

Section 5
ENGINEERING ANALYSIS

REDUCTION

The catalyst reduction operation for the 40-day run was more stable and better controlled than the prior shakedown run reduction. At the beginning of reduction, the reaction rate is very sensitive to temperature, especially above 140°C, and temperature increases have to be programmed carefully. At the bulk reduction stage during the shakedown run, the feed gas temperature was increased from 140°C to 165°C in about one hour and the bed temperatures increased too rapidly, necessitating rapid corrective action. For the 40-day run the temperature of the reduction gas was increased from 140° to 164°C in six hours, thus leading to a more gradual bulk reduction (see Table 4-3).

Abrupt increases in hydrogen concentration should also be avoided, and preheat temperature by itself is not enough to control the maximum hot spot temperature owing to the "heat sink" effect of the bed. During the shakedown run, the hydrogen concentration was increased to above one volume percent with a simultaneous feed gas temperature decrease from 165°C to 135°C. Possibly the temperature change was too severe and in consequence the reduction operation became difficult to stabilize. Hydrogen uptake and temperatures oscillated for a period of several hours. For the 40-day run the concentration changes did not take place and most of the reduction occurred at concentrations less than one percent.

The extent of catalyst dryout for the 40-day run was less than the shakedown run. The observed heat wave and rapidly increasing temperatures experienced in the latter run were not experienced here. The drying stage, as examined in the shakedown run, begins when the catalyst bed temperature is between 100-110°C and is usually completed at about 130°C.

For the LaPorte PDU reactor, the initial reduction reaction rate creates a hot spot when the preheat temperature is above 140°C at the prevailing hydrogen partial pressure of about 10 kPa. When the reduction of the catalyst was about 60 percent complete and the hot spot was at 180°C, the hydrogen uptake reached a level of 4,200 liters/hr as compared to about 6,300 liters/hr in the shakedown run.

From the analysis of data generated in the 40-day run, the principal steps of the reduction operation may be categorized as shown in Table 5-1. The total calculated hydrogen uptake per unit of catalyst oxide weight was 147.3 liters/kg, which is less than the value obtained for the shakedown run, 185 liters/Kg. There is no explanation for this difference, and more knowledge on the reduction operation, specially temperature programming and its influence on catalyst activity, may be required.

The principal reduction variables are plotted in Figure 5-1. One of the parameters that varied considerably was the hydrogen concentration. A better sized control valve could have resulted in smoother concentrations and perhaps a more accurate hydrogen uptake determination. Also, for better accuracy it is preferable to maintain hydrogen concentration and temperature during bulk reduction at conditions that give a 100 percent hydrogen uptake and thus zero hydrogen in reactor effluent.

CATALYST PERFORMANCE

Attrition Resistance Analysis of Transition to Entrained Operation

Summary. The rate of attrition of the catalyst extrudates during the early part of the run was considerably higher than for the prior shakedown run. The transition to fully entrained operation took only one day instead of a week as was originally expected. Although more data at higher space velocities are required, the analysis of the three-phase and conversion data indicates that catalyst productivity improves with the presence of fines. However, the effect appears to decrease rapidly reaching a maximum when the fines content approaches 20 percent of the total catalyst weight in the reactor.

The higher-than-expected attrition rate experienced in the 40-day run is probably a twofold effect of lower bed expansions and higher gas superficial velocities. The initial bed expansion during the 40-day run was less than 15 percent compared with an average expansion close to 30 percent for the shakedown run. However,

Table 5-1

PRINCIPAL OPERATIONS DURING REDUCTION

	Hydrogen Partial Pressure, kPa	Temperature Range, °C	Hydrogen Uptake, Nm ³ /hr	Preheat, °C	Hot Spot, °C
Catalyst dryout	-	100-110	-	-	-
First-stage reduction	10	110-140	2	110-140	150
Second-stage reduction (bulk of reduction)	10	140-160	4	140-160	190
Third-stage reduction	20	160-200	1	160-200	200
Polishing step	20	200-230	1	200-240	230

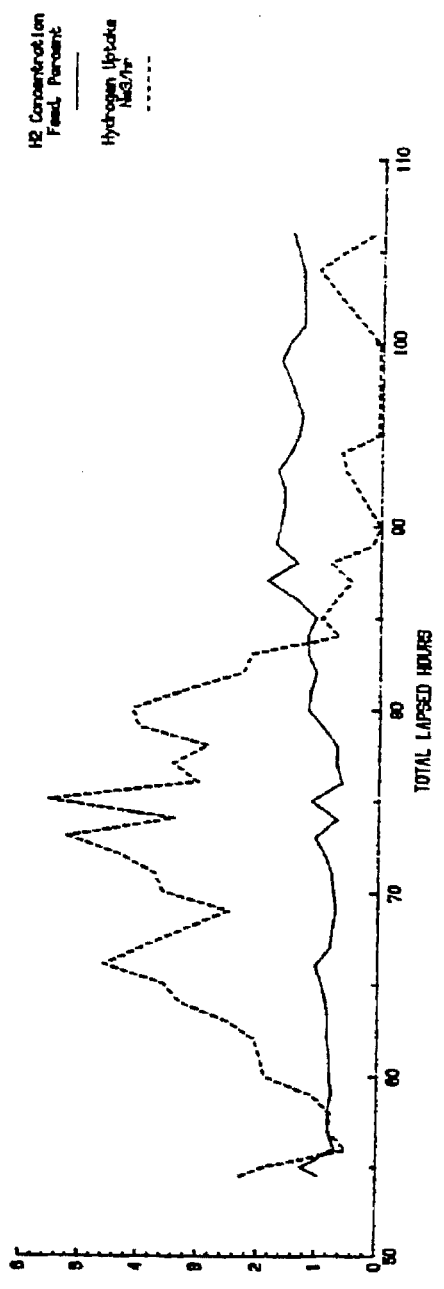
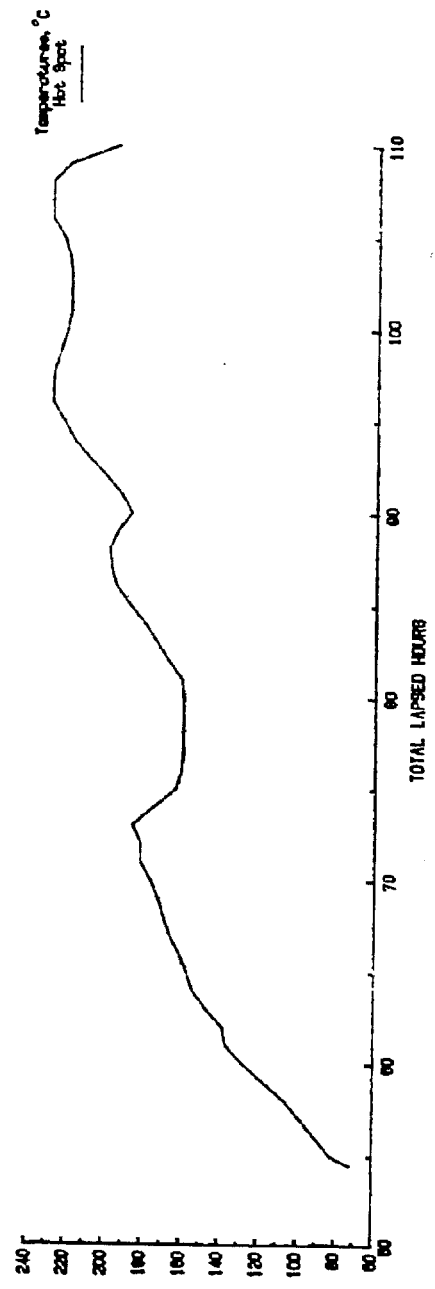


Figure 5-1. LaPorte PDU Reduction Data

the higher superficial gas velocity utilized in the 40-day run may have had a stronger effect on attrition rate than bed expansion, which is related primarily to liquid superficial velocity. The analysis of the data of both runs shows that the attrition rate is almost proportional to the superficial gas velocity.

Three-Phase Data Analysis and Methodology

Three full-bed catalyst density profile scans were obtained for this run (see Table 5-2). The first two showed a distinct bed with approximately the same height, and the last scan resulted in an almost uniform density throughout the reactor indicating that a distinct bed of catalyst pellets no longer existed. For analysis purposes, the transition to entrained operation was divided into the following periods:

- Period between the first two bed profile determinations.
- Period after the second profile and the disappearance of the bed.
- Period after the disappearance of the bed.

The analysis of the first period, which comprises hours 7.5 through 16.5, is complicated due to the lack of analytical slurry concentration determinations. A sensitivity analysis, however, results in a solution that agrees closely with an analysis performed on the shakedown run data (2). A useful parameter for studying the effect on the gas holdup and other properties is the ratio of gas holdup in the bed to the gas holdup above the bed, E_{GB}/E_{GO} . When varying this ratio between 0.8 and 1.5:1, the following effects were obtained (see Figure 5-2):

- The gas holdup above the bed fluctuated between 0.25 and 0.207.
- The slurry concentration for the first bed profile became zero when $E_{GB}/E_{GO} = 1.12$.

Assuming that the gas holdup above the bed does not exceed the two-phase LaPorte data, a minimum E_{GB}/E_{GO} ratio of 1.10:1 is obtained. Since the minimum slurry concentration defines a maximum gas holdup ratio of 1.12:1, a solution to the density and mass balance equations can be obtained.

Table 5-2
BED PROFILE DETERMINATIONS

Date Time Hours on synthesis gas*	4/11		4/11		4/12	
	09:30 - 12:00	8.5	18:45 - 20:15	16.8	02:45 - 03:30	24.0
	Height Above Tray, cm	Volts	Height Above Tray, cm	Volts	Height Above Tray, cm	Volts
	61	-0.126				
	152	-0.158	91	-0.180	102	-0.268
	243	-0.210	213	-0.245	203	0.280
	284	-0.171	306	-0.285	305	-0.288
	287	-0.213	315	-0.308		
	305	-0.245	318	-0.330		
	320	-0.284	321	-0.345		
	325	-0.317	323	-0.360		
	328	-0.290	326	-0.385		
	330	-0.324	328	-0.455		
	333	-0.373	330	-0.550		
	325	-0.435			381	-0.310
	339	-0.600			447	-0.335
	447	-0.980	447	-0.853		

* End of scan.

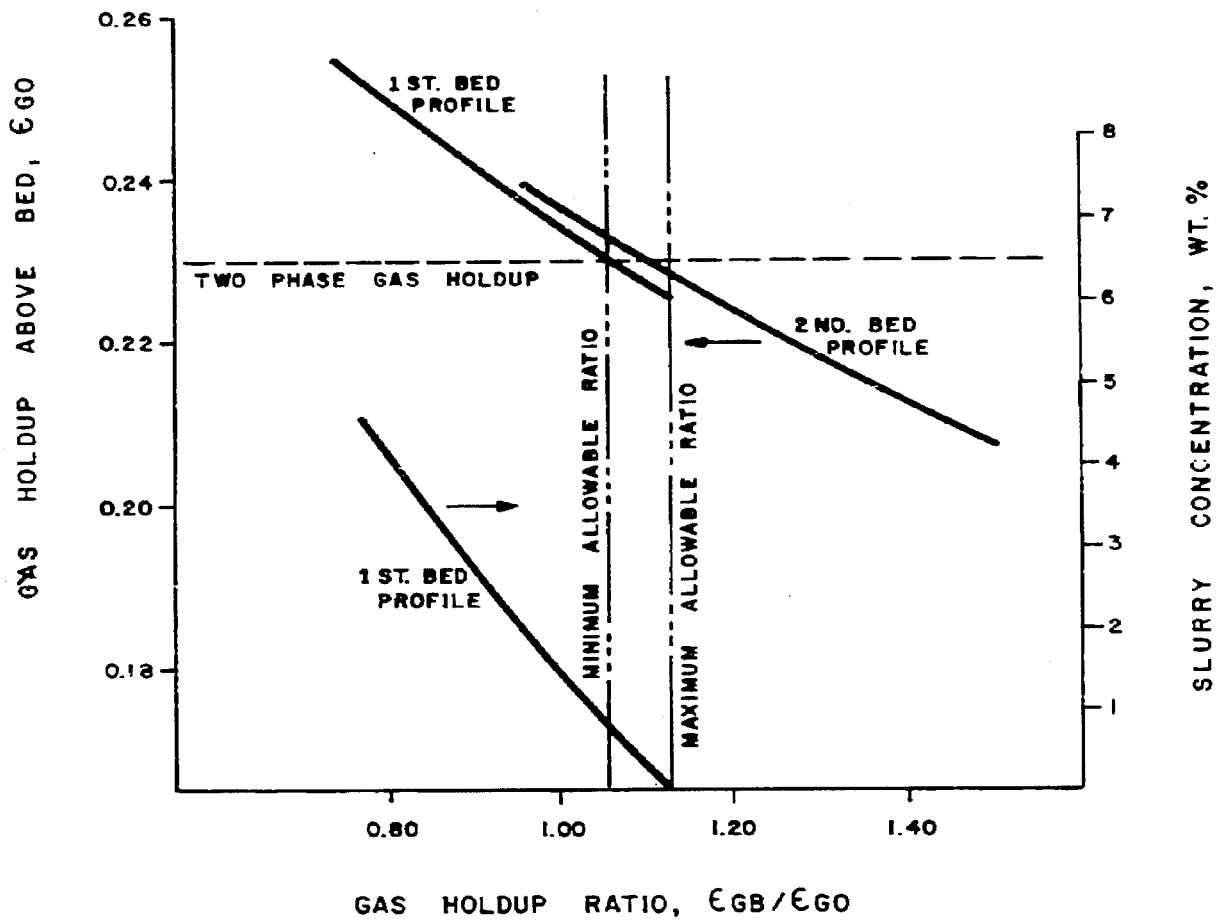


Figure 5-2. Sensitivity Analysis in Transition to Entrained Operation Period

A gas holdup ratio of 1.10:1 gives a slurry concentration for the first and second bed profile determinations of 0.30 and 9.9 weight percent, respectively. Also, a rate of fines generation of 13.3 kg/hr, or about two percent weight loss of the catalyst bed per hour, can be calculated. This weight loss is approximately three times the attrition rate of the shakedown run.

