V. 10-DAY SHAKEDOWN RUN (RUN F-1)

A. Objectives

Immediately after the completion of the chemical wash, a 10-day shakedown operation Run F-1 with catalyst extrudates (R71/OF12-26)* was conducted in the LaPorte LPMEOH PDU. The objectives of the shakedown operation were to:

- Establish operation of the unit under methanol production conditions.
- Determine the source and magnitude of carbonyl formation.
- Test the effectiveness of downstream product separation equipment.
- Determine the carbonyl removal capacity of a charcoal adsorbent bed.
- Check the system mass balances and reactor heat balance.
- Check the data acquisition system, analytical equipment, and sampling systems.
- Obtain conversion data at variable flow, temperature, and pressure conditions for balanced and CO-rich gas.
- Determine the attrition characteristics of R71/OF12-26 catalyst extrudates.
- Measure gas holdup and catalyst inventory in the reactor.

* This catalyst is also designated as EPJ-19LR.

- Check for trace components in the fresh feed.

- Perform catalyst postmortem analyses to establish Cu crystallite size, Cu^{+1}/Cu^{0} ratio, and accumulation of poisoning agents.

B. Catalyst Reduction

Approximately 408 kg (900 lb) of catalyst extrudate R71/OF12-26 (EPJ-19LR) supplied by United Catalysts Inc. were screened with a 20-mesh screen and loaded into the reactor. This catalyst had been batch-checked by Chem Systems Inc. in the Lab PDU in July/August 1983 (Reference 4), and its properties are listed in Table V-1. The bed height was checked with a dip stick and with the nuclear density gauge. Both measurements yielded a bed height of 82 in. (208 cm) above the tray.

A chronology of the catalyst reduction procedure is presented in Table V-2. Upon the completion of reduction, nitrogen was used to purge the system and the catalyst bed was cooled to 200°C (392°F). The cumulative hydrogen consumption during reduction was determined to be 827 g-mol hydrogen per kilogram catalyst, which corresponded to a 13% weight loss, assuming that a stoichiometric amount of oxygen was removed as water.

C. Catalyst Bed Studies

In order to determine the hydrodynamics of the ebullated-bed operation with the R71/OF12-26 catalyst, a series of three-phase catalyst fluidization tests was conducted before synthesis gas was introduced and methanol synthesis was initiated. Extensive data on ebullated-bed expansion (similar to those developed in the Lab PDU) and three-phase gas holdup were obtained.

TABLE V-1

CATALYST R71/OF12-26 (EPJ-19LR) PARTICLE PROPERTIES

	Fresh[1] Oxided Catalyst
Average Particle Length, cm	0.4831
Average Particle Diameter, cm	0.1756
Average Particle Volume, cm^3	1.170×10^{-2}
Average Side Crush[2] Strength, kg/cm	7.0
Average Dry Particle Density, g/cm^3	1.4747
Average Dry Particle Weight, mg	17.2
Average L.O.A.[3], %	6.8
Solid Density, g/cm^3 (Immersion in oil)	3.636

(1) Based on the average of three samples collected by the coning and quartering method of sampling.

(2) Weight necessary to crush a catalyst particle oriented on its side and expressed as kg/cm length.

(3) Loss on attrition; wt% smaller than 20 mesh as determined by the standard 8-hour cold attritionometer test.

TABLE V-2

LAPORTE LPMEOH PDU CATALYST REDUCTION CHRONOLOGY

WITH CATALYST R71/0F12-26 (EPJ-19LR)

Date	Time	Cumulative Time On Reduction Gas (Hours)	Milestone
3/5/84	1750		Approximately 408 kg (900 lb) screened catalyst (EPJ-19LR) was loaded into reactor. The catalyst bed height was determined with a dip stick and with the nuclear density gauge. Both methods gave a bed height of 82 inches (208 cm) above the tray. The total volume of catalyst loaded was calculated to be 0.521 m^3 (18.4 ft^3).
	2330		Heated up the catalyst bed with 525 Nm^3/h (20,000 SCFH) N_2 at 790 kPa (115 psia). The heatup rate was controlled at 10°C/h (18°F/h).
3/6/84	1415		Increased reactor pressure to 1,140 kPa (165 psia) and N_2 flow to 790 Nm^3/h (30,000 SCFH) in order to accelerate the heatup of the catalyst bed.
	1745		The average bed temperature reached 120°C (250°F). Bypassed hot N_2 to obtain an H_2 concentration of 1 mol%. Verified the H_2 concentration on GC. Reduced the reactor pressure to 790 kPa (115 psia).
	1945	0	The average bed temperature had dropped to ~99°C (210°F) when the heatup was resumed with 525 Nm^3/h (20,000 SCFH) hot reduction gas (1 mol% H_2 in N_2). Monitored H_2 outlet concentration closely on H_2 analyzer for first sign of reduction.
	2230	2-3/4	Observed first sign of reduction when average bed temperature reached 103°C (217°F).
3/7/84	0630	10-3/4	Increased H_2 concentration in the reduction gas to 1.5 mol% when average bed temperature reached 177°C (350°F).

TABLE V-2

LAPORTE LPMEOH PDU CATALYST REDUCTION CHRONOLOGY

WITH CATALYST R71/0F12-26 (EPJ-19LR)

(continued)

Date	Time	Cumulative Time On Reduction Gas (Hours)	Milestone
3/7/84	1815	22-1/2	Bulk reduction completed; raised H_2 concentration in the reduction gas to 2 mol% and started heating the catalyst bed to 230°C (446°F).
3/8/84	0130	29-3/4	Increased reactor pressure to 1,140 kPa (165 psia) and reduction gas flow to 790 Nm^3/h (30,000 SCFH) to accelerate the heatup rate.
	0500	33-1/4	Catalyst reduction completed.

Dry Catalyst Bed Density

Table V-3 lists the NDG measurements of the density of the dry oxide bed, and Tables V-4 and V-5 list the corresponding information for the bed after the completion of the bulk and polishing reduction steps. Assuming no change in bed height, these measurements show about a 12% weight loss during the bulk reduction, but no detectable loss during the final reduction. This agrees with the hydrogen consumption measurements, which showed a 13% weight loss during bulk reduction and no measurable hydrogen consumption during final reduction.

The measured bulk densities are about 2-3% less than that required to account for the known mass of catalyst charged. Initially, about 408 kg (900 lb) of oxide were charged, and the top of the bed was 82 in. (208 cm) above the tray, both by dip stick and by NDG observations. This corresponds to a bulk density (after excluding the 0.5 ft^3 (.014 m^3) column occupied by the bubble caps) of 0.785 g/cm^3 for the oxide, and, assuming 12.5% weight loss on reduction, 0.687 g/cm^3 for the reduced catalyst.

Table V-6 lists the properties of the reduced catalyst extrudates; these values are used in all density calculations.

Initial Wet Settled Bed Density

Table V-7 provides the data for the initial wet settled bed density measurements. Results are given in terms of the true volume fraction of solids, ϵ_S, the volume fraction of liquid in the particle pores, ϵ_{LP}, and the volume fraction of free liquid, ϵ_{LF}. The values of ϵ_S are also shown in Figure V-1. It can be seen that the wet settled bed had a uniform bulk catalyst density of 0.68 g/cm^3, and that the particles were packed somewhat more tightly than in the dry settled bed (ρ_B = 0.67 g/cm^3). The

TABLE V-3

NDG MEASUREMENTS OF OXIDE BED DENSITY

(5 March 1984, V_o = -66 mV)

NDG Position Above Tray, in.	NDG Reading volts	Bed Density ρ g/cm^3	Bulk Catalyst Density, $\rho_B=\rho-\varepsilon_G\rho_G$ g/cm^3
15 (38 cm)	-0.437	0.789	0.782
24 (61 cm)	-0.485	0.764	0.757
36 (91 cm)	-0.679	0.762	0.755
48 (122 cm)	-0.678	0.762	0.755
60 (152 cm)	-0.641	0.776	0.769
72 (183 cm)	-0.667	0.764	0.757
Average			0.763

TABLE V-4

NDG MEASUREMENTS OF DRY CATALYST BED DENSITY AFTER BULK REDUCTION

(1800, 7 March 1984, V_o = -46 mV)

NDG Position Above Tray, in.	NDG Reading, volts	Bed Density ρ g/cm^3	Bulk Catalyst Density, ρ_B g/cm^3
15-3/4 (40 cm)	-0.588	0.691	0.686
24 (61 cm)	-0.640	0.675	0.670
36 (91 cm)	-0.911	0.674	0.669
48 (122 cm)	-0.914	0.673	0.668
60 (152 cm)	-0.891	0.677	0.672
72 (183 cm)	-0.911	0.671	0.666
Average			0.672

TABLE V-5

NDG MEASUREMENTS OF DRY CATALYST BED DENSITY AFTER POLISHING REDUCTION

(0630, 8 March 1984; V_o = -43 mV)

NDG Position Above Tray, in.	NDG Reading, volts	Bed Density ρ g/cm^3	Bulk Catalyst Density, ρ_B g/cm^3
15-3/4 (40 cm)	-0.583	0.692	0.685
24 (61 cm)	-0.637	0.675	0.668
36 (91 cm)	-0.897	0.677	0.670
48 (122 cm)	-0.901	0.676	0.669
60 (152 cm)	-0.887	0.678	0.671
72 (183 cm)	-0.901	0.673	0.666
Average			0.672

TABLE V-6

REDUCED CATALYST PROPERTIES

Bulk Density, ρ_B, g/cm^3	0.687
Dry Particle Density, ρ, g/cm^3	1.290
True Solids Density, ρ_S, g/cm^3 (by oil immersion)	4.4
Bed Porosity, ϵ_{mf}	0.467
Particle Porosity, α	0.707
True Volume Fraction Solids, ϵ_S	0.155

