TABLE IV-2

LAPORTE LPMEOH PDU

RUN E-4 CHRONOLOGY WITH CATALYST F21/OE75-35

Date	Time	Cumulative Time on Synthesis Gas (Hours)	Milestone
7/15/85	1150		Plant being pressurized to 5,270 kPa (765 psia). Slurry temperature maintained at 222°C (432°F).
	1400	0	Synthesis gas introduced to the PDU. Began Case E-4A: CO-rich gas, T=250°C (482°F), P=5,270 kPa (765 psia), V_L=5.6 cm/s (0.18 ft/s), V_G=12.2 cm/s (0.40 ft/s).
	1420	0-1/3	Gas chromatograph detected 1.4% MeOH in reactor effluent.
	1830	4-1/2	Product methanol flow first taken to day tank.
7/16/85	0515	15-1/4	First indication of existence of solids density profile in reactor from nuclear density gauge readings.
	1900	29	Ended Case E-4A. Raised superficial liquid velocity to check for effect on solids density reactor profile. Began Case E-4B: CO-rich gas, T=250°C (482°F), P=5,270 kPa (765 psia), V_L=6.5 cm/s (0.21 ft/s), V_G=12.3 cm/s (0.40 ft/s).
7/17/85	0200	36	Ended Case E-4B. Increased superficial gas velocity. Began Case E-4C: CO-rich gas, T=250°C (482°F), P=5,270 kPa (765 psia), V_L=6.3 cm/s (0.21 ft/s), V_G=15.6 cm/s (0.51 ft/s).
	1100	45	Drained slurry from slurry loop to slurry prep tank in preparation for dilution. Ended Case E-4C. Began Case E-4D: CO-rich gas, T=250°C (482°F), P=5,270 kPa (765 psia), V_L=6.0 cm/s (0.20 ft/s), V_G=15.3 cm/s (0.50 ft/s).
7/18/85	0400	62	Drained additional slurry from loop to slurry prep tank. Ended Case E-4D. Began Case E-4E: CO-rich gas, T=250°C (482°F), P=5,270 kPa (765 psia), V_L=5.7 cm/s (0.19 ft/s), V_G=15.4 cm/s (0.51 ft/s).

TABLE IV-2

LAPORTE LPMEOH PDU

RUN E-4 CHRONOLOGY WITH CATALYST F21/0E75-35

(continued)

Date	Time	Cumulative Time on Synthesis Gas (Hours)	Milestone
7/19/85	1530	97-1/2	Started lowering slurry flow rate to reactor. Ended Case E-4E. Began Case E-4F: CO-rich gas, T=250°C (482°F), P=5,270 kPa (765 psia), V_L=1.8 cm/s (0.06 ft/s), V_G=15.3 cm/s (0.50 ft/s).
7/24/85	0000	202	Ended Case E-4F. Changed feed gas to balanced gas and began Case E-4G: T=250°C (482°F), P=5,270 kPa (765 psia), V_L=1.9 cm/s (0.06 ft/s), V_G=15.4 cm/s (0.51 ft/s).
7/25/85	0500	231	Ended Case E-4G. Stopped synthesis gas to reactor.

The PDU was shut down in a controlled manner at 0500 hours on 25 July 1985 after 231 hours of synthesis gas operation. On-stream time was 100%, and catalyst carry-over from the slurry loop was significantly lower than the high slurry loading operation in June 1984 (Run E-2). The 10.50 slurry pump performed well at each of the various slurry concentrations, and there was no evidence of blockage or fouling in either the 21.10 feed/product exchanger or the 21.20 slurry heat exchanger. This operation demonstrates that the LaPorte LPMEOH PDU can mechanically accommodate slurry concentrations in the 30-47 wt% oxide range with a high degree of reliability.

D. Discussion of Results

Table IV-3 summarizes the reactor performance data for Run E-4. Due to the steady decline in methanol productivity, results for several one-hour "snapshots" for the initial case (E-4A) are presented. The CO conversion and methanol productivity for the cases using CO-rich gas (E-4A through E-4F) are plotted in Figure IV-2; the curve for the autoclave results is also given for comparison. Similar information for the balanced gas condition (E-4G) is shown in Figure IV-3. Detailed data sheets generated by the Data Acquisition System are attached in Appendix A.

