The form of Equation (IV-1) is very similar to the correlation proposed by Shah et. al. (Reference 4) based on the two-phase gas holdup data obtained for the H_2/kerosene system:

$$\epsilon_G \propto \rho^{0.18} \qquad \text{(Eq. IV-2)}$$

During the carbonyl survey period, some gas holdup data were obtained for the CO-rich/Freezene-100 system. A nonuniform axial gas holdup profile, similar to those observed for N_2/Freezene-100, was also observed for CO-rich gas at a superficial gas velocity of 12 cm/s. The profile was flat at a lower gas velocity (2 cm/s). The gas holdup data from both surveys, as a function of height above the tray, are listed in Table IV-4 and are plotted in Figure IV-6. The gas holdup observed for the CO-rich/Freezene-100 system at 5,270 kPa (765 psia) and 250°C (482°F) are noticeably lower than the corresponding N_2/Freezene-100 gas holdup, but compare reasonably well with earlier (1983-1984) high-pressure data (see Figure IV-7). It should be noted that the gas holdup data from March/April 1985 for CO-rich gas and N_2 were taken at different liquid velocities, which may explain some of the difference shown in Figure IV-7. The volatilization of light ends of Freezene-100 oil at 250°C (482°F) may also be responsible for part of the difference.

B. Carbonyl Surveys

Iron and nickel carbonyl are known poisons of the methanol synthesis catalyst and have been suspected as a major cause of the high rate of catalyst deactivation observed in Run E-1 (Reference 2 and 5). The metallurgical upgrades completed in February and April 1985 (see Section III-D) were designed to minimize the carbonyl generation and to permit the measurement of catalyst activity maintenance in a poison-free environment. To verify the effectiveness of the material change-outs, carbonyl surveys were conducted following each PDU modification. The results of the surveys are presented below.

TABLE IV-4

LAPORTE LPMEOH PDU

TWO-PHASE GAS HOLDUP FOR CO-RICH/FREEZENE-100 SYSTEM

(March/April 1985)

Survey No.	Pressure, kPa (psia)	Temperature °C (°F)	Superficial Gas Velocity, cm/s	Superficial Liquid Velocity, cm/s	Gas Holdup, (@ 54-in. Position) %
E-3-37	5310 (770)	248 (478)	1.0	5	7
E-3-38	5310 (770)	248 (478)	1.0	2	8
E-3-39	5280 (766)	248 (478)	1.0	5	8
E-3-40	5270 (765)	250 (482)	2.1	5	14
E-3-48	5300 (768)	250 (482)	2.2	5	10
E-3-49	5300 (768)	250 (482)	11.9	5	38

