Section 4

DATA SUMMARIES

RESULTS FOR APRIL-MAY 1984

Table 4-1 contains the summary of the data generated during the 40-day run. Due to the relatively low conversions inherent in CO-rich operation, small variations in flows lead to much larger changes in conversions. When errors occur in compositional analyses or in flow measurements, the effect upon conversion results can be significant. The LaPorte PDU is highly instrumented and computerized. Consequently, errors can be isolated and corrected by thorough and flexible engineering analysis of results obtained from the data reduction programs. Unfortunately, simplistic forced balances around the PDU reactor do not yield accurate results in all instances. Thus, the data analysis of LaPorte PDU results has involved a more thorough approach as outlined in Section 2. Several illustrations of these techniques are discussed below.

In general, at the beginning of the run not all the flows were available and the raw data indicated several inconsistencies in the material balances (overall mass and individual component balances). In order to arrive at the correct catalyst and plant performance results, adjustments had to be made to some flow rates, and in some cases, concentrations.

A straightforward procedure for arriving at correct conversion values is to assume that one of the gas flows around the reactor is incorrect and, by modifying either the reactor feed or the reactor effluent flow, a match in the nitrogen or the mass flow across the reactor is obtained. However, if the correct absolute reactor feed flow is to be obtained for space velocity and similar extensive property considerations, more attention has to be paid to the overall plant material balances. For example, as seen in Table 4-2 none of the plant balances for period E-1A-1 were better than 95 percent and the originally calculated carbon monoxide conversion of 35.8 percent could have been in error.

Table 4-1

LAPORTE PDU AVERAGED DATA SUMMARY WITH R71/OF12-26 CATALYST AND FREEZENE OIL
RESULTS FOR APRIL - MAY 1984

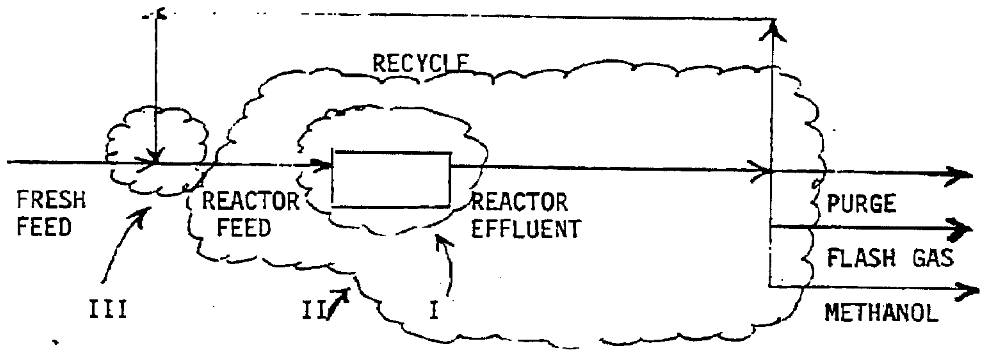
End of Period		Balance Period (Hours)	Synthesis Hours on Stream	Feed Gas Type	Reactor		Gas S.V. (cm/sec)	Space Vel. (l/kg-hr)	Oil S.V. (cm/sec)	Slurry Conc. (Wt. %)	H Conv. (%)	CO Conv. (%)	MeOH Prod. (gmol/kg-hr)	Equil. Appr. (°C)
Date	Time				Temp. (°C)	Press (kPa)								
4/11/84	1400	5	10.5	B	250	5,380	5.7	2,400	3.8	1.0	22.2	40.0	7.0	22.4
4/11	1800	4	14.5	B	250	5,380	6.0	2,770	4.0	5.9	24.1	39.2	8.8	19.3
4/12	0500	10	25.5	B	250	5,370	5.4	3,210	4.1	15.0	26.4	40.5	10.9	15.2
4/14	0800	22	76.5	B	250	6,430	11.6	11,000	5.6	29.4	23.4	28.8	30.0	39.1
4/15	0900	21	101.5	B	250	5,480	17.0	14,400	6.8	28.7	13.5	19.5	27.0	41.1
4/16	1300	11	129.5	U	250	5,420	10.3	9,390	7.6	26.9	28.3	10.4	23.5	-
4/16	2400	7	140.5	U	250	5,420	10.6	8,910	7.6	27.2	28.9	11.3	21.7	-
4/17	0800	8	148.5	U	250	5,410	10.7	10,000	7.6	27.5	28.1	9.9	23.6	-
4/18	2200	5	186.5	U	250	5,380	10.6	11,100	5.5	25.1	26.5	9.3	22.5	-
4/20	2400	24	236.5	U	250	5,370	10.5	10,200	5.6	26.3	27.4	9.5	21.8	35.0
4/21	2400	24	260.5	U	250	5,380	10.3	10,300	5.6	26.4	27.4	9.6	22.1	-
4/22	1900	19	279.5	U	250	5,400	10.5	9,710	5.5	26.3	27.3	9.4	21.3	-
4/25	0800	27	340.5	U	250	5,400	10.3	10,300	5.4	26.1	26.5	9.1	20.4	36.6
4/27	0900	33	389.5	U	250	5,400	10.5	10,900	5.5	25.8	25.4	8.7	21.0	39.2
4/28	2400	24	428.5	U	249	5,400	10.5	10,400	5.4	26.1	25.2	8.6	20.4	39.3
5/01	0900	25	485.5	U	250	5,400	10.6	10,800	5.5	25.9	23.7	8.0	19.4	41.9
5/02	2400	24	524.5	U	250	5,400	10.5	10,900	5.5	25.6	23.1	7.7	19.3	42.3
5/03	2400	24	548.5	U	249	5,400	10.5	11,000	5.5	25.1	23.1	7.8	19.6	43.4

Table 4-1 (Continued)