From these results, it is clear that the performance of catalyst F21/0E75-35 in Run E-4 was less than that which was anticipated from autoclave tests. A similar sharp decline in initial methanol productivity was also observed in the previous high slurry concentration run (Run E-2, Reference 2). It is interesting to note that the sharp decline in methanol productivity corresponds approximately to the development of a high solids density zone in the bottom of the reactor and the decrease in gas holdup. It appears that the rheological properties of the slurry may have changed as the result of the methanol synthesis reaction, which leads to a lower mass transfer rate and/or an inadequate gas/slurry

TABLE IV-3

LAPORTE LPMEOH PDU

DATA SUMMARY FOR RUN E-4

Case	Balance Period Date	Balance Period Time	Feed Gas Type*	Hrs. on Syngas	Temp. °C	Press. kPa	V_G c cm/s	V_L c cm/s	Space Velocity l/hr-kg	Slurry Conc. wt% ox.	CO Conv. %	Appr. to Equil. %	MeOH in Rx Effluent %	MeOH Prod. gmol/hr-kg	Net MeOH Prod TPD
E-4A	16 July	1900-2000	U	5	250	5270	11.8	5.5	4,900	47.4	14.2	76.8	8.06	14.38	7.290
E-4A	16 July	0000-0100	U	10	250	5270	12.4	5.6	5,100	47.4	13.8	69.5	7.48	13.24	6.712
E-4A	16 July	0500-0600	U	15	250	5270	12.2	5.6	4,900	47.4	12.8	69.6	7.34	11.90	6.264
E-4A	16 July	1000-1100	U	20	250	5270	12.2	5.5	4,900	47.4	11.05	59.7	6.97	11.16	5.828
E-4A	16 July	1500-1600	U	25	250	5270	12.2	5.6	4,900	47.4	11.2	60.5	6.46	10.26	5.401
E-4B	16-17 July	2200-0200	U	32-36	250	5270	12.3	6.6	6,800	47.4	10.4	56.2	6.00	10.03	5.365
E-3C	17 July	0700-1100	U	41-45	250	5270	15.6	6.3	6,200	47.4	8.5	45.9	5.28	11.23	6.007
E-4D	17-18 July	2000-0400	U	54-62	250	5270	15.3	6 0	8,000	40.3	9.3	50.3	5.59	16.09	6.624
E-4E	18-19 July	1000-1500	U	68-97	250	5270	15.4	5.7	10,600	34.2	9.5	51.6	5.91	21.63	6.729
E-4F	20 July	0000-2400	U	106-130	250	5270	15.3	1.9	11,800	33.5	9.6	51.9	6.02	24.51	6.877
E-4F	21 July	0000-2400	U	130-154	250	5270	15.3	1.8	11,800	32.9	9.6	51.9	6.04	25.29	6.882
E-4F	22 July	0000-2400	U	154-178	250	5270	15.3	1.8	11,400	33.7	9.5	51.4	6.01	24.69	6.949
E-4F	23 July	0000-2400	U	178-202	250	5270	15.3	1.9	11,200	34.0	9.6	51.9	6.04	23.99	6.874
E-4G	24-25 July	1200-0500	B	214-231	250	5270	15.4	1.9	11,100	33.9	23.4	45.9	6.09	23.84	6.911

