TABLE B-1

LAPORTE LPMEOH PDU

SLURRY LOOP METALLURGICAL CHANGE-OUT

(April 1985)

- OBJECTIVE Replace or coat, where necessary, remaining carbon steel or low alloy steel surface in the slurry loop.

- SCOPE

	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*	Replace 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.

APPENDIX C

NUCLEAR DENSITY GAUGE CALIBRATION

To obtain accurate density measurement, the nuclear density gauge (NDG) requires frequent calibration to check the parameters used in density calculation. NDG readings for the empty reactor were initially obtained on 23 February 1985. After a correction was made for the 13-mV background reading and the absorption of N_2 in the reactor, a value of 8,640 mV was determined as the empty vessel reading at 54 in. (137 cm) above the bubble cap tray. This compares with 11,100 mV for the empty reactor in previous surveys; most of the reduction is due to the new 1/16-in. thick, 304 stainless steel liner. The NDG was further calibrated with Freezene-100 oil. At various temperatures, these readings are listed in Table C-1 and plotted as a function of the oil density in Figure C-1.

The data yield a straight calibration line for Freezene-100 oil at the position 54-in. (137 cm) above the tray. The equation for this calibration line is:

$$\rho_L = 0.222 \ln \frac{8,640}{V - V_o} \qquad \text{(Eq. C-1)}$$

Where ρ_L = density of Freezene-100 oil (g/cm^3)
V = NDG voltage output (mV)
V_o = NDG background voltage with source shutter closed (mV)

The parameter of 0.222 g/cm^3 is consistent with the previous calibration done in 1983 (Reference 1). The calibration at other elevations of the reactor is given by:

$$\rho_L = 0.222 \ln \frac{8,640\ C_R}{V - V_o} \qquad \text{(Eq. C-2)}$$

where C_R is the ratio of the reading at a given elevation to that at 54 in. (137 cm) above the tray. Table C-2 lists values of C_R measured at various elevations with the reactor empty and with oil in the reactor. The readings with oil at 130 in. (330 cm) show a significant change relative to the empty

TABLE C-1

LAPORTE LPMEOH PDU
REACTOR NDG READING WITH FREEZENE-100 OIL

Temperature, °C (°F)	ρ_L, g/cm3	NDG Reading, mV	$V-V_o$, mV
13 (55)	0 (Empty)		8,640
13 (56)	0.853	198	185
23 (73)	0.846	204	191
72 (161)	0.815	232	219
76 (169)	0.812	236	223
233 (434)	0.717	258	245