End of Period		Balance Period (Hours)	Synthesis Hours on Stream	Feed Gas Type	Reactor		Gas S.V. (cm/sec)	Space Vel. (l/kg-hr)	Oil S.V. (cm/sec)	Slurry Conc. (Wt. %)	H Conv. (%)	CO Conv. (%)	MeOH Prod. (gmol/kg-hr)	Equil. Appr. (°C)
Date	Time				Temp. (°C)	Press (kPa)								
5/04	2400	24	572.5	U	249	5,400	10.6	10,900	5.5	25.2	22.7	7.5	19.0	44.0
5/05	2400	23	596.5	U	249	5,400	10.6	11,100	5.5	25.1	22.7	7.7	19.2	43.9
5/06	2400	24	620.5	U	249	5,410	10.6	11,200	5.5	25.0	22.0	7.4	18.9	45.3
5/07	2400	24	644.5	U	250	5,410	10.6	11,400	5.5	24.9	21.0	7.2	18.7	46.6
5/08	1400	14	658.5	U	250	5,400	10.7	11,400	5.5	24.8	21.0	7.1	18.4	47.3
5/09	2400	14	692.5	U	250	5,410	10.7	11,600	5.5	24.6	20.5	6.7	18.1	48.2
5/10	2400	24	716.5	U	250	5,400	10.6	11,500	5.5	24.4	20.3	6.5	17.8	49.0
5/11	2400	24	740.5	U	250	5,400	10.5	11,600	5.4	24.4	19.6	6.6	17.5	49.8
5/12	2400	24	764.5	U	250	5,400	10.5	11,900	5.5	24.2	18.6	6.4	17.6	50.3
5/13	2400	24	788.5	U	250	5,400	10.5	11,900	5.4	24.2	18.1	6.3	17.4	52.2
5/14	2400	24	812.5	U	250	5,400	10.4	12,000	5.4	24.0	17.7	5.9	16.3	53.9
5/15	2400	24	836.5	U	250	5,410	10.4	12,100	5.4	23.9	17.2	5.7	15.9	55.4
5/16	2400	24	860.5	U	250	5,400	10.5	12,200	5.4	23.9	16.6	5.5	15.6	56.5
5/17	2400	24	884.5	U	250	5,400	10.5	12,300	5.4	23.7	16.2	5.4	15.3	56.6
5/18	2400	24	908.5	U	249	5,400	10.6	12,500	5.4	23.6	15.4	5.2	15.0	59.4
5/19	2400	24	932.5	U	249	5,400	10.5	12,600	5.5	23.4	14.8	4.8	14.7	59.4
5/20	2400	24	956.5	U	250	5,400	10.5	12,500	5.5	23.3	14.9	4.6	14.3	59.0
5/21	0800	8	964.5	U	251	5,400	10.5	12,400	5.5	23.3	14.9	4.8	14.3	59.1

Table 4-2

CORRECTIONS TO RAW DATA DURING SELECTED PERIODS
AT INITIATION OF OPERATIONS



	E-1A-1	E-1A-3	E-1B
Period From	0900 April 11	1900 April 11	1000 April 13
To	1400 April 11	0500 April 12	0800 April 14
Raw Data			
Mass balances (out/in); %			
Envelope I	107.1	104.6	101.6
II	NA	98.1	96.5
III	92.9	96.9	102.4
Nitrogen balance (out/in); %			
Envelope I	108.4	103.2	101.2
II	95.4	101.8	94.5
III	93.4	98.8	102.9
After Adjustment			
Adjustment	N_2 tie to Front-end	Mass flow to Front-end	Nitrogen Balance Cptimization
Mass balances (out/in); %			
Envelope I	100.1	100.00	100.4
II	NA	100.2	100.4
III	99.4	100.00	98.5
Nitrogen balance (out/in); %			
Envelope I	101.2	98.6	100.00
II	89.2	98.6	98.3
III	100.00	102.0	98.9
MeOH selectivity to CO + CO_2; %			
Envelope I	96.6	104.3	101.1
II	NA	95.8	103.4

However, since there was a relatively good check in the nitrogen balance between the plant front-end (recycle plus fresh feed) and the reactor effluent (a combined envelope I and III balance in Table 4-2 yields a 101.2 percent closure), the reactor feed was increased 7 percent to match the nitrogen flow with the plant front-end. This correction was then checked by the mass balance and the calculated selectivity across the reactor (100.1 and 96.6 percent, respectively). This resulted in a carbon monoxide conversion of 40.0 percent.

For the period E-1A-3, the H_2, CO, and CO_2 component balances for the raw data, show a consistent variance in the reactor feed of about 3 percent. However, the nitrogen variance was only 1 percent. For this reason it was decided not to use nitrogen balance, but instead to tie the reactor feed and reactor effluent mass flows to the plant front-end. The plant back-end flows were not utilized as a tie, since the methanol product rate appeared to be low. In the corrected version, an average methanol product rate for periods E-1A-3 (low) and E-1A-2 (high) was employed.

After the corrections, the component balances in the reactor feed and the reactor effluent adjusted to within +/- 1 percent with the exception of nitrogen in the reactor feed with a variance of -2 percent and methanol in the reactor effluent with a difference of about +10 percent. Selectivity across the reactor remained high (104 percent) and the value calculated from an overall balance (96 percent) was considered more accurate.

The procedure to upgrade the raw data for period E-1B shown in Table 4-2 was slightly more involved. The hydrogen concentrations as measured by GC #2 were considered in error and new values were calculated by difference. After the hydrogen concentration change the molecular weights of the streams involved were corrected and a nitrogen balance optimization across the plant was made.

For the short-term operation with CO-rich gas, the corrections to the feed gas flow were consistent and the component balance checks across the plant show variations less than one percent relative.

REDUCTION DATA

Table 4-3 contains a summary of the parameters of interest during the reduction operation. Although there were two chromatographs in operation, the data correspond to GC#1, which was considered more accurate.