TABLE V-7

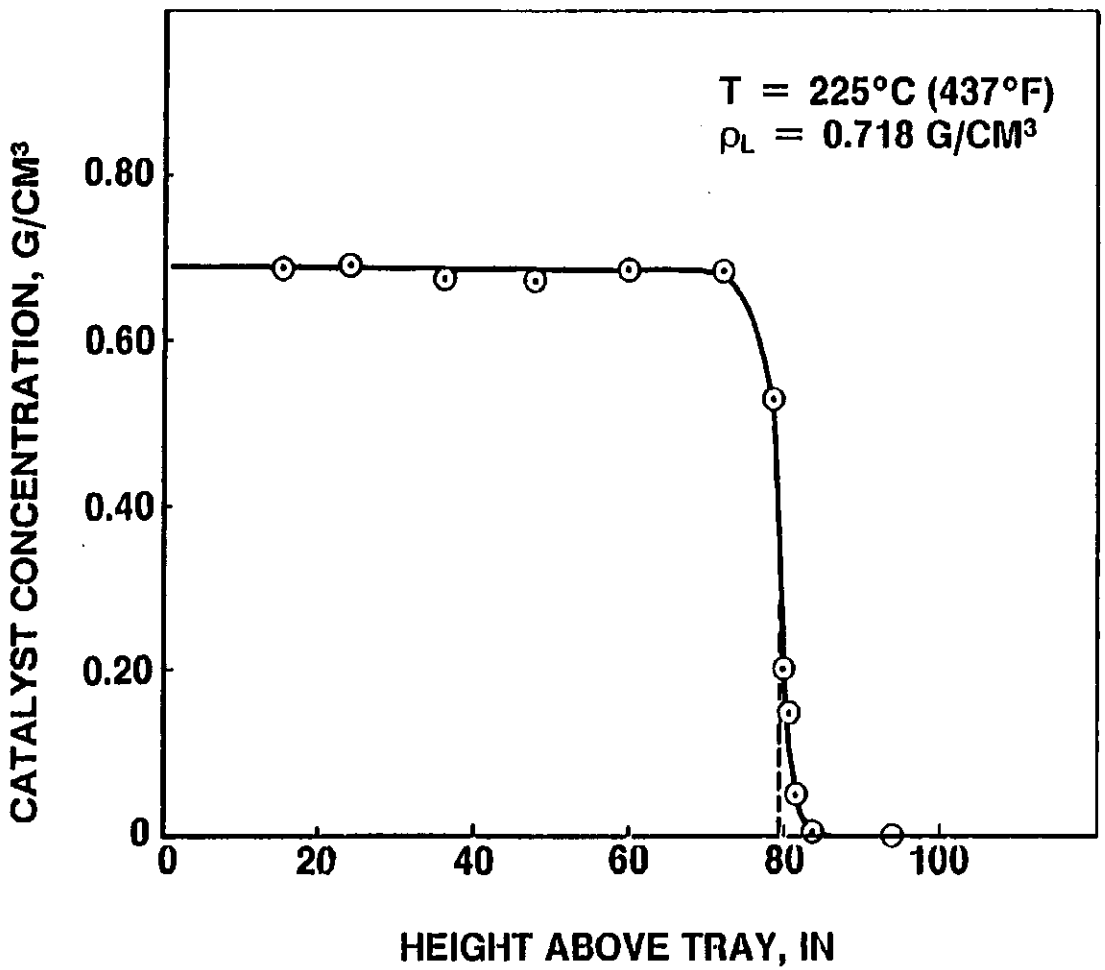
INITIAL WET SETTLED BED DENSITY MEASUREMENTS - NDG SURVEY NO. BE-01-A0

(225°C, Vo = -43 mV, ρ_S = 4.4 g/cm^3, ρ_L = 0.718 g/cm^3)

NDG Position Above Tray, in.	NDG Reading, millivolts	Vol. Fraction of Solids ϵ_S, %	Vol. Fraction of Liq. in Particle Pores ϵ_{LP}, %	Vol. Fraction of Free Liq. ϵ_{LF}, %	Bed Density g/cm^3
15-3/4 (40 cm)	- 79	15.5	37.3	47.2	1.29
24 (61 cm)	- 79	15.7	37.9	46.4	1.30
36 (91 cm)	- 98	15.3	36.9	47.8	1.28
48 (122 cm)	- 98	15.3	36.9	47.8	1.28
60 (152 cm)	- 96	15.5	37.4	47.1	1.29
72 (183 cm)	- 97	15.4	37.1	47.5	1.28
78-1/2 (199 cm)	-128	12.0	28.9	59.1	1.16
78-15/16 (200 cm)	-275	4.5	10.8	84.7	0.88
80-1/8 (204 cm)	-405	1.2	2.8	96.0	0.76
84 (213 cm)	-459	0	0	100	0.72
94 (239 cm)	-454	0	0	100	0.72

FIGURE V-1

INITIAL WET SETTLED BED HEIGHT (SURVEY BE-01-AO, 2230 HRS., 8 MARCH 1984)



average value of ϵ_S in the bed calculated from NDG readings was in close agreement with the value of 0.162 obtained from the known amount of catalyst charged and the 79 in. (201 cm) bed height. However, considering the high radiation attenuation of the dense catalyst/liquid mixture in the wet settled bed, the accuracy of the NDG readings in the measurement of the wet bed density was little better than ±5%.

The data in Figure V-2 show that the wet settled bed height dropped to about 77 in. (196 cm), with no significant change in bed density, during the 1-day bed expansion test period. This represents a 4% catalyst particle loss of attrition.

Equations for Three-Phase Gas Holdup Data Analysis

Upon completion of the wet settled bed study, tests on the effects of gas and liquid velocity on bed dynamics were initiated. It should be noted, however, that the definition of the solid phase must consider the presence of catalyst as both ebullated particles and attrited fines. Also, liquid is present both in the pores of the ebullated particles and as slurry liquid. Thus, a full description of the reactor requires expanding Equation (IV-2) to:

$$(\epsilon_{SB} + \epsilon_{SF})\, a_S \rho_S^L + (\epsilon_{LP} + \epsilon_{LF})\, a_L \rho_L^L + \epsilon_G a_G \rho_G^L = \ln \frac{C_R\,[V(o) - V_o]}{V - V_o} \qquad \text{(Eq.V-1)}$$

where ϵ_{SB} = volume fraction of true solids in ebullated pellets,

ϵ_{SF} = volume fraction of fines,

ϵ_{LP} = volume fraction of liquid in the ebullated catalyst pores,

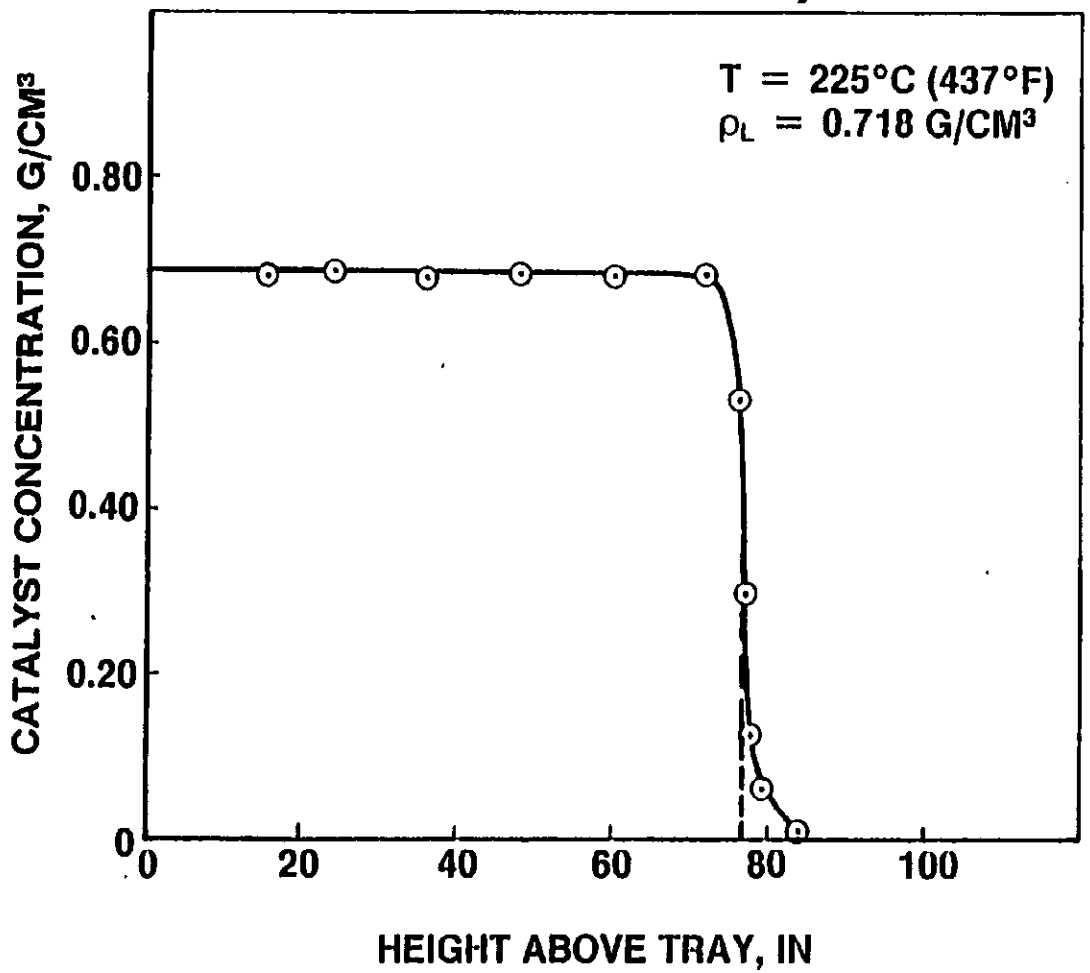
ϵ_{LF} = volume fraction of liquid not in the ebullated catalyst pores, and

ϵ_G = volume fraction of gas, assumed to be a constant value both within and above the bed.

Two additional equations may be written immediately:

FIGURE V-2

WET SETTLED BED AFTER BED EXPANSION STUDY (SURVEY BE-01-A0-1, 1630 HRS., 9 MARCH 1984)



$$\varepsilon_{SB} + \varepsilon_{SF} + \varepsilon_{LP} + \varepsilon_{LF} + \varepsilon_{G} = 1, \text{ and} \qquad \text{(Eq. V-2)}$$

$$\frac{\varepsilon_{LP}}{\varepsilon_{LP} + \varepsilon_{SB}} = \alpha = \text{particle porosity.} \qquad \text{(Eq. V-3)}$$

With the current data, $[V(o) - V_o]$ is -11.1 volts and α, the particle porosity, is 0.707 (see Table V-6).

Given values for V (the NDG output voltage) and V_o (the "zero" or offset output voltage), Equations (V-1, 2, and 3) constitute three equations with five unknowns. More information is required to obtain a solution.

One additional equation can be obtained by considering the overall solids and oil material balances. Let

M_L = total mass of liquid in the system,
M_{LP} = total mass of liquid in the ebullated pellet pore,
M_{LF} = total mass of liquid in the slurry,
M_S = total mass of catalyst in the system,
M_{SB} = total mass of catalyst in the bed, and
M_{SF} = total mass of the catalyst as fines.

Then, assuming a constant slurry concentration throughout the slurry loop,

$$\frac{\varepsilon_{SF}}{\varepsilon_{LF}} = \frac{M_{SF}/\rho_S}{M_{LF}/\rho_L} = \frac{\rho_L\,(M_S - M_{SB})}{\rho_S\,(M_L - M_{LP})} \qquad \text{(Eq. V-4)}$$

M_S and M_L are known quantities from the catalyst and oil inventories. From Equation (V-3),

$$\frac{M_{LP}}{\rho_L} = \frac{M_{SB}}{\rho_S} \cdot \frac{\alpha}{1-\alpha} \qquad \text{(Eq. V-5)}$$

Finally, M_{SB} can be found by integrating the bed density profile in the reactor:

$$\frac{M_{SB}}{\rho_S} = \int_0^h A_C \cdot \epsilon_{SB} \cdot dz \qquad \text{(Eq. V-6)}$$

where A_C = reactor cross-sectional area, cm^2 (ft^2),
z = distance above tray, and
h = bed height, the point of inflection in the catalyst concentration vs. reactor height curve, cm (ft).

Note that the fraction of the total catalyst charge in the bed is M_{SB}/M_S, and the slurry concentration is $M_{SF}/(M_{LF} + M_{SF})$.

Since the bed density is clearly not constant in the present data, Equation (V-6) must be numerically integrated.

The five equations (V-1, 2, 4, 5, 6) are solved by trial and error iteration using a computer. A sample calculation is attached as Appendix B.

Ebullated-Bed Expansion Studies

Table V-8 and Figures V-3 to V-5 summarize the results of the initial bed expansion studies (NDG survey Nos. BE-01-A1 to BE-01-D2). These tests were run with nitrogen at 225°C (437°F). Since complete bed profiles were not obtained for the "A" series surveys, these points were calculated assuming no catalyst attrition. The remaining data were reduced by the method described above. Relative bed expansions are based on the initial wet settled bed height of 79 in. (201 cm).