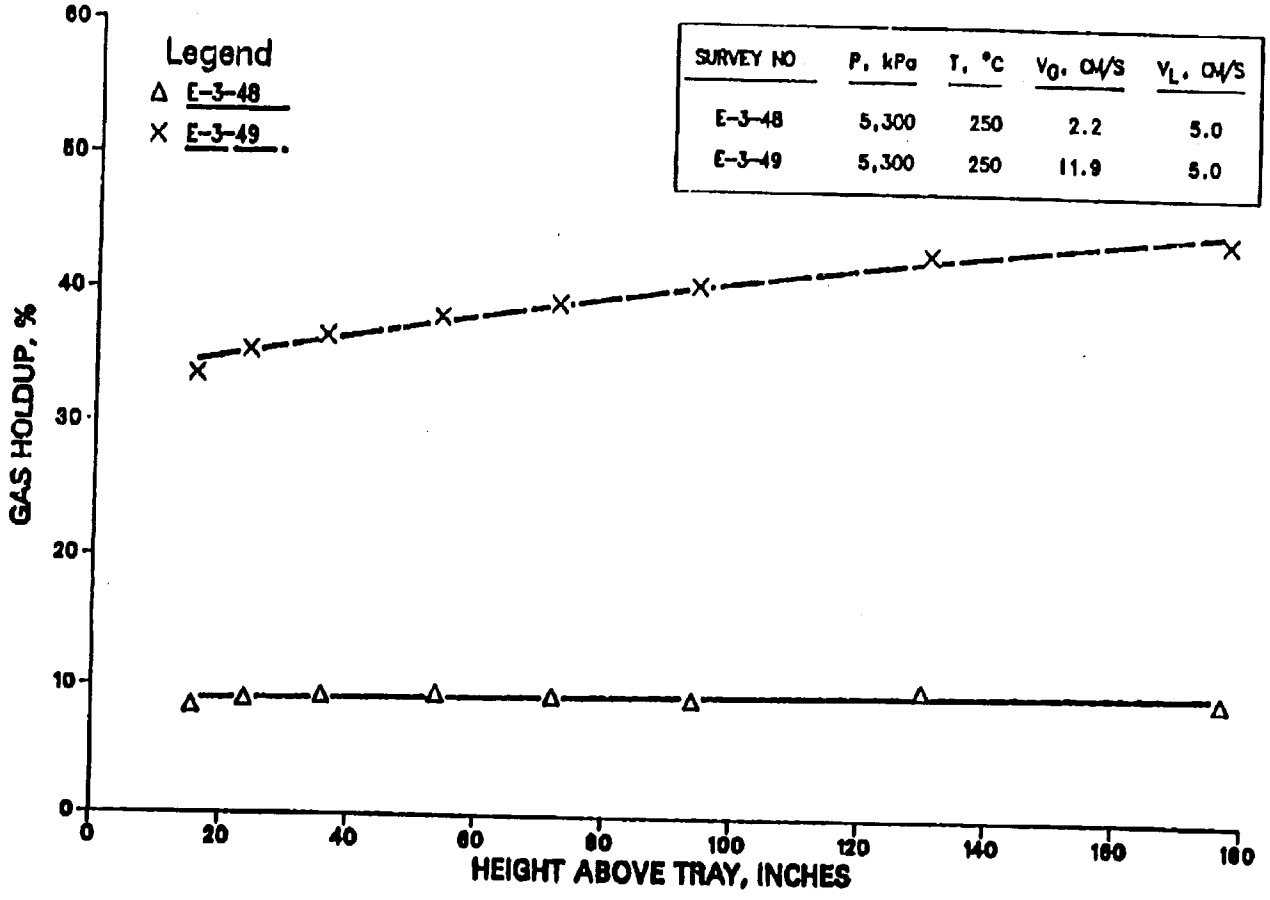

Figure IV-6. LaPorte LPMEOH PDU Axial Gas Holdup Profile for CO-Rich/Freezene-100 System

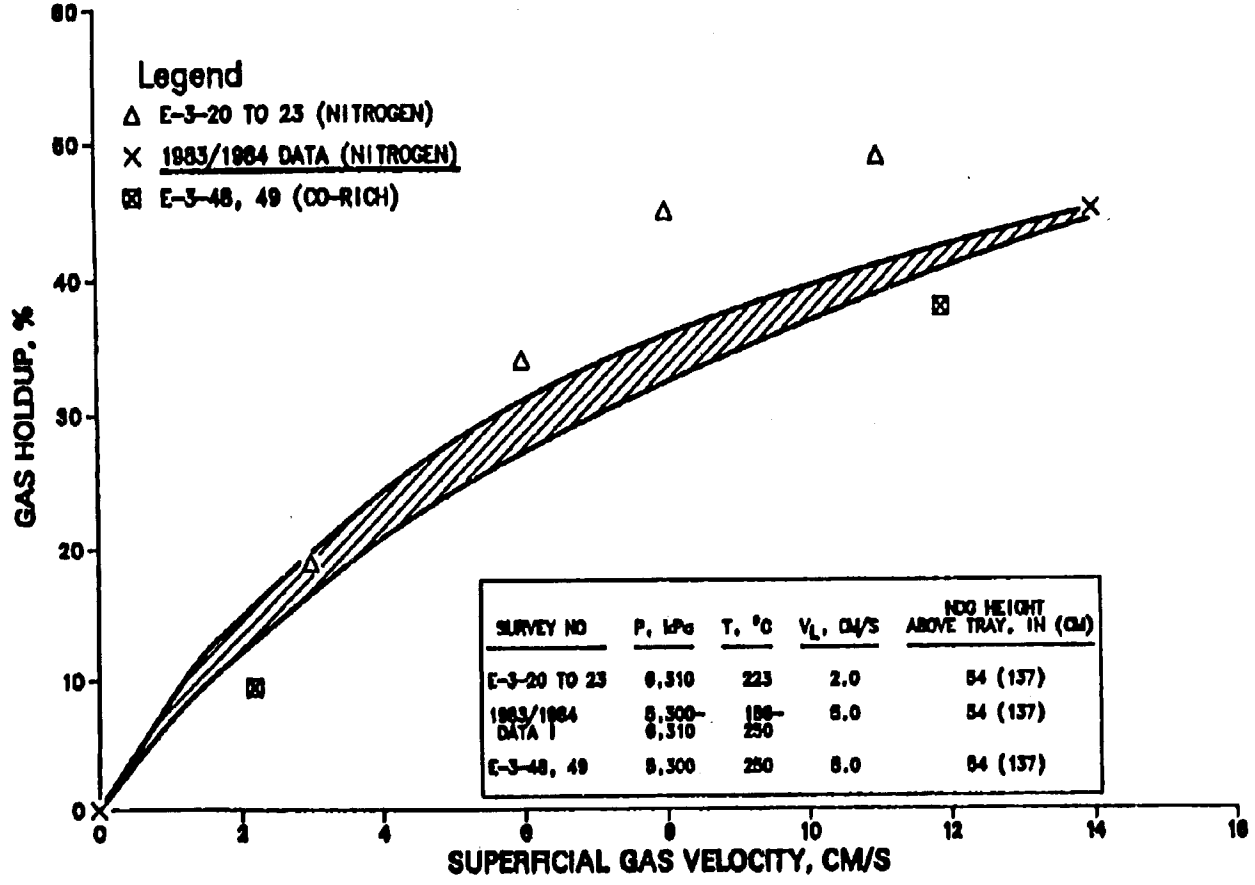

Figure IV-7. LaPorte LPMEOH PDU Comparison of Gas Holdup Data for N_2/Freezene-100 System and CO-Rich/Freezene-100 System