Note: $\rho_L = 0.861 - 0.000643 * T(°C)$
V_o (Background NDG reading) = 13 mV

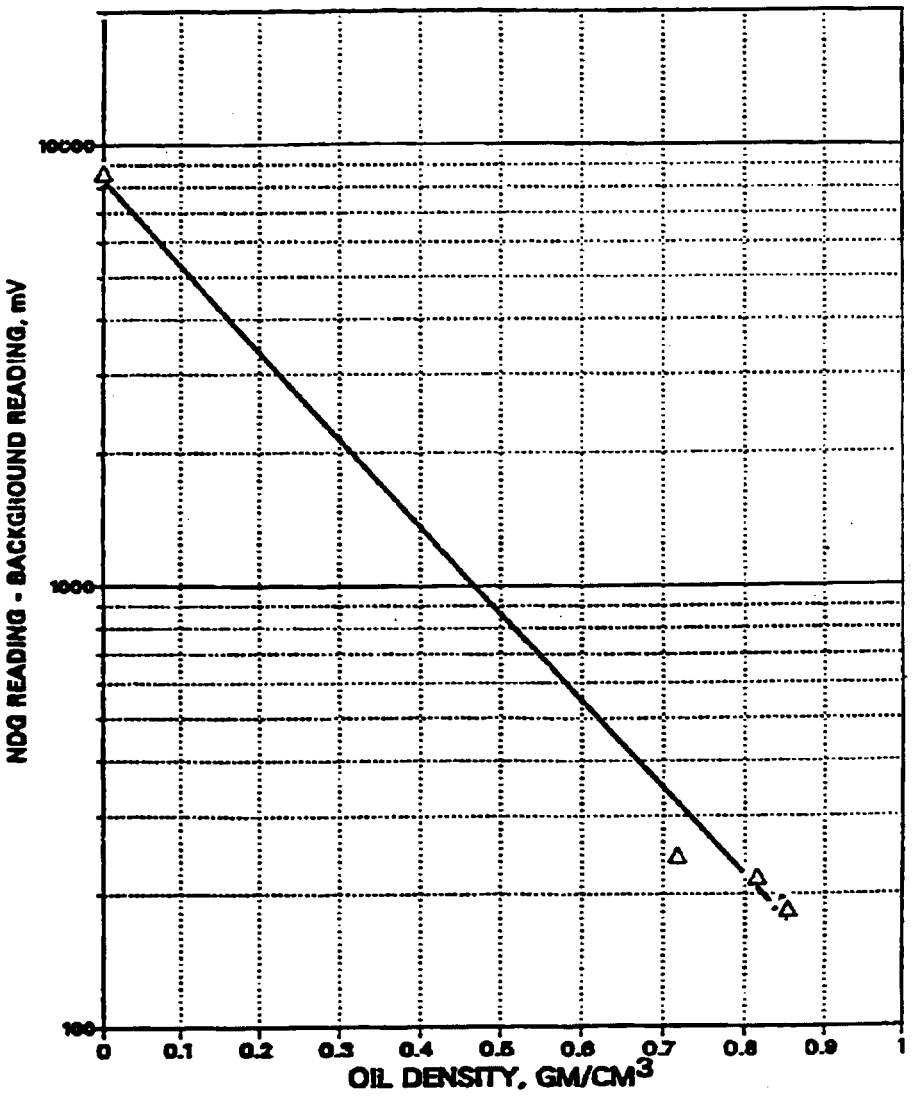

Figure C-1. LaPorte LPMEOH PDU Calibration of Reactor NDG with Freezene-100 Oil

TABLE C-2

LAPORTE LPMEOH PDU
REACTOR NDG CALIBRATION (MARCH 1985)

Position Above Tray, in. (cm)	Empty Reactor (NDG Survey E-3-1) NDG Reading,* mV	Calibration Ratio, C_R	Oil Only at 76°C, 650 kPa (NDG Survey E-3-7) NDG Reading,** mV	Calibration Ratio, C_R	Oil Only at 74°C, 100 kPa (NDG Survey E-3-25) NDG Reading,** mV	Calibration Ratio, C_R	Oil Only at 76°C, 170 kPa (NDG Survey E-3-30) NDG Reading,** mV	Calibration Ratio, C_R	Avg. C_R For Survey E-3-1 To E-3-40
15-3/4 (40)	6,020	0.70	157	0.70	149	0.67	150	0.67	0.69
24 (61)	6,060	0.70	156	0.70	152	0.68	155	0.70	0.70
36 (91)	8,900	1.03	226	1.01	223	1.00	223	1.00	1.01
54 (137)	8,640	=1.00	224	=1.00	223	=1.00	223	=1.00	1.00
72 (183)	8,700	1.01	224	1.00	223	1.00	223	1.00	1.00
94 (239)	8,870	1.03	225	1.00	226	1.01	226	1.01	1.02
130 (330)	8,820	1.02	212	0.95	219	0.98	216	0.97	0.98
176-3/4 (449)	8,820	1.02	218	0.97	-	-	221	0.99	1.00

*Corrected for background reading (13 mV) and N_2 density.
**Corrected for background reading (13 mV).

vessel readings; otherwise, differences are probably within the ability to reproduce the exact position of the NDG in its traverse between surveys and other sources of noise in the data. The average values for C_R that are used in reducing the two-phase gas holdup data are listed in the last of column Table C-2.