The step change in bed density that occurred shortly after 22.0 hours on syngas had been logged, as shown by the NDG readings of Table 5-3, was probably indicative of a massive elutriation of the catalyst bed. This phenomenon may have been triggered by a pulse induced by an increase in seal flush oil flow that took place in this same period. The voltage reading at the 447 cm mark in the freeboard zone at 22.0 hours on synthesis gas was probably symptomatic of a catalyst bed that had expanded to near the top of the reactor. If it is assumed that the attrition rate during the second period was the same as the one calculated before, the catalyst inventory in the reactor including pellets and fines can be estimated. Therefore, use of a constant attrition rate, catalyst and oil mass balances, a gas holdup ratio of 1.10:1, and the density equations for the freeboard, enabled the calculation of the catalyst inventory for NDG readings at 20.3 and 22.0 hours on synthesis gas.

For the period after the massive elutriation of the bed it can be assumed that the catalyst was pulverized very rapidly to a 30 weight percent slurry of catalyst (oxide) and the required catalyst inventories can be obtained from the voltage readings. However, when an instantaneous breakdown is assumed, extremely low (and probably incorrect) gas holdups are obtained from the readings after the 02:20 hour nuclear density gauge scan as illustrated by the numbers in parentheses in Table 5-3. What probably existed in the slurry loop was a circulating mass of catalyst fines and small catalyst pellets. No significant settling of catalyst pellets occurred, however, until after 25.5 hours on synthesis gas as manifested by the decreasing methanol concentrations after that hour.

The inventory of catalyst immediately before the methanol concentration in the reactor effluent dropped could be estimated assuming an attrition rate higher than the one experienced in the previous period and a constant gas holdup. In addition to the results of the analysis of the previous periods, Table 5-4 includes the results for 25.5 hours on synthesis gas for which an attrition rate of roughly three times the attrition rate of the first period and an even

Table 5-3

VOLTAGE READINGS DURING THE TRANSITION TO ENTRAINED OPERATION

<u>Date</u>	<u>Time</u>	<u>Hours on Syngas</u>	<u>Voltage @ 447 cm</u>	<u>Gas Holdup Above Bed</u>	<u>Density of Freeboard, g/cm³</u>
4/11	20:00	16.5	-0.853	0.2297	0.614
	23:45	20.3	-0.597	0.1348	0.706
4/12	01:30	22.0	-0.525	0.1023	0.737
	02:20	22.8	-0.334	(0.0750)	(0.879)
	02:50	23.3	-0.335	(0.0762)	(0.878)
	03:50	24.3	-0.316	(0.0581)	(0.895)
	04:00	24.5	-0.320	(0.0620)	(0.891)
	04:40	25.2	-0.295	(0.0364)	(0.914)
	05:30	26.0	-0.276	(0.0151)	(0.934)

distribution of the remaining pellets in the slurry loop were utilized. It may be important to mention here that the inventory calculated using the procedure described above is only 7 percent lower than the value calculated using the voltage readouts and an assumed instantaneous catalyst fragmentation.

Methanol Productivity During the Transition Period

Three process data averages were performed to cover the transition to entrained operation. The selected time spans for every process average do not coincide strictly with the periods of the above analysis as shown in Figure 5-3. The selection of the data averages was based on steady-state considerations (flows, methanol concentrations, etc.).

The results of the process averages are shown in Table 5-5. Figure 5-4 illustrates how methanol productivity increased with the presence of fines. The shape of the curve drawn through the experimental points shows a relatively rapid slowdown of the enhanced productivity effect of the catalyst fines. This effect was also observed in the shakedown run in which a change from 51 to 61 percent fines in the reactor did not have a noticeable effect on methanol productivity at a space velocity of 5,900 liters/hr-kg catalyst and a superficial gas velocity of 5.2 cm/sec (runs F-1F-1 and F-1F-2).

Table 5-4

TRANSITION TO ENTRAINED OPERATION PERIOD
SUMMARY OF INVENTORY CALCULATIONS

Date	4/11	4/11	4/12	4/12	4/12
Time	11:00	20:00	23:45	01:35	02:20
Hours on syngas	7.5	16.5	20.3	22.1	22.8
Bed height, cm	322	314	(1)	(1)	(2)
Slurry conc., wt %	0.30	9.9	13.4	14.8	15.5
Oil weight					21.5 (4)
(total), kg	1,468.7	1,468.7	1,446.1	1,446.1	1,446.1
Attrition rate, kg/hr	-	13.3	13.3	13.3	45.4 (4)
Fines in reactor, %	0.38	8.8	16.2	20.0	22.2
					60.3

(1)

(2)

(3)

(4)

(5)

Assume bed expanded to full reactor length.
Catalyst elutriated from bed at this point.
Circulating mass of catalyst pellets (small), 54 percent of which inside reactor at a given time.
Assume attrition rate increased due to higher velocities in duct work and pump impeller.
Catalyst solid density of 4.4 g/cm³ utilized for all data points.

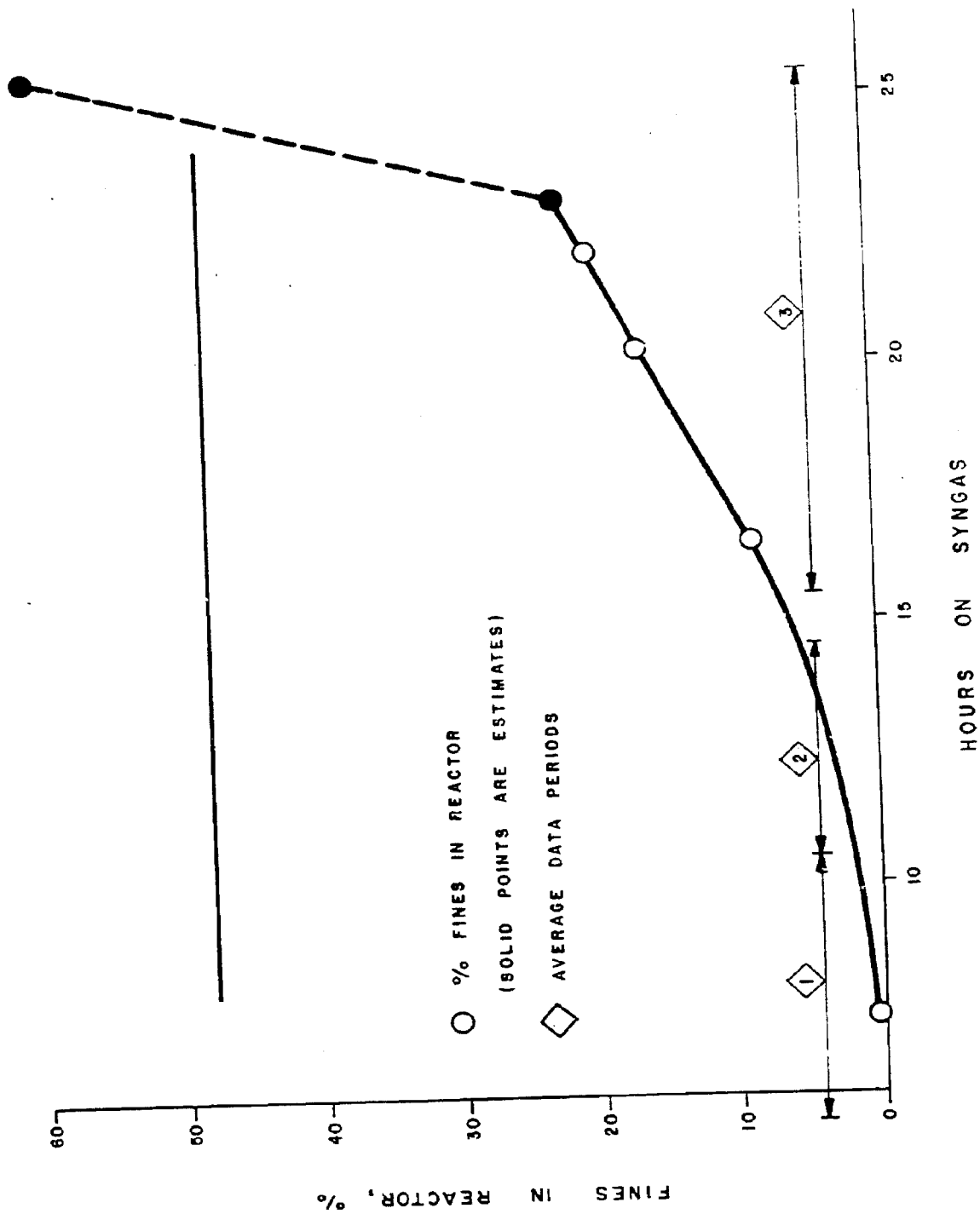


Figure 5-3. Operation in Transition to Entrained Mode for Balanced Gas

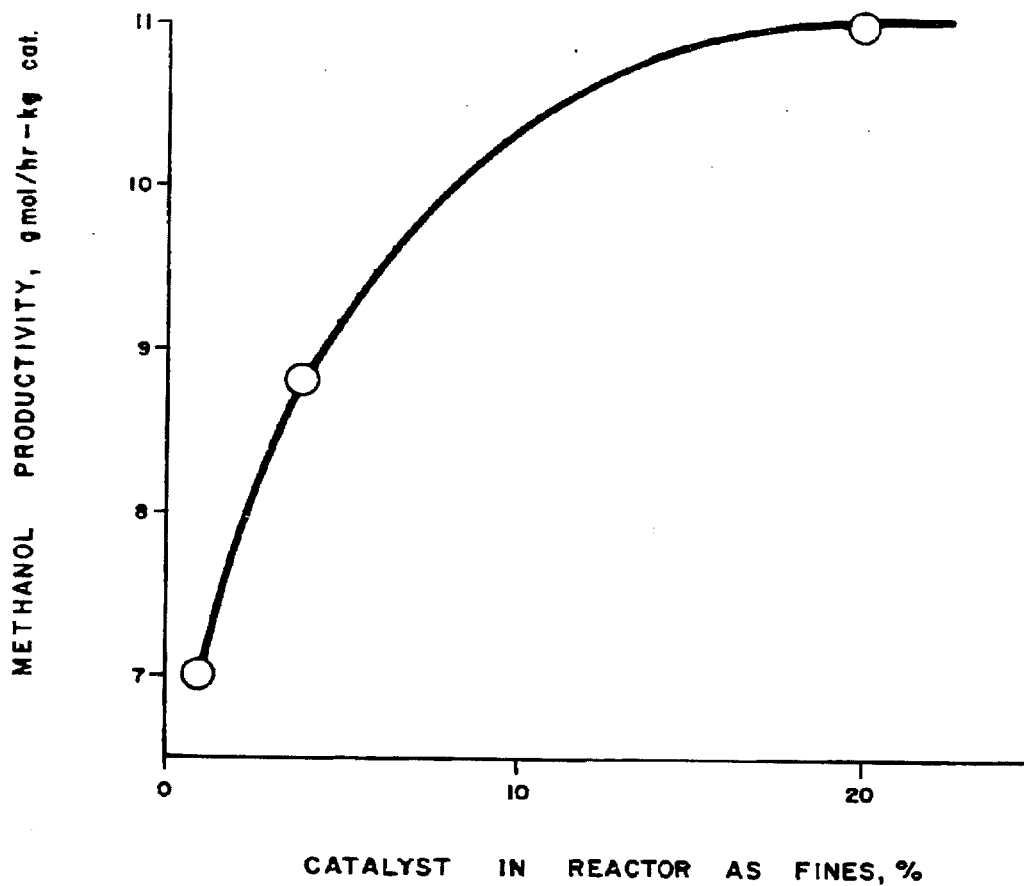


Figure 5-4. Effect of Catalyst Fines on Reactor Performance

ACTIVITY MAINTENANCE WITH UNBALANCED GAS

Catalyst Analyses

Perusal of the LaPorte catalyst analyses presented in Table 4-8 reveals that several activity-related catalyst characteristics changed during the run:

- Different surface copper states under balanced and CO-rich gases.
- Increased Cu^0 crystal size.
- Continuous buildup of iron and nickel.