A series of carbonyl surveys was conducted from 2-9 March to determine the level of carbonyl generation in the LaPorte LPMEOH PDU after the completion of the metallurgical upgrade and chemical wash (February 1985). The PDU was maintained at 250°C (482°F) and 5,270 kPa (765 psia) throughout the survey, with only Freezene-100 oil circulating in the reactor-slurry loop. CO-rich gas was directed in a single pass through the PDU so that areas of metal carbonyl generation could be easily identified. Gas and oil flow rates were varied to determine the effect of gas and liquid velocities on carbonyl generation. The wet chemical analysis technique developed by Air Products' Analytical Group was employed to measure the concentration of carbonyls.

A simplified flow diagram identifying the sampling points is given in Figure IV-8. The results of the surveys are summarized in Table IV-5. The data confirmed the elimination of iron and nickel carbonyl sources in the feed gas supply to the reactor. The initial detection of high iron and nickel carbonyl levels at the outlet of the 01.10 feed compressor was probably due to contamination of the sampling line. Upon correction of this problem, the carbonyl levels in the 01.10 outlet dropped to very low levels. In the early stages of the survey period, a low level of nickel carbonyl was detected at locations downstream of the 27.10 reactor. The nickel carbonyl concentration at those locations dropped to the order of 10 ppbv by the end of the survey work. This represents an improvement of 10 to 20 times in the level of nickel carbonyl generation over the activity maintenance run E-1 (Reference 2) performed in April/May 1984. It appeared that the trace nickel contamination had been eliminated as a result of chemical cleaning.

Throughout the carbonyl surveys, the LaPorte LPMEOH PDU was operated in a single-pass mode. The purge flow for the plant was taken at a location upstream of the 01.20 recycle compressor, which was operating on total recycle. This resulted in a high nickel carbonyl concentration (>6,600 ppbv) in the loop around the recycle

