Section 3

RUN DESCRIPTION

BACKGROUND

Liquid-Fluidized Tests

Catalyst R71/OF12-26, also designated EPJ-19LR, was developed by United Catalysts, Inc. under contract to the Electric Power Research Institute (EPRI Contract No. RP1656-1) specifically for the Liquid Phase Methanol process in the liquid-fluidized mode. This 40-day run is a continuation of several tests with R71/OF12 type catalysts, which were previously tested at the lab PDU scale (10-cm diameter reactor) and at the LaPorte PDU scale (57-cm diameter reactor) of operation. Table 3-1 summarizes all major PDU scale tests with liquid-fluidized catalysts and synthesis gas.

The R71/OF12 type catalysts were found to have good activity maintenance properties; however, their attrition resistance was found unacceptable for commercial application as liquid-fluidized catalysts.[4,5,6] The shakedown run of the LaPorte facility showed that the attrition of the catalyst in the larger diameter reactor was particularly severe since the catalyst completely attrited in ten days.[3]

As a result of the absence of suitable liquid-fluidized catalysts, and in view of the progress of the liquid-entrained mode in lab PDU the continuation of LaPorte PDU testing after the shakedown run had to be primarily in the liquid-entrained mode.

Liquid-Entrained Tests

Selected tests with liquid-entrained catalysts and synthesis gas are shown in Table 3-2. The liquid-entrained research program at the autoclave scale of operation had resulted in a catalyst candidate that was an intermediate product in the manufacture of a commercial catalyst pellet. Seven commercial methanol synthesis catalyst powders were evaluated as well as three candidates developed by

Table 3-1

PDU TESTS WITH LIQUID-FLUIDIZED CATALYSTS AND SYNTHESIS GAS

Catalyst	Unit	Period	Hours on Synthesis Gas	Observations
FX2/1F15-02	Lab PDU	Oct.-Nov. 1978	645	2.4-mm mini-tablets. CO-rich gas. High attrition rate. Bed decreased to 60% of its initial size.
R71/0F12-02	Lab PDU	Feb.-March 1982	540	Extrudates 2 x 6.4 mm. Most of run with 2/1 H_2/CO gas. Better activity than mini-tablets. Attrition rate 1.4% per day.
R71/0F12-26	Lab PDU	July-Aug. 1983	501	Extrudates obtained by recalcining LaPorte batch R71/0F12-22 to obtain higher attrition resistance. Similar activity and attrition rate as -02 in the series.
R71/0F12-25	Lab PDU	Oct. 1983	510	Another LaPorte candidate batch with different finishing step. Attrition tests by manufacturer were better than previous catalysts tested. However, methanol productivity and attrition resistance at the PDU were found to be surprisingly lower.
R71/0F12-26	LaPorte	March 1984	248	Shakedown run. Periods with both balanced and unbalanced gas. Higher attrition rate obtained at this larger scale as expected (about 11% per day). At the end of the run all the bed had attrited to a nominal 20% slurry (oxide basis).
R71/0F12-26	LaPorte	April-May 1984	965	Short-term testing with unbalanced gas (CO-rich). Catalyst load intentionally attrited to a 27% (oxide) slurry.