The catalyst had very different surface copper states under balanced and CO-rich gases. The change in copper state occurred quickly after switching gas feed compositions, with much lower Cu/Zn and Cu^+/Cu^0 ratios on CO-rich gas. The lower copper state ratios were stable throughout the CO-rich operation. It is surprising to see: (1) the surface Cu/Zn ratio reduced to less than 0.1 when the bulk composition of the catalyst has a Cu/Zn ratio of approximately 1.5 and (2) Cu^+/Cu^0 dropped to nil after 200 hours on stream despite the fact that the catalyst was still active.

Copper crystallite size was observed to increase with time on stream. Crystal size is regarded as an important measurement of catalyst surface area available for reaction. An increase in crystal size signals a decrease in available surface area, which would create a decline in catalyst activity. The crystal sizes reported in Table 4-8 were calculated from XRD traces using the Warren equation (7). However, a slightly different equation recommended by the catalyst manufacturer gives improved results for relatively large sizes (more than 200 Angstroms). The Warren equation values show the crystal size increased through the first 300 hours of operation, and then held constant at approximately 360 Angstroms for the remainder of the run. The values from the revised equation, however, suggest the crystal size continued growing past the 300-hour mark to the end of the run. The trend outlined by the revised equation crystal sizes is more consistent with the observed continued activity decline during the 40-day run.

Iron analyses of the catalyst samples by X-ray fluorescence (XRF) and atomic absorption (AAS) differ in absolute iron levels, yet both show the same continuous buildup of iron on the catalyst throughout the run. On balanced gas,

Table 5-5
TRANSITION TO ENTRAINED OPERATION PERIOD
PROCESS AVERAGED DATA

	<u>4/11</u>	<u>4/11</u>	<u>4/12</u>
Time (end of period)	14:00	18:00	05:00
Averaged hours	5	4	10
Temperature, °C	249.5	250.3	250.0
Pressure, kPa	5,380	5,380	5,370
Superficial velocity			
Gas, cm/sec	5.7	6.0	5.4
Liquid cm/sec	3.8	4.0	4.1
Slurry concentration, wt. %	1.0	5.9	15
Fines in reactor, %	1	3.9	20
Space velocity, l/hr-kg	2,398	2,769	3,207
Hydrogen conversion, %	22.2	24.1	26.4
Carbon monoxide conversion, %	40.0	39.2	40.5
Productivity, gmol/hr-kg	7.0	8.8	10.9
Approach to MeOH eq., °C	22.4	19.3	15.2
MeOH production rate, kg/hr	140	164	152

no carbonyls were observed above the detection limit of 10 ppbv. However, under CO-rich gas, iron and nickel carbonyl were generated in various parts of the plant. The main source of nickel carbonyl was some residual nickel catalyst present in the feed section of the plant (01.10 compressor filter) and iron carbonyl apparently originated at surfaces made of low alloy steel (carbon - 1/2 molybdenum steel).

The composite iron and nickel carbonyl concentration in the feed gas shown in Figure 5-5 agrees reasonably well with the measured iron and nickel uptake in the catalyst. The results also indicate a slow nickel buildup on the catalyst. The increased content of iron and nickel on the catalyst must also have contributed to the activity decline observed in the run. No sulfur or chloride increases were observed on the catalyst.

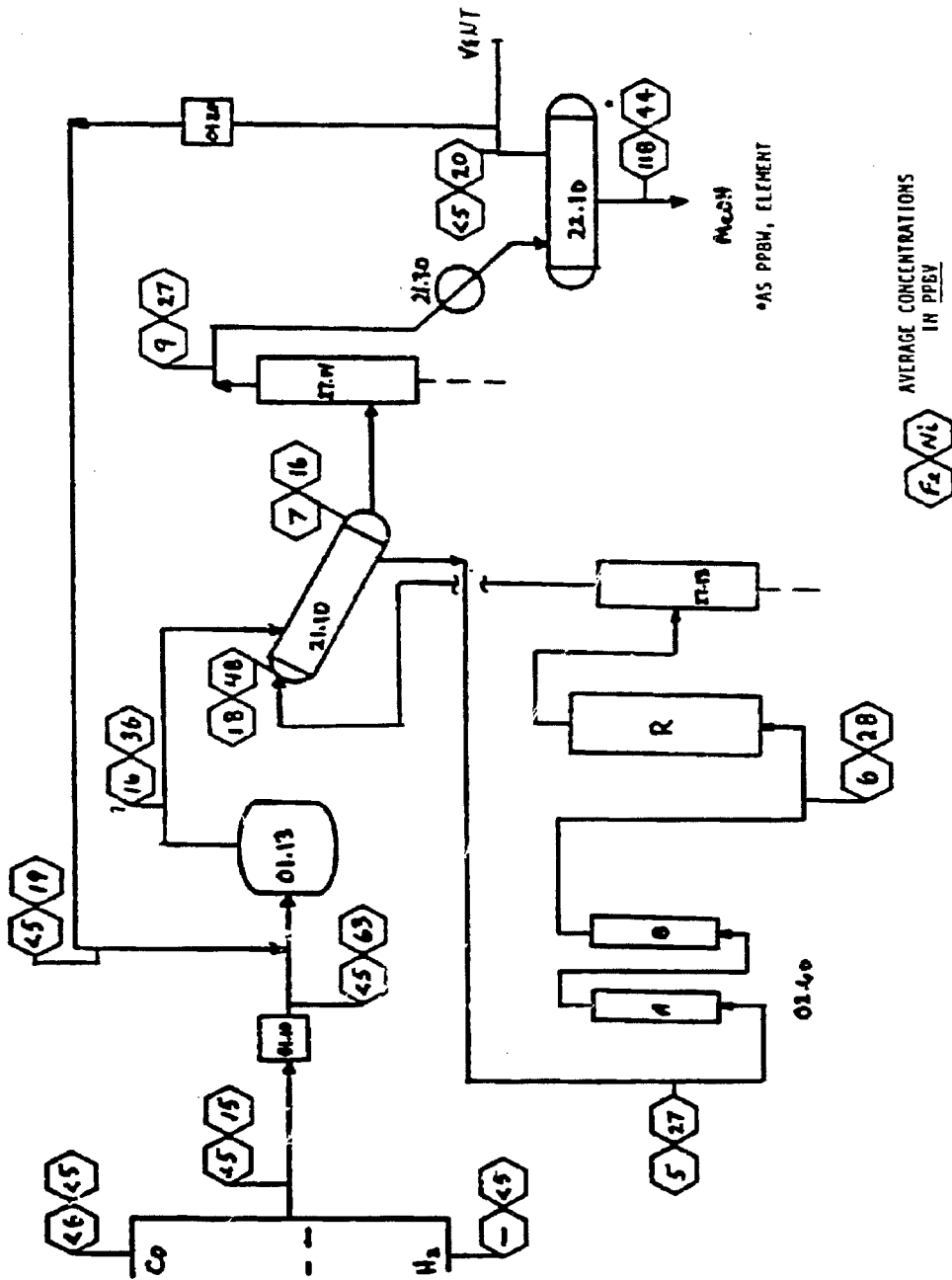


Figure 5-5. Carbonyl Survey: Latter Half of 40-Day Run - 630-960 Hours on Stream

Catalyst Performance

Methanol productivity and carbon monoxide conversion declined steadily from the start of CO-rich gas (103 hours on synthesis gas). However, carbon dioxide conversion as calculated from the water balance actually had a small increase. Table 5-6 includes the pertinent process data and the catalyst characteristics that show a continuous variation with run time. The operating conditions for the activity maintenance portion of the run with CO-rich gas were:

250°C reactor temperature
5,400 kPa reactor pressure
10,000-12,500 Nl/hr-kg catalyst
27.5-23.3 weight percent catalyst as oxide

The productivity and CO conversion fell from about 23 to 14 gmol/hr-kg catalyst and from 10.7 to 4.8 percent, respectively. This represents a drop in catalyst performance close to 50 percent in about 850 hours of operation.

Calculated methanol productivity as a function of time on synthesis gas is presented in Figure 5-6 and as a function of cumulative methanol production in Figure 5-7. The decline in methanol productivity versus time has the following straight-line representation:

$$P = 24.5 - 9.804 \times 10^{-3}T$$

where:

P = methanol productivity, gmol/hr-kg catalyst
T = hours on synthesis gas

The slope of the line is equivalent to a 1.0 percent decrease in catalyst activity per day. The decline in methanol productivity versus cumulative methanol production follows:

$$P = 25.5 - 0.0173 \text{ CMP}$$

where:

CMP = Cumulative methanol produced, kg/kg catalyst

Table 5-6

LAPORTE PDU ACTIVITY MAINTENANCE DATA WITH R71/OF 12-26 CATALYST - UNBALANCED GAS

HOURS OF SYNTHESIS GAS	FEED GAS FLOW (M ³ /hr)	CO CONVERSION (%)	CO ₂ (G) CONVERSION (%)	APPROACH TO RHOH EQUILIBRIUM (deg C)	IRON IN CATALYST (1000)		NICKEL IN CATALYST (1000)		CRYSTAL SIZE BY IRD (μ)	Cumulative Space Velocity hr ⁻¹ /ft ³	Cumulative Methanol Productivity kg/mol/kg cat.	Methanol Productivity g/mol/hr ft ³
					IRF	ARS	IRF	ARS				
					(g)	(g)	(g)	(g)				
0.0	--	--	--	--	250	(162)	45	(42)	96	--	--	--
10.5	1439	0	--	0	--	--	--	--	25.2	2.36	--	
12.0	--	--	--	--	582	(540)	--	(56)	166	--	--	
14.5	1334	0	--	0	--	--	--	--	35.4	3.49	--	
25.5	1379	0	--	0	--	--	--	--	71.7	7.23	--	
34.0	--	--	--	--	--	--	--	--	146	--	--	
37.0	--	--	--	--	375	--	70	--	171	--	--	
76.5	3460	0	--	0	--	--	--	--	631.9	56.30	--	
81.0	--	--	--	--	304	--	52	--	215	--	--	
101.5	4307	0	--	0	--	--	--	--	990.9	77.93	--	
125.0	--	--	--	--	553	--	66	--	231	--	--	
129.5	2500	10.4	0.30	--	--	--	--	--	1240.9	90.90	23.5	
140.5	2520	11.3	--	--	--	--	--	--	1345.0	105.63	21.7	
146.5	2540	9.9	0.30	--	--	--	--	--	1423.2	112.67	23.6	
179.0	--	--	--	--	623	--	69	--	249	134.03	(22.6)	
186.5	2560	9.3	--	--	--	--	--	--	1044.4	140.20	(22.5)	
203.0	--	--	--	--	446	(310)	63	(44)	320	151.01	(22.3)	
230.5	2510	9.5	1.03	--	--	--	--	--	2356.2	175.22	21.0	
250.5	2530	9.6	1.04	--	--	--	--	--	2603.7	192.23	22.1	
275.5	2625	9.4	1.00	--	--	--	--	--	2795.6	203.20	21.3	
290.0	--	--	--	--	442	--	67	--	357	215.99	(21.1)	
340.5	2506	9.1	0.76	--	--	--	--	--	3426.6	245.07	20.4	
344.0	--	--	--	--	553	--	86	(51)	371	247.43	(20.4)	
379.5	2600	8.7	1.02	39.2	--	--	--	--	3553.1	270.04	21.0	
392.0	--	--	--	--	916	(650)	75	(60)	267	279.67	(21.0)	
420.5	2799	8.6	0.96	39.3	--	--	--	--	4364.5	303.49	20.4	
425.5	2602	8.0	1.01	41.9	--	--	--	--	4902.5	330.00	19.4	
446.0	--	--	--	--	517	--	70	--	357	319.19	(19.4)	
524.5	2602	7.0	1.10	42.3	--	--	--	--	5400.9	361.03	19.3	
532.0	--	--	--	--	510	--	87	(83)	361	360.37	(19.4)	
540.5	2619	7.0	1.02	43.4	--	--	--	--	5673.0	370.12	19.6	
572.5	2620	7.5	1.19	44.0	--	--	--	--	5935.0	392.73	19.0	
580.0	--	--	--	--	606	--	110	--	371	397.35	(19.1)	
596.5	2620	7.7	1.14	43.9	--	--	--	--	6200.3	407.53	19.2	
620.5	2620	7.4	1.26	45.3	--	--	--	--	6460.7	422.02	18.9	
644.5	2626	7.2	1.24	46.6	--	--	--	--	6741.5	436.41	18.7	
656.0	--	--	--	--	576	(382)	120	(94)	342	443.20	(18.5)	
658.5	2633	7.1	1.19	47.3	--	--	--	--	6901.0	444.60	18.4	
692.5	2640	6.7	1.39	48.2	--	--	--	--	7297.2	464.35	18.1	
704.0	--	--	--	--	572	--	120	--	342	470.92	(18.0)	
716.5	2607	6.5	1.44	49.0	--	--	--	--	7574.0	470.07	17.8	
740.5	2625	6.6	1.43	49.0	--	--	--	--	7852.0	471.54	17.5	
750.0	--	--	--	--	504	(401)	130	(112)	362	496.00	(17.5)	
764.5	2619	6.4(3)	1.33	50.3	--	--	--	--	8137.2	505.04	17.4	
780.5	2620	6.3(3)	1.39	52.2	--	--	--	--	8422.2	510.41	17.4	
812.5	2620	5.9(3)	1.41	53.9	--	--	--	--	8709.3	530.94	16.3	
822.0	--	--	--	--	597	--	150	--	364	535.79	(16.2)	
836.5	2633	5.7	1.30	55.4	--	--	--	--	9000.5	543.20	15.9	
860.5	2630	5.5	1.42	56.5	--	--	--	--	9293.6	555.24	15.6	