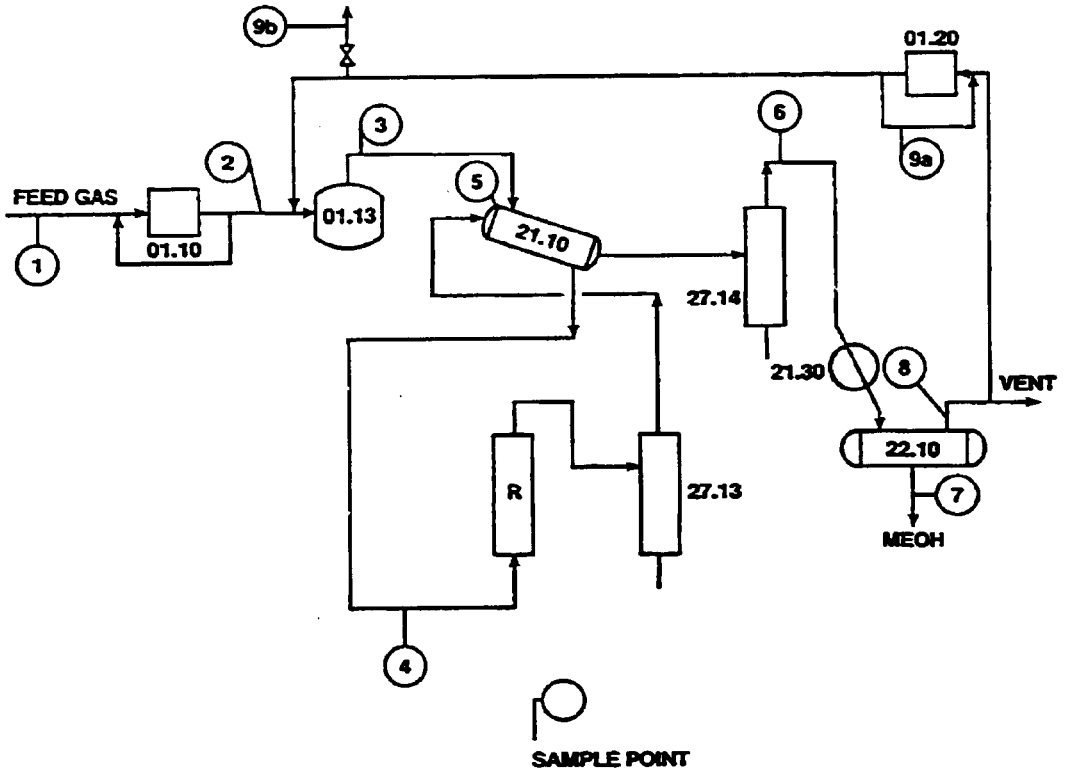

Figure IV-8. LaPorte LPMEOH PDU Carbonyl Survey Sample Points

TABLE IV-5

LAPORTE LPMEOH PDU

CARBONYL SURVEY WITH CO-RICH GAS (2-9 MARCH 1985)

P=5,270 kPa (765 psia), T=250°C (482°F), F=260 Nm3/h (10,000 SCFH)

concentrations in ppbv,

Hours on Syngas		1* Fresh Feed	2 01.10 Outlet	3 01.13 Ovhd.	4 Reactor Feed	5 27.13 Ovhd.	6 27.14 Ovhd.	8 22.10 Ovhd.	9a Recycle Compressor	Remarks
8	$Fe(CO)_5$	<5						1,730	150	V_L = 5.0 cm/s
	$Ni(CO)_4$	<5						500	>3,300	Vg = 1.1 cm/s
18	$Fe(CO)_5$	<5			15	2,250		2,850		
	$Ni(CO)_4$	<5			<10	120		84		
22	$Fe(CO)_5$		56			1,470	1,380			
	$Ni(CO)_4$		760			<10	26			
31	$Fe(CO)_5$			<8	<8				260	
	$Ni(CO)_4$			<8	<6				>6,600	
43	$Fe(CO)_5$	<3	36	<6						
	$Ni(CO)_4$	<3	596	<3						
55	$Fe(CO)_5$					78	963	811		New sample location for 22.10 Ovhd.
	$Ni(CO)_4$					33	64	<5		
67	$Fe(CO)_5$				<5			484	673	
	$Ni(CO)_4$				<20			<10	118	
78	$Fe(CO)_5$		15			606	715			
	$Ni(CO)_4$		<5			28	24			
90	$Fe(CO)_5$					855	561		555	
	$Ni(CO)_4$					84	53		86	

*Sample point number.

TABLE IV-5 (continued)

LAPORTE LPMEOH PDU

CARBONYL SURVEY WITH CO-RICH GAS (2-9 MARCH 1985)

P=5,270 kPa (765 psia), T=250°C (482°F), F=260 Nm3/h (10,000 SCFH)

concentrations in ppbv,

Hours on Syngas		1* Fresh Feed	2 01.10 Outlet	3 01.13 Ovhd.	4 Reactor Feed	5 27.13 Ovhd.	6 27.14 Ovhd.	8 22.10 Ovhd.	9a Recycle Compressor	Remarks
					Change Oil After 95 Hours on Syngas					
	$Fe(CO)_5$					542	537	551		
101	$Ni(CO)_4$					<60	<29	<35		
	$Fe(CO)_5$					343	317	372		
113	$Ni(CO)_4$					<30	<30	<30		
	$Fe(CO)_5$					194	194	187		Pump stopped
117	$Ni(CO)_4$					<30	<30	<30		VL = 0.0 cm/s
	$Fe(CO)_5$					151	168	202		Gas Flow
143	$Ni(CO)_4$					11	36	11		Doubled Vg = 2.0 cm/s VL = 5.0 cm/s

1544S-W2

compressor. The concentration of the nickel carbonyl dropped to a level comparable to the other sections of the PDU after the purge was relocated to a point downstream of the recycle compressor.

Unexpectedly high concentrations of iron carbonyl were measured at the sampling points downstream of the reactor-slurry loop. Since there was no upward trend in iron carbonyl measurements downstream of the 27.13 primary V/L separator, it appeared that all the iron carbonyl was being generated in the reactor-slurry loop. The iron carbonyl concentration showed a continuous decline during the survey period. After 95 hours on CO-rich syngas, the initial Freezene-100 oil charge was replaced because of oil contamination, which was suspected to have contributed to the high rates of iron carbonyl generation. However, no significant improvement resulted from the oil change. A steep drop in iron carbonyl levels was observed when the oil circulation was stopped, which suggested that the slurry loop piping (1-1/4% Cr- 1/2% Mo) may have been the major source of iron carbonyl formation. Doubling the synthesis gas flow to 500 NM^3/hr (19,000 SCFH) reduced the iron carbonyl concentration by half. This implied that the rate of iron carbonyl generation was independent of the gas velocity.