Table 4-3

LAPORTE PDU REDUCTION DATA - R71/OF 12-26 CATALYST, 1200 kPa (170 psia)

TOTAL LAPSED HOURS	H_2 CONC. % FEED	H_2 CONC. % EFFL.	GAS FLOW Kg Mol/hr	HYDROGEN UPTAKE Nm3/hr	HYDROGEN UPTAKE Nl/Kg cat.	H_2O CONC. IN EFFL. %	WATER EVOLUTION Kg Mol/hr	WATER EVOLUTION Kg Mol	TEMPERATURES, C FEED GAS	TEMPERATURES, C BOTTOM	TEMPERATURES, C 193cm
54.50	0.985	0.523	22.045	2.29	3.7	--	--	--	78	70	72
55.00	1.245	0.868	22.490	1.90	6.8	--	--	--	90	90	82
56.00	0.690	0.594	22.490	0.49	7.6	--	--	--	99	96	90
57.00	0.787	0.629	22.490	0.79	8.9	--	--	--	109	105	98
58.00	0.797	0.646	22.490	0.76	10.2	--	--	--	116	109	106
59.00	0.738	0.522	22.490	1.09	11.9	--	--	--	125	120	117
60.00	0.776	0.408	22.490	1.90	15.0	0.082	0.019	0.019	131	130	128
61.00	0.779	0.386	22.544	1.98	18.3	0.181	0.040	0.059	129	132	137
62.00	0.820	0.407	22.153	2.07	21.6	0.252	0.057	0.116	138	137	139
63.00	0.808	0.302	22.408	2.54	25.8	0.275*	0.062	0.177	141	141	148
64.00	0.854	0.194	22.408	3.31	31.2	0.297	0.067	0.244	141	139	155
65.00	0.924	0.218	22.317	3.59	37.0	0.332*	0.074	0.318	144	139	158
66.00	1.034	0.122	22.408	4.59	44.5	0.366	0.082	0.401	150	144	162
67.00	0.782	0.000	22.317	3.91	50.9	0.461	0.103	0.504	151	145	167
68.00	--	--	--	--	--	0.426	0.095	0.599	157	149	170
69.00	0.649	0.107	22.317	2.51	55.0	0.605	0.136	0.734	160	152	173
70.00	0.719	0.000	22.362	3.60	60.9	0.511	0.115	0.849	164	155	177
71.00	0.747	0.000	22.362	3.74	67.0	0.624	0.140	0.989	165	157	182
72.00	0.862	0.000	22.362	4.32	76.0	0.591	0.132	1.121	164	158	182
73.00	1.041	0.000	22.362	5.22	82.5	0.490	0.110	1.231	158	159	186
74.00	0.680	0.000	22.362	3.41	88.0	0.469	0.105	1.336	164	158	175
75.00	1.109	0.000	22.362	5.56	97.1	0.532	0.119	1.456	166	160	164
76.00	0.684	0.000	22.317	3.42	102.0	0.439	0.098	1.554	164	160	161
77.00	0.685	0.000	22.317	3.43	107.6	0.393	0.088	1.642	165	160	160
78.00	0.670	0.109	22.362	2.86	112.3	0.430	0.096	1.738	164	160	160
79.00	0.916	0.110	22.226	4.02	118.8	0.348	0.078	1.816	164	160	160
80.00	1.162	0.349	22.090	4.13	125.6	0.431	0.096	1.912	164	160	160
81.00	1.146	0.483	21.954	3.26	130.9	0.330	0.073	1.985	173	165	161
82.00	1.055	0.594	22.181	2.30	134.6	0.268	0.059	2.045	180	172	168
83.00	1.102	0.750	22.408	2.16	138.1	0.193	0.043	2.088	184	178	174
84.00	1.205	1.069	21.999	0.67	139.2	0.151	0.034	2.121	195	185	180
85.00	1.073	0.878	21.999	0.97	140.8	0.188	0.042	2.163	206	193	188
86.00	1.308	n.a.	21.999	--	140.8	0.168	0.037	2.200	207	190	195
87.00	1.895	1.799	21.999	0.48	141.6	0.192	0.043	2.243	205	197	198
88.00	1.395	1.230	22.090	0.81	142.9	0.216	0.048	2.291	204	201	199
89.00	1.751	1.723	22.226	0.14	143.1	0.279*	0.062	2.353	189	188	195
90.00	1.680	1.677	22.453	0.01	143.2	0.279*	0.062	2.415	194	191	188
91.00	1.619	1.619	22.453	--	143.2	0.279*	0.062	2.478	206	198	193
92.00	1.619	1.619	22.453	--	143.2	0.343	0.076	2.554	217	207	201
93.00	1.729	1.618	22.453	0.58	144.1	0.366	0.082	2.635	227	215	210
94.00	1.515	1.385	22.453	0.65	145.2	0.393	0.087	2.722	226	223	218
95.00	1.385	1.375	22.453	0.05	145.2	0.337	0.074	2.796	240	229	223
96.00	1.334	1.359	22.408	--	145.2	0.327	0.072	2.868	237	231	229
97.00	1.435	1.443	22.490	--	145.2	0.273	0.060	2.928	233	228	229
98.00	1.536	1.605	22.408	--	145.2	0.273	0.059	2.987	230	227	228
99.00	1.685	1.685	22.453	--	145.2	0.219	0.048	3.035	226	223	225
100.00	1.550	1.540	22.362	0.05	145.3	0.211	0.047	3.082	223	220	222
101.00	1.315	1.582	22.408	--	145.3	0.172	0.038	3.119	223	219	220
102.00	n.a.	n.a.	22.045	--	145.3	0.151	0.033	3.152	224	220	220
103.00	n.a.	n.a.	22.045	--	145.3	0.152	0.034	3.186	224	220	220
104.00	1.339	1.123	22.045	1.07	147.1	0.133	0.029	3.216	227	221	221
105.00	n.a.	n.a.	21.999	--	147.1	0.146	0.032	3.248	235	228	221

Table 4-3 (Continued)