*B = Balanced Gas
U = CO-rich Gas

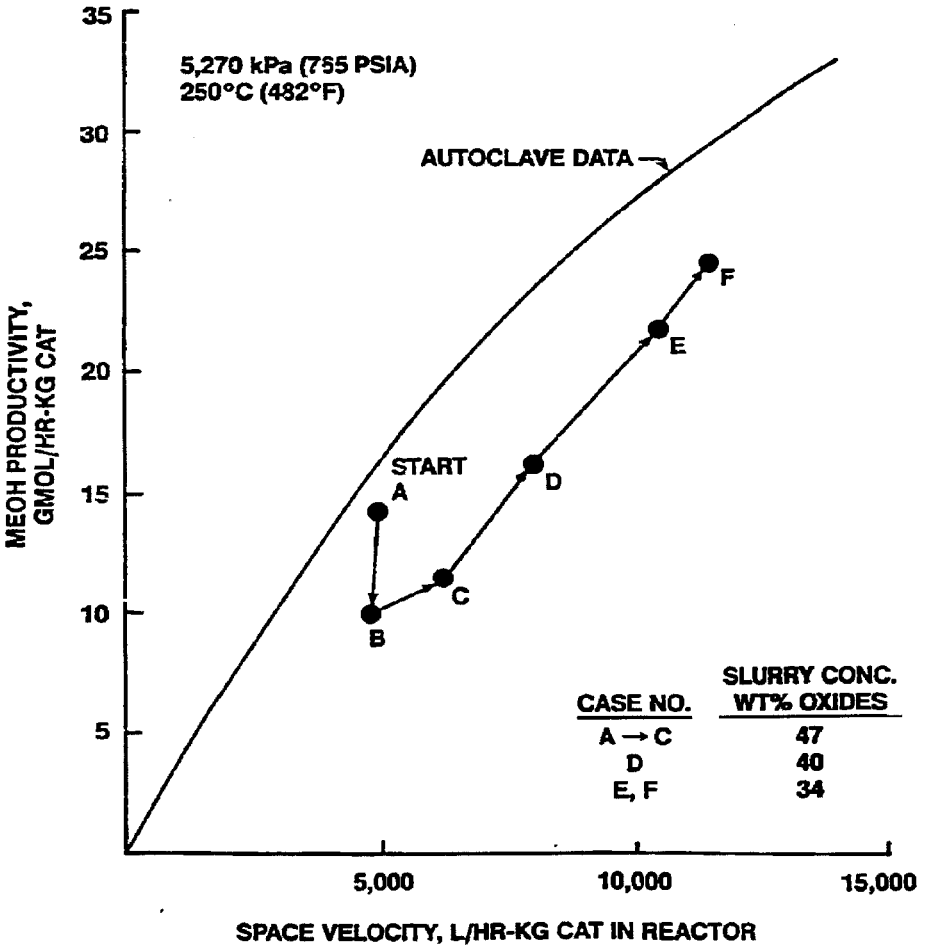

Figure IV-2. Laporte Lpmeoh PDU, Reactor Performance, Run E-4: Co-Rich Gas

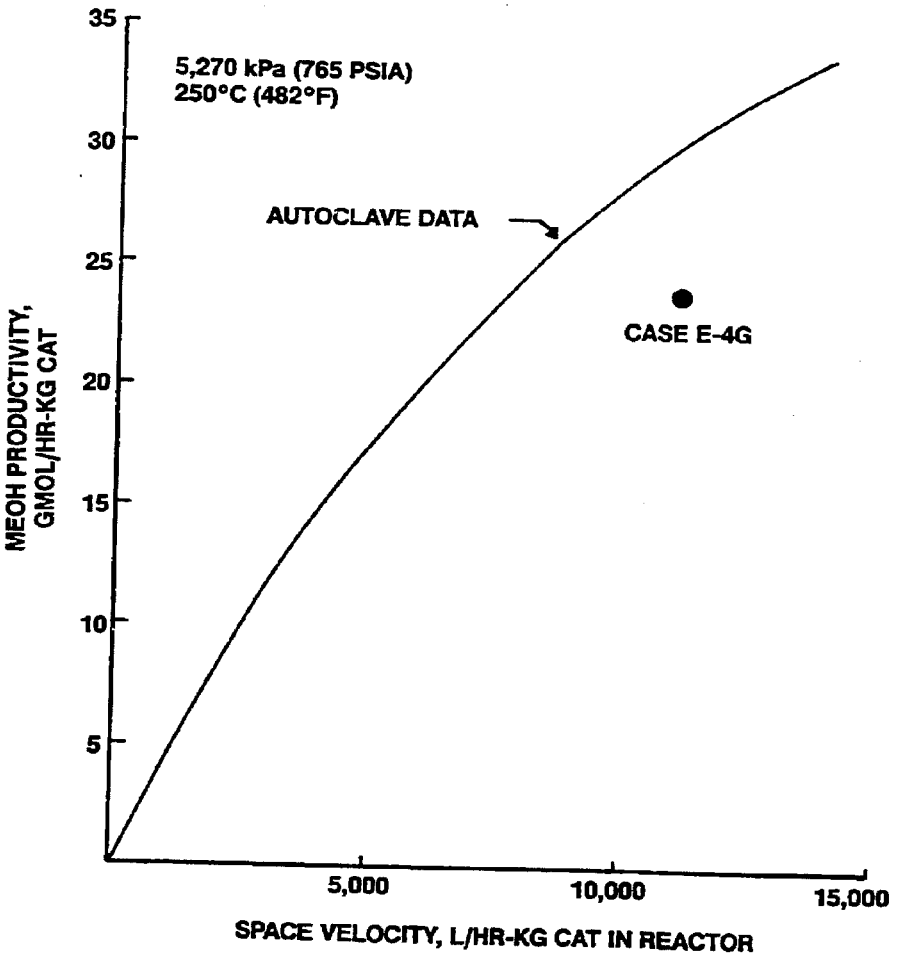

Figure IV-3. Laporte Lpmeoh PDU, Reactor Performance, Run E-4: Balanced Gas

mixing and limits the methanol productivity. The methanol productivity was stabilized after about 20 hours on synthesis gas and remained approximately 58% to 63% of the autoclave performance in Cases E-4B and E-4C. After the slurry concentration was reduced by dilution steps, the methanol productivity increased relative to autoclave data. Figure IV-4 shows a plot of the percent approach of the methanol productivity at the LaPorte LPMEOH PDU to the corresponding autoclave prediction as a function of slurry concentration. Data for the CO-rich gas conditions E-4B through E-4F are given. Results representative of the high solids loading operation in June 1984 (Run E-2) are also plotted. In Run E-2, the slurry catalyst had not been adequately activated; this was believed to have been the primary cause for the low level of performance (Reference 2). Figure IV-4 illustrates the magnitude of the improvement in methanol productivity at the LaPorte LPMEOH PDU resulting from the use of the revised in-situ reduction procedure. It is believed that a mass transfer limitation and/or poor gas/slurry mixing are the major contributors to the remainder of the difference between the results of Run E-4 and the autoclave data.

There was little change in performance when superficial gas and liquid velocities were altered, although a decrease in the superficial liquid velocity, which was tested in Case E-4F, did show slight improvement in comparison with Case E-4E. This is believed to be the result of increasing gas holdup at a lower superficial liquid velocity.

The impact of feed gas composition (CO-rich vs. balanced) on methanol productivity is negligible, although the partial pressure of the reactants of the two feeds differs significantly. The relative LaPorte PDU performances with respect to autoclave data are 83% and 81% for the CO-rich (Case E-4F) and the balanced (Case E-4G) feed gases, respectively. This result suggests that inadequate gas/slurry mixing and/or low product methanol mass transfer might be the limiting factors for the LaPorte bubble-column reactor