By extension of Equation (C-2), the NDG calibration in the presence of gas/oil and catalyst becomes:

$$\ln \frac{8640 \cdot C_R}{V - V_O} = \frac{\epsilon_L \rho_L}{0.222} + \frac{\epsilon_G \rho_G}{a_G L} + \frac{\epsilon_S \rho_S}{0.265} \qquad \text{(Eq. C-3)}$$

Where
- ϵ_G = volume fraction of gas
- ϵ_L = volume fraction of oil
- ϵ_S = volume fraction of catalyst
- ρ_G = density of gas (g/cm^3)
- ρ_L = density of oil (g/cm^3)
- ρ_S = density of catalyst (g/cm^3)
- $a_G L$ = product of specific absorbance of gas and the effective path length (cm^3/g), which is equal to 0.254 for N_2 and 0.244 for CO-rich syngas.

For the calculation of two-phase gas holdup, the last term of Equation (C-3) drops out.

A repeat set of empty reactor readings was obtained on 1 March after the reactor had been heated to 227°C (440°F) and cooled. The reading at 54 in. (137 cm) above the bubble cap tray had increased slightly to 8,760 mV. Thus, the empty reactor voltage reading in Equation (C-3) should be replaced by 8,760 mV in calculating the gas holdup data for NDG survey E-2-24 and later. However, this change corresponds to only 0.003 g/cm^3 in the density measurements, which is not significant.

After the completion of the second metallurgy changes in April, new sets of empty reactor and oil-only readings were obtained and are shown in Table C-3. The empty reactor reading at 54 in. (137 cm) above the tray declined slightly to 8,380 mV. The correction factor, C_R, with respect to the 54-in. (137-cm)

TABLE C-3

LAPORTE LPMEOH PDU
REACTOR NDG CALIBRATION (APRIL 1985)

Position Above Tray, in. (cm)		Empty Reactor (NDG Survey E-3-1) NDG Reading,* mV	Calibration Ratio, C_R	Oil Only at 76°C, 650 kPa (NDG Survey E-3-7) NDG Reading,** mV	Calibration Ratio, C_R	Oil Only at 74°C, 100 kPa (NDG Survey E-3-25) NDG Reading,** mV	Calibration Ratio, C_R	Oil Only at 76°C, 170 kPa (NDG Survey E-3-30) NDG Reading,** mV	Calibration Ratio, C_R	Avg. C_R For Survey E-3-1 To E-3-40
15-3/4	(40)	5,441	0.65	128	0.67	270	0.66	255	0.68	0.67
24	(61)	5,665	0.68	131	0.68	276	0.67	256	0.68	0.68
36	(91)	8,478	1.01	193	1.01	413	1.00	377	1.00	1.01
54	(137)	8,380	≡1.00	192	≡1.00	412	≡1.00	376	≡1.00	≡1.00
72	(183)	8,550	1.02	196	1.02	417	1.01	382	1.02	1.02
94	(239)	8,688	1.04	199	1.04	426	1.03	388	1.03	1.03
130	(330)	8,711	1.04	185	0.96	406	0.99	375	1.00	1.00
176-3/4	(449)	8,847	1.06			419	1.02	393	1.05	1.05

*Corrected for background reading (13 mV) and N_2 density.
**Corrected for background reading (13 mV).

position also changed slightly. The values selected for NDG surveys E-3-41 to E-3-60 are listed in the last column of Table C-3. The remaining parameters in Equation C-3 are unchanged. Table C-4 shows the empty reactor readings taken on 1 May before the start of in-situ reduction for Run E-3. The reading at 54 in. (137 cm) above the bubble cap tray declined slightly to 8,342 mV, corresponding to only 0.001 g/cm^3 in the density measurement. Therefore, the empty reactor reading of 8,380 mV obtained on 26 April (NDG survey E-3-47) is still used for the subsequent gas holdup calculations. Slightly different correction factors were obtained, and these values were used for NDG surveys E-3-53 to E-3-104.