TABLE V-8

SUMMARY OF BED EXPANSION TEST RESULTS

NDG Survey No.	P kPa (psia)	Liquid Velocity cm/s	Gas Velocity cm/s	Gas Holdup (above bed) %	Bed Height in.	Bed Expansion* %
BE-01-A1	4450 (645)	2.4	0	--	82 (208 cm)	4
BE-01-A2	4180 (606)	3.7	0	--	90 (229 cm)	14
BE-01-A3	4060 (589)	4.9	0	--	98 (249 cm)	24
BE-01-A4	3930 (570)	6.1	0	--	113 (287 cm)	43
BE-01-A3A	3870 (561)	4.9	0	--	98 (249 cm)	24
BE-01-A2A	3810 (553)	3.7	0	--	90 (229 cm)	14
BE-01-B1	5360 (778)	6.1	2.1	12.3	112 (284 cm)	42
BE-01-B2	5390 (781)	4.9	2.4	14.3	97 (246 cm)	23
BE-01-B3	5320 (772)	3.7	2.4	16.1	94 (239 cm)	19
BE-01-C1	5240 (760)	6.1	3.7	15.9	113 (287 cm)	43
BE-01-D1	5260 (763)	6.1	4.9	21.4	109 (277 cm)	38
BE-01-D2	5240 (760)	4.9	4.9	24.2	101 (257 cm)	28

*Based on the initial wet settled bed height of 79 in. (201 cm).

FIGURE V-3
EXPANDED BED PROFILES: N_2

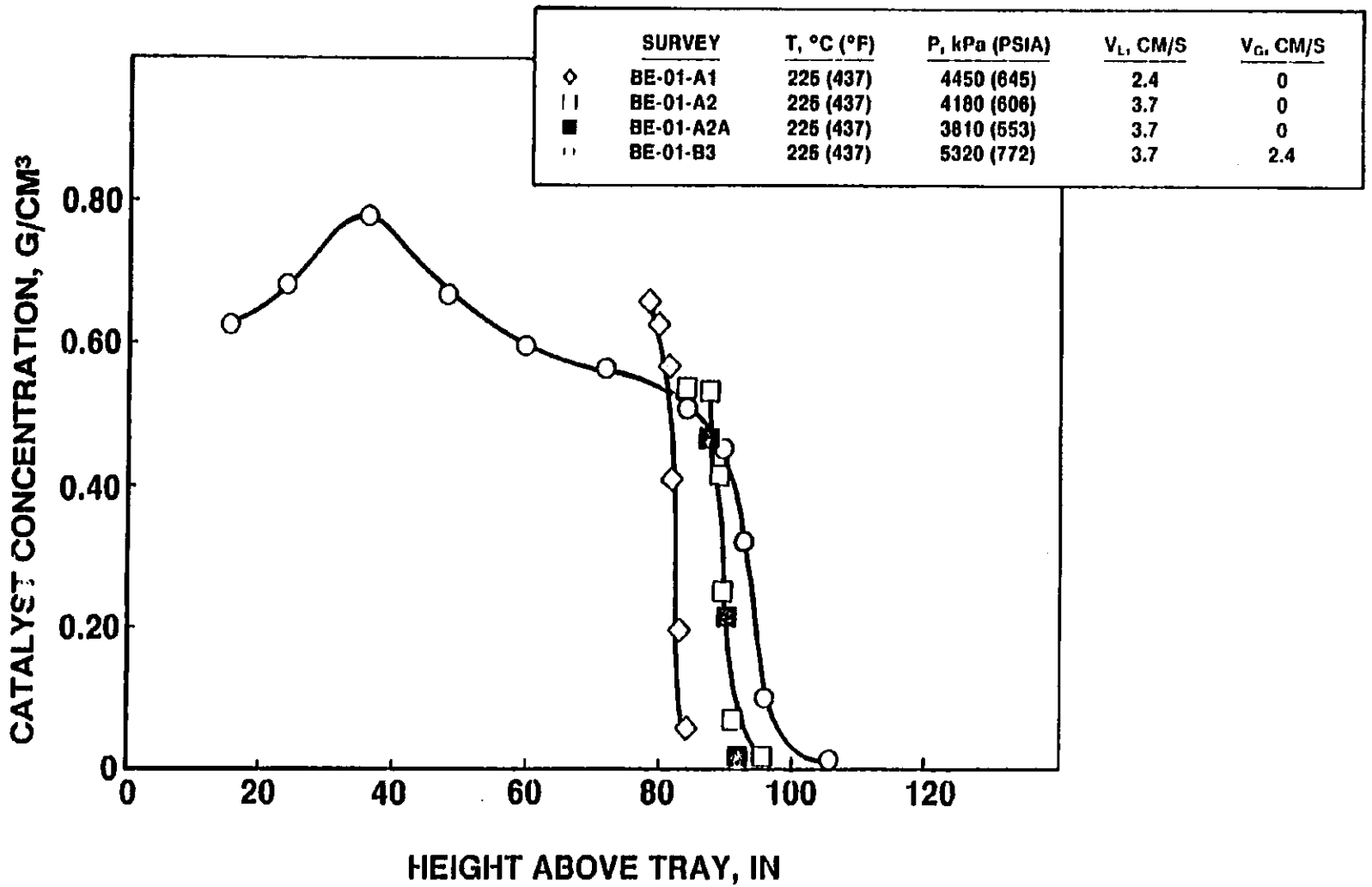


FIGURE V-4
EXPANDED BED PROFILES: N_2 (CONT'D)

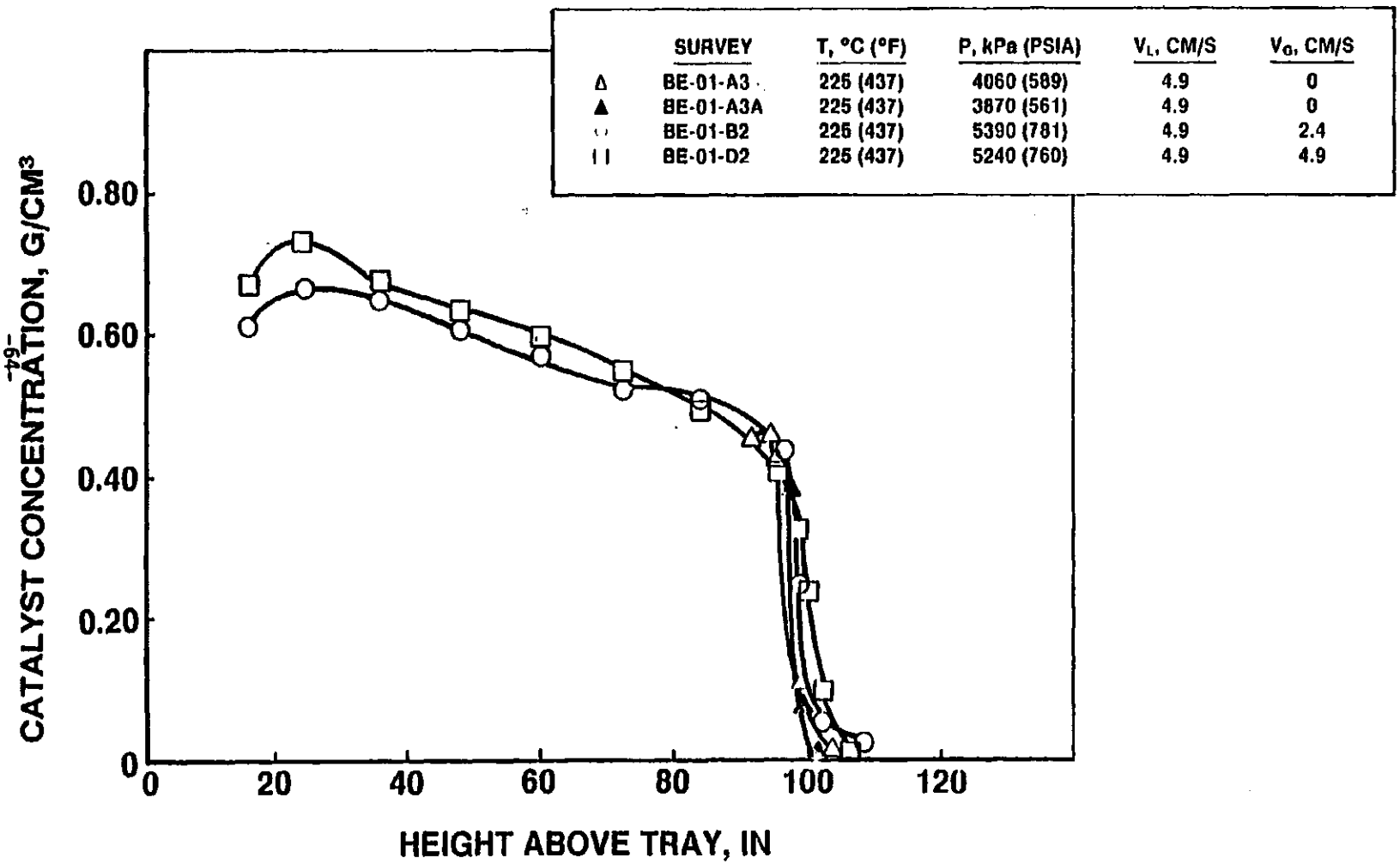


FIGURE V-5
EXPANDED BED PROFILES: N_2 (CONT'D)