TOTAL LAPSED HOURS	H_2 CONC. % FEED	H_2 CONC. % EFFL.	GAS FLOW Kg Mol/hr	HYDROGEN UPTAKE Nm^3/hr	HYDROGEN UPTAKE Nl/Kg cat.	H_2O CONC. IN EFFL. %	WATER EVOLUTION Kg Mol/hr	WATER EVOLUTION Kg Mol	TEMPERATURES, C FEED GAS	TEMPERATURES, C BOTTOM	TEMPERATURES, C 193cm
106.00	1.509	1.475	21.999	0.16	147.3	0.132	0.029	3.277	237	232	230
107.00	--	--	21.999	--	147.3	0.133	0.029	3.306	234	230	230
108.00	--	--	21.999	--	147.3	0.122	0.027	3.334	232	230	230
109.00	--	--	21.999	--	147.3	B.D.L.	--	--	193	206	221
110.00									138	166	196

*Estimated

CATALYST INVENTORY

As mentioned earlier, an oil and catalyst balance was systematically performed to maintain an account of all oil additions and withdrawals and catalyst losses. Table 4-4 summarizes all such balances. The final oil inventory of 1,830 liters and slurry concentration of 23.3 weight percent shown in Table 4-4 was verified against the following:

- Nuclear density gauge at zero gas flow, end of run: 22 weight percent slurry (reduced), 23.8 percent oxide.

- Final liquid inventory via direct liquid level measurement, end of run:

  2,139 liters slurry at 184°C
  1,893 liters slurry at 20°C
  1,783 liters pure oil at 20°C

- Via tote bin collection plus 10 percent assumed holdup:

  1,764 liters pure oil at 20°C

- From the calculated oil inventory from liquid level measurements and a reduced catalyst concentration of 22 percent, a total catalyst weight of 428 kg is obtained. This weight implies a loss of 118 kg of catalyst (reduced) which is close to the calculated catalyst loss from the final inspection (see Section 3).

Table 4-5 lists the reactor density measurements, all at the 137-cm elevation and reactor catalyst inventory values for syngas operation during the 40-day run. Slurry concentrations are from inventory estimates from Table 4-4, and a solids density of 4.76 g/cc was used for reducing the data. Nuclear density gauge data reduction techniques have been explained elsewhere.(3) A vertical scan at the end of the run indicated no significant density variation as a function of elevation. The "zero" reading drifted slightly from -59 mv early in the run to -70 mv at shutdown.

The catalyst inventory data for the transition to entrained operation period is covered in Section 5.

Table 4-4

LAPORTE OIL AND CATALYST BALANCE SHEET

Date	Time	Process Oil Inventory, Liters: Additions	Losses: Leaks	Losses: Soluble In MeOH	Losses: Insoluble In MeOH	Net	Intermediate Separator Inventory, Liters	Oil In Reactor Loop*: Liters	Oil In Reactor Loop*: Kg	Catalyst Oxide, kg: Est'd Loss	Catalyst Oxide, kg: Inventory	Est'd Slurry Wt % Oxide
4/10/84	1200	1,703	-	-	-	1,703	0	1,703	1,449	-	612	-
	2400	284	106	-	-	1,881	0	1,881	1,601	-	612	-
4/11	1200	174	8	9	9	2,029	303	1,726	1,469	-	612	-
	2400	-	19	27	24	1,961	261	1,700	1,446	-	612	-
4/12	1200	382	-	26	23	2,294	307	1,987	1,691	-	612	26.6
	2400	-	-	26	26	2,241	273	1,968	1,675	-	612	26.8
4/13	1200	-	-	53	53	2,135	424	1,711	1,456	1.8	611	29.6
	2400	-	-	53	53	2,029	318	1,711	1,456	1.8	609	29.5
4/14	1200	-	-	53	53	1,923	151	1,772	1,507	1.8	607	28.7
	2400	242	-	45	49	2,071	322	1,749	1,488	1.8	605	28.9
4/15	1200	238	8	45	45	2,210	216	1,995	1,697	1.8	603	26.2
	2400	-	-	34	34	2,142	185	1,957	1,665	1.8	601	26.5
4/16	1200	-	-	38	34	2,071	170	1,900	1,616	1.8	600	27.1
	2400	-	8	38	34	1,991	125	1,866	1,588	1.8	598	27.4
4/17	1200	432	8	49	46	2,320	473	1,847	1,572	1.8	596	27.5
	2400	314	257	34	34	2,309	291	2,018	1,716	1.8	595	25.7
4/18	1200	-	-	42	42	2,226	189	2,037	1,733	1.8	593	25.5
	2400	235	19	38	38	2,366	291	2,074	1,765	1.8	591	25.1
4/19	1200	-	-	49	45	2,271	280	1,991	1,694	1.8	589	25.8
	2400	19	19	38	38	2,196	216	1,980	1,684	1.8	587	25.9
4/20	1200	-	-	30	30	2,135	208	1,927	1,392	1.8	586	26.3
	2400	318	-	30	30	2,392	462	1,931	1,642	1.8	584	26.2
4/21	1200	19	19	30	30	2,332	416	1,915	1,630	1.8	582	26.3
	2400	-	-	26	26	2,279	382	1,896	1,613	1.8	580	26.4
4/22	1200	-	8	26	26	2,218	341	1,878	1,598	1.8	578	26.6
	2400	-	-	30	30	2,158	257	1,900	1,617	1.8	577	26.3
4/23	1200	352	19	34	34	2,423	591	1,832	1,559	1.8	575	27.0
	2400	15	-	30	30	2,377	481	1,896	1,613	1.8	573	26.2
4/24	1200	-	-	30	30	2,317	394	1,923	1,636	1.8	571	25.9
	2400	19	22	34	34	2,245	356	1,889	1,607	1.8	569	26.2
4/25	1200	-	-	34	34	2,177	288	1,889	1,607	1.8	567	26.1
	2400	280	-	34	34	2,385	454	1,931	1,643	1.8	566	25.6
4/26	1200	15	-	34	30	2,336	413	1,923	1,636	1.8	564	25.6
	2400	-	-	34	30	2,271	413	1,859	1,581	1.8	562	26.2
4/27	1200	19	-	34	34	2,222	344	1,878	1,598	1.8	560	26.0
	2400	34	19	30	30	2,177	291	1,885	1,604	1.8	559	25.8

*From oil balance (net - intermediate separator).