Table 3-2

SELECTED TESTS WITH LIQUID-ENTRAINED CATALYSTS AND SYNTHESIS GAS

Catalyst	Unit	Period	Hours on Syngas	Observations
F50/4E75-01	Lab PDU	Sep. 1983	83	Successful in-situ reduction of a 10 wt. % catalyst slurry. Catalyst activity with balanced gas comparable to autoclave runs. Activity with unbalanced gas somewhat lower than autoclave.
F50/4E75-01	2000 cc Autoclave	July-Oct. 1983	2,267	Activity maintenance test with unbalanced gas and activated carbon guard beds. Rate of catalyst deactivation comparable to that achieved with balanced gas in the vapor phase.
F50/4E75-01	Lab PDU	Nov. 1983	-	Tried higher concentration of slurry (35% by weight). Problems with reduction, low synthesis gas conversions. Unit voluntarily shutdown.
F50/4E75-27	Lab PDU	Dec 1983	261	Sample of catalyst batch manufactured for LaPorte liquid-entrained operations. Same catalyst as -01 above but with a more extensive calcining step. Catalyst coated vessels and lines and plugged heat exchanger tubes of the PDU when a 30 wt. % slurry loading was tested.
F50/4E75-84	300 cc Autoclave	Jan. 1984	314	Same material as F50/4E75-01. "High" slurry concentration utilized (37 wt. %). Performance consistent with prior work at lower catalyst concentrations.
F20/4E77-09	2000 cc Autoclave	NA	NA	Commercial catalyst. Performance at reduced slurry loading (10 wt. %) similar to previously tested catalysts.
F20/4E77-09	2000 cc Autoclave	April 1984	38	Results with balanced gas at a 31 wt. % slurry loading found to be comparable to previous tests with same catalyst (different batch). The catalyst seemed to be 5-15% less active than the original candidate for La Porte F50/4E75-01.

APCI. Three of the ten catalysts tested (F50/4E75-01, F20/4E77-09 and FX0/4E75-06) achieved the best results. However, the base case liquid-entrained catalyst, F50/4E75-01, outperformed the other two candidates by 10-13 percent (relative) in methanol productivity over a range of synthesis conditions (as shown in Table 3-3).

Table 3-3

EARLY LIQUID-ENTRAINED CATALYST SCREENING
SUMMARY OF AVERAGED SYNTHESIS RESULTS FOR CATALYST CANDIDATES

Reaction condition: low severity (3,500 kPa, 250°C, 4,000 l/hr-kg catalyst)

Catalyst type	F50/4E75-01	F20/4E77-09	FX0/4E75-06
Reduction techniques	2,3	5,6	8,8
H_2 conversion, %	24.8	20.9	22.1
CO conversion, %	25.3	21.2	22.4
CO_2 conversion, %	1.7	3.7	2.2
MeOH productivity, g mol/kg-hr	12.0	10.6	10.9

Reaction condition: high severity (7,000 kPa, 250°C, 6,000 l/hr-kg catalyst)

Catalyst type	F50/4E75-01	F20/4E77-09	FX0/4E75-06
H_2 conversion, %	41.6	37.8	40.0
CO conversion, %	41.5	37.8	39.5
CO_2 conversion, %	8.7	7.2	5.0
MeOH productivity, g mol/kg-hr	31.3	27.8	27.7

A series of activity maintenance tests with unbalanced synthesis gas was performed in the autoclaves at CSI using F50/4E75-01 catalyst powder. In October 1983 a 2,300-hour run was completed by eliminating catalyst poisons such as chlorine and iron carbonyl using activated carbon guard beds. These guard beds were frequently changed to eliminate the possibility of catalyst poisoning with feed contaminants.

A test at the Lab PDU scale using the F50/4E75-01 catalyst was successful. However, a second attempt using a sample of the catalyst batch manufactured for LaPorte operations (F50/4E75-27) caused considerable problems to the unit by coating vessels, lines and plugging heat exchanger tubes. Apparently, the Lab PDU problems with this catalyst could be attributed to different operating conditions at the powder calcining step prior to pelletizing. As a result of blockage and sticking problems encountered in the Lab PDU with the LaPorte batch of F50/4E75-27 catalyst powder, it was decided to demonstrate technical feasibility of the liquid-entrained mode at LaPorte using attrited liquid-fluidized catalyst R71/0F12-26.

TEST OBJECTIVES

The overall goal of the run was to achieve sustained operations with CO-rich gas at high catalyst loading using R71/0F12-26 catalyst. In order to obtain a 40 weight percent slurry, the original plan envisioned a fresh charge of catalyst extrudates and the addition of the required amount of the 20 weight percent slurry left from the earlier shakedown run. However, soon after the initial fresh catalyst load was dried with hot nitrogen in the reactor, it was found that the 20 percent slurry had a low intrinsic activity. In consequence, the maximum attainable slurry concentration became limited to approximately 30 weight percent after addition of a second fresh charge of catalyst extrudates.

