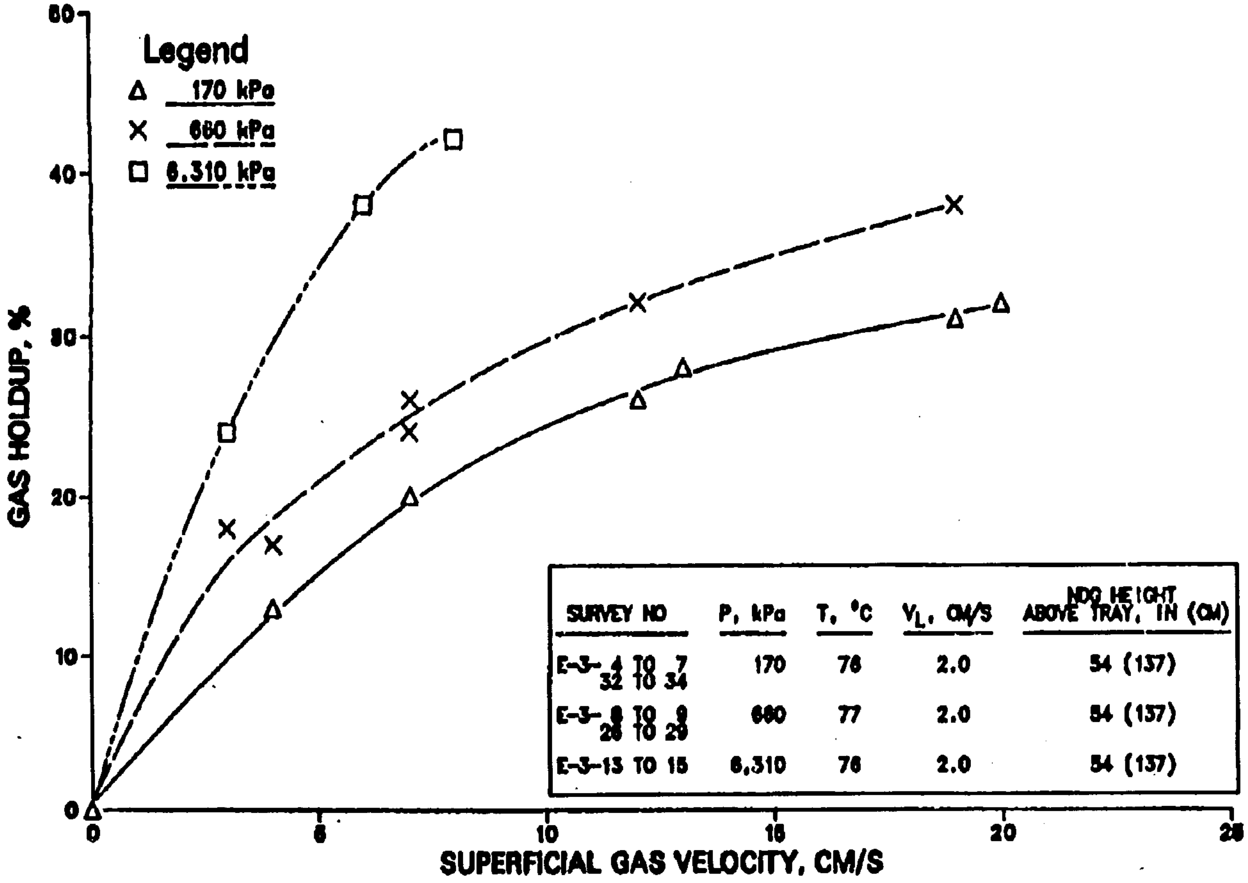
(March 1985)

Survey No.	Date	Time Hours	Temperature °C (°F)	Liquid Rate GPM	Slurry Line NDG Reading mV	Indicated Density g/cm3
E-3-37	4 March	1000	248 (478)	203	2590	0.707
E-3-38	4 March	-	247 (477)	69	2580	0.713
E-3-39	7 March	0915	248 (479)	202	2570	0.719
E-3-40	9 March	1105	252 (483)	189	2562	0.723



SURVEY NO	P, kPa	T, °C	V_L, CM/S	NDG HEIGHT ABOVE TRAY, IN (CM)
E-3-13 TO 15	6,310	76	2.0	54 (137)
E-3-16 TO 18	6,310	150	2.0	54 (137)
E-3-20 TO 23	6,310	223	2.0	54 (137)
1983/1984 DATA	5,300-6,310	186-250	5.0	54 (137)

Figure IV-4. LaPorte LPMEOH PDU Effect of Temperature on Gas Holdup for N_2/Freezene-100 System



SURVEY NO	P, kPa	T, °C	V_L, CM/S	NDG HEIGHT ABOVE TRAY, IN (CM)
E-3-4 TO 7 32 TO 34	170	76	2.0	54 (137)
E-3-8 TO 9 28 TO 29	660	77	2.0	54 (137)
E-3-13 TO 15	6,310	76	2.0	54 (137)

Figure IV-5. LaPorte LPMEOH PDU Effect of Pressure of Gas Holdup for N_2/Freezene-100 System