After a cumulative 155 hours of operation, carbonyl surveys indicated that the measured amounts of iron carbonyl had only dropped to a level comparable with the observations during 1984 PDU operation. Iron carbonyl concentrations at sample points downstream of the reactor were converted to generation rates to demonstrate the rate of decline in iron carbonyl formation shown in Figure IV-9. At this point, visual inspection of oil samples taken from the slurry circulation loop revealed the presence of minute metallic particles dispersed in the oil. On the basis of this observation, the PDU was shut down and inspected to confirm its mechanical integrity. Upon inspection, a particular pitting action was found to have attacked the 1-1/4% Cr - 1/2% Mo steel alloy piping of the slurry loop. A section of 1-1/4% Cr - 1/2% Mo pipe from the slurry loop that had been removed from the PDU after the 1984 operating program did not display this pitting.

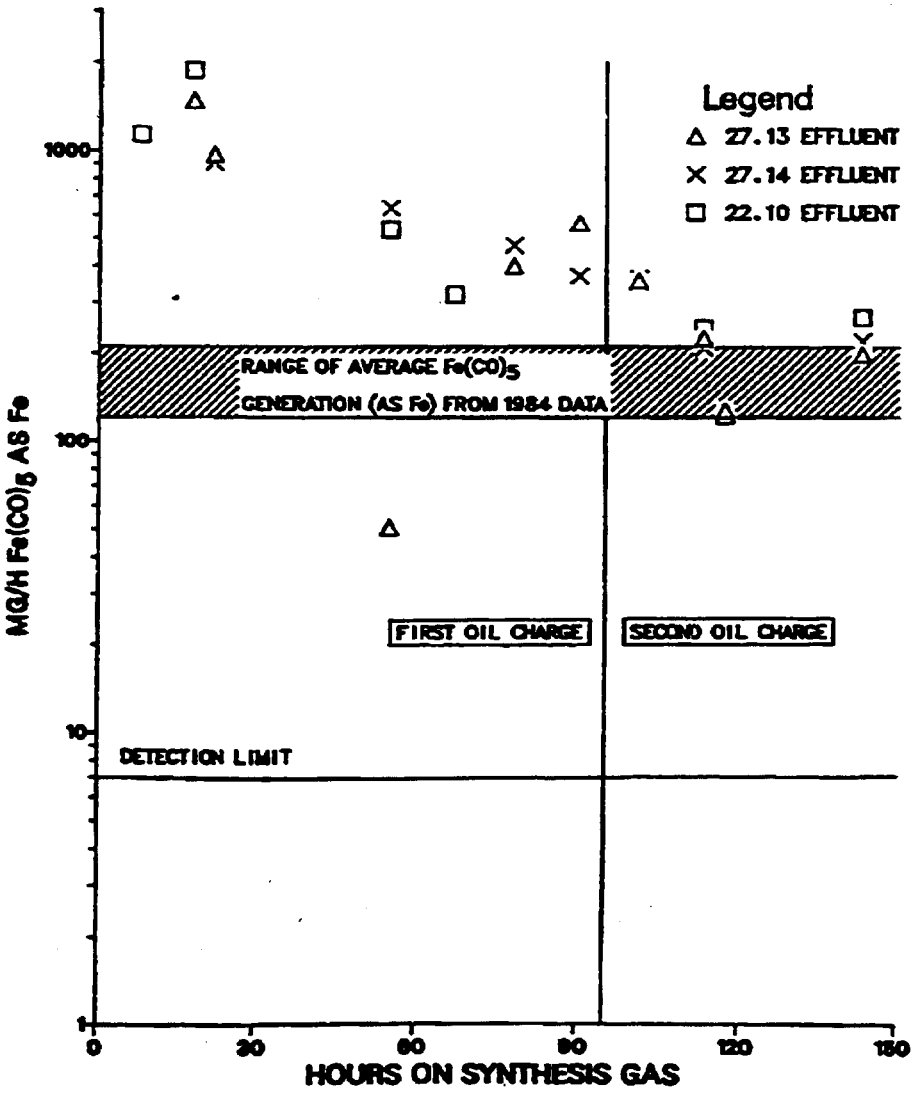

Figure IV-9. LaPorte LPMEOH PDU Iron Carbonyl Generation from Reactor/Slurry Loop (2-9 March 1985)

It is suspected that the various chemical wash procedures conducted in January 1985 may have activated the 1-1/4% Cr - 1/2% Mo piping of the slurry loop and made it susceptible to attack under synthesis gas conditions. A detailed post-survey inspection report is given in Appendix D.

Additional data taken during the carbonyl survey period 2-9 March are listed in Tables IV-6 and IV-7. These include analyses of liquids and suspended solids from the slurry loop. The steep change in metals content in the oil after the oil change is evident from these tables.