The specific objectives of the liquid-entrained run were as follows:

1. Slow attrition of catalyst extrudates to make a slurry with a solids concentration of 30 weight percent oxide (Run E-1A).

2. Obtain conversion data on balanced gas at a high slurry concentration, high space velocity, and high linear superficial velocity (Run E-1B).

3. Obtain conversion data on balanced gas at a high slurry concentration, high space velocity, and maximum permissible superficial velocity (Run E-1C).

4. Obtain conversion data on unbalanced gas (CO-rich gas) at a high slurry concentration and high space velocity. Test the short-term activity maintenance of the catalyst with CO-rich gas (Run E-1D).

The planned operating conditions of each run appear in Table 3-4.

Table 3-4

LIQUID-ENTRAINED RUN PLANNED OPERATING CONDITIONS - HIGH SLURRY CONCENTRATION[1]

Run No.	Reactor Feed Flow[2] NM^3 per hr/SCFH	Pressure kPa/psig	Temperature $^oC/^oF$	Estimated Space Velocity, l/kg-hr	Planned Run Time Days
E-1A	1,300/50,000	5,300/750	250/482	2,700	7-10[3]
E-1B	3,600/136,000	6,300/900	250/482	7,300	1-3
E-1C	4,600/175,000	5,300/750	250/482	9,300	1-3
E-1D	2,600/100,000	5,300/750	250/482	6,500	40

(1) 610 kg (1,350 lb) of R71/OF12-26 extrudates.
(2) NM^3/hr measured at 0°C and 760 mm Hg. (22.4 m^3/kg mol).
SCFH measured at 70°F and 760 mm Hg (386.8 cu ft/lb mol).
(3) As necessary for slow attrition of fresh R71/OF12-26 catalyst.

In addition to the main test objectives, some special recommendations were issued regarding surveillance of critical equipment and process performance. Of particular concern was the operation of the slurry pump with high concentration slurries and possible carryover of oil and catalyst to the reactor overhead.

Sampling frequencies and trace component analyses were also established. A higher sampling frequency for slurry samples was planned for the initiation of operations than for the short-term activity maintenance portion of the run. Carbonyl trace component analyses were deemed necessary to evaluate the possible sources of catalyst poisoning. Carbonyl analyses were to take place at the middle and end of CO-rich gas operation, and sample frequency for trace component analyses was established at one sample of fresh feed gases per week.

OPERATING HISTORY

Preliminary Operations

Fresh catalyst was charged to the reactor on April 5-6, 1984. A total of 613.5 kilograms (1,353 lb) of R71/OF12-26 catalyst was added in two steps. An initial load of 409.1 kilograms was dried in the first 19 hours of operation as shown in the major event summary of Table 3-5. This quantity was then topped with an additional 204.5 kilograms to complete the catalyst charge. Another 30 hours were required to complete the dry-out of the combined load.

Catalyst dryout and reduction was accomplished during April 6-9, 1984. The reduction with R71/OF12-26 was smooth. A discussion of the reduction operation is given in Section 5.

Process oil circulation began on April 10, 1984. In order to thoroughly soak the catalyst with oil, a low oil flow of 190 liters/min at 120°C was utilized. Because some leaks were found on the feed gas line check valves, draining of the oil was necessary to repair the valves. Oil pumping was resumed and the required volume, 1,890 liters of cold oil, was charged to the reactor/primary separator system to achieve a 28 weight percent slurry following catalyst attrition.