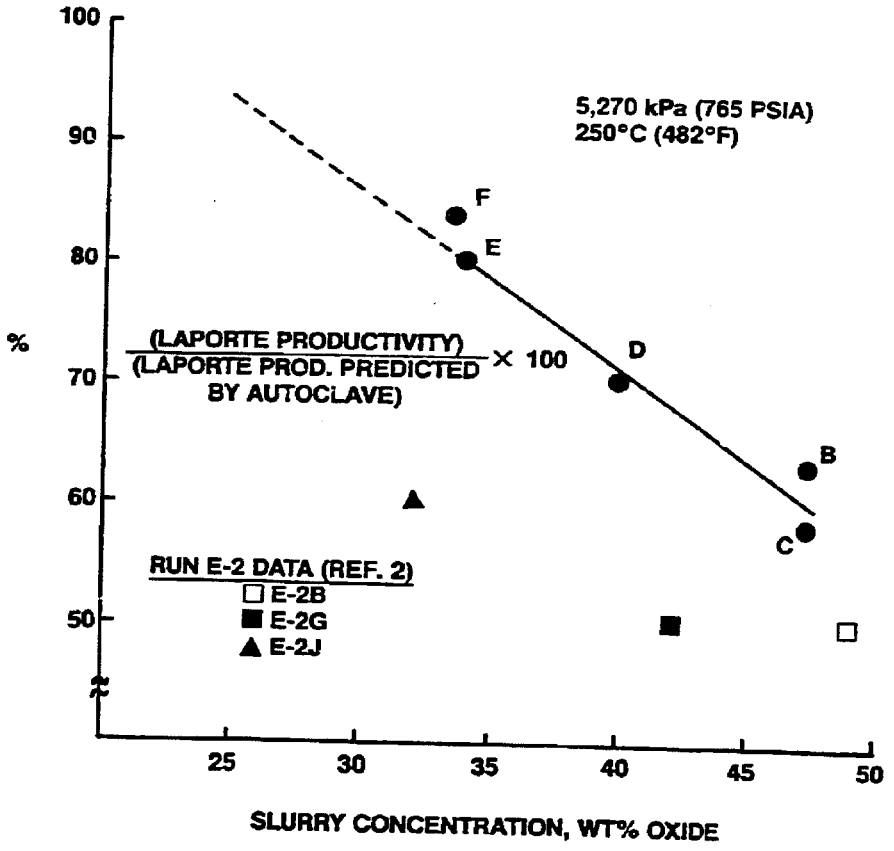

Figure IV-4. Laporte Lpmeoh PDU, Run E-4 Relative Performance As A Function of Slurry Concentration: Co-Rich Gas

performance at high slurry concentrations. In the future developmental work, alternate liquid media and reactor internals that will overcome the limits of the present LPMEOH reactor system at solids loadings above about 30 wt% should be investigated.

Analytical Results and Activity Tests

Catalyst slurry samples were taken during the in-situ reduction and throughout the synthesis gas operation. The analysis of a slurry sample at the end of in-situ reduction showed surface properties of a properly reduced catalyst. Details regarding in-situ reduction are covered in the Supplementary Volume.

Catalyst samples taken during the synthesis operation were selectively analyzed. These results are summarized in Table IV-4. Three hours into the synthesis gas operation, the ESCA results indicated a negligible Cu^{+1}/Cu^{0} ratio and a Cu/Zn ratio of 0.15. This is not unexpected. The XRD results show expected values for copper and ZnO crystallite sizes with little change throughout the run. Analysis by atomic absorption (AA) indicated no increase of Fe and Ni concentrations, indicating the total lack of metal carbonyls during the run. Reliable sulfur and chloride analyses for the end-of-run samples were not obtained due to analytical difficulties.

To further confirm that the catalyst had been properly activated and did not deteriorate during the run, samples at 33 hours on stream and at the end of run were subjected to autoclave tests. The slurry samples were carefully diluted with degassed Freezene-100 and tested with CO-rich gas at 5,270 kPa (765 psia), 250°C (482°F), and a nominal space velocity of 5,000 l/hr-kg. Activity results are summarized in Table IV-5 and compared in Figure IV-5 with the standard autoclave curve for a properly activated catalyst. It is concluded that the catalyst in LaPorte Run E-4 was intrinsically active throughout the run.

TABLE IV-4

LAPORTE LPMEOH PDU

CATALYST ANALYSES FOR RUN E-4

Sample	Hours On Gas	ESCA/AUGER		XRD, Å		Quantitative Analysis (ppmw)			
		Cu^{+1}/Cu°	Cu/Zn	Cu	ZnO	Fe	Ni	S	Cl
E4-1	3	nil	0.15	87.5	62.0				
E4-2	9								
E4-3	19.75	nil		87.5	64.4	68.8	33.1		<60
E4-4	33								
E4-5	56								
E4-6	73.3								
E4-7	119.3	nil	0.18	87.5	65.7				
E4-9	225	nil	0.1	87.5	65.7				
E4-10	230								
E4-EOR	231		0.13	87.5	63.1	67	29	<0.2%	

TABLE IV-5

LAPORTE LPMEOH PDU

AUTOCLAVE TESTS OF CATALYST SAMPLES

Sample No.	Hours On-stream at LaPorte	Autoclave			
		Space Velocity	CO Conversion (%)	Methanol Productivity g-mol/hr-kg	Approach to Standard Curve
E4-4	33	4700	16.2	16.0	100
E4-EOR	231	5200	15.1	16.7	100

Conditions: CO-rich gas
5,270 kPa (765 psia)
250°C (482°F)