Table 5-6 (Continued)

HOURS ON SYNTHESIS BPS	FEED GAS FLOW (mm ³ /hr)	CO CONVERSION (1)	CO ₂ (16) CONVERSION (5)	APPROX TO M ₀ N EQUILIBRIUM (deg C)	IRON IN CATALYST (mm)		NICKEL IN CATALYST (mm)		CRYSTAL SIZE BY XRD (μ)	Cumulative Space Velocity hr ⁻¹ /g	Cumulative Methanol Productivity g/molH ₂ /g cat.	Methanol Productivity g/mol/hr kg
					XRF	ARG	XRF	ARG				
878.8	—	—	—	—	646	(397)	—	—	368	—	339.91	(13.3)
884.5	2641	5.4(3)	1.34	56.5	—	—	—	—	2588.4	—	557.84	13.3
908.5	2638	5.2(3)	1.42	59.4	—	—	—	—	3287.9	—	578.59	13.8
928.8	—	—	—	—	613	—	157	—	348	—	581.41	(14.9)
932.5	2642	4.8(3)	1.47	59.4	—	—	—	—	—	10198.8	589.91	14.7
956.5	2637	4.8(3)	1.68	59.8	—	—	—	—	—	18448.5	608.98	14.3
964.8	—	—	—	—	649	(394)	188	(137)	362	—	604.33	(14.3)
964.5	2631	4.6	1.56	59.1	—	—	—	—	18588.7	—	604.56	14.3

- (1) All Conversions from reactor balance and M₀N₂ unless otherwise noted
- (2) Corrected from carbon balance
- (3) Conversions and Methanol rate from "overall" balance
- (4) * Indicates balanced gas data
- (5) () Indicates interpolated data
- (6) from meter balance across plant

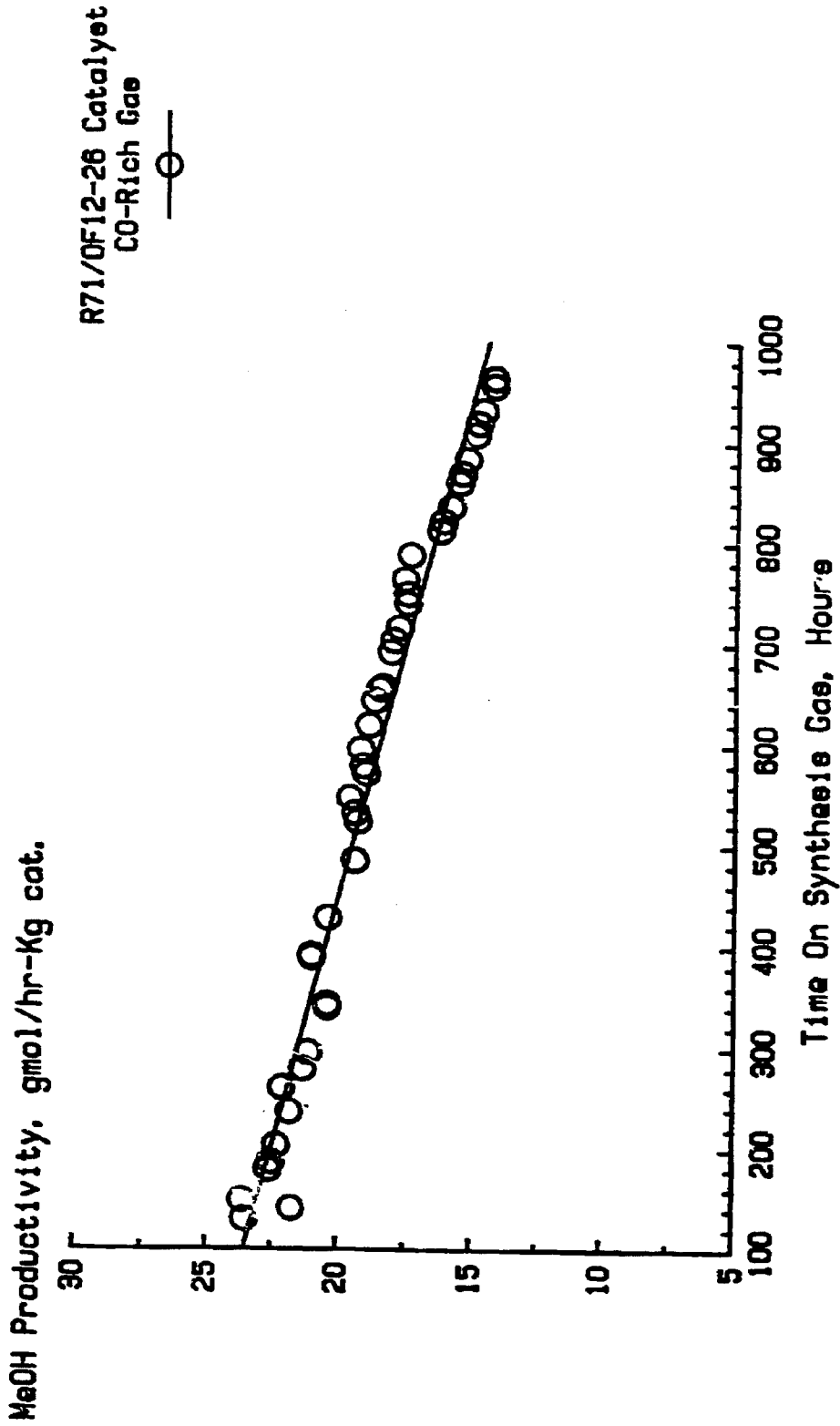
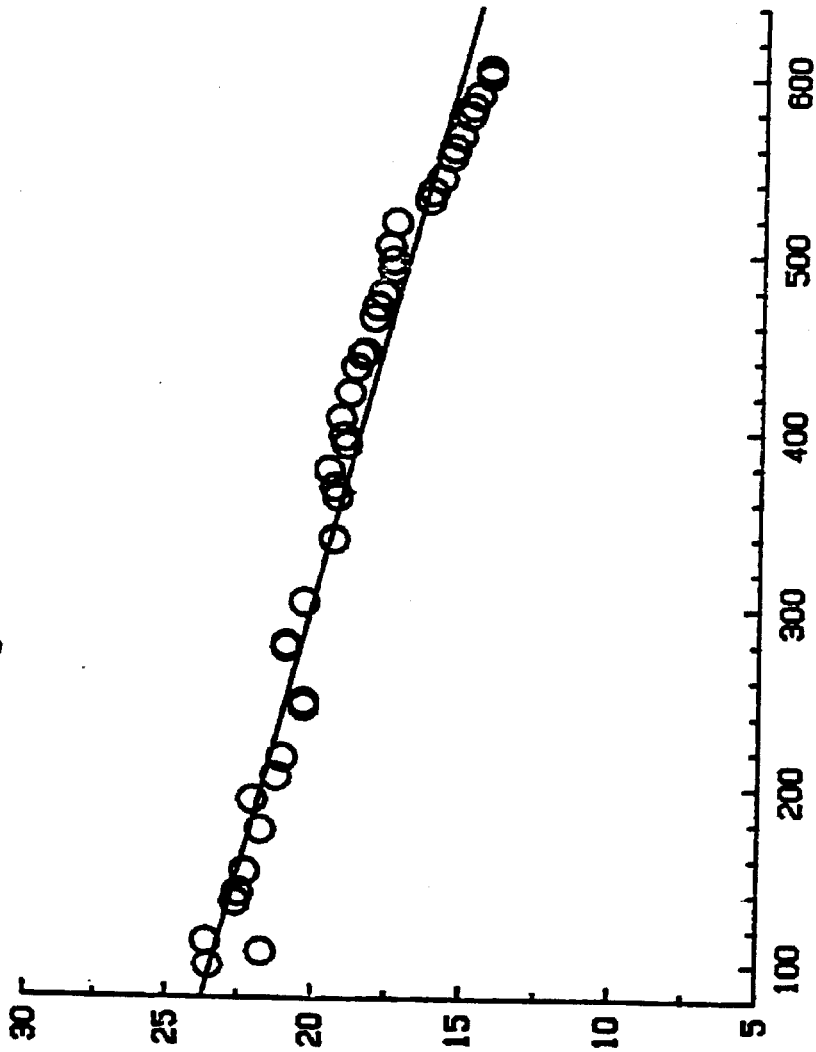


Figure 5-6. Activity Maintenance in LaPorte PDU, MeOH Productivity vs. Time on Synthesis Gas

MeOH Productivity, gmol/hr-Kg cat.

R71/OF12-28 Catalyst
CO-Rich Gas

—○—



Cumulative Methanol Production, KgMeOH/Kg cat.

Figure 5-7. Activity Maintenance in LaPorte PDU, MeOH Productivity vs. Cumulative MeOH Production

During this run, the space velocity at the end of the test was 25 percent higher than at the initiation. For this reason and in order to obtain a better correlating parameter, cumulative space velocity or the equivalent cumulative gas flow per unit weight of catalyst was utilized (Figure 5-8). A straight-line correlation of methanol productivity with cumulative gas flow follows:

$$P = 24.2 - 8.9706 \times 10^{-4} \text{ CSV}$$

where:

$$\text{CSV} = \text{cumulative gas flow, Nm}^3/\text{kg catalyst}$$

Nickel content in the catalyst increased more steadily than iron content. It correlates very well with catalyst deactivation even though the data are not as numerous as that for iron. A straight-line correlation for methanol productivity as a function of nickel buildup, as shown in Figure 5-9, has the form:

$$P = 25.3 - 0.0751 N$$

where:

$$N = \text{Nickel in catalyst, ppm by XRF}$$

Approach to methanol equilibrium also correlates well with the extent of catalyst deactivation. Figures 5-10 and 5-11 illustrate its variation versus cumulative space velocity and nickel content in the catalyst.

Commercial catalysts for vapor-phase methanol synthesis achieve 6,000 kilograms of methanol per kilogram of catalyst throughout their useful lifetime, but at much less severe synthesis gas conditions in terms of CO partial pressure and with temperature programming to neutralize the effect of catalyst deactivation. Figure 5-12 illustrates how far the R71/OF12-26 catalyst was from arriving at such a level of performance under the conditions imposed by the 40-day run.