Because of the high levels of iron carbonyl formation measured during these surveys and the pitting discovered on the 1-1/4% Cr - 1/2% Mo slurry piping and valves, it was decided to upgrade the slurry loop piping and valves to 304-SS and 316-SS, respectively, and to apply a plasma-arc spray of 310-SS material to the remaining low-alloy steel surfaces on the slurry heat exchanger heads, two slurry valves, and on the inner casing of the slurry pump (see Section III-D). This second metallurgical change-out was completed in mid-April 1985, and the PDU was restarted for a follow-up series of carbonyl surveys on 24 April.

As in the previous test, CO-rich synthesis gas was directed in a single pass through the PDU with no catalyst present in the system. Reactor conditions of 250°C (482°F) and 5,270 kPa (765 psia) were maintained, while the feed flow was varied from 265 NM^3/hr (10,000 SCFH) to 525 NM^3/hr (20,000 SCFH). Sensitivity tests from this baseline included various reactor temperatures, operation with and without gas recycle, and variation of the circulation rate in the slurry loop. The data on carbonyl generation collected during this operation are summarized in Table IV-8.

The results confirmed both the elimination of iron carbonyl sources from the feed gas supply up to the reactor and the absence of any appreciable nickel contamination in the entire PDU. Evidence of

TABLE IV-6

LAPORTE LPMEOH PDU

ANALYSES OF OIL SAMPLES FROM INITIAL OIL CHARGE

(3-6 March 1985)

Hours on Synthesis Gas	Solid Conc, Wt%	Metals in Oil	
		Fe, PPMW	Ni, PPMW
0.0	0.3*	1.7	<1.0
14.5		125.0	<1.0
17.0		68.0	<1.0
24.0		31.0	<1.0
38.0		48.0	<1.0
49.5		35.5	<1.0

*The solids were analyzed as 0.42 wt% Fe, 28.5 wt% Cu, 28.8 wt% Zn, 1.22 wt% Al, 294 ppmw Ni, <200 ppmw S.

TABLE IV-7

LAPORTE LPMEOH PDU

ANALYSES OF OIL SAMPLES FROM SECOND OIL CHARGE

(7-9 March 1985)

	Metals in Oil		Metals in Solids*					
Hours on Synthesis Gas	Fe, PPMW	Ni, PPMW	Fe, Wt%	Cu, Wt%	Zn, Wt%	Cr, PPMW	Ni, PPMW	Mo, PPMW
65**	<1.5		0.94	12.9	13.5	1300	208	<34
99	4.4		0.67	15.6	18.0	714	188	<19
118	3.2	<0.2	0.63	13.8	16.4	1400	<38	<38
139	5.1	<0.2						
150	1.8	<0.2						

*Solids were still present in the second oil charge, but at a substantially lower concentration.

**Immediately after second oil-charge.

TABLE IV-8

LAPORTE LPMEOH PDU

CARBONYL SURVEY WITH CO-RICH GAS (24-29 APRIL 1985)

P = 5,270 kPa (765 psia)

Hours on Syngas	Reactor Feed (SCFH)	Reactor Temp. °C		Concentration in ppbv, 1* Reactor Feed	5 27.13 Ovhd.	8 22.10 Ovhd.	9b Recycle Comp. Purge	Remarks
7.5	10,000	250	$Fe(CO)_5$		47	<53	36	Reactor - slurry loop still generates small quantities of carbonyls.
			$Ni(CO)_4$		25	<45	18	
13.0	10,000	250	$Fe(CO)_5$		89	96	104	No carbonyl generation downstream of 27.13.
			$Ni(CO)_4$		20	21	26	
27.5	10,000 (3/4 hr) 20,000 (3/4 hr) 80,000 (6-1/2 hr)	250	$Fe(CO)_5$		60	58	59	
			$Ni(CO)_4$		10	11	11	
Decision was made to change oil on 4/25/85 due to presence of a small quantity of solids in oil samples.								
36.5	20,000	250	$Fe(CO)_5$		32	40	46	The appearance of second batch of oil is clean. $Ni(CO)_4$ level has reduced to near detection limit.
			$Ni(CO)_4$		5	<5	8	
43.0	20,000	250	$Fe(CO)_5$	<3	35		41	No carbonyls in reactor feed.
			$Ni(CO)_4$	<3	<3		5	
49.5	20,000	250	$Fe(CO)_5$	<3	35		40	
			$Ni(CO)_4$	3	5		6	
62.0	20,000	225	$Fe(CO)_5$		36	39	38	Lowering reactor temp. to determine the temperature effect on carbonyl generation
			$Ni(CO)_4$		6	5	<4	

*Sample point number.