Transition to Fully-Entrained Operation

A few hours before synthesis gas was introduced to the reactor, the catalyst bed was expanded from 287 cm (wet settled bed) to 335 cm (132 in) above the

Table 3-5

SECOND LAPORTE PDU RUN - MAJOR EVENT SUMMARY

Date	Time	Total Hours	Hours with Liquid	Hours on Synthesis Gas	Event
4/05/84	17:00	0	0	0	409.1 kg R71/OF12-26 loaded, bed height = 190.2 cm.
	19:45	2.75	0	0	System being pressurized with nitrogen to 1,050 kPa.
	21:00	4.00	0	0	Nitrogen flowing (1,420 M^3/hr) in reactor, begin heat-up of catalyst
4/06/84	11:45	18.75	0	0	Catalyst at 124°C, dry-out complete
	16:15	23.25	0	0	Begin cooling reactor
	19:00	26.00	0	0	Charged additional 204.5 kg of fresh R71/OF12-26 to reactor, bed height = 286.1 cm
	21:00	28.00	0	0	Reactor pressurized with nitrogen to 1,050 kPa, begin heating. Heat-up rate less than 10°C/hr.
4/07/84	11:30	42.50	0	0	Catalyst at 125°C, holding steady.
	13:30	44.50	0	0	Begin heating catalyst to 135°C
	14:30	45.50	0	0	Nitrogen flow decreased to 1,236 M^3/hr.
	18:30	49.50	0	0	Catalyst dry-out complete, begin cooldown with N_2 flow.
	20:00	51.00	0	0	Blending 1% H_2/N_2, reactor bypassed
	22:30	53.50	0	0	Begin reduction gas flow
4/08/84	04:00		0	0	Water in reactor effluent (on set of reduction) when max. bed temp. 125°C. Reduction with 0.8-1.0% H_2/N_2 heat-up rate less than 10°C/hr to 150°C.
	17:00	72.00	0	0	Reactor at 180°C
	17:15	72.25	0	0	Increasing hydrogen content to 1.5%
	18:00	73.00	0	0	Reactor temp. went up to 185°C, decreasing hydrogen content back to 1.0%, temp. decreased and stabilized at 177°C
4/09/84	06:00	85.00	0	0	Bulk reduction complete. Polishing step increase H_2 to 1.5-2.0 mol % and continue heat-up.

Table 3-5 (Continued)

Date	Time	Total Hours	Hours with Liquid	Hours on Synthesis Gas	Event
4/10/84	02:45	105.75	0	0	Reactor at 230°C
	03:45	106.75	0	0	Reduction complete, H_2 off
	04:00	107.00	0	0	Begin cooling reactor
	07:45	110.75	0	0	Depressurizing reactor
	08:00	111.00	0	0	Catalyst sample taken from reactor
	13:00	116.00	0	0	Pressurize to 3,500 kPa using nitrogen
	14:30	117.50	0	0	Oil introduced to reactor at 190 L/min
	20:00	123.00	5.50	0	Total oil inventory = 1,890 liter (cold)
	22:00	125.00	7.50	0	Settled bed height = 287 cm (wet)
4/11/84	00:00	127.00	9.50	0	Liquid only expansion = 30% at 250°C and oil flow = 520 L/min; U_l = 3.4 cm/sec
	00:30	127.50	10.00	0	System being pressurized to 5,400 kPa with nitrogen
	01:30	128.50	11.00	0	Nitrogen to reactor @ 450 N m^3/hr
	02:30	129.50	12.00	0	Nitrogen flow increased to 700 Nm^3/hr
	03:30	130.50	13.00	0	Introduce balanced gas: 5,400 kPa; 200°C
	05:45	132.75	15.25	2.25	Bed height = 335 cm @ U_l = 3.6 cm/sec; 5,250 kPa; 240°C; Ug = 2.3 cm/sec
	06:15	133.25	15.75	2.75	Bed height = 338 cm @ U_l = 3.6 cm/sec; 5,250 kPa; 250°C; Ug = 3.4 cm/sec
	06:45	133.75	16.25	3.25	Increased Ug to 4.5 cm/sec
	07:30	134.50	17.00	4.00	Bed height = 350.0 cm @ U_l = 3.6 cm/sec, Ug = 4.5 cm/sec
	09:00	136.00	18.50	5.50	U_l = 3.8 cm/sec; Ug = 5.7 cm/sec
	09:30	136.50	19.00	6.00	Expanded bed height = 332.7cm
	19:00	146.00	28.50	15.50	Expanded bed height = 332.7cm @ 5,400 kPa; 250°C; Ug = 4.1 cm/sec; U_l = 5.2 cm/sec, freeboard zone increasing in density
4/12/84	02:30	153.50	36.00	23.00	Reactor density profile shows no interface
	03:45	154.75	37.25	24.25	U_l decreased to 3.4 cm/sec, reactor density profile shows no interface
	04:15	155.25	37.75	24.75	U_l back to 4.2 cm/sec
	05:30	156.50	39.00	26.00	Slurry heat exchanger fouling becomes evident