The newly installed NDG on the slurry line was calibrated in the same manner. Table C-5 and Figure C-2 show the change of NDG voltage output as a function of oil density in the pipe. The equation representing the calibration line drawn through the data is simply:

$$\rho_L = 1.5 \ln \frac{4,150}{V} \qquad \text{(Eq. C-4)}$$

Extension of Equation (C-4) to the case in which entrained gas and/or catalyst are present gives:

$$\ln \frac{4,150}{V} = \frac{\epsilon_L \rho_L}{1.53} + \frac{\epsilon_G \rho_G}{1.72^*} + \frac{\epsilon_S \rho_S}{1.79} \qquad \text{(Eq. C-5)}$$

The slurry line NDG was recalibrated on 22 April 1985. Due to the change of slurry piping to stainless steel, the NDG voltage output from an empty pipe fell to 3,690 mV. The background reading (with shutter closed) was negligible, as before. Based on a single oil-only, zero-flow reading of 2,131 mV at 32°C (89°F), ρ_L = 0.841 g/cm^3, NDG survey E-3-41, the new calibration for the slurry line NDG becomes:

$$\ln \frac{3,690}{V} = \frac{\epsilon_L \rho_L}{1.53} + \frac{\epsilon_G \rho_G}{1.75^{*+}} + \frac{\epsilon_S \rho_S}{1.83} \qquad \text{(Eq. C-6)}$$

*Value for nitrogen only.
+Value for CO-rich gas should be 1.70.

With known oil and catalyst densities, the solids concentration can be calculated using Equation (C-6).

TABLE C-4

REACTOR NDG CALIBRATION

(May 1985)

Position Above Tray, in. (cm)	Empty Reactor (NDG Survey E-3-52) NDG Reading,* mV	Calibration Ratio CR
15-3/4 (40)	5,628	0.68
24 (61)	5,729	0.69
36 (91)	8,495	1.02
54 (137)	8,342	1.00
72 (183)	8,523	1.02
94 (239)	8,645	1.04
130 (330)	8,670	1.04
176-3/4 (449)	8,808	1.06

*Corrected for background reading (29 mV) and N_2 density.

TABLE C-5

SLURRY LINE NDG READING WITH FREEZENE-100 OIL

Temperature °C (°F)	ρ_L, g/cm3	NDG Reading, mV
13 (55)	Empty	4,150
13 (55)	0.853	2,350
76 (169)	0.812	2,415
148 (435)	0.766	2,490
224 (55)	0.717	2,575

*ρ_L = 0.861-0.000643 * T(°C)

**The background readings (22 mV for empty pipe and 7 mV for oil-filled pipe) are small relative to normal voltage output and are neglected in calculations.