Table 4-4 (Continued)

Date	Time	Oil in Reactor Loop* Liters	Kg	Catalyst Oxide, kg Est'd Loss	Inventory	Estimated Slurry Wt % Oxide
4/28	1200	1,840	1,565	1.8	557	25.9
	2400	1,862	1,584	1.8	555	25.9
4/29	1200	1,859	1,581	1.8	553	25.9
	2400	1,847	1,571	1.8	552	26.0
4/30	1200	1,840	1,565	1.8	550	26.0
	2400	1,840	1,565	1.8	548	25.9
5/01	1200	1,840	1,565	1.8	546	25.9
	2400	1,840	1,565	1.8	544	25.9
5/02	1200	1,847	1,571	1.8	542	25.7
	2400	1,847	1,571	1.8	541	25.6
5/03	1200	1,847	1,571	1.8	539	25.5
	1400	1,904	1,619	1.8	537	24.9
	2400	1,862	1,584	1.8	535	25.3
5/04	1200	1,839	1,565	1.8	534	25.4
	2400	1,855	1,578	1.8	532	25.2
5/05	1200	1,862	1,584	1.8	530	25.1
	2400	1,855	1,577	1.8	528	25.1
5/06	1200	1,840	1,565	1.8	527	25.2
	2400	1,821	1,549	1.8	525	25.3
5/07	1200	1,855	1,578	1.8	523	24.9
	2400	1,821	1,549	1.8	521	25.2
5/08	1200	1,855	1,578	1.8	519	24.8
	2400	1,839	1,565	1.8	517	24.9
5/09	1200	1,847	1,571	1.8	516	24.7
	2400	1,832	1,558	1.8	514	24.8
5/10	1200	1,855	1,578	1.8	510	24.5
	2400	1,840	1,565	1.8	510	24.6
5/11	1200	1,847	1,571	1.8	508	24.4
	2400	1,840	1,565	1.8	507	24.5
5/12	1200	1,855	1,578	1.8	505	24.2
	2400	1,832	1,558	1.8	503	24.4
5/13	1200	1,840	1,565	1.8	501	24.3
	2400	1,840	1,565	1.8	499	24.2
5/14	1200	1,855	1,578	1.8	498	24.0
	2400	1,840	1,565	1.8	496	24.1
5/15	1200	1,847	1,571	1.8	494	23.9
	2400	1,847	1,571	1.8	493	23.9
5/16	1200	1,840	1,565	1.8	491	23.9
	2400	1,847	1,571	1.8	489	23.7
5/17	1200	1,847	1,571	1.8	487	23.7
	2400	1,855	1,577	1.8	485	23.5
5/18	1200	1,862	1,584	1.8	484	23.4
	2400	1,840	1,565	1.8	482	23.5
5/19	1200	1,840	1,565	1.8	480	23.5
	2400	1,840	1,565	1.8	479	23.4
5/20	1200	1,870	1,591	1.8	477	23.1
	2400	1,847	1,571	1.8	475	23.2
5/21	1200	1,832	1,558	1.8	473	23.3

*Via level measurement.

Table 4-5

LAPORTE PDU CATALYST INVENTORY

Date	Time	Slurry Conc. Wt. % Oxide	NDG Reading, mv
13 April	11:15	29.6	-380
	19:00	29.5	-407
14 April	05:45	29.1	-461
	22:30	28.9	-548
15 April	03:20	28.2	-550
16 April	02:00	26.6	-447
	11:30	27.1	-439
	17:00	27.2	-443
17 April	08:00	27.5	-464
18 April	01:00	25.7	-512
	23:00	25.1	-527
20 April	09:25	26.3	-496
22 April	00:30	26.6	-492
22 April	15:30	26.3	-518
23 April	13:30	26.2	-524
24 April	19:30	26.2	-516
25 April	04:00	26.1	-534
26 April	11:00	25.6	-545
27 April	12:00	26.0	-527
28 April	07:50	26.2	-535
29 April	04:30	25.9	-551
30 April	09:20	26.0	-553
1 May	16:15	25.8	-555
2 May	10:40	25.7	-561
3 May	11:30	25.5	-562
3 May	14:05	24.9	-527
3 May	24:00	25.3	-534
4 May	11:30	25.4	-527
5 May	11:40	25.2	-548
6 May	11:10	25.1	-545
7 May	12:00	24.9	-555
8 May	12:00	24.8	-565
9 May	12:00	24.7	-567
10 May	12:00	24.5	-569
11 May	12:05	24.4	-563
12 May	12:00	24.2	-578
13 May	12:00	24.3	-574
14 May	12:00	24.0	-584
15 May	12:13	23.9	-595
16 May	10:10	23.9	-594
17 May	12:38	23.7	-596
18 May	24:00	23.5	-606
19 May	08:40	23.5	-608
20 May	10:10	23.1	-606
21 May	03:00	23.3	-595

ANALYTICAL RESULTS

Slurry Concentration Measurements

Slurry concentration measurements, on a reduced and oxide basis, are presented in Table 4-6. These measurements were made on actual samples taken from the PDU slurry loop during operation. Also shown are the slurry concentration estimates developed from the oil and catalyst balances. The concentration measurements show little change in slurry concentration over the run, while the slurry inventory estimates (and the nuclear density gauge) indicated a gradual lightening of the slurry. However, the differences between the analytical measurements and the estimates are within 2-4 weight percent absolute.