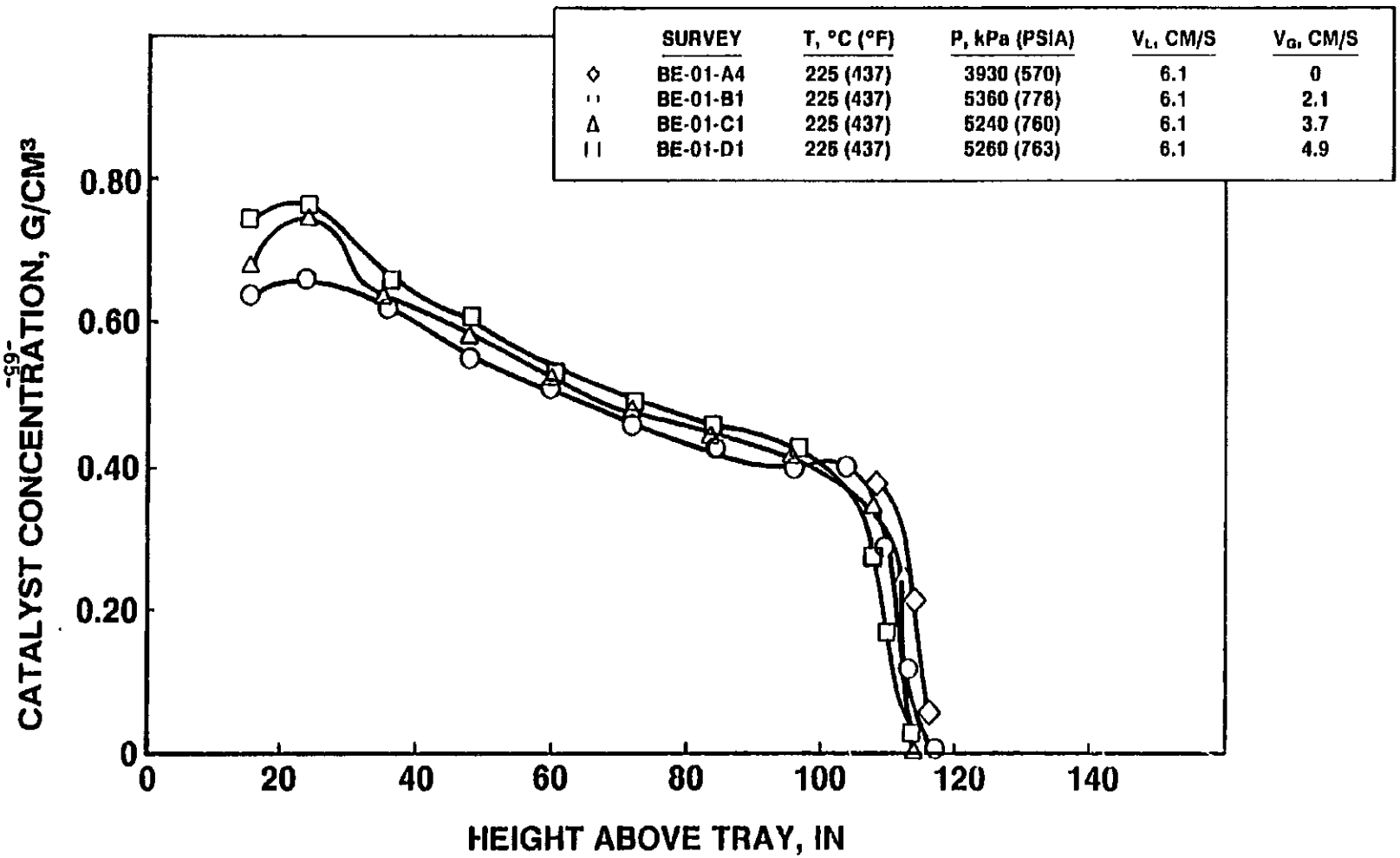
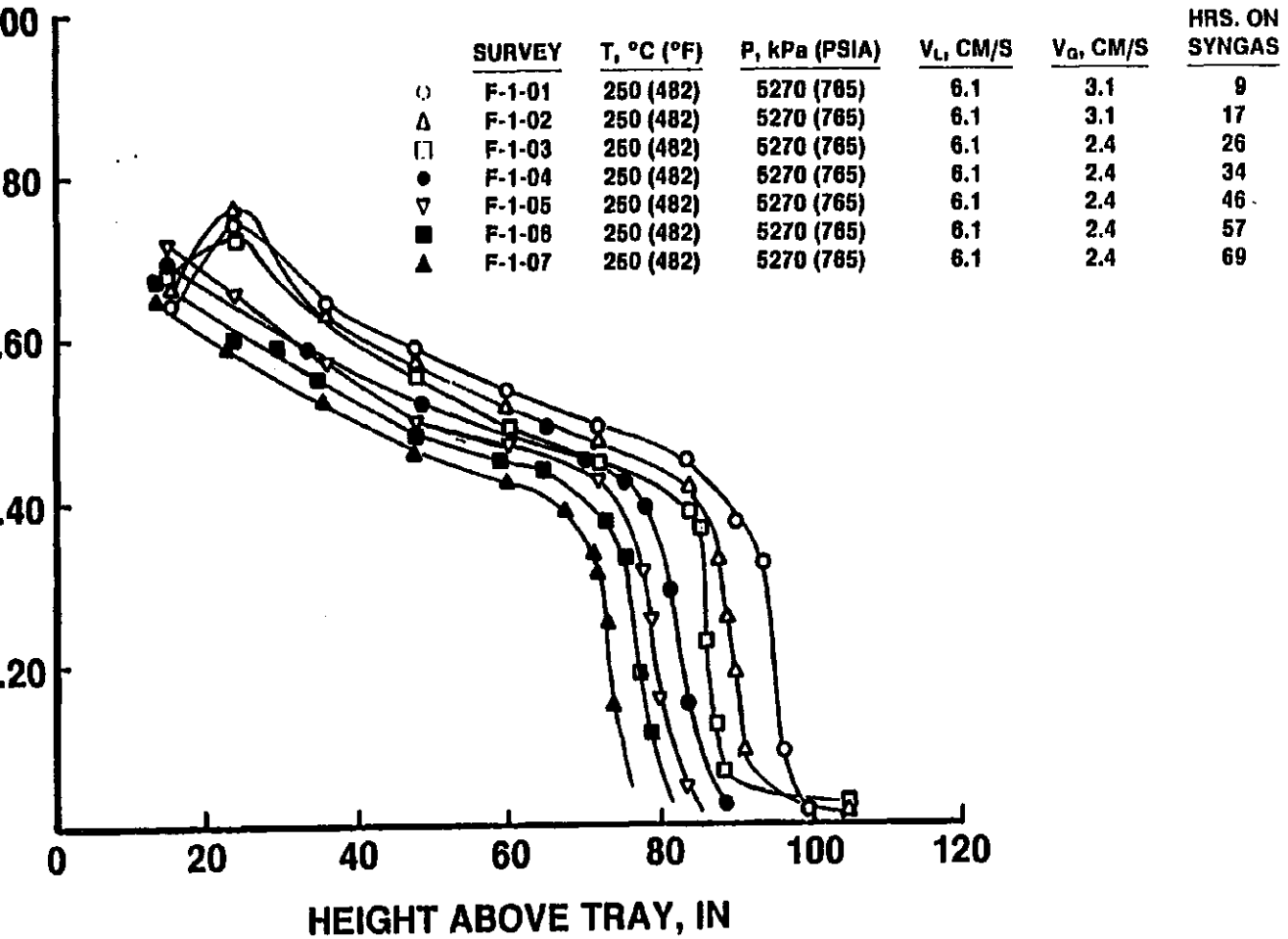


FIGURE V-7
EXPANDED BED PROFILES: BALANCED GAS



	SURVEY	T, °C (°F)	P, kPa (PSIA)	V_L, CM/S	V_G, CM/S	HRS. ON SYNGAS
○	F-1-01	250 (482)	5270 (765)	6.1	3.1	9
△	F-1-02	250 (482)	5270 (765)	6.1	3.1	17
□	F-1-03	250 (482)	5270 (765)	6.1	2.4	26
●	F-1-04	250 (482)	5270 (765)	6.1	2.4	34
▽	F-1-05	250 (482)	5270 (765)	6.1	2.4	46
■	F-1-06	250 (482)	5270 (765)	6.1	2.4	57
▲	F-1-07	250 (482)	5270 (765)	6.1	2.4	69

FIGURE V-8
EXPANDED BED PROFILES: BALANCED GAS (CONT'D)

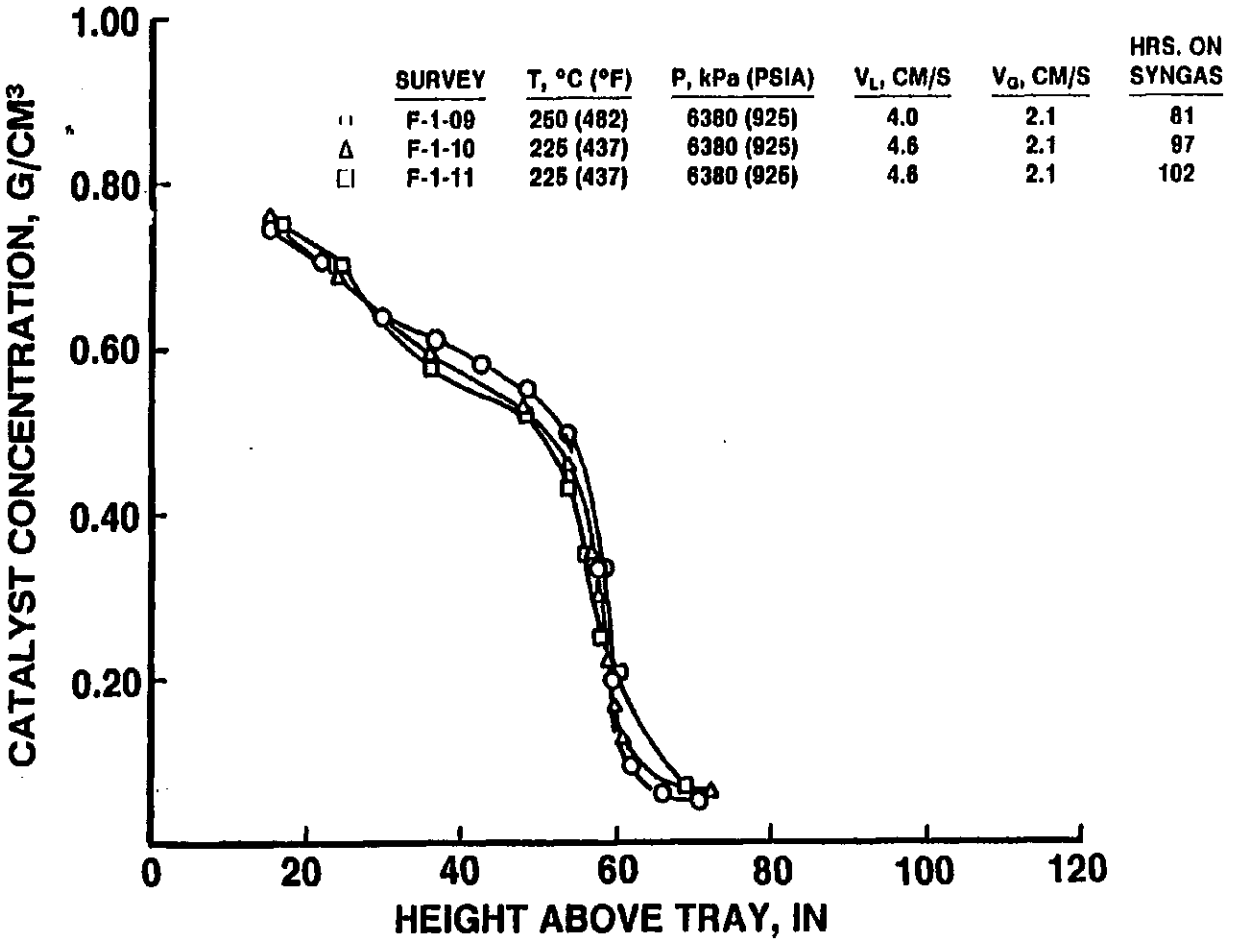
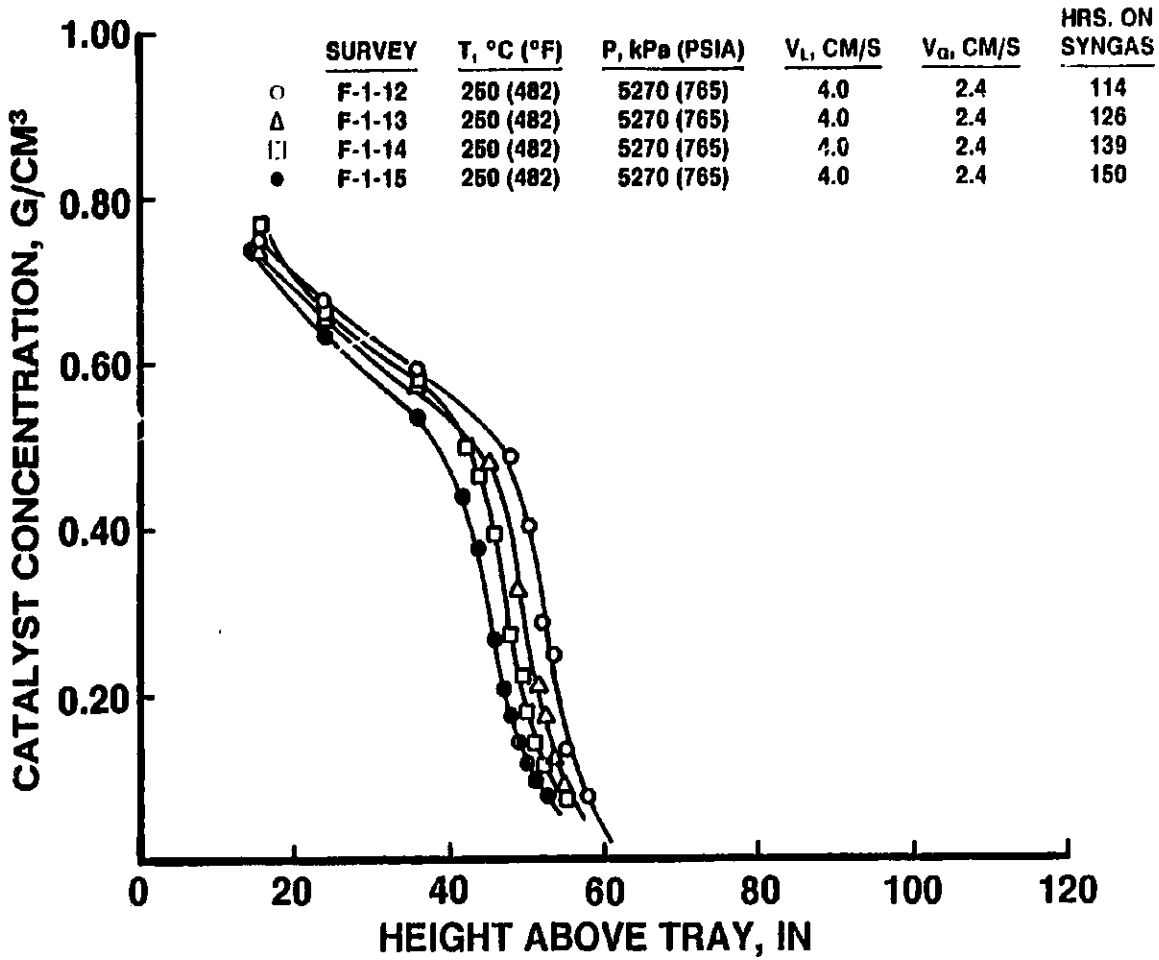