TABLE IV-8 (continued)

LAPORTE LPMEOH PDU

CARBONYL SURVEY WITH CO-RICH GAS (24-29 APRIL 1985)

P = 5,270 kPa (765 psia)

Hours on Syngas	Reactor Feed (SCFH)	Reactor Temp. °C		Concentration in ppbv, 1* Reactor Feed	5 27.13 Ovhd.	8 22.10 Ovhd.	9b Recycle Comp. Purge	Remarks
66.0	20,000	225	$Fe(CO)_5$		30	39	36	
			$Ni(CO)_4$		<4	<4	<5	
73.0 (Slurry Pump off)	20,000	255-193 (224 avg.)	$Fe(CO)_5$		16	14	21	With slurry pump stopped, the conc. of $Fe(CO)_5$ almost reduced by half.
			$Ni(CO)_4$		<6	<5	<6	
84.5	20,000	279	$Fe(CO)_5$		22	27	24	High temp. appears to reduce the level of of $Fe(CO)_5$ generation.
			$Ni(CO)_4$		7	9	7	
90.5	20,000	250	$Fe(CO)_5$		30	31	29	
			$Ni(CO)_4$		<5	<6	<5	
96.0	100,000 20,000 Fresh Feed 80,000 Recycle 20,000 Purge	250	$Fe(CO)_5$	21	26		21	$Fe(CO)_5$ and $Ni(CO)_4$ generation across reactor slurry loop very small as expected.
			$Ni(CO)_4$	12	<7		9	
100.0	100,000	250	$Fe(CO)_5$		26	27	26	
			$Ni(CO)_4$		<5	<7	<8	
102.5	20,000	250	$Fe(CO)_5$		26	28	22	Slurry pump speed reduced 20%.
			$Ni(CO)_4$		<5	<8	<6	
108.0	20,000	250	$Fe(CO)_5$		20	18	18	Slurry pump speed reduced 50%.
			$Ni(CO)_4$		<6	<5	<6	

iron carbonyl generation was again limited to the reactor-slurry loop; however, the initial concentration was about one fourth of the level detected during the March 1985 carbonyl survey and decreased with time. The downward trend of the rate of iron carbonyl generation is illustrated in Figure IV-10. The sensitivity of iron carbonyl generation rate to the reactor temperature was not significant in the range of 225 to 280°C (437 to 536°F), although generation rates appeared to be slightly lower at the higher temperature.

Iron carbonyl levels were consistently lower as the rate of oil circulation through the slurry loop was reduced. When this circulation flow was stopped, iron carbonyl concentrations were reduced by approximately 50% relative to the baseline. This is consistent with the results of carbonyl surveys obtained in March 1985.

Additional data on the analyses of oil samples from the slurry loop are listed in Table IV-9. All oil samples appeared very clean with only trace solids dispersed in the liquid. Both iron and nickel concentrations in the oil were low compared to the previous surveys.

The results of this series of carbonyl surveys indicated a decrease in the generation rate of 9 to 15 times for $Ni(CO)_4$ and 2 to 8 times for $Fe(CO)_5$ when compared to the 40-day activity maintenance run made in April/May 1984 (Run E-1). Due to the significant improvement, a decision was made to proceed with the second 40-day activity maintenance run (Run E-3).