Table 4-6

SLURRY CONCENTRATION MEASUREMENTS FOR LAPORTE 40-DAY RUN
SAMPLES FROM SLURRY LOOP

Sample ID#	Date	Hours On Stream	Measured Slurry Conc. (wt %)		Slurry Inventory Estimates (wt % Oxide)
			Reduced	Oxide	
LO 365	4/12/84	37	13.9	-	26.6
LO 367	4/14/84	81	24.6	-	28.7
LO 388	4/25/84	344	-	27.1	27.6
LO 389	4/25/84	344	-	27.2	27.6
LO 408	4/27/84	392	25.3	25.8	26.0
LO 412	5/01/84	486	25.0	26.8	25.9
LO 428	5/08/84	653	25.5	27.1	24.8
LO 439	5/12/84	750	24.8	26.7	24.2
LO 447	5/17/84	870	26.0	27.6	23.7
	5/21/84	964	25.0	26.5	23.3

Gas Trace Contaminant Analysis

Results of analyses for trace quantities of sulfur and chlorides in the PDU feed gases are shown in Table 4-7. The fresh mixed feed was sampled once per week, and the CO_2 supply was sampled when a new shipment was delivered. The recycle gas was sampled as a "blank", since trace sulfur or chlorine poisons would be adsorbed on the catalyst, leaving the recycle gas clean. High-purity standard

Table 4-7

TRACE GAS CONTAMINANT ANALYSES
(ppm weight)

Sample ID#	Date	Blank S	Blank Cl	Feed Gas S	Feed Gas Cl	CO_2 S	CO_2 Cl
LO 367	4/15/84			1.25	-		
LO 368	4/15/84	1.21	0.1				
LO 381	4/28/84					0.44	0.22
LO 414	4/30/84	0.42	2.12			0.22	0.87
LO 425	5/02/84	0.21	0.21				
LO 416	5/02/84			0.30	0.60		
LO 417	5/02/84	0.22	0.88				
LO 426	5/07/84					.06	.06
LO 430, 429, 431	5/08/84	.11	.48	.14	.58	.11	.11
LO 440	5/14/84					.05	.21
LO 440, 445 444,443	5/16/84	.01	.36	.02	.6	.04	.06

gases were also used as blanks. The detection limit for sulfur and chlorides decreased as the analysis method was improved over the run, indicated by the decreasing levels reported in the blank samples. The sulfur and chloride levels in the feed gases and CO_2 were always at or very near the detection limits, even as the detection limits were improved.

Catalyst Analyses

Slurry samples were taken from the circulation loop after the slurry pump at various stages of PDU operation. To avoid air contamination, each sample was taken under inert atmosphere and shipped to APCI Allentown facilities for catalyst analyses. A total of 21 samples was shipped. Each slurry sample was first filtered and then thoroughly washed with cyclohexane to remove residual oil on the catalyst before submitting for analyses.

Results for copper state, crystal size, and poisons are presented in Table 4-8. The CO-rich gas condition during the 40-day run began at 103 hours on stream.

Table 4-8

LAPORTE 40-DAY RUN CATALYST ANALYSES

Sample I.D.	Date Taken	Hours On Stream	Chemical Composition		Crystal Size	Poisons (ppm)					
						Fe		Ni			
			Cu/Zn	Cu^{+1}/Cu^{0}	Cu^{0}	XRF	AAS	XRF	AAS	Cl	S
Solid #22 (fresh reduced catalyst)	4/09/84	0	.7	.41	96A	258	165	45	42	49	81
011 53	4/11/84	13	.3	.53	166A	582	540		560	69	81
011 54	4/12/84	34	.37	.42	146A						
011 55	4/12/84	37	.31	.71	171A	375		70		43	95
011 57	4/14/84	81	.28	.48	215A	384		52		46	88
011 63	4/16/84	129	.4	3.6	231A	553		66		110	142
011 64	4/18/84	179			249A	633		69		63	95
011 65	4/19/84	203	.07	0	320A	446	310	65	44	47	78
011 67	4/23/84	296	.09	0	357A	482		67		52	85
011 72	4/25/84	344			371A	553	310	86	51	63	118
011 74	4/27/84	392	.1	0	267A	916	650	75	60	52	86
011 76	5/01/84	486	.05	0	357A	517		70		43	96
011 78	5/03/84	533	.06	0	361A	510	410	87	83	38	92
011 80	5/05/84	580	.09	0	371A	606		110		81	108
011 88	5/08/84	656	.06	0	342A	576	382	120	94	63	122
011 89	5/10/84	704	.06	0	342A	572		128		57	146
011 91	5/12/84	750	.05	Trace	362A	584	401	130	112	64	99
011 93	5/15/84	822	.06	0	368A	597		150		49	88
011 94	5/17/84	870	.06	0	368A	640	397	163	128	50	88
011 96	5/19/84	920	.07	Trace	348A	615		157		46	86
011 97	5/21/84	964	.08	Trace	362A	649	394	180	137	52	104

Carbonyl Survey

Carbonyl surveys of the PDU were made during the 40-day run at LaPorte to determine the carbonyl formation during long-term CO-rich operation. The first survey was undertaken in the early part of the run on CO-rich gas (150 hours cumulative run time, 50 hours of CO-rich gas). Carbonyl levels in the plant were all below the detection limit as shown in Table 4-9. These levels, at 2,600 Nm^3/hr gas rate, are consistent with the levels at high gas rates in the shakedown run. The initial high nickel carbonyl concentrations in the 27.14 intermediate oil separator effluent were attributed to sample system contamination.

A second survey was conducted in the middle of the run (650 hours cumulative run time, 550 hours on CO-rich gas). The detection limit was improved to 5 ppbv. A low level of iron carbonyl (6-9 ppbv) was observed in the reactor feed gas as shown in Table 4-10. This level is comparable with the slow buildup of iron on the catalyst reported in a previous section of this report. Nickel carbonyl levels of finite value were first observed in the second survey. $Ni(CO)_4$ was detected at 20-40 ppbv in the outlet of the 01.13 feed surge tank and in the reactor feed gas, and nickel was detected in the slurry sample from the 27.13 primary separator. A third carbonyl survey was undertaken to determine the source of the nickel carbonyl as summarized in Table 4-11. The source of nickel carbonyl was determined to be in the feed compressor section.