FIGURE V-9
EXPANDED BED PROFILES: CO-RICH GAS



Increasing the gas velocity by means of recycle flow, beginning with Survey F-1-16 (159 hours on synthesis gas), resulted in a rapid decrease in the density of the remaining bed (Figure V-10). Without a clear inflection point in these curves, it became impossible to determine the catalyst bed height. The further increase in gas velocity following Survey F-1-21 eliminated essentially all traces of an ebullated bed.

Three-Phase Gas Holdup

Three-phase gas holdup data were obtained during the syngas operation. The results are presented in the Supplementary volume of this report.

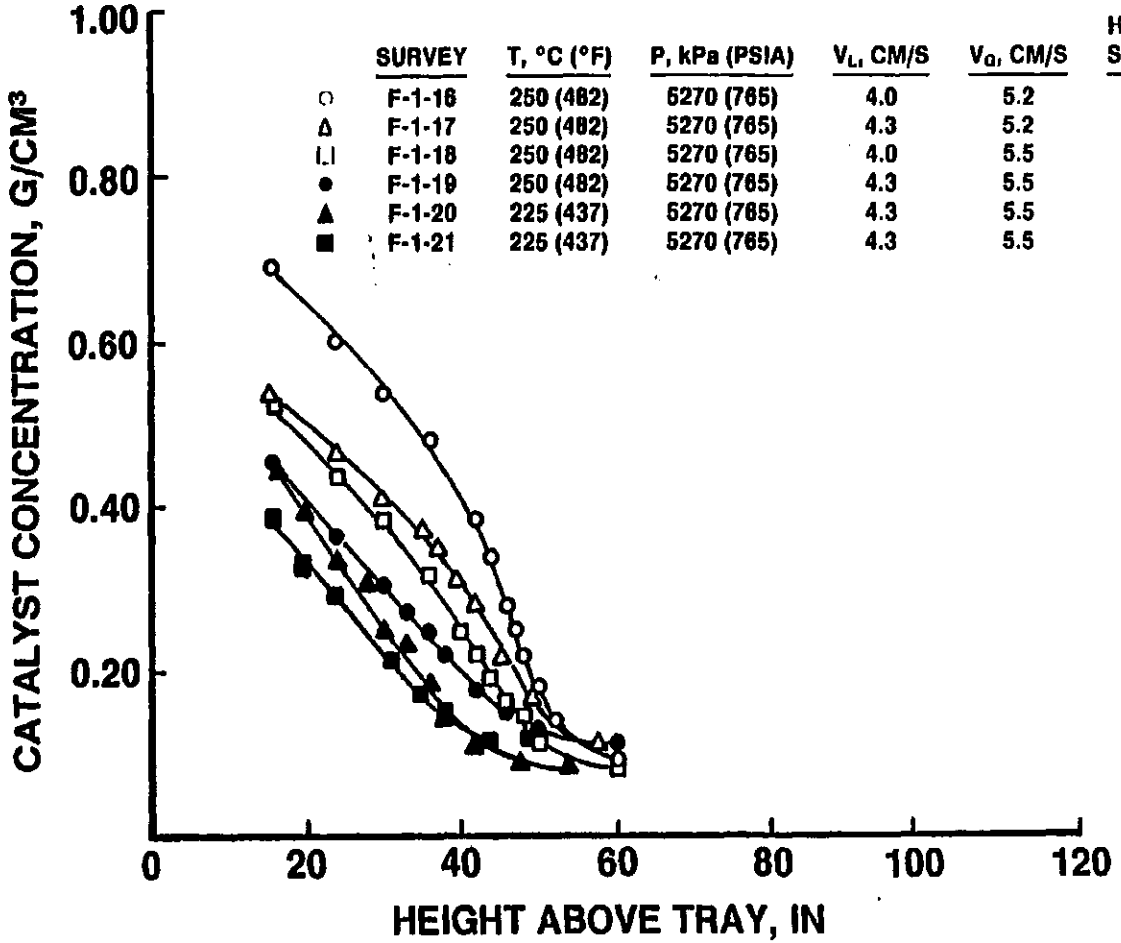
At the end of the shakedown run, additional three-phase gas holdups were measured using nitrogen. The data are tabulated in Table V-9 and plotted in Figure V-11. The gas holdups measured during the initial bed expansion studies (Surveys BE-01-A1 to D2, Table V-8) and the two-phase gas holdups measured for the N_2/Freezene-100 system at 186°C (367°F) and 5,270 kPa (765 psia) are also shown in Figure V-11 for comparison. At the higher linear gas superficial velocities, the gas holdups with solids present are moderately reduced with respect to the two-phase gas holdup data.

D. Methanol Synthesis Operation (Run F-1)

Catalyst Performance Data

After the completion of the bed expansion studies with N_2, the synthesis gas supplies were lined up in a once-through (no recycle) mode, and the first methanol was produced at the LaPorte LPMEOH PDU. The gas chromatograph indicated the presence of methanol in the reactor effluent sample stream, and liquid inventories began to increase in the product separation equipment. Throughout this first LaPorte run, PDU performance was smooth; plant upsets due to mechanical problems were infrequent and of short duration.

FIGURE V-10
EXPANDED BED PROFILES: CO-RICH GAS (CONT'D)



	SURVEY	T, °C (°F)	P, kPa (PSIA)	V_L, CM/S	V_G, CM/S	HRS. ON SYNGAS
○	F-1-16	250 (482)	5270 (765)	4.0	5.2	159
△	F-1-17	250 (482)	5270 (765)	4.3	5.2	175
□	F-1-18	250 (482)	5270 (765)	4.0	5.5	184
●	F-1-19	250 (482)	5270 (765)	4.3	5.5	199
▲	F-1-20	225 (437)	5270 (765)	4.3	5.5	210
■	F-1-21	225 (437)	5270 (765)	4.3	5.5	218

TABLE V-9

SHAKEDOWN RUN

THREE-PHASE GAS HOLDUP DATA FOR N_2

NDG Survey No.	Gas	Slurry Conc. wt%	T °C (°F)	P kPa (psia)	u_L cm/s	u_G cm/s	ϵ_G %
F-1-25	N_2	18.2	178 (352)	6240 (905)	4.9	9.8	31.7
F-1-26	N_2	18.2	187 (369)	6320 (916)	4.9	6.7	25.5
F-1-27	N_2	18.2	193 (379)	6310 (915)	5.2	2.7	19.7
F-1-28	N_2	18.2	193 (379)	6310 (915)	0	0	2.5

FIGURE V-11
TWO-PHASE AND THREE-PHASE GAS HOLDUP: N_2

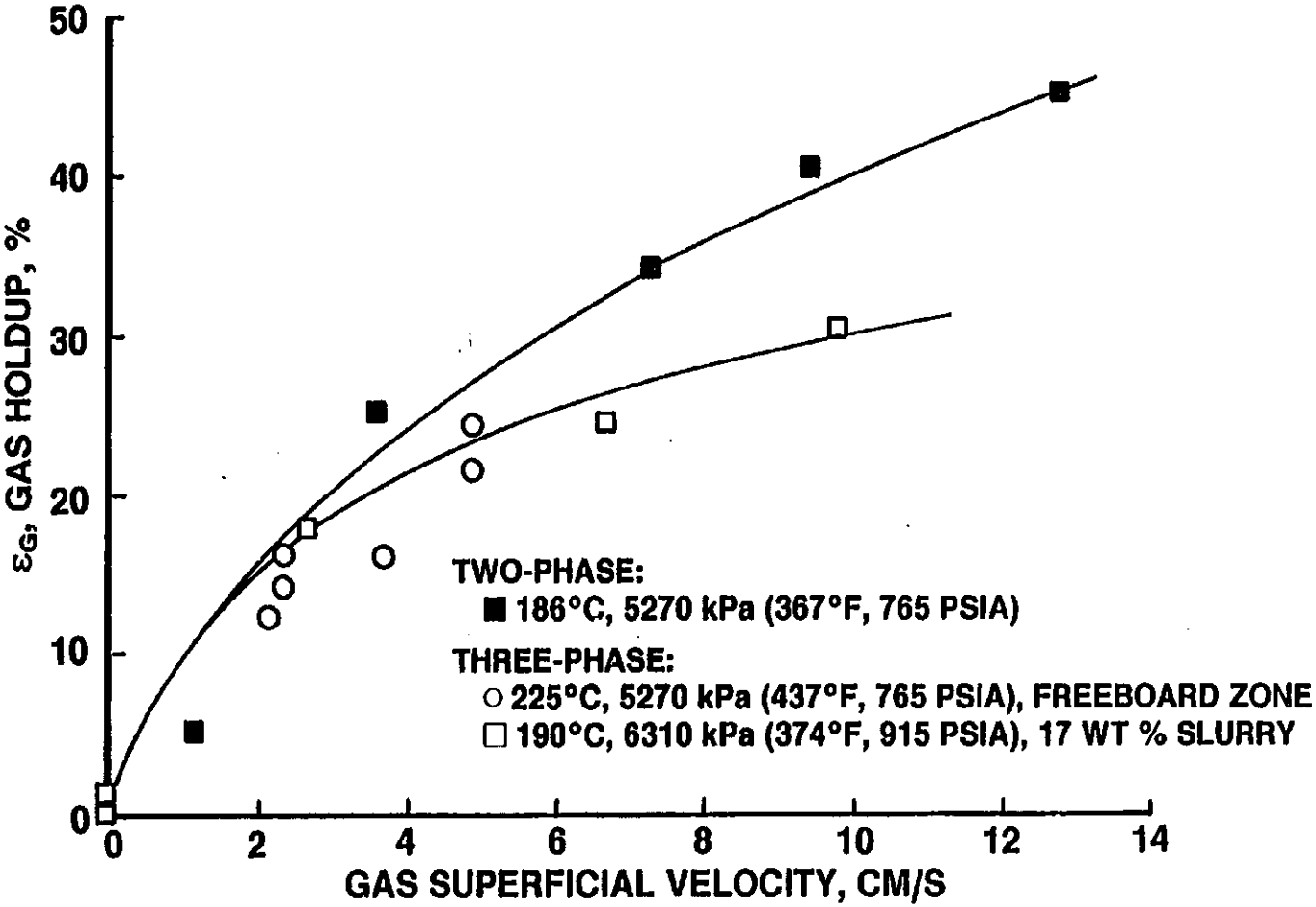


Table V-10 summarizes the operating conditions of the shakedown run, and a complete chronology is presented in Table V-11. The reactor was operated at nominal conditions of 5,270 kPa (765 psia) and 6,310 kPa (915 psia), 225°C (437°F) and 250°C (482°F). Superficial gas velocities varies from 2.1 cm/s (0.07 ft/s) to 12.5 cm/s (0.41 ft/s), and superficial liquid velocities ranged from 4.0 cm/s (0.13 ft/s) to 6.1 cm/s (0.20 ft/s). The key process variables and performance data are summarized in Table V-12, while the detailed data sheets generated by the Data Acquisition System for these test periods are attached in Appendix C.