There are no straightforward explanations for the deactivation phenomena of attrited R71/OF12-26 catalyst, and comparisons with autoclave data are difficult due to the different operating conditions and nature of the catalysts. However, the rather drastic changes in catalyst surface properties may indicate a catalyst structure instability that could be related to the attrition mechanism or the

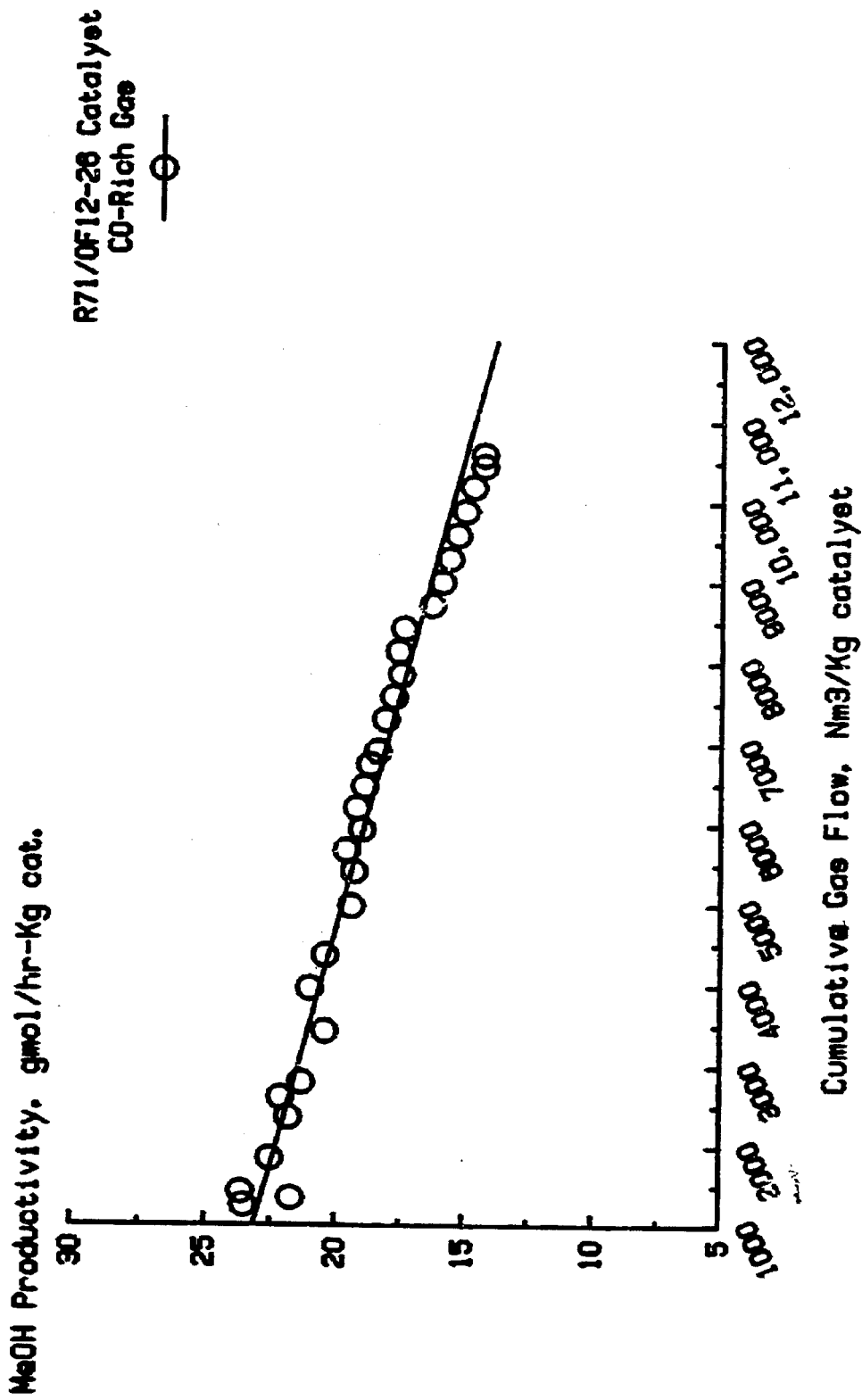


Figure 5-8. Activity Maintenance in LaPorte PDU, MeOH Productivity vs. Cumulative Gas Flow

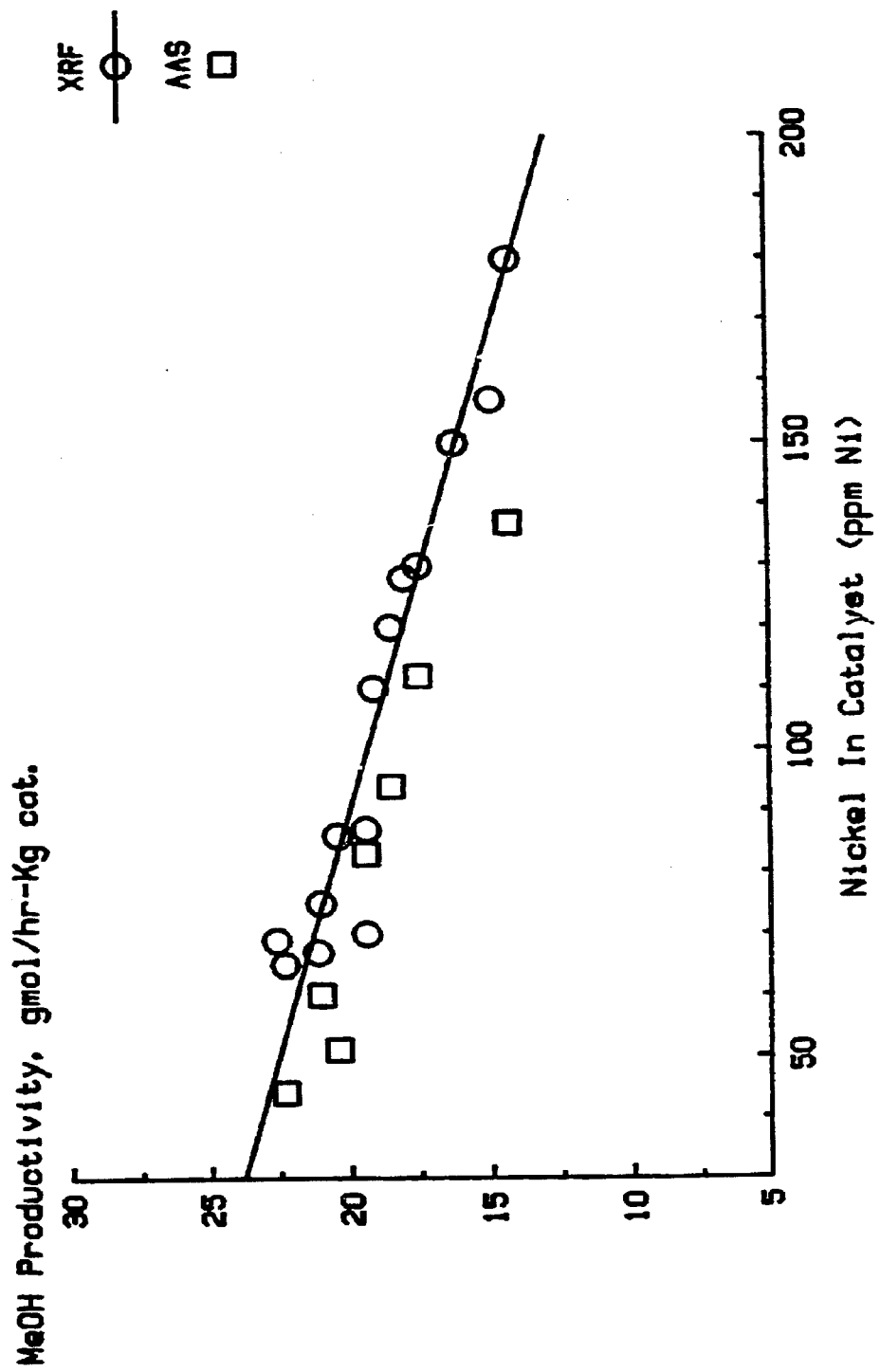


Figure 5-9. Activity Maintenance in LaPorte PDU, MeOH Productivity vs. Nickel in Catalyst

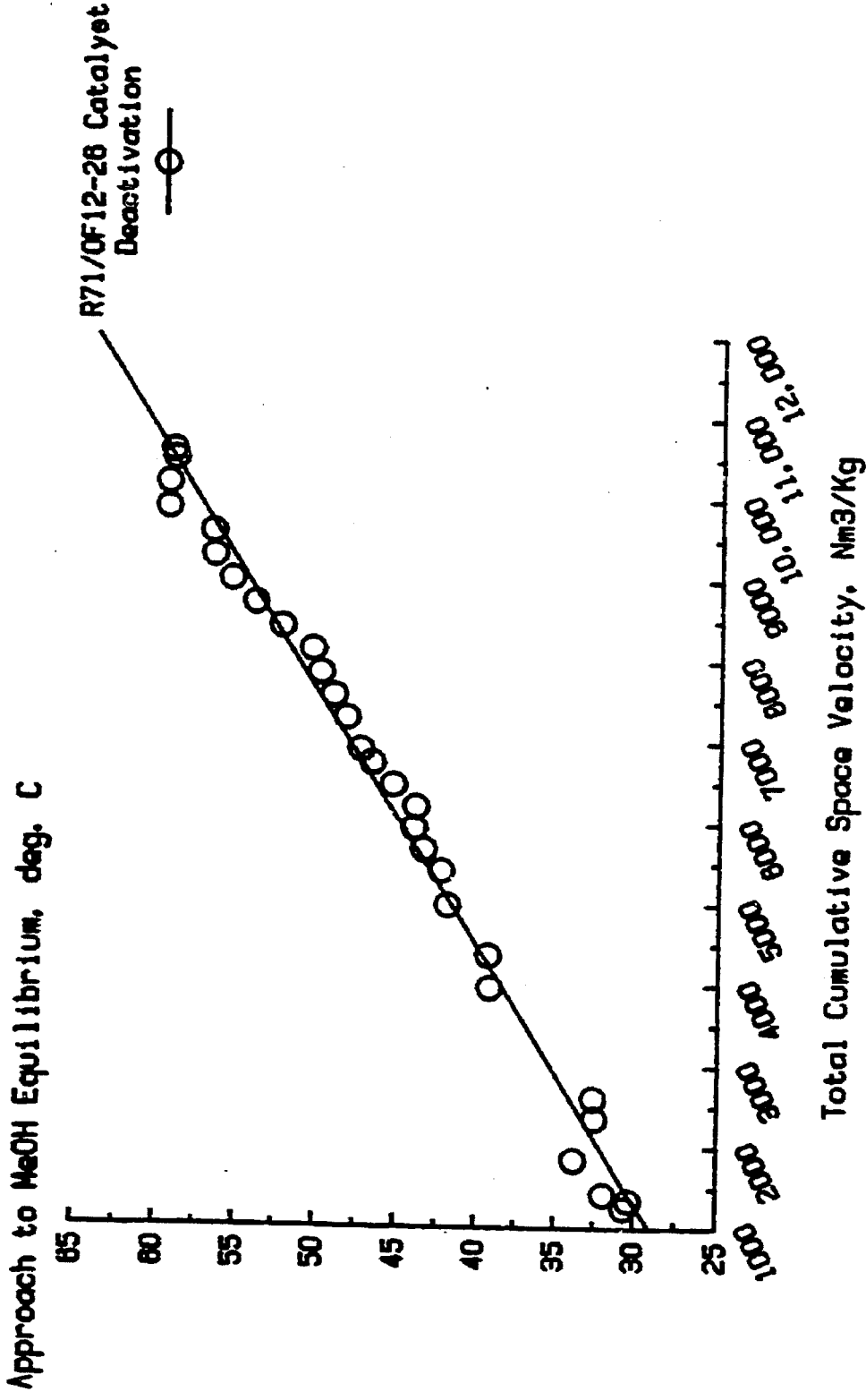


Figure 5-10. Activity Maintenance in LaPorte PDU, MeOH Equilibrium vs. Cumulative Space Velocity