Freezene-100 Boiling Points

Figure 4-1 shows the the boiling point curves of fresh and used Freezene-100 oil. The used oil is appreciably heavier than the fresh oil due to the loss of light ends in the liquid (methanol) product and the purge gas.

Methanol Product Analyses

Methanol product analyses are included on Table 4-12 and on computerized sheets in the Appendix. The first four analyses correspond to balanced gas operation. The remaining analysis for the CO-rich portion of the run show a gradual increase in water concentration probably due to a relative increase in CO_2 conversion.

Table 4-9

FIRST CARBONYL SURVEY - 40 DAY RUN

Time	Exit 2.60B (Reactor Feed)[A]		Exit 21.10 (Tubeside)[A]		Exit 27.14 (2^T V/L Sep.)[A]		27.13 Bottoms[B]		27.14 Bottoms[B]		Crude MeOH Product[B]		Freezene Oil (Blank)[B]	
	Fe	Ni	Fe	Ni	Fe	Ni	Fe	Ni	Fe	Ni	Fe	Ni	Fe	Ni
4/17/84 1230-1500	<.01	<.01			<.013	.07	28.5	<.7	18.7	<.8	.34	<.03		
4/17/84 1545-1745	<.01	<.01			.017	.32								
4/18/84 0930-1230			<.02	.26	<.01	<.01	10.7	<.8	4.7	<.8	.19	<.03	3.6	<.1
4/18/84 1300-1715			<.01	<.01	<.01	<.01								

[A] ppmv as carbonyl
[B] ppmw as metal

Table 4-10

SECOND CARBONYL SURVEY - 40 DAY RUN

Time	Exit 2.60B (Reactor Feed)[A] Fe	Ni	Exit 27.14 (2° V/L Sep.)[A] Fe	Ni	Exit 21.10 (Tubeside)[A] Fe	Ni	Inlet 21.10 (Tubeside)[A] Fe	Ni	Exit 01.13[A] Fe	Ni	27.13 Bottoms[B] Fe	Ni	27.14 Bottoms[B] Fe	Ni	22.15 Oil[B] Fe	Ni	Crude MeOH[B] Fe	Ni
5/7/84 1300-1700	0.006	0.03	0.007	0.118							69.3	7.2	7.7	<0.5	4.9	<0.5	1.4	<0.5
5/7/84 1930-0930	0.006	0.026	0.006	0.025														
5/8/84 1230-1630	0.009	0.043	0.005	0.051					0.10[C]		0.069[C] 67.5	15.1	6.7	<0.5	5.3	<0.5	6.7	<0.5
5/8/84 1930-0900	0.007	0.031			0.006	0.012			0.02	0.032								
5/9/84 1140-1540			0.006	0.044	<0.005	0.023			0.018	0.024								
5/9/84 1630-0800			0.008	0.017	0.006	0.01	0.01	0.028										
5/10/84 1100-1700			0.012	0.026	0.008	0.024	0.028	0.047										

[A] ppmv as carbonyl
[B] ppmw as metal
[C] suspected contamination from regulator

Table 4-11

THIRD CARBONYL SURVEY - 40 DAY RUN

Time	LaPorte CO Supply[A] Fe	LaPorte CO Supply[A] Ni	LaPorte H_2 Supply[A] Fe	LaPorte H_2 Supply[A] Ni	01.10 In[A] Fe	01.10 In[A] Ni	01.10 Out[A] Fe	01.10 Out[A] Ni	01.20 In[A] Fe	01.20 In[A] Ni	01.20 Out[A] Fe	01.20 Out[A] Ni	01.11 Out[A] Fe	01.11 Out[A] Ni
1015-1415														
1440-1840														
1915-0010														
1350-1745							<.005	.07					<.005	.019
1920-0255							<.005	.057					<.021	.04
1130 1650 5/18/84		<.005			<.005	.016					<.005	.011		
1900-0900 5/18-19/84	<.006	<.005			<.005	.015					<.006	.02		
1000-1400 5/19/84				<.003					.024[C]	.041				
1400-1800 5/19/84									<.006	.021				
2000-0400 5/20/84									<.005	.019				
5/20/84														
1000-1400 5/20/84											.007	.026		

Time	02.60A In[A] Fe	02.60A In[A] Ni	02.60B Out[A] Fe	02.60B Out[A] Ni	21.10 Tubeside In[A] Fe	21.10 Tubeside In[A] Ni	21.10 Tubeside Out[A] Fe	21.10 Tubeside Out[A] Ni	21.10 Cond. Out[B] Fe	21.10 Cond. Out[B] Ni	27.14 Out[A] Fe	27.14 Out[A] Ni	Crude MeOH[B] Fe	Crude MeOH[B] Ni
1015-1415			<.005	.02							.005	008		
1440-1840			<.005	.014							<.005	.016		
1915-0010	<.005	.027	.005	.03										
1350-1745														
1920-0255														
1130 1650 5/18/84														
1900-0900 5/18-19/84														
1000-1400 5/19/84											.016	.028	.171	.075
1400-1800 5/19/84					.017	.059					<.005	.024		
2000-0400 5/20/84					.015	.043					.021	.027	.076	073
5/20/84													.106	.035
1000-1400 5/20/84					.02	.061	.007	.01	0	.06				