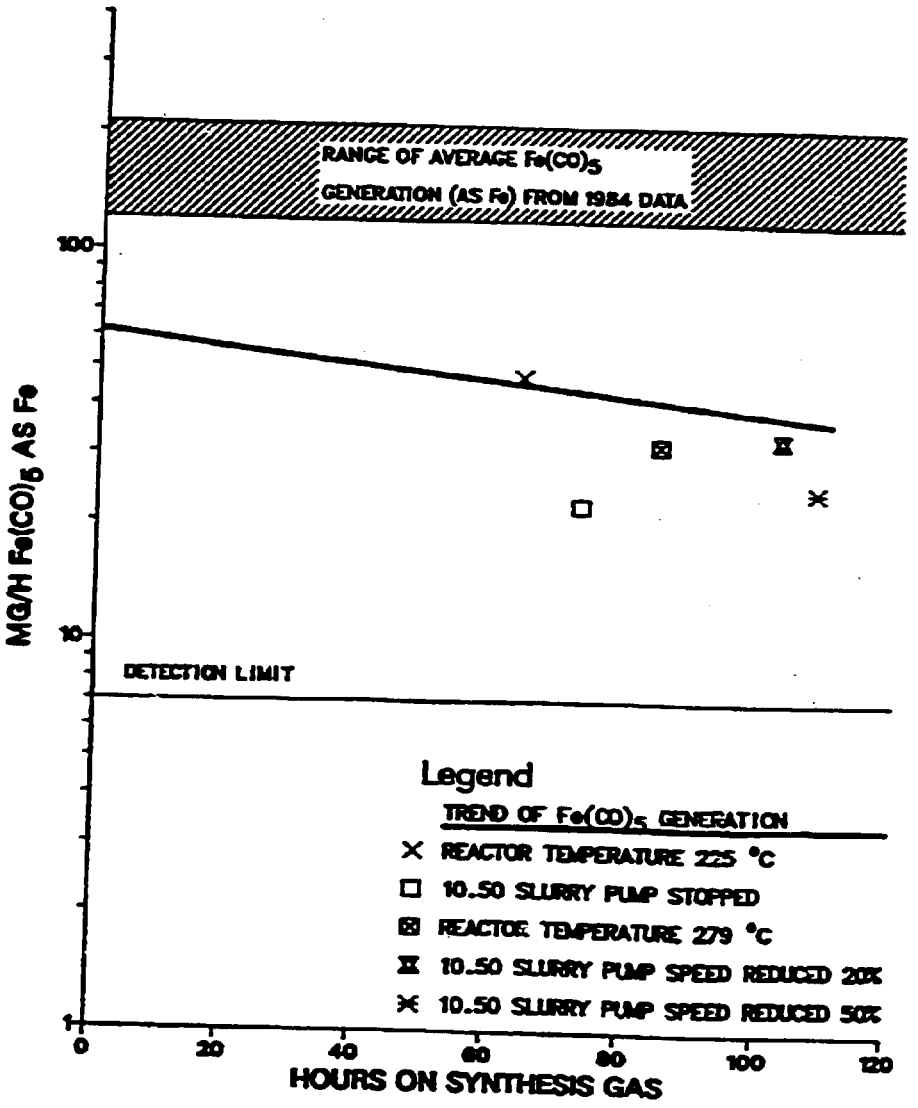

Figure IV-10. LaPorte LPMEOH PDU Iron Carbonyl Generation from Reactor/Slurry Loop (24-30 April 1985)

TABLE IV-9

LAPORTE LPMEOH PDU

ANALYSES OF OIL SAMPLES

(24-25 April 1985)

Hours on Synthesis Gas	Metals in Oil	
	Fe, PPMW	Ni, PPMW
0	0.59	<0.05
2	1.14	<0.05
15	1.19	<0.05

V. HIGH SLURRY CONCENTRATION RUN (RUN E-2)

A. Objectives

A liquid-entrained run was made in the LaPorte LPMEOH PDU with a commercially available slurry catalyst (F21/OE75-29) in June 1984. A 43 wt% (oxide basis) slurry was prepared in the 28.30 slurry prep tank and successfully transferred to the slurry loop. The catalyst was activated in the slurry form. PDU performance data were obtained at 6,310 kPa (915 psia), 250°C (482°F), and various space velocities and slurry concentrations. The mechanical performance of the LaPorte PDU in this run was excellent. However, the catalyst activity was not as high as projected from the laboratory autoclaves. The low activity has been attributed in part to an inadequate catalyst activation.

The objectives of the run were to demonstrate slurry preparation and transfer, in-situ reduction of a catalyst powder, and liquid-entrained operation at high slurry loading and high superficial gas velocity. The run also provided the first opportunity to study the change of catalyst characteristics during in-situ reduction and how that translates into performance on synthesis gas. The details of the PDU operation and run results are discussed below.

B. In-Situ Reduction

A batch of 43 wt% (oxide basis) slurry using Freezene-100 oil and catalyst powder F21/OE75-29 was prepared in the 28.30 slurry prep tank. The agitator for the slurry prep tank operated without difficulty throughout the catalyst loading operation. The slurry was pressure-transferred into the slurry loop, and catalyst reduction procedure was followed. Further details are presented in the supplementary volume to this topical report. No operational problems with the 10.50 slurry pump at this elevated slurry loading were encountered during the reduction procedure. The final hydrogen consumption was about 77% of the stoichiometric value for the

catalyst. When no further hydrogen consumption was detected, the reducing gas flow was stopped and synthesis gas feed was lined up for methanol synthesis operation.

C. Methanol Synthesis Operation

After the reduction was completed, the reactor was maintained at 240-250°C (464 to 482°F) under nitrogen for approximately 10 hours to vaporize the excess oil added to the reactor-slurry loop as the pump seal fluid during catalyst activation. When the slurry concentration reached 46.5 wt% (as oxide) solids, balanced feed gas was introduced to the reactor. During the early stages of the run, the slurry concentration was increased to 49 wt% by limiting the pump seal flush flow.

The range of operating conditions for Run E-2 is given in Table V-1. In addition to varying temperature and gas and liquid superficial velocities, the effect of solids loading was also studied. A series of process variable scans was performed to obtain a measure of process performance at these different conditions. Associated with the process variable scans, slurry samples were taken for solids concentration measurement and catalyst analysis. Reactor hydrodynamics were monitored using the nuclear density gauge mounted on the reaction vessel.

Process equipment operated smoothly throughout the run. The 10.50 slurry circulation pump and the 21.20 slurry heat exchanger performed well at the high slurry concentrations. After 145 hours on synthesis gas, the run was terminated as scheduled on 20 June. The overall on-stream factor of this run exceeded 99%. The run chronology is presented in Table V-2.