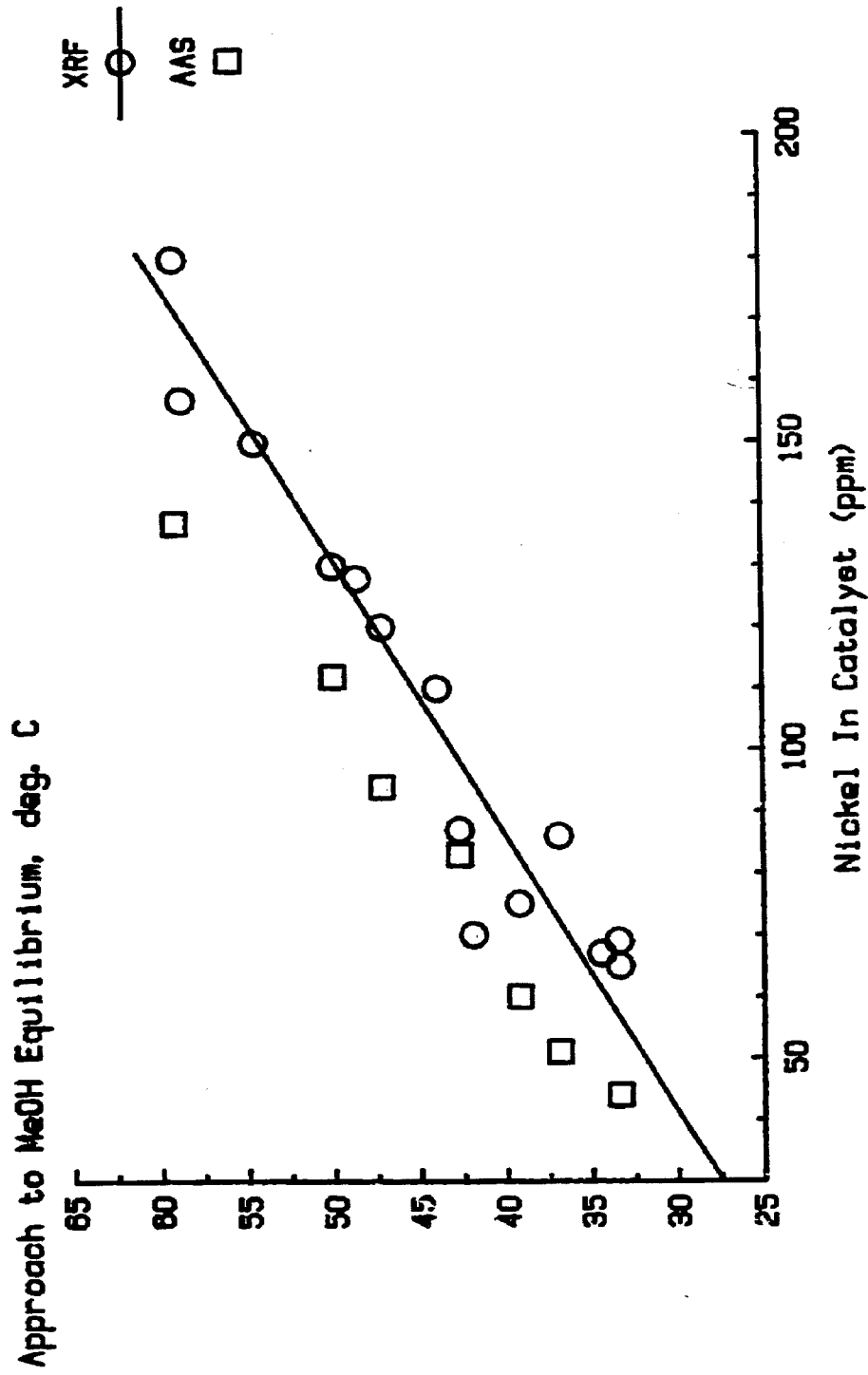


Figure 5-11. Activity Maintenance in LaPorte PDU, MeOH Equilibrium vs. Nickel in Catalyst

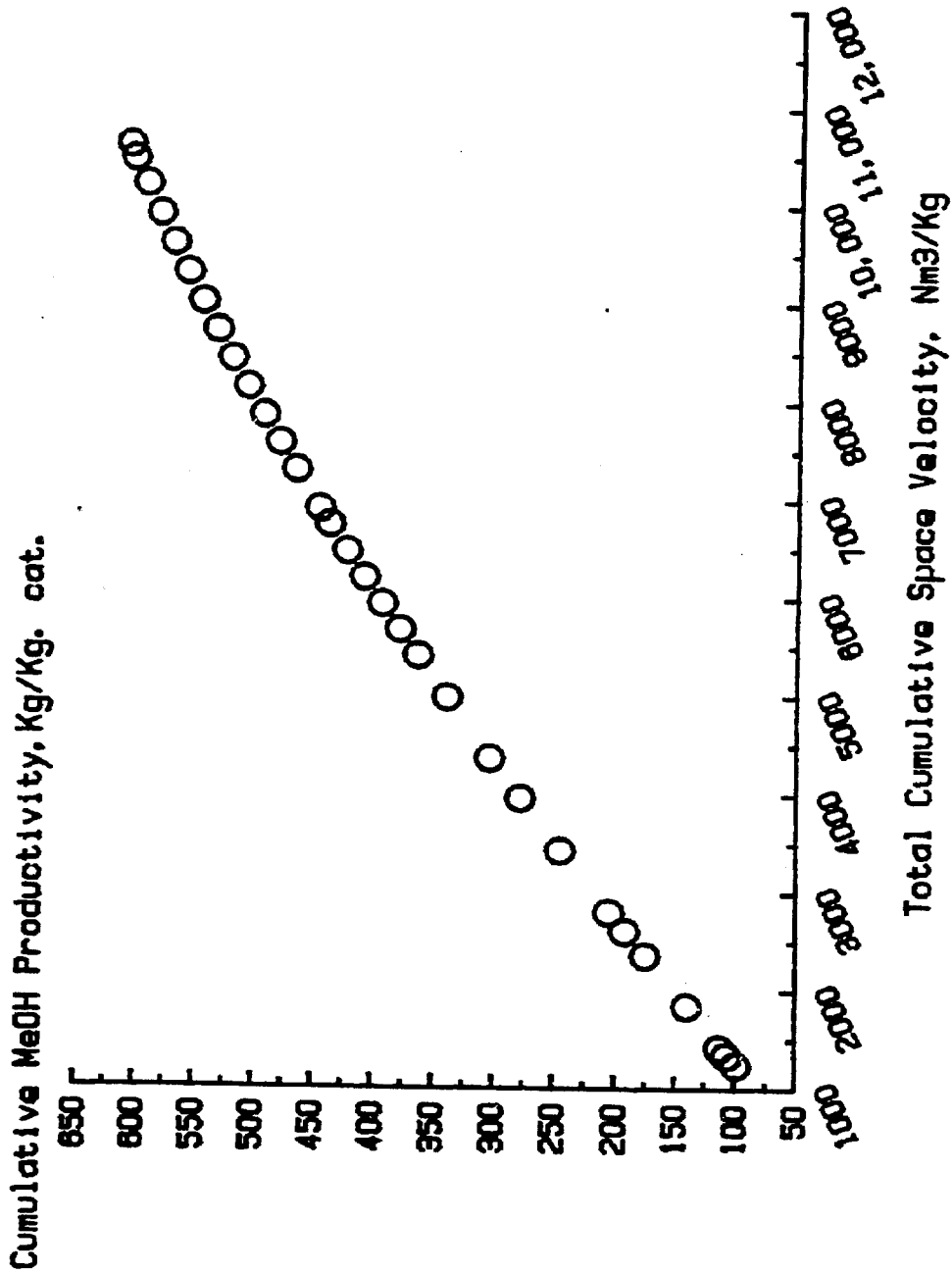


Figure 5-12. Activity Maintenance in LaPorte PDU, Cumulative MeOH Productivity vs. Cumulative Space Velocity

reduction operation. This instability may allude to the unsuitability of some pelletized catalysts that have been transformed by attrition to operate in the entrained mode. The effect of carbonyl poisoning probably does not completely explain completely the deactivation of the catalyst. A rough estimate of the effect of iron and nickel accumulation suggests an incremental loss in activity of only 0.3 percent per day. However, the complete elimination of the nickel catalyst contamination from prior methanation operations with some of this equipment and some metallurgical changes in the plant may contribute to better future tests.

It is interesting to note that even though CO conversion decreased steadily during the run, the corresponding conversion for CO₂ actually increased slightly. The conversion of CO₂ was calculated using a water balance assuming all the water originates from the reaction of CO₂ with hydrogen. This neglects the small generation of water from higher alcohols and oxygenates-forming reactions. The increase in CO₂ conversion probably reflects different rates of deactivation via the methanol and CO-shift reactions. If the predominant methanol-producing reaction is from CO,



and CO₂ is converted via the reverse shift reaction



then the methanol-forming reaction deactivated faster. On the other hand, if the main methanol-producing reaction is from CO₂



the opposite phenomenon is true. In this case, the forward shift reaction deactivated faster and was unable to consume the water at the same rate as was generated by the methanol-from-carbon-dioxide reaction.

PROCESS VARIABLES SCANS WITH R71/OF12-26 CATALYST

The effects of superficial gas velocity, reactor pressure and synthesis gas composition at high slurry concentrations were studied during the LaPorte 40-day run. The data generated can be grouped as follows:

Balanced gas:

- Low space velocity transition period (Runs E-1A1 through E-1A3)
- High pressure, high space velocity (Run E-1B)
- High superficial velocity and space velocity (Run E-1C)

Unbalanced gas:

- Initial activity at high space velocity (Run E-1D)

The 40-day run and some prior shakedown run data⁽³⁾ are shown on Table 5-7 and are presented in a series of parametric plots (Figures 5-13 through 5-18) with catalyst performance expressed as CO conversion, approach to methanol equilibrium and methanol productivity, respectively. In addition to the R71/OF12-26 catalyst data, the model predictions and Lab PDU performance are included to assist the analysis process given the rather limited data base for the LaPorte PDU. The following paragraphs describe qualitative observations that can be made from the plots.

For balanced gas operation, CO conversion decreased to about 80 percent of equilibrium in the 2,000 to 3,000 NLiters/hr-kg space velocity range. A similar drop with respect to equilibrium for previous work at the Lab PDU with F50/4E75-01 catalyst was not obtained until the space velocity was higher than 5,000 NLiters/hr-kg. This indicates poorer performance of partially attrited R71/OF12-26 catalyst with respect to the F50/4E75-01 powder as shown in Figure 5-14.

The performance in the highest slurry concentration balanced-gas run (E-1B) appears to be somewhat low in relation to the curve drawn through shakedown runs F-1B and F-1H in Figure 5-13. Although the variation is small, the decrease in performance may indicate a mass transfer or hydrodynamic limitation. In general, the balanced gas liquid-entrained data for catalyst R71/OF12-26 are fairly consistent with the Lab PDU and autoclave data. A plot of approach to methanol

Table 5-7

R71/OF 12-26 CATALYST ACTIVITY DATA, SUMMARY FOR SHAKEDOWN AND 40-DAY RUNS

Run No. (1)	Synthesis Hours On Stream	Reactor Temp. (deg C)	Press (MPa)	Space Velocity (NI/Mg-hr)	Gas Sup. Vel. (cm/sec)	Slurry Conc. (wt. %)	Percent Fines In Reactor	CO Conversion (%)	CO ₂ Conversion (%)	Approach to MeOH Equil. (deg C)		MeOH Productivity (gmo)/hr kg)
										CO Conversion (%)	CO ₂ Conversion (%)	
F-1A	54.0	250	5350	1800	2.4	7.0	13.3	44.2	1.2	13.0	6.0	
E-1A1	10.5	250	5300	2400	5.7	1.0	1.0	40.0	6.7	22.4	7.0	
E-1A2	14.5	250	5300	2770	6.0	5.9	3.9	39.2	3.4	19.3	8.8	
E-1A3	25.5	250	5370	3210	5.4	15.0	20.0	40.5	3.2	15.2	10.9	
E-1C	101.3	250	5400	14400	17.0	20.7	100.0	19.5	6.0	41.1	27.0	
F-1B	68.0	250	6370	2140	2.2	9.7	23.0	49.0	3.6	13.3	6.6	
E-1B	76.5	250	6430	11000	11.6	29.4	100.0	20.0	5.6	39.1	30.0	
F-1H	247.0	250	6510	20600	12.5	20.3	100.0	24.9	6.1	47.6	50.6	
UNBALANCED GAS												
F-1E	130.0	250	5350	2950	2.4	11.0	31.0	10.0	(0.03)	8.0	7.5	
F-1F1	192.0	250	5370	5840	5.3	15.6	51.3	11.0	1.7	25.4	15.3	
F-1F2	203.0	250	5370	5900	5.1	16.7	60.0	11.7	1.6	27.4	15.1	
E-1D	236.5	250	5370	10200	10.5	26.3	100.0	9.5	1.0	35.0	21.0	