The CO conversion and methanol productivity data obtained during the shakedown run are plotted as a function of space velocity in Figures V-12 and V-13 for the balanced and CO-rich reactor feeds, respectively. Data from autoclaves and the Lab PDU, as well as curves predicted by the fundamental model (Reference 5), are also included in the figures for comparison. Near equilibrium CO conversion was achieved at the low space velocities, and productivities as high as 50.6 g-mol methanol/hr-kg catalyst in the reactor as oxide (1.62 kg methanol/hr-kg catalyst) were realized at the high space velocities. At these conditions, the LaPorte PDU reactor clearly performed as a well-mixed reactor and without mass transfer limitations. It is evident that the activity of the catalyst extrudate F71/OF12-26 (EPJ-19LR) was comparable to that of slurried catalyst powder F51/0E75-01 tested in the autoclave at variable space velocities. At the high velocity condition the PDU was producing 8 tons per day of methanol.

In the previous section, it was noted that both the catalyst bed height and bed density were declining throughout the run due to attrition of the catalyst. Figure V-14 illustrates the increased level of catalyst fines (reduced basis) in the circulating Freezene-100 oil as measured by NDG readings and by actual samples taken via the slurry sampling system. The calculated concentrations are in good agreement with the lower edge of directly measured concentrations. The samples having higher

TABLE V-10

LAPORTE LPMEOH PDU SHAKEDOWN RUN (F-1) OPERATING CONDITIONS

Case	Gas	P kPa (psia)	T °C (°F)	V_G cm/s (ft/s)	V_L cm/s (ft/s)	Hrs at Condition
F-1A	Balanced	5340 (775)	250 (482)	2.4 (0.08)	6.1 (0.20)	76
F-1B	Balanced	6370 (924)	250 (482)	2.2 (0.07)	4.0 (0.13)	12
F-1C	Balanced	6370 (925)	225 (437)	2.1 (0.07)	4.6 (0.15)	14
F-1E	CO-rich	5320 (772)	250 (482)	2.4 (0.08)	4.1 (0.13)	55
F-1F	CO-rich	5310 (770)	250 (482)	5.2 (0.17)	4.1 (0.13)	46
F-1DR	CO-rich	5310 (770)	225 (437)	4.5 (0.15)	4.3 (0.14)	15
F-1G	CO-rich	5310 (770)	250 (482)	10.7 (0.35)	5.9 (0.19)	11
F-1H	Balanced	6360 (922)	250 (482)	12.5 (0.41)	6.0 (0.20)	18
						248

TABLE V-11

LAPORTE LPMEOH PDU SHAKEDOWN RUN (F-1) CHRONOLOGY

WITH CATALYST R71/OF12-26 (EPJ-19LR)

Date	Time	Cumulative Time On Synthesis Gas (Hours)	Milestone
3/8/84	1230		Oil temperature reached 193°C (380°F); introduced oil into reactor and established oil circulation around the reactor loop.
	1700		Reactor temperature reached 250°C (482°F); began bed expansion tests on N_2.
3/9/84	1800	0	Completed the bed expansion tests. Balanced feed gas was introduced to the PDU. Began Case F-1A: T=250°C (482°F), P=5,270 kPa (765 psia), v_L=6.1 cm/s (0.20 ft/s), v_G=2.4 cm/s (0.08 ft/s).
	1845	3/4	GC detected 2 mol% MEOH in reactor effluent.
3/12/84	2330	77-1/2	Ended Case F-1A; checked wet settled bed height. V-333 on reactor gas inlet stuck in closed position.
3/13/84	0330	77-1/2	V-333 opened; restored balanced feed gas to the reactor.
	0500	79	Began Case F-1B: Bal. gas, T=250°C (482°F), P=6,310 kPa (915 psia), v_L=4.0 cm/s (0.13 ft/s), v_G=2.2 cm/s (0.07 ft/s).
	1400	88	Ended Case F-1B. Began Case F-1C: Bal. gas, T=225°C (437°F), P=6,310 kPa (915 psia), v_L=4.6 cm/s (0.15 ft/s), v_G=2.1 cm/s (0.07 ft/s).
3/14/84	0400	102	Ended Case F-1C. Changed feed gas to CO-rich gas and began Case F-1E: T=250°C (482°F), P=5,270 kPa (765 psia), v_L=4.1 cm/s (0.13 ft/s), v_G=2.4 cm/s (0.08 ft/s).

TABLE V-11

LAPORTE LPMEOH PDU SHAKEDOWN RUN (F-1) CHRONOLOGY

WITH CATALYST R71/OF12-26 (EPJ-19LR)

(continued)

Date	Time	Cumulative Time On Synthesis Gas (Hours)	Milestone
3/16/84	1030	156-1/2	Ended Case F-1E. Began Case F-1F: CO-rich gas, T=250°C (482°F), P=5,270 kPa (765 psia), v_L=4.1 cm/s (0.13 ft/s), v_G=5.2 cm/s (0.17 ft/s).
3/18/84	0930	203-1/2	Ended Case F-1F. Began Case F-1DR: CO-rich gas, T=225°C (437°F), P=5,270 kPa (765 psia), v_L=4.3 cm/s (0.14 ft/s), v_G=4.5 cm/s (0.15 ft/s).
3/19/84	0100	219	Ended Case F-1DR. Began Case F-1G: CO-rich gas, T=250°C (482°F), P=5,270 kPa (765 psia), v_L=5.9 cm/s (0.19 ft/s), v_G=10.7 cm/s (0.35 ft/s).
	1200	230	Ended Case F-1G. Changed feed gas to Bal. gas and began Case F-1H: T=250°C (482°F), P=6,310 kPa (915 psia), v_L=6.0 cm/s (0.20 ft/s), v_G=12.5 cm/s (0.41 ft/s).
3/20/84	0530	247-1/2	Stopped syngas to the reactor. Began N_2/slurry gas holdup tests.
	1030		Shut down slurry circulation pump and transferred slurry into slurry prep tank.

TABLE V-12

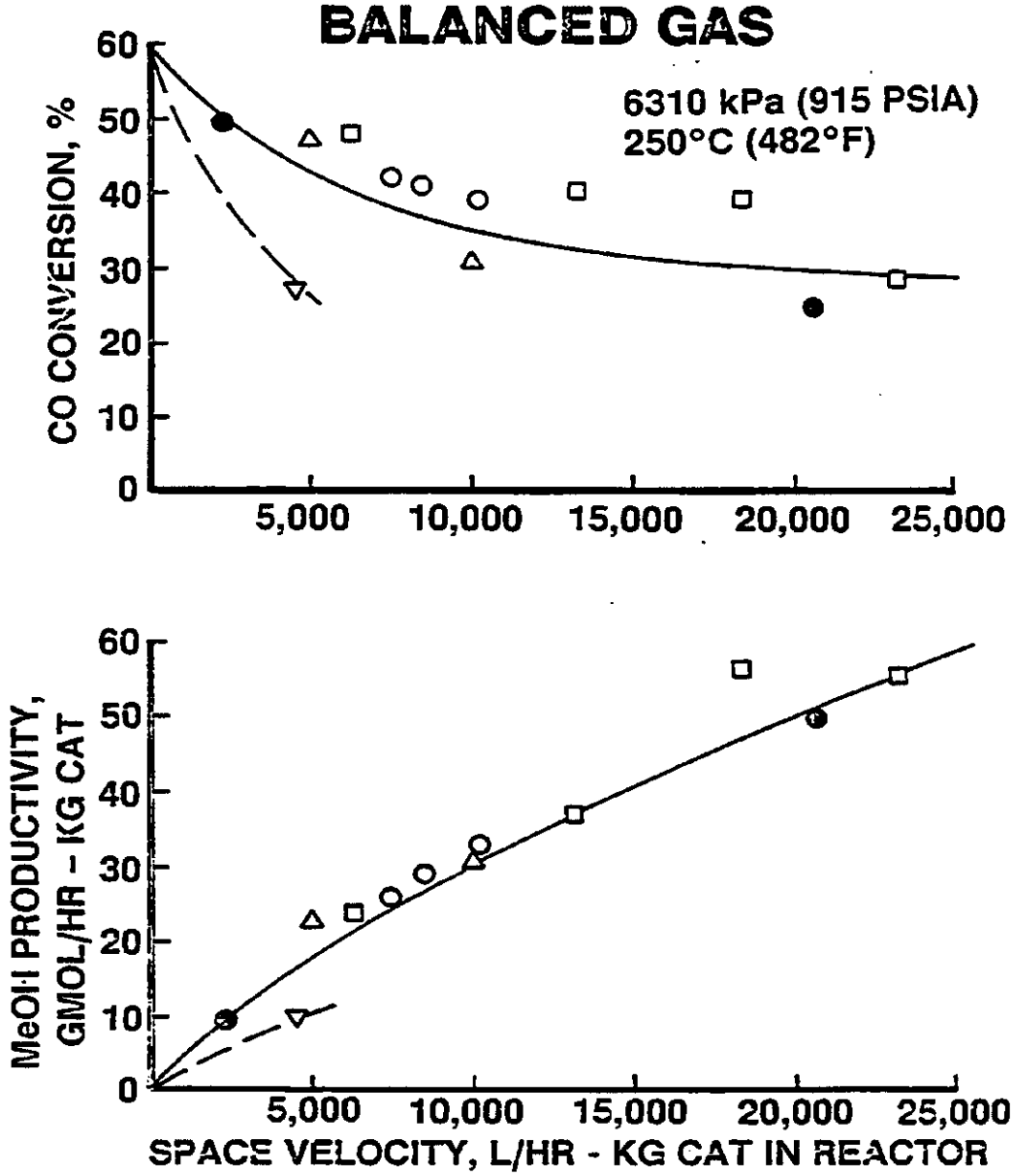
LAPORTE LPMEOH PDU SHAKEDOWN RUN DATA SUMMARY

Case No.	End of Period Date	End of Period Time	Balance Period (Hours)	Cumulative Synthesis Hours on Stream	Feed Gas Type*	Reactor Temp. (°C)	Reactor Press (kPa)	Gas S.V. (cm/s)	Space Velocity (l/kg-hr)	Oil S.V. (cm/s)	Slurry Conc. (wt. % ox)	H2 Conv. %	CO Conv. %	Prod. (gmol/ kg-hr)	Equil. Appr. (°C)
F-1A	3/11	24:00	24	54	B	250	5,340	2.4	1,800	6.1	7.0	26.6	44.2	6.0	13.0
F-1B	3/13	14:00	8	88	B	250	6,370	2.2	2,140	4.0	9.7	35	49	8.6	13.3
F-1C	3/14	04:00	6	102	B	225	6,380	2.1	2,190	4.6	9.9	37	50	9.7	39.2
F-1E	3/15	16:00	12	138	U	250	5,320	2.4	2,050	4.1	11.8	43.7	18.8	7.5	8.8
F-1F-1	3/17	22:00	12	192	U	250	5,310	5.3	5,840	4.0	15.6	32.2	11.8	15.3	26.4
F-1F-2	3/18	09:00	9	203	U	250	5,310	5.1	5,900	4.2	16.7	32.2	11.7	15.1	27.4
F-1DR	3/18	24:00	11	218	U	225	5,310	4.5	5,900	4.3	17.4	28.0	9.6	14.4	59.5
F-1G	3/19	11:10	6.7	229	U	250	5,310	10.7	15,070	5.9	19.3	26.4	8.5	30.7	36.7
F-1H	3/20	05:00	7	247	B	250	6,360	12.5	20,600	6.0	20.3	20.9	24.9	50.6	47.6