[A] ppmv as carbonyl
[B] ppmw as metal
[C] suspect leak

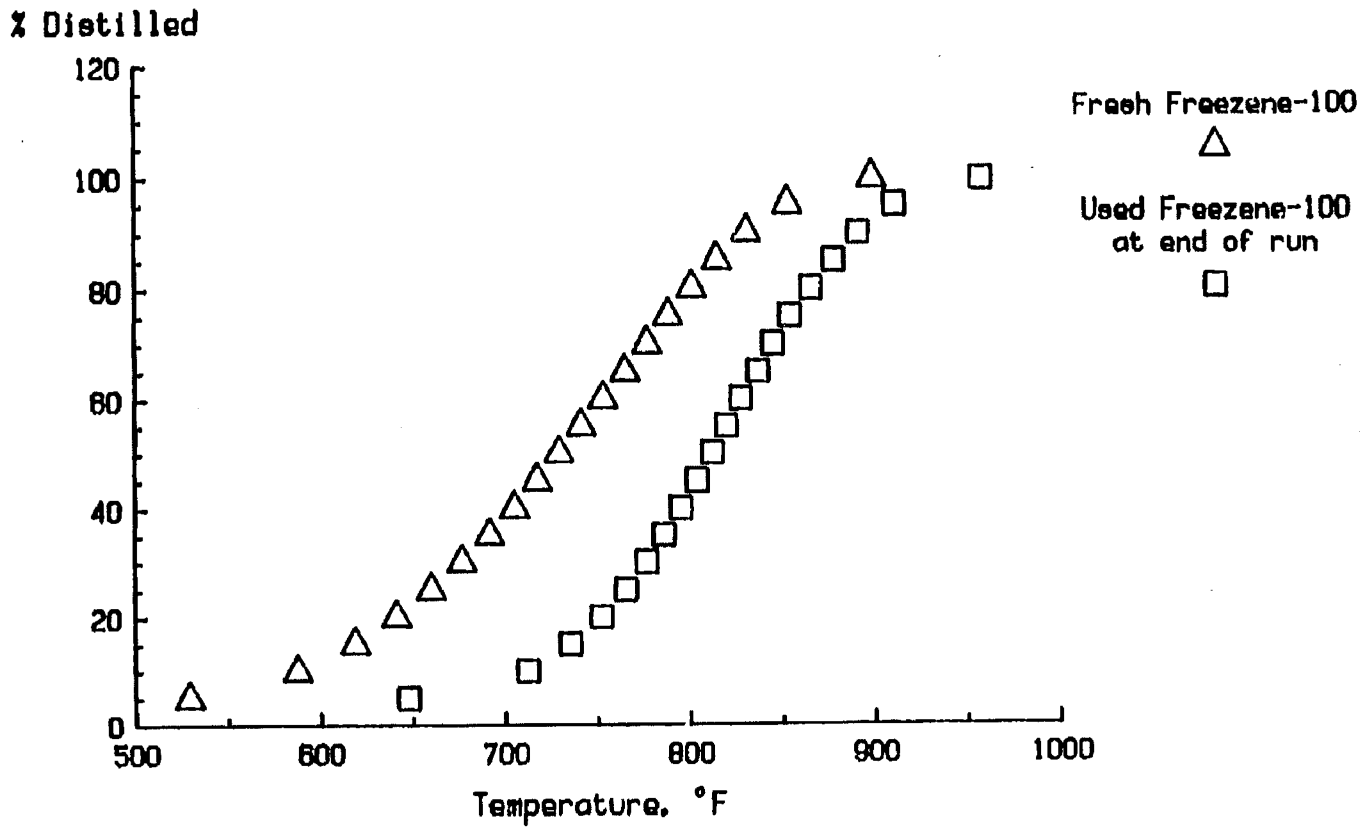


Figure 4-1. Boiling Point Distribution of Fresh and Used Process Oil

Table 4-12

METHANOL PRODUCT ANALYSES
(Weight Percent)

Sample I.D.	L0353	L0354	L0364	L0355	L0356	L0357	L0358	L0359	L0361	L0362	L0363
Date	4/11/84	4/12/84	4/13/84	4/14/84	4/15/84	4/16/84	4/17/84	4/18/84	4/19/84	4/20/84	4/21/84
Time	18:00	19:15	18:15	17:45	18:10	17:30	19:00	17:50	18:00	18:16	18:00
MeOH	95.18	95.31	95.78	95.07	95.68	95.93	96.36	95.92	96.58	96.63	96.78
EtOH	0.51	0.41	0.12	0.08	0.37	0.48	0.39	0.364	0.367	0.345	0.313
Oil	1.36	1.26	1.36	1.38	1.35	1.36	1.50	1.56	1.21	1.25	1.15
H_2O	2.28	2.55	2.49	3.26	1.75	1.14	1.42	1.43	1.54	1.50	1.50
Esters	0.24	0.21	0.20	0.18	0.60	0.71	0.05	0.48	0.049	0.049	0.042
C_3 alcohols	0.20	0.15	0.04	0.02	0.12	0.16	0.13	0.121	0.120	0.111	0.10
C_4 alcohols	0.16	0.12	0.02	0.01	0.10	0.15	0.11	0.097	0.102	0.092	0.090
C_5 alcohols	0.07	0.003	-	-	0.03	0.06	0.05	0.031	0.037	0.021	0.027

Sample I.D.	L0374	L0375	L0376	L0377	L0378	L0379	L0380	L0382	L0409	L0411	L0415
Date	4/22/84	4/23/84	4/24/84	4/24/84	4/25/84	4/26/84	4/27/84	4/28/84	4/29/84	4/30/84	5/01/84
Time	19:10	18:00	18:00	18:00	18:00	18:00	18:00	18:00	18:00	18:00	18:00
MeOH	97.00	97.02	96.81	96.804	96.729	96.755	96.938	97.014	96.986	96.686	96.567
EtOH	0.288	0.251	0.254	0.247	0.206	0.229	0.208	0.200	0.200	0.186	0.182
Oil	1.070	1.105	1.225	1.24	1.355	1.335	1.180	1.135	1.160	1.150	1.121
H_2O	1.42	1.410	1.53	1.524	1.525	1.530	1.530	1.530	1.530	1.82	1.93
Esters	0.038	0.036	0.032	0.034	0.027	0.026	0.025	0.019	0.020	0.018	0.016
C_3 alcohols	0.088	0.085	0.077	0.078	0.076	0.067	0.070	0.055	0.059	0.050	0.050
C_4 alcohols	0.083	0.078	0.066	0.064	0.066	0.050	0.042	0.040	0.039	0.035	0.035
C_5 alcohols	0.016	0.015	0.008	0.009	0.016	0.008	0.007	0.007	0.006	0.005	0.005