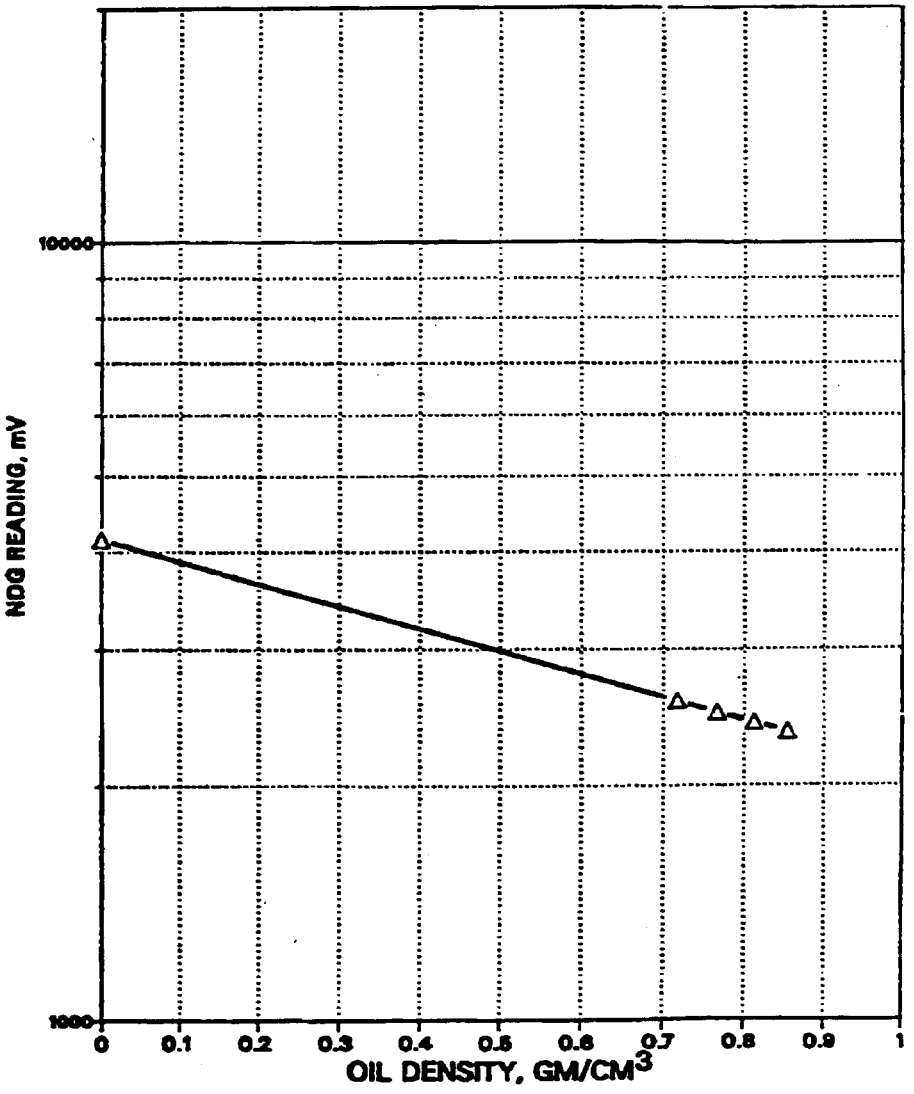

Figure C-2. LaPorte LPMEOH PDU Calibration of Slurry Line NDG with Freezene-100 Oil

APPENDIX D

LAPORTE LPMEOH PDU

INSPECTION AFTER CARBONYL SURVEY

(11-12 March 1985)

After completion of the carbonyl poisons survey, selected areas of the slurry loop piping, the slurry pump, and the outlet head of the 21.10 feed/product heat exchanger were disassembled for inspection on 11 and 12 March.

A small quantity of debris/slurry material (less than 2.27 kg (5 lb), was found in the slurry pump casing and in the annular space behind the sleeve of two expansion joints around the slurry pump. Otherwise, the slurry loop was generally clean. The debris/slurry material left in these areas is suspected to be the source of solids found in the circulation oil during the carbonyl survey. All stainless steel surfaces appeared to be in good condition; however, evidence of pitting and material displacement was found on carbon steel and 1-1/4% Cr - 1/2% Mo steel surfaces.

Details of the inspection are described below:

Reactor

The 6-in. catalyst loading nozzle was opened. The reactor walls were clean with no apparent solid deposits. It was difficult to see the bubble caps and the tray clearly because of the distance from the loading nozzle; however, they appeared to be clean.

The reactor overhead spool pipe, which had a 1-1/4% Cr - 1/2% Mo flange on one end, was disconnected for inspection. Although the surface of the Cr-Mo flange was pitted, no apparent metal loss was observed on the stainless steel pipe and the stainless steel flange on the other end of the spool.