* B = Balanced gas
  U = CO-rich gas

FIGURE V-12

LAPORTE PDU PERFORMANCE COMPARED TO LAB PDU, AUTOCLAVES, AND MODEL: BALANCED GAS



- ● LAPORTE PDU DATA
- — MODEL PREDICTION FOR LAPORTE PDU
- □ FAIRFIELD LAB PDU DATA CORRECTED TO 6310 kPa (915 PSIA)
- △ APCI 1-LITER AUTOCLAVE DATA
- ○ CSI 2-LITER AUTOCLAVE DATA CORRECTED TO 6310 kPa (915 PSIA)
- ▽ FAIRFIELD LAB PDU EBULLATED DATA CORRECTED TO 6310 kPa (915 PSIA)

FIGURE V-13

LAPORTE PDU PERFORMANCE COMPARED TO LAB PDU AUTOCLAVES, AND MODEL: CO-RICH GAS

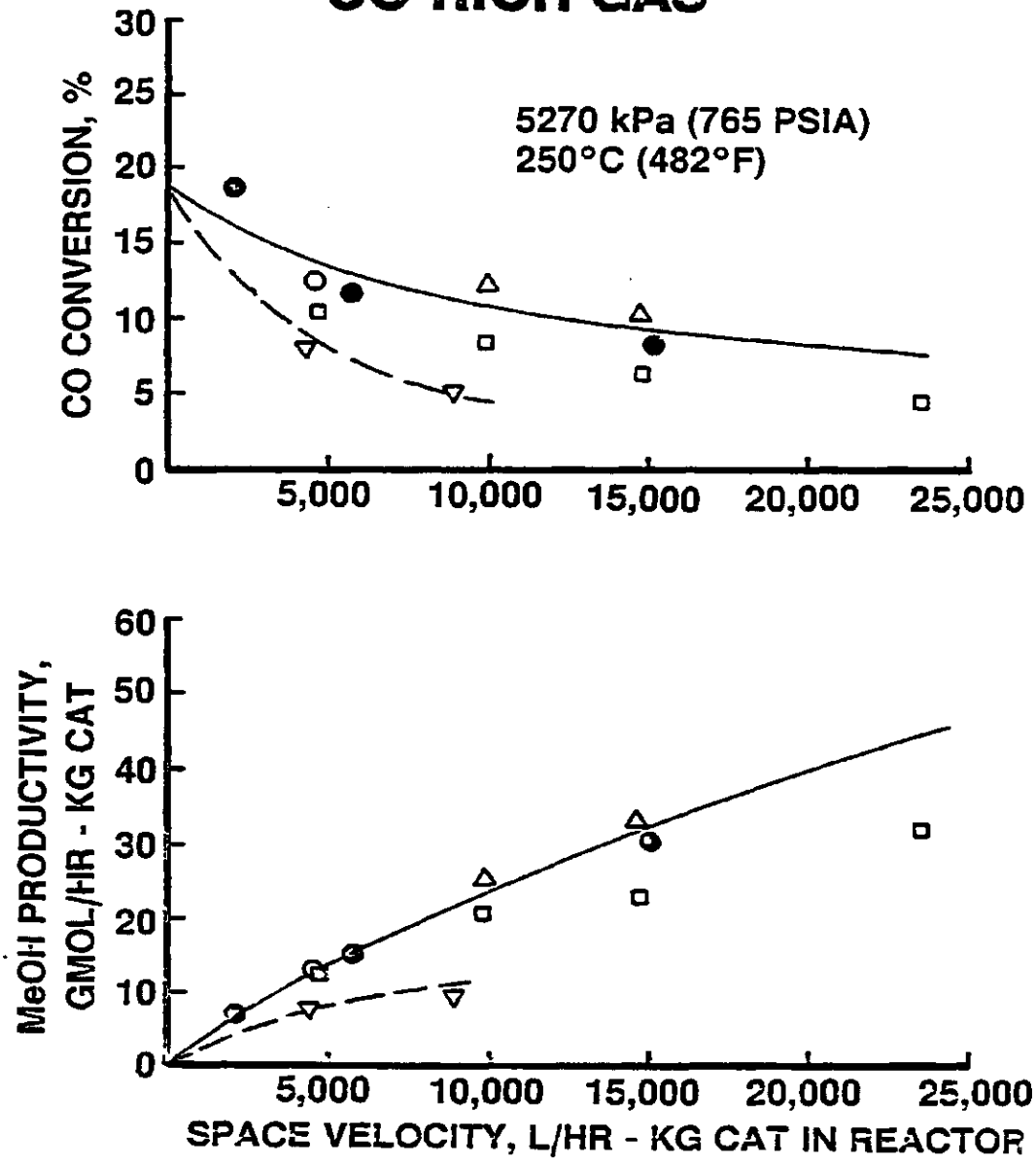
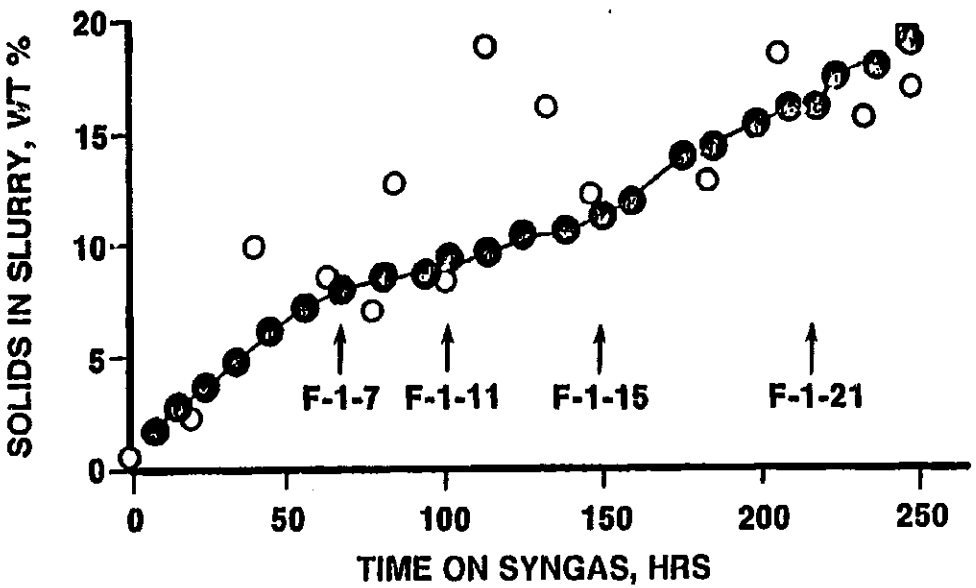


FIGURE V-14
INCREASE IN SLURRY SOLIDS LOADING DURING LAPORTE PDU SHAKEDOWN RUN

○ SOLIDS CONCENTRATION VIA SLURRY SAMPLES
● SOLIDS CONCENTRATION VIA NUCLEAR DENSITY GAUGE
□ SOLIDS CONCENTRATION VIA FINAL LIQUID INVENTORY



concentrations are probably not representative of the circulating slurry. By the end of the shakedown run, a fully developed liquid-entrained condition existed. The LaPorte LPMEOH PDU continued to operate without interruption, however, as a result of the "unified design" concept. The final slurry concentration was found to be 17 wt% (19 wt% on a catalyst oxide basis), based on a postrun inventory check. The 10.50 slurry circulation pump was able to operate with this slurry loading without difficulty. After the reactor NDG profiles had indicated that the ebullated bed profile had disappeared, the gas superficial velocity was increased to test PDU performance at the maximum design flow for liquid-entrained operation.

As the run proceeded, measurements from the NDG were used to calculate the amount of the initial catalyst bed which had attrited to fines; Table V-13 indicates the extent of this decline. This added variable was included in the calculations of catalyst performance for each condition.

Metal Carbonyl Survey

In order to determine the source and magnitude of metal carbonyl formation in the LaPorte LPMEOH PDU, a program of gas analyses was undertaken during synthesis gas operation. Drager tubes were used to indicate the presence of iron and nickel carbonyl at various sample locations; wet chemical tests provided quantitative results. In balanced gas operation, iron carbonyl was not observed above the detectable limit of 0.01 ppmv. Levels of iron and nickel carbonyl, on the order of 0.04 and 0.01 ppmv, were present on both the shell and tube sides of the 21.10 feed/product heat exchanger during CO-rich process variable scans. A sample carbonyl survey for an operating period on CO-rich gas and using plant recycle gas is presented in Figure V-15.

Details of the materials of construction and operating conditions for the PDU are provided in Figure V-16. Analysis of these data identified that the primary sources of iron carbonyl formation were

TABLE V-13

SUMMARY OF SOLIDS HOLDUP DATA - SHAKEDOWN RUN

NDG Survey No. F-1-	Cumulative Hours On Syngas	% of Initial Reduced Catalyst Remaining in Bed	Wt% Solids In Slurry (Reduced)	Reduced Catalyst in Reactor kg (lb) In Bed	As Fines	Total
1	9	91	2.1	322 (709)	13 (29)	335 (738)
2	17	87	3.0	307 (677)	20 (43)	327 (720)
3	25	82	4.1	289 (637)	28 (61)	317 (698)
4	34	76	5.2	270 (595)	36 (79)	306 (674)
5	46	72	6.2	253 (557)	44 (97)	297 (654)
6	57	67	7.1	236 (520)	51.2 (113)	287 (633)
7	69	62	8.1	218 (480)	60.3 (133)	278 (613)
8*	77-1/2	61	8.2	217 (478)	67.6 (149)	285 (627)
9	81	59	8.6	209 (461)	62.6 (138)	272 (599)
10	96	60	8.5	210 (463)	64.0 (141)	274 (604)
11	102	57	9.1	200 (441)	68.5 (151)	269 (592)
12	114	53	9.7	189 (416)	72.1 (159)	261 (575)
13	125	49	10.4	173 (382)	78.5 (173)	252 (555)
14	139	49	10.5	171 (378)	79.8 (176)	251 (554)
15	151	44	11.3	155 (342)	88.5 (195)	244 (536)
16	160	41	11.4	154 (340)	74.5 (164)	229 (504)
17	175	31	13.4	110 (242)	99.8 (220)	210 (462)
18	185	28	13.9	98.9 (218)	104 (230)	203 (448)
19	200	21	14.9	75.3 (166)	117 (257)	192 (423)
20	211	17	15.6	61.7 (136)	126 (278)	188 (413)
21	218	14	16.1	48.5 (107)	132 (292)	181 (399)
22	226	5	17.3	16 (36)	142 (314)	159 (350)
23	237	1	17.9	3 (7)	150 (331)	153 (338)

* Wet settled bed.