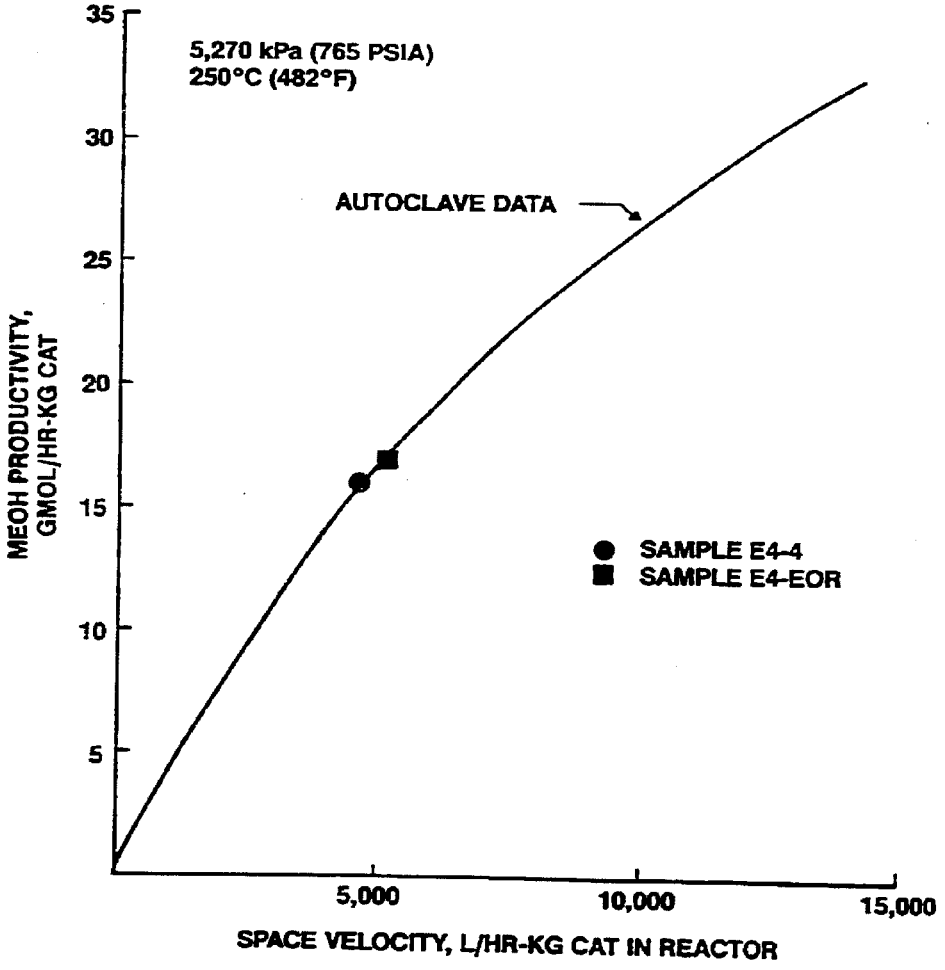

Figure IV-5. Autoclave Check on Co-Rich Gas

Nuclear Density Gauge Results

The readings from the nuclear density gauge had indicated the presence of a change in solids density with respect to reactor height during the early stages of Run E-4. The apparent high catalyst density in the lower portion of the reactor could be attributed to either solids accumulation or low gas holdup. The apparent solids density profiles for Cases E-4A through E-4E were developed based on the assumption that slurry concentration was constant throughout the reactor/slurry loop and gas holdup was changing along the reactor; these are plotted in Figure IV-6. Combining this information with the observation of regions of flow instability during Cases E-4A through E-4D shows that it is possible that unstable, large bubbles were formed in the bottom of the reactor, limiting the mass transfer between the gas and liquid phases and leading to the lack of performance in the early hours on synthesis gas.

Although constant solids density profiles were observed starting with Case E-4E, it is possible that flow irregularities could still have been present. Since measurements from the nuclear density gauge cannot be made below a height of 15-7/8 in. (40 cm) above the gas/slurry distributor system (due to the obstruction of the bottom head of the vessel), any instability in the bottom section would not be detected. Also, the profile is determined using a point source and detector which scans only through the center of the reactor cross-sectional area; the hydrodynamics in other radial positions cannot be measured.

The results of three-phase gas holdup measurements for Run E-4 are presented in the Supplementary Volume of this report.