Expansion Joints

Two horizontal expansion joints, EJ-1 and EJ-2, at the discharge and inlet to the slurry pump were removed for inspection. The stainless steel sleeves of the expansion joints appeared to be in good condition, with no apparent metal loss. There was an approximately 1.3-cm (0.5-in.) thick accumulation of debris/slurry material in the bottom half of the annular space behind the sleeves. The debris/slurry material is believed to consist of the methanol synthesis catalyst left from the previous runs. It was removed and the expansion joints cleaned with steam.

Slurry Circulation Pump

The mechanical seal of the slurry circulation pump was removed for repair. The pump liner, which is made of a high chromium alloy, was in good condition with no evidence of pitting. An accumulation of debris/slurry material was found in the pump casing and in the cavities around the internal casing assembly nuts. The debris/slurry material was later removed and the pump internals cleaned with steam.

Valve 304-S

This valve is made of carbon steel. Both inlet and outlet flanges showed evidence of apparent metal loss.

Valves 307-S and 308-S

These valves have a carbon steel body with hard alloy coated plug and plug well. There was evidence of pitting on both valves. After the inspection, it was learned that the hard alloy coating on the valve plugs contained a significant nickel alloy component.

Slurry Heat Exchanger

The bottom cone-shaped head made of 1-1/4% Cr - 1/2% Mo steel was removed for inspection. All tubes were open. There were some apparent rough spots on the surface of the bottom head, which were attributed to pitting. The condition of the tube sheet, which is made of Carbon - 1/2% Mo steel, was difficult to see due to its position approximately 30 cm (1 ft) up into the exchanger shell.

Slurry Sampling Line

The spool piece between valves 307-S and 308-S was removed for inspection. The inside surface showed apparent signs of metal loss. Metal analysis using a Texas Nuclear Alloy Analyzer identified a 0.34 wt% content of nickel on the outside surface of this 1-1/4% Cr - 1/2% % Mo pipe. However, no nickel was identified on the internal surface of the pipe. It is speculated that during the Cr-Mo pipe manufacture, some scrap stainless steel material may have been included in the 'heat' as the source of the chromium. The nickel on the internal surface is suspected to have been reacted away by forming nickel carbonyl.

Subsequent surveying of the remainder of the Cr-Mo slurry loop piping with the Texas Nuclear Alloy Analyzer did not indicate any other nickel-containing Cr-Mo pipe in the slurry loop.

Slurry Transfer Line

The 4-in. carbon steel header of the slurry transfer lines was opened for inspection. The header appeared to be in good condition with no evidence or erosion or pitting. The header, along with the slurry loop, was washed with ammoniated citric acid in January 1985, but was not in contact with CO-rich gas during the carbonyl survey.

Feed/Product Heat Exchanger

The entire heat exchanger is made of stainless steel. The outlet head of the exchanger was removed for inspection. All tubes were clean. A brownish stain on the tube sheet indicated that oil carry-over containing a small quantity of residual catalyst was condensed and flowed through the tubes. A thin layer of residue, about 5 cm (2 in.) wide, was found in the lower portion of the head. The stainless steel head and flanges were in good condition with no evidence of metal loss.