FIGURE V-15
CARBONYL SURVEY OF LAPORTE PDU

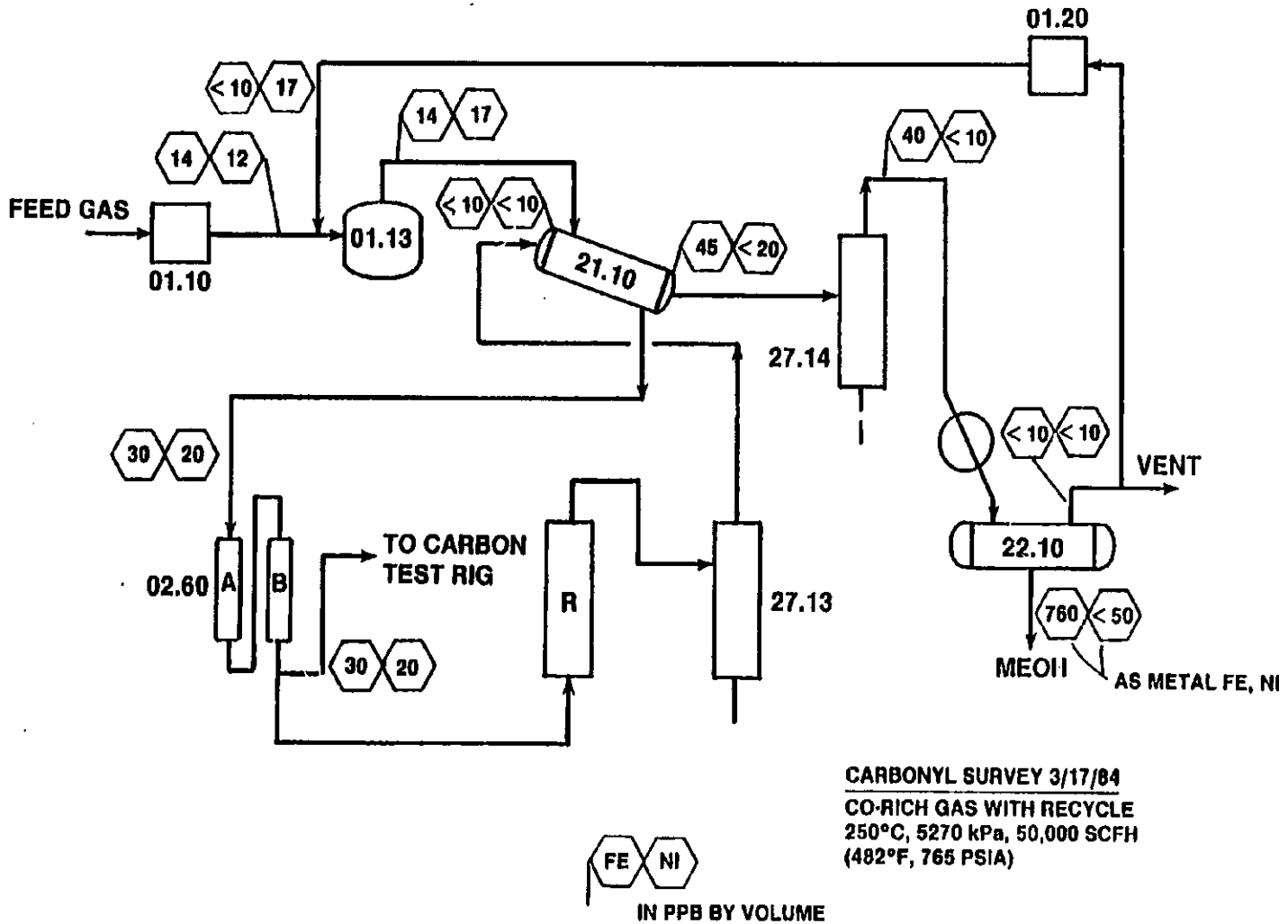
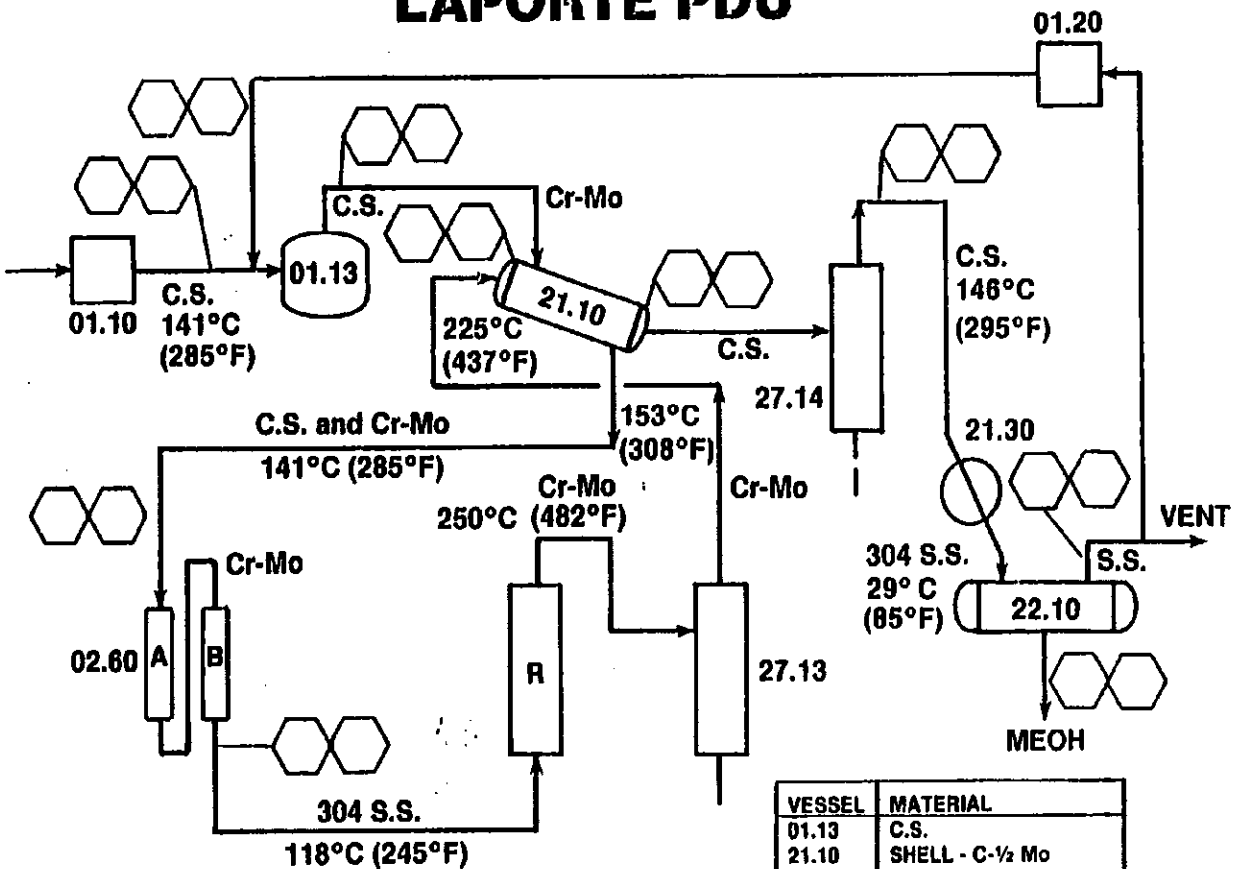


FIGURE V-16
MATERIALS OF CONSTRUCTION AND OPERATING CONDITIONS OF LAPORTE PDU



VESSEL	MATERIAL
01.13	C.S.
21.10	SHELL - C-½ Mo
	TUBES - 304 S.S.
	TUBESHEET - C-½ Mo
02.60's	Cr-Mo
27.13	Cr-Mo
27.14	C-½ Mo
21.30	TUBES - 304 S.S.
22.10	C.S.

the shell-side pass of the 21.10 feed/product heat exchanger (reactor feed side) and the tubesheets and exchanger heads (carbon-1/2% Mo) on the exchanger tube-side section (reactor effluent side). Nickel carbonyl levels were very low and were probably generated from the residual nickel contamination in the compressor recycle line, which could not be treated during the chemical wash. At higher gas rates (2,630 Nm^3/h, 100,000 SCFH), all carbonyl levels were below the detection limit, 0.01 ppmv.

In conjunction with the carbonyl survey, a carbon adsorption test was conducted to determine the effectiveness of activated carbon (Calgon BPL) in removing carbonyls. A side stream of the reactor inlet gas, which contained recycled methanol and oil vapors, was passed through a 1-in. (2.54 cm.)-diam x 1-ft (30 cm.) long carbon bed, and carbonyl levels in the inlet and outlet of the bed were measured. Because carbonyl levels during the shakedown run were very low, accurate determination of the adsorption capacity was not possible. Qualitatively, carbonyl breakthrough was observed early in the test, and a subsequent methanol/oil breakthrough indicated that, during PDU operation, a carbon guard bed would be quickly saturated with organics. The test results suggested that a carbon system would have limited effectiveness in removing carbonyls in a gas stream containing methanol and oil, especially at the low levels observed in the LaPorte LPMEOH PDU.

Catalyst Analyses

Catalyst slurry samples were obtained from the LaPorte LPMEOH PDU slurry loop during the shakedown run, and were analyzed for solids concentration, copper crystal size, oxidation state, and the presence of poisons. A detailed description of the samples and results of the analyses are presented in Table V-14. Catalyst copper crystal size remained essentially constant during the run, and was comparable to the crystal size of the circulating fines in the Lab PDU run on catalyst F71/OF12-26 (207 Å) (Reference 4).

TABLE V-14

LAPORTE LPMEOH PDU SHAKEDOWN RUN CATALYST SAMPLE ANALYSES

Sample No.	Description	Solid Conc., wt%	Cu^{o} Crystal Size, Å	Cu/Zn	Cu^{+1}/Cu^{o}	Poisons, ppmw Fe	Ni	Cl
Solid 17	Fresh oxide					314	10	33
Oil 32	0 hours on stream	0.5	183					
Oil 33	18 hours on stream, Run F-1A, Balanced Gas	2.7	207					
Oil 35	42 hours on stream, Run F-1A, Balanced Gas	9.9						
Oil 36	66 hours on stream, Run F-1A, Balanced Gas	8.5						
Oil 37	78 hours on stream, Run F-1A, Balanced Gas	7.1						
Oil 38	88 hours on stream, Run F-1B, Balanced Gas	13.7	183					
Oil 39	102 hours on stream, Run F-1C, Balanced Gas	8.4						
Oil 40	112 hours on stream, Run F-1E, CO-rich Gas	19.0	197	0.14	0.60			
Oil 42	134 hours on stream, Run F-1E, CO-rich Gas	16.1						
Oil 43	160 hours on stream, Run F-1F, CO-rich Gas	12.2						
Oil 44	184 hours on stream, Run F-1F, CO-rich Gas	12.8						
Oil 45	206 hours on stream, Run F-1DR, CO-rich Gas	18.4						
Oil 46	230 hours on stream, Run F-1G, CO-rich Gas	15.5	197	0.20	0.14			
Oil 47	248 hours on stream, Run F-1H, Balanced Gas	16.9	192	0.13	0.14	830	15	36
Oil 49	Slurry from Slurry Preparation Tank, 27 March 1984		183	0.17	0.40			
Oil 50	Slurry from Slurry Preparation Tank, 8 April 1984	17.0	183					
Oil 52	Slurry from Slurry Preparation Tank, 11 April 1984	21.0 (oxide)	192	0.14	0.15	1852		
Oil 52A	Oil Sample After Autoclave Test		203	0.18	0.13	2002	60	43

However, the Cu^{+1}/Cu^{0} ratios for the LaPorte samples are somewhat lower than those for the fines from the Fairfield Lab PDU run (Cu^{+1}/Cu^{0} = 0.8). The presence of metal carbonyls in the reactor feed gas resulted in the increase in both iron and nickel levels on the catalyst.