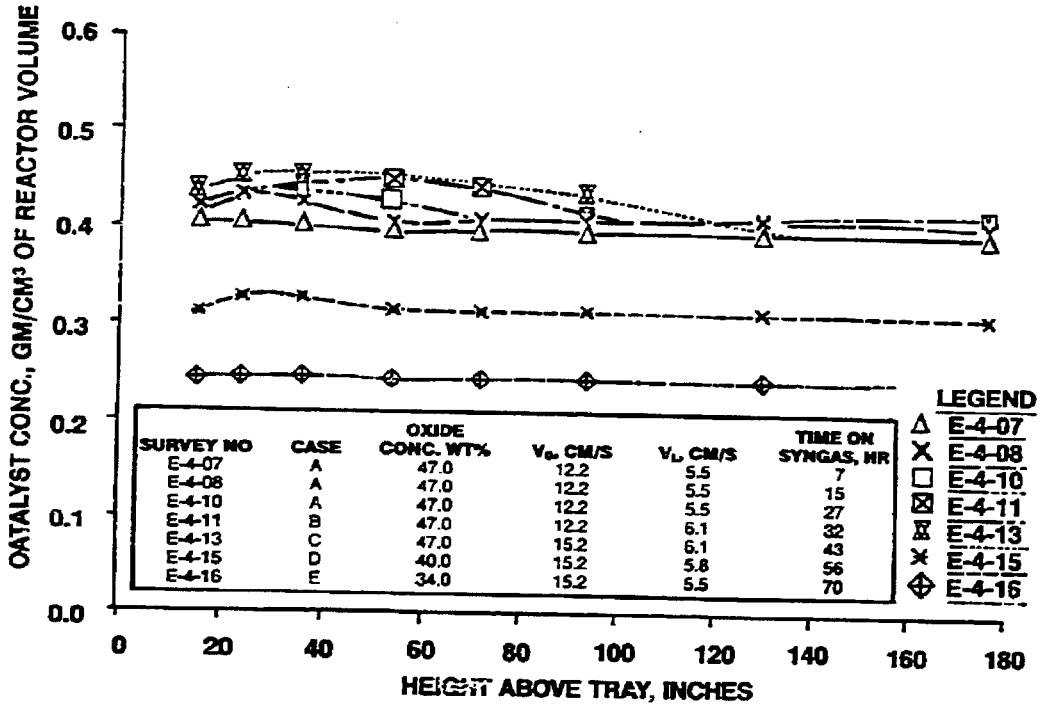

Figure IV-6. Laporte Lpmeoh PDU, Solid Concentration Profile For Run E-4

Product Methanol Results

During the operation of Run E-4 on CO-rich gas, a trend in the composition of the crude methanol samples was evident. Table IV-6 lists the typical product methanol analyses for each of the run conditions. Early samples showed higher selectivities to ethanol and higher alcohols than had been measured in previous PDU campaigns. The product composition for Case E-4F, however, is more typical of crude methanol product for the CO-rich reactor feed gas. Diffusional resistances may have caused a higher residence time for both reactants and products in the vicinity of the catalyst. This could have led to the formation of secondary products such as higher alcohols.

Wet Chemical Analysis for Carbonyls

A set of wet chemical tests was performed to determine whether catalyst poisoning had contributed to the decline in methanol productivity during the initial hours of Run E-4. Table IV-7 summarizes the result of this single survey (at 25 hours on synthesis gas). The levels of iron and nickel are very low and consistent with data from an earlier activity maintenance operation (Run E-3, Reference 2) under CO-rich synthesis gas, during which reactor performance was acceptable. Therefore, it is concluded that the rapid decrease in methanol productivity during the initial period of Run E-4 was not caused by catalyst poisoning.

Post-Run Inspection

The major pieces of PDU equipment were opened for inspection following the completion of Run E-4. No major blockages or plugs of solids were found in any lines or equipment. However, upon opening the 27.10 reactor, a layer of ~60 wt% slurry about 10 to 13 cm (4 to 5 in.) thick was found on the perimeter of the bottom head. A