APPENDIX E

RUN E-2 DETAILED DATA ACQUISITION SHEETS

LaPORTE LPMETHANOL PROCESS AVERAGE REPORT
ENTRAINED MODE
PROCESS VARIABLES & ANALYTICAL SUMMARY

AVERAGE : 06/15/0300—>1100
CASE A

DATE :	27-Jun-84
TIME :	02:42 PM
RUN ID NUMBER :	EB-X954
FEED GAS TYPE:	BALANCED GAS
REACTOR FEED GAS INLET TEMP. (deg.C) :	142.6
OIL/SLURRY INLET TEMP. (deg.C) :	251.8
AVE. REACTOR TEMPERATURE (deg.C) :	250.2
REACTOR OUTLET TEMP. (deg.C) :	251.8
GUARD BED FEED PRESSURE (kPa) :	6358
PRIMARY SEPARATOR GAS PRESSURE (kPa) :	6308
GAS SUPERFICIAL VELOCITY (cm/sec) :	8.9
LIQUID SUPERFICIAL VELOCITY (cm/sec) :	4.5
SLURRY CONCENTRATION (wt%) :	43.9
CATALYST OXIDE WT IN REACTOR (kg oxide) :	-
GAS HOLD-UP :	-
SPACE VELOCITY (l/kg-hr) :	4230
RECYCLE/FRESH FEED RATIO :	2.53281
OIL/SLURRY CIRCULATION RATE (m3/hr) :	41.9
PROD.SEPARATOR GAS FLOWRATE <50> + <55> (kgmol/hr) :	94.84
PURGE GAS FLOW RATE <50> (kgmol/hr) :	6.42

STREAM #	1	55	10	15	25#	25#	68	
STREAM NAME	FRESH FEED	RECYCLE GAS	GUARD-BED FEED	REACTOR FEED	V/L SEP	V/L SEP	MEOH PRODUCT	
ON-LINE GC#	1	2	1	2	2	1		
COMPONENT	<MOL%>	<MOL%>	<MOL%>	<MOL%>	<MOL%>	<MOL%>	<MOL%>	<WT%>
H2	63.99(1)	57.90	57.75	59.34	53.92	52.87	———	———
CO	27.77	15.35	19.81	19.33	14.68	14.51	———	———
CO2	2.42	4.80	4.14	4.05	4.38	4.46	———	———
N2	5.69	20.11	15.74	15.77	17.98	18.30	———	———
CH4	0.12	0.58	0.40	0.49	0.52	0.49	———	———
H2O	0.01	0.00	0.04	0.00	0.34	0.43	2.55	1.40
CH3OH	0.00	0.36	0.35	0.24	8.40 (2)	8.80 (2)	97.10	95.00
DME	0.00	0.00	0.01	0.00	0.00	0.01	0.36	0.50
C2H5OH	———	———	———	———	———	———	0.00	0.00
C3OH'S	———	———	———	———	———	———	0.00	0.00
C4OH'S	———	———	———	———	———	———	0.00	0.00
C5OH'S	———	———	———	———	———	———	0.00	0.00
ALKANES	———	———	———	———	———	———	0.00	0.00
ESTERS	———	———	———	———	———	———	0.00	0.00
ALDEHYDES	———	———	———	———	———	———	0.00	0.00
OIL	———	———	———	———	———	———	0.00	0.00
TOTAL :	100.00	99.59	98.24	99.21	100.21	99.86	100.00	100.00
DENSITY g/cc	0.004	0.033	0.024	0.024	0.022	0.001	———	0.790
AV.MOL.WT	11.75	13.62	13.37	13.07	14.97	15.22	32.75	———
Nm3/hr	782.5	1981.9	2649.7	2768.4	2416.8	2377.1	———	———
kgmol/hr	34.91	88.42	118.21	123.51 (4)	107.82 (3)	106.05	8.75	———
l/hr@prod	———	———	———	———	———	———	———	354.24

Compositions correspond to STREAM#32
(1)Corrected by difference.
(2)Decreased to match carbon balance
(3)Increased to match front end mass balance
(4)Adjusted to match across reactor mass balance

CONVERSIONS ACROSS REACTOR :

		GC#1	GC#2
HYDROGEN CONVERSION	(Z) :	17.9	20.7
CARBON MONOXIDE CONVERSION	(Z) :	34.3	33.7
CARBON DIOXIDE CONVERSION	(Z) :	3.4	5.5

*** See next page for conversions as calc. by overall bal.

SELECTIVITIES:

		ACROSS REACTOR GC Average	OVERALL *
CO (+CO2) SELECTIVITY TO METHANOL	(Z) :	107.0	92.6
CO (+CO2) SELECTIVITY TO ETHANOL	(Z) :		0.0

* Methanol in flashed gas not measured
Ethanol only measured in product flow

METHANOL PRODUCTIVITIES & YIELDS

MEOH SOURCE	gmol/hr-kg cat	kg/1000 Nm3 fresh feed	kg/1000 Nm3 reactor feed
As calculated ACROSS REACTOR	13.49	362.0	102.3
As Net MeOH produced, OVERALL balance	12.71	340.7	96.3

REACTOR FEED (H2/(CO+1.5CO2)) :	2.34
REACTOR FEED ((H2-CO2)/(CO+CO2)) :	2.37
APPROACH TO METHANOL EQUILIBRIUM (deg.C) :	36.5
APPROACH TO WATER-GAS EQUILIBRIUM (deg.C) :	22.4
METHANOL COLLECTED AS Z OF CALCULATED :	93.9
CALCULATED METHANOL PRODUCTION RATE (Kgmol/hr) :	8.84

LaPORTE LPMETHANOL PROCESS HOURLY REPORT
MATERIAL BALANCE SUMMARY

COMPONENT BALANCE (IN-OUT)/IN :

STREAMS # / STREAMS LOCATION / COMPONENT :	[PURE GASES - 1] FRESH FEED GAS	[(1+55)-15] REACTOR FEED	[25 - (50+51+62+68)] REACTOR EFFLUENT
	<% diff.>	<% diff.>	<% diff.>
H2	-0.80274	-0.81684	5.38049
CO	5.18307	-0.68930	4.85602
CO2	-30.69480	1.79284	3.51138
N2	-34.21070	1.45227	1.43501
CH4	74.78580	-10.73370	1.66691
H2O	———	100.00000	38.92870
CH3OH	———	7.86655	2.25540

OVERALL ELEMENTAL BALANCE (Kg-atoms/hr) :

	INPUTS	OUTPUTS					(IN-OUT)/IN
STREAM # / STREAM NAME	15 REACTOR FEED	55 RECYCLE	50 PURGE GAS	62 FLASH GAS	68 MeOH PRODUCT	TOTAL	%
CARBON:							
CO	23.8681	14.0119	1.0179	0.0269	———	15.0567	36.9172
CO2	4.9966	4.2418	0.3081	0.0083	———	4.5582	8.7729
CH3OH	0.2961	0.3214	0.0233	0.0163	8.4915	8.8525	-2889.5804
OTHERS	0.6111	0.5112	0.0371	0.0009	0.0622	0.6114	-0.0538
TOTAL C	29.7718	19.0862	1.3865	0.0524	8.5537	29.0788	2.3278
HYDROGEN:							
H2	146.5710	102.3820	7.4375	0.1963	———	110.0160	24.9402
H2O	0.0000	0.0000	0.0000	0.0016	0.4452	0.4468	n.a.
OTHERS	3.6287	3.3302	0.2419	0.0689	34.1524	37.7935	-941.5189
TOTAL H	150.2000	105.7130	7.6794	0.2668	34.5976	148.2560	1.2949
OXYGEN:							
TOTAL O	34.1573	22.8169	1.6575	0.0606	8.7451	33.2801	2.5861
NITROGEN:							
TOTAL N	19.4774	17.7795	1.2916	0.0340	———	19.1050	1.9116
TOTAL MASS FLOW (kg/hr)	1613.9200	1203.8600	87.4532	2.8248	279.8450	1573.9800	2.4745

REACTOR GAS BALANCE (OUT/IN) :

	GC#1	GC#2
MASS BALANCE, (%) :	100.000	100.000
ELEMENTAL BALANCE, (%) :		
CARBON	102.554	101.319
HYDROGEN	108.728	103.505
OXYGEN	102.849	101.577