(1) F1 Shakedown Run Data; E1 40-Day Run Data

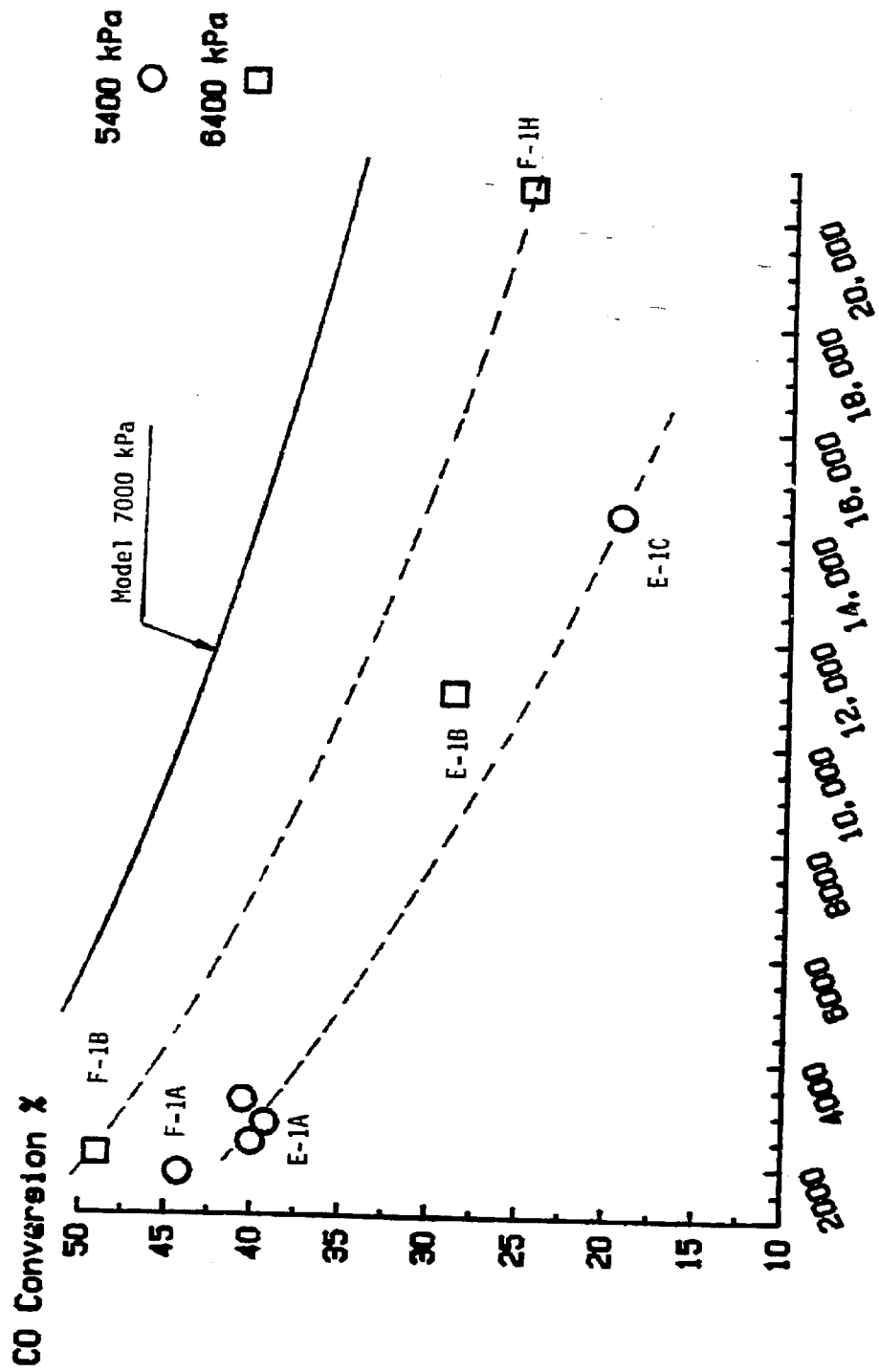


Figure 5-13. Process Variables Scans, CO Conversion vs. Space Velocity

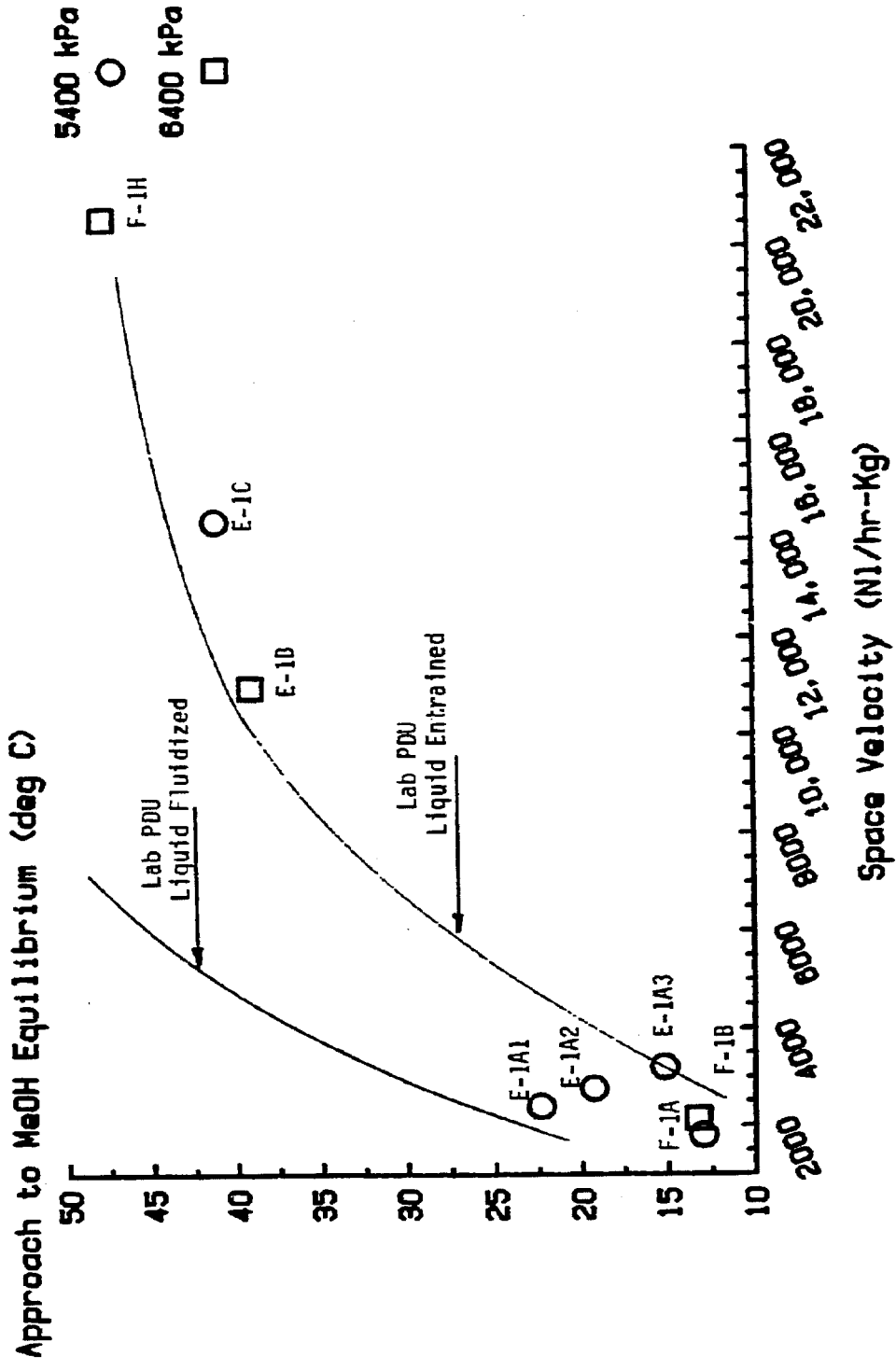


Figure 5-14. Process Variables Scans, Approach to Equilibrium vs. Space Velocity

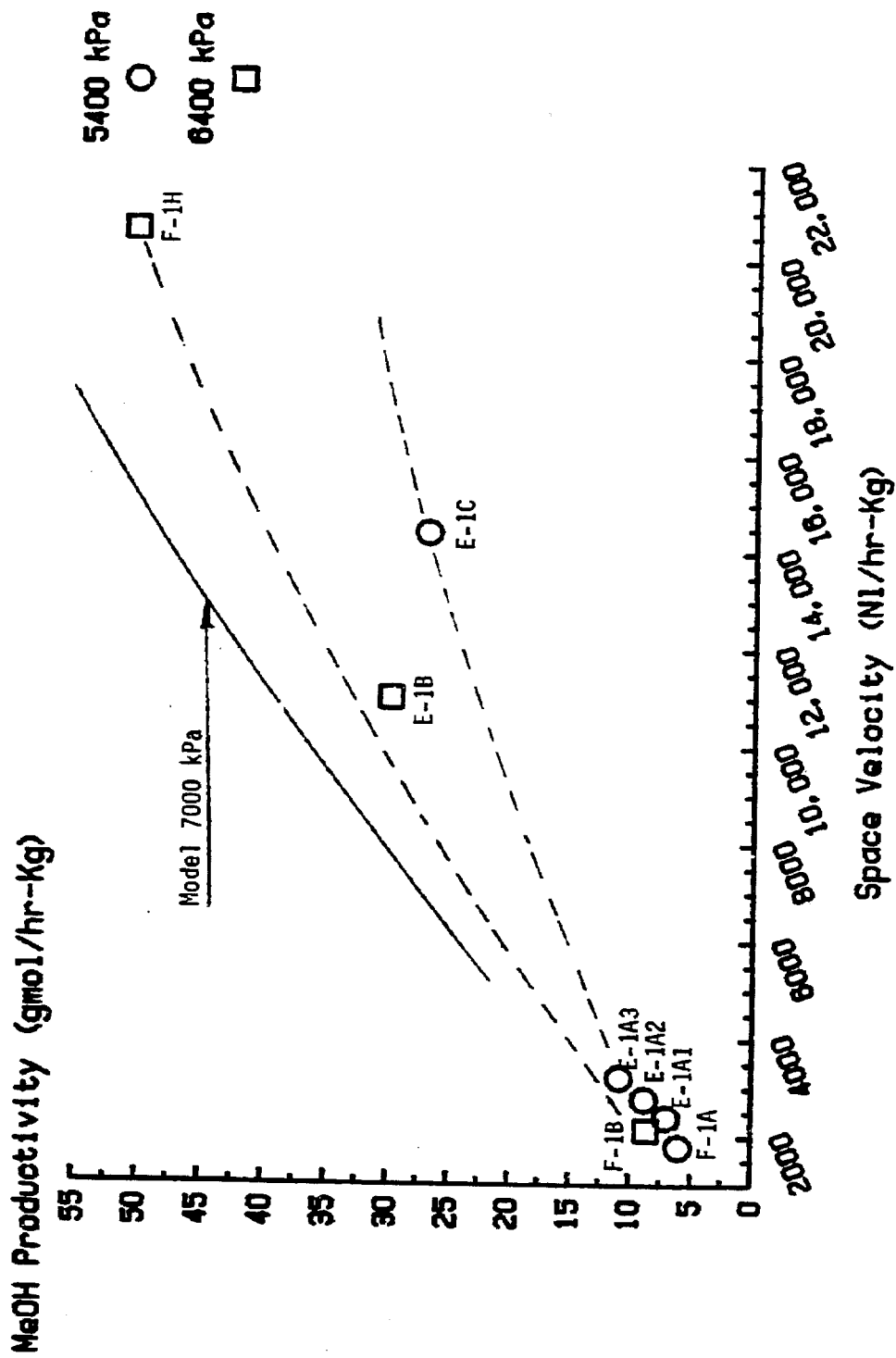


Figure 5-15. Process Variables Scans, MeOH Productivity vs. Space Velocity

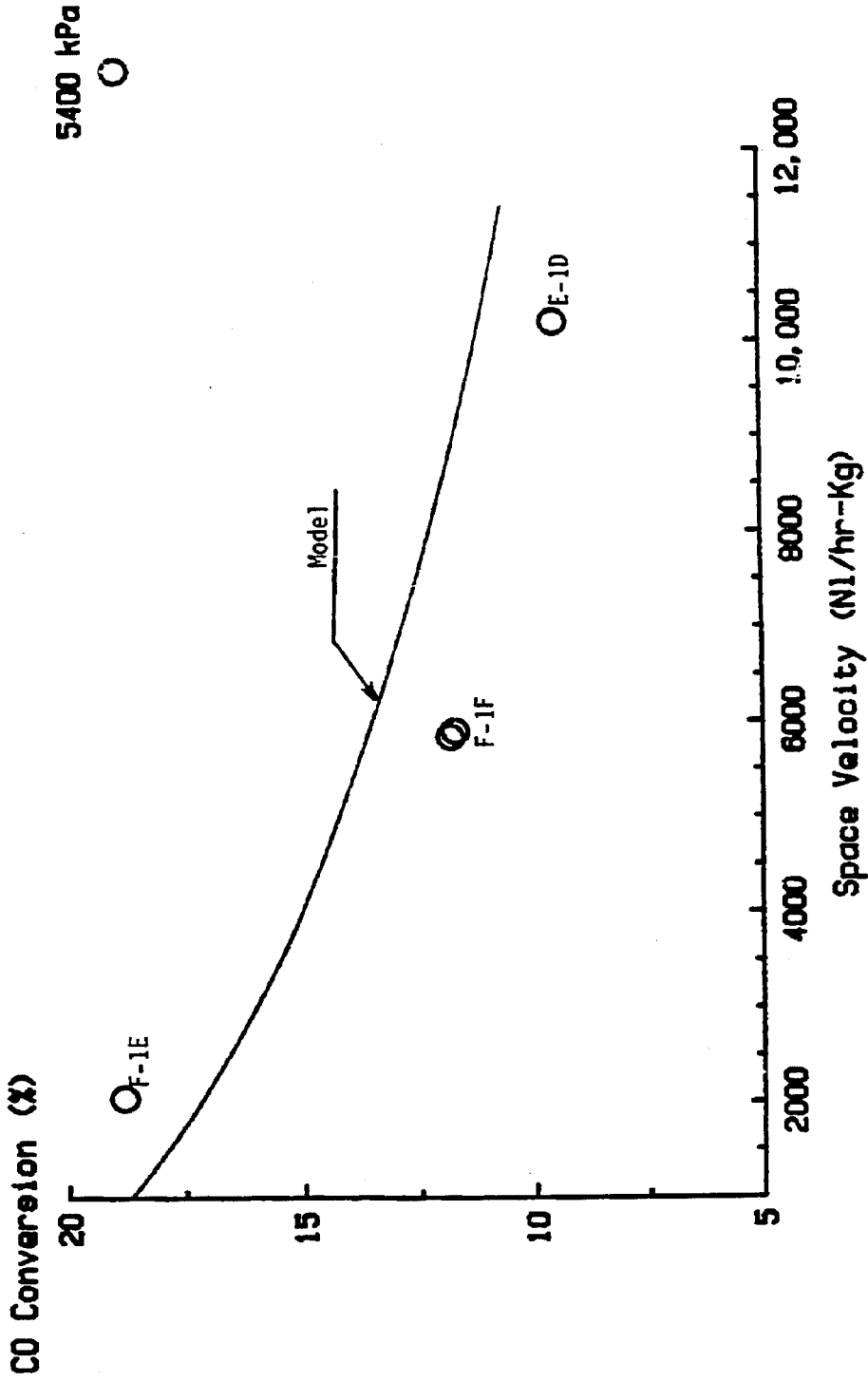


Figure 5-16. Process Variables Scans, CO Conversion vs. Space Velocity

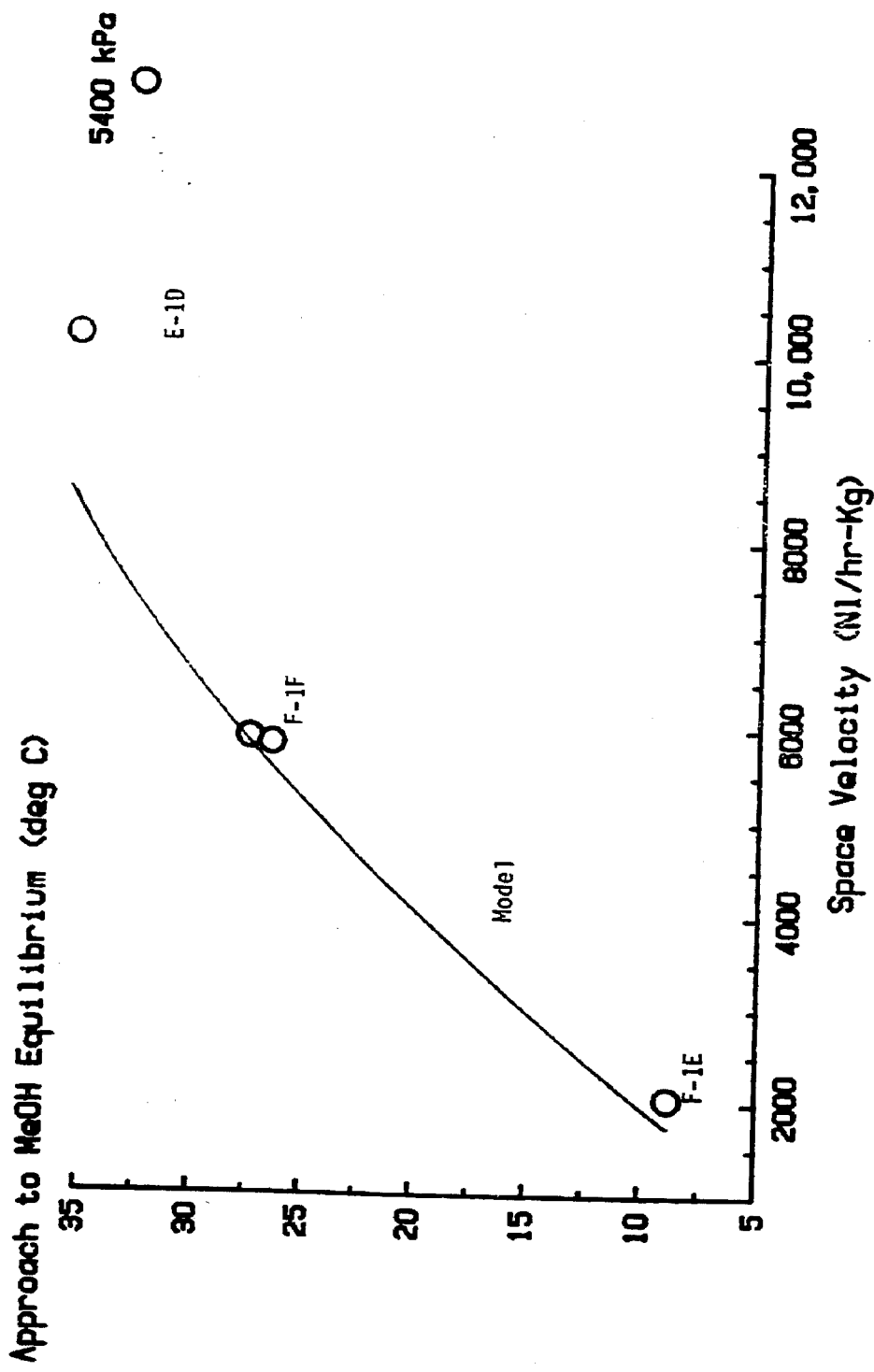


Figure 5-17. Process Variables Scans, Approach to Equilibrium vs. Space Velocity

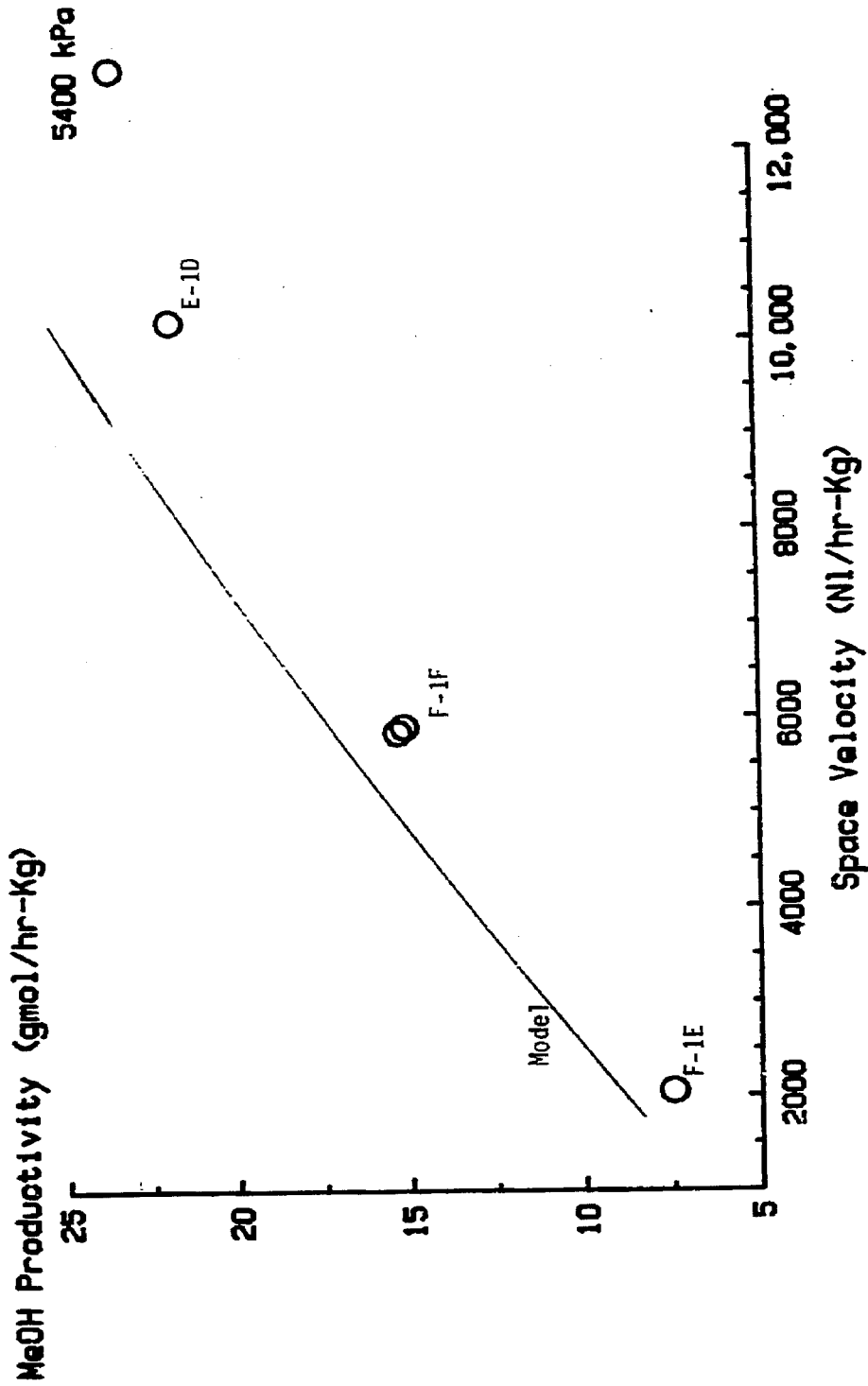


Figure 5-18. Process Variables Scans, MeOH Productivity vs. Space Velocity

equilibrium versus space velocity (Figure 5-14) reveals such agreement and it also denotes very clearly the transition from liquid-fluidized to liquid-entrained operation (runs E-1A1 through E-1A3).

For balanced gas it appears that higher pressures are desirable when operating at increasing space velocities. Figure 5-15 shows that at 16,000 NLiters/hr-kg, an approximate increase of 50 percent in productivity is gained when pressure is increased from 5,400 to 6,400 kPa. A gain of only 40 percent is obtained at half the space velocity.

Performance with unbalanced gas at the LaPorte PDU for catalyst R71/OF12-26 was close to, but perhaps slightly lower than, that predicted by the model, as shown in Figures 5-16 through 5-18.