TABLE IV-6

LAPORTE LPMEOH PDU

TYPICAL PRODUCT METHANOL COMPOSITIONS FOR RUN E-4

Case No.	E-4A	E-4B	E-4C	E-4D	E-4E	E-4F	E-4G
Gas Composition	CO-rich---------->						Balanced
Slurry Conc., wt% oxide	47	47	47	40	34	34	34
Space Velocity, l/hr-kg cat	5000	4800	6200	8000	10400	11500	11100
Composition, wt%							
Methanol	92.87	92.79	92.78	93.15	94.68	95.25	95.49
Water	0.72	0.73	0.86	0.97	1.00	1.07	2.65
Ethanol	1.77	1.79	1.68	1.52	1.03	0.82	0.18
C3+ Alcohols	2.12	2.11	2.14	1.89	1.04	0.76	0.12
Esters	1.02	1.08	1.04	0.97	0.75	0.62	0.18
Freezene-100 Oil	1.50	1.50	1.50	1.50	1.50	1.48	1.38
	100.00	100.00	100.00	100.00	100.00	100.00	100.00

TABLE IV-7

LAPORTE LPMEOH PDU

CARBONYL SURVEY--25 HOURS ON SYNTHESIS GAS

Location	Fe, ppbv	Ni, ppbv
Fresh Feed	<2	<3
Reactor Feed	<2	<4
22.10 Gas Outlet	<3	<5

greater buildup was seen behind and above the gas inlet nozzle on the gas sparger. This type of accumulation was also found after the earlier high-slurry concentration operation (Run E-2). Both the gas and liquid spargers were coated with slurry, but the outlet holes were open. The solids on the perimeter of the head appeared drier than the thick slurry in the bottom of the head. This could be a result of the nitrogen purge flow maintained to the reactor during the transfer of slurry to the 28.30 slurry prep tank. The tray had an uneven coating of slurry adhering to the base, bubble caps, and stems. A total of 37 kg (80 lb) of thick black slurry was cleared from the bottom head and spargers, and an additional 2 kg (5 lb) was removed from the distributor tray. A 10-cm (4-in.) ball of red catalyst was also found in an unused nozzle on the bottom head. This dead space had not been exposed to the flow of either slurry or synthesis gas; this is believed to be a reason for the difference in color.

The manway on the 27.13 primary separator was opened. Approximately 11 kg (25 lb) of black slurry had accumulated in the manway. The vessel walls were also coated with a thin black film of slurry.

Approximately 27 kg (60 lb) of thick black slurry were found in the casing of the 10.50 slurry pump and the suction expansion joint. The dead space of the pump contained about 4 kg (10 lb) of red/black slurry.

Both the inlet and outlet heads were removed from the 21.10 feed/product exchanger. All tubes were clear from blockage. A coating about 0.04 cm (1/64 in.) thick had accumulated along the first 1.8 m (6 ft) of the tubeside inlet (the overhead line from the primary separator). The outlet head only had a gray/black film with no evidence of solids buildup.

A gray film coated the sides of the walls of the 27.14 intermediate V/L separator. About 39 kg (85 lb) of black sludge were found below the top of the stand pipe in the bottom head of the vessel.

A single 22.5l oil condensate filter had been used for service in the seal flush return line to the slurry pump. A total of 2 kg (5 lb) was found in this filter.

The manway to the 22.10 product separator was opened. No solids were found, but a gray film in the portion of the vessel which had contained a liquid level during the run was observed.

It is noteworthy that the amount of catalyst that had accumulated in the feed/product exchanger intermediate V/L separator and oil condensate filter was low. This is an illustration of the low rate of solids carry-over from the primary V/L separator at superficial gas velocities as high as 15.6 cm/s (0.51 ft/s).

V. CONCLUSIONS AND RECOMMENDATIONS

The results of Run E-4 have led to the following conclusions and recommendations:

- The ability to handle catalyst slurries in excess of 40 wt% solids has been successfully demonstrated at the LaPorte LPMEOH PDU. However, the likelihood of catalyst carry-over from the slurry circulation loop is greater if higher superficial gas velocities are tested. Evaluations of devices that could reduce the rate of catalyst carry-over are being performed under this contract (DE-AC22-85PC80007).

- The modifications to the in-situ reduction procedure have been successfully demonstrated in the LaPorte LPMEOH PDU with a slurry concentration of 41 wt%.

- The LaPorte LPMEOH PDU achieved a 100% on-stream factor during the synthesis gas operation of Run E-4. Methanol productivity was below the laboratory prediction for all cases tested. It is believed that a product methanol mass transfer limitation and/or an inadequate gas/slurry mixing which are related to the slurry concentration exist within the present LaPorte reactor system. Studies into alternate liquid media and reactor designs to enhance the gas/liquid mass transfer at high slurry concentrations are planned within this contract.