Table 4-12 (Continued)

Sample I.D.	L0418	L0420	L0421	L0423	L0424	L0427	L0432	L0433	L0435	L0436	L0437
Date	5/02/84	5/03/84	5/04/84	5/05/84	5/06/84	5/07/84	5/08/84	5/09/84	5/10/84	5/11/84	5/12/84
Time	18:00	18:00	18:00	18:00	18:00	18:30	18:00	18:00	18:15	18:00	18:00
MeOH	96.647	96.453	96.445	96.431	96.557	95.907	96.125	95.967	96.105	95.97	95.90
EtOH	0.188	0.181	0.118	0.119	0.108	0.135	0.091	0.089	0.103	0.113	0.105
Oil	1.155	1.275	1.425	1.245	1.015	1.49	1.25	1.21	1.06	1.27	1.25
H ₂ O	1.926	1.998	1.934	2.133	2.250	2.40	2.47	2.69	2.68	2.59	2.69
Esters	0.016	0.018	0.015	0.014	0.012	0.011	0.011	0.009	0.01	0.01	0.007
C ₃ alcohols	0.045	0.046	0.042	0.040	0.031	0.035	0.034	0.026	0.028	0.028	0.027
C ₄ alcohols	0.023	0.024	0.021	0.018	0.022	0.022	0.019	0.009	0.028	0.019	0.019
C ₅ alcohols	0.000	0.005	-	-	-	-	-	-	-	-	-
Sample I.D.	L0438	L0441	L0442	L0446	L0448	L0449	L0450	L0451			
Date	5/13/84	5/14/84	5/15/84	5/16/84	5/17/84	5/18/84	5/19/84	5/20/84			
Time	18:00	18:00	17:35	18:00	18:20	16:30	18:00	18:00			
MeOH	95.53	95.52	95.36	95.19	95.15	94.89	94.68	95.07			
EtOH	0.099	0.099	0.097	0.083	0.077	0.062	0.069	0.083			
Oil	1.36	1.26	1.38	1.35	1.28	1.28	1.32	1.15			
H ₂ O	2.97	3.09	3.12	3.34	3.46	3.74	3.90	3.67			
Esters	0.007	0.006	0.007	0.005	0.005	-	-	0.003			
C ₃ alcohols	0.023	0.021	0.027	0.018	0.018	0.022	0.024	0.017			
C ₄ alcohols	0.014	0.013	0.012	0.007	0.007	0.005	0.006	0.012			
C ₅ alcohols	-	-	-	-	-	-	-	-			