Table 3-5 (Continued)

Date	Time	Total Hours	Hours with Liquid	Hours on Synthesis Gas	Event
4/12/84	10:00	161.00	43.50	30.15	Slurry flow increased to 8.0 cm/sec to rid exchanger of fouling
	14:00	165.00	47.50	34.50	Increased oil flow has eliminated fouling
4/13/84	01:00	176.00	58.50	45.50	Increasing gas flow and pressure
	05:00	180.00	62.50	49.50	Gas flow at 3,800 M^3/hr, reactor at 6,300 kPa; Ug = 11 cm/sec; U_l = 5.9 cm/sec
4/14/84	02:00	201.00	83.50	70.50	MeOH liquid product meter being calibrated (0.85* reading = actual)
	09:45	208.75	91.30	78.30	Begin decreasing system pressure
	11:00	210.00	92.50	79.50	System at 5,400 kPa; 250°C
	13:30	212.50	95.00	82.00	Ug = 18 cm/sec, U_l = 6 cm/sec
4/15/84	05:00	228.00	110.50	97.50	Noting some catalyst in methanol product
	10:00	233.00	115.50	102.50	End of balanced gas run, switch to unbalanced gas
	12:45	235.75	118.25	105.25	System pressure dropped twice to remove nitrogen
	20:30	243.50	126.00	113.00	Slurry flow dropping off, suspect plugging, increasing flow to 950 L/min
	21:45	244.75	127.25	114.25	Slurry sample taken
	22:00	245.00	127.50	114.50	Pump output increased to 100%, voltage is constantly increasing indicating possible loosening of plug
4/16/84	00:30	247.50	130.00	117.00	Seal flush pump not unloading resulting in full oil flow (25 L/min) to seal flush, system temp. beginning to fall
	00:45	247.75	130.25	117.25	Pump manually unloaded, temps. returning to normal
4/17/84	06:15	277.25	159.75	146.75	Lost seal flush due to catalyst in suction filter
	06:45	277.75	160.25	147.25	Filter changed, seal flush back on
	12:45	283.25	166.25	153.25	Heater trip

Table 3-5 (Continued)

Date	Time	Total Hours	Hours with Liquid	Hours on Synthesis Gas	Event
4/17/85	13:00	284.00	166.50	153.50	Heater on, lost 3°C in reactor
	15:15	286.25	168.75	155.75	Switched seal flush pump filter due to plug
	17:30	288.50	171.00	158.00	Spare filter plugged, fresh filter on-line
	18:15	289.25	171.75	158.75	Pump rate decreased from 950 L/min to 850 L/min in attempt to stop catalyst carryover from V/L separator, new U_1 = 5.~ cm/sec
4/18/84	14:00	309.00	191.50	178.50	Seal flush filter changed
4/19/84	14:00	333.00	215.50	202.50	Gas compressor trip, oil flow, and reactor temp. remained steady, gas back to plant
	15:00	334.00	216.50	203.50	Seal flush filter changed
4/20/84	01:30	344.50	227.00	214.00	Barrier fluid pumps switched
	22:15	365.25	247.75	234.75	Compressor recycle valve failure, caused full gas flow (3,800 M^3/hr) to go into plant
	23:00	366.00	248.50	235.50	Recycle valve reset manually, gas to plant back down to 2,800 M^3/hr
4/21/84	01:00	368.00	250.50	237.50	Seal flush filter changed
	11:15	378.25	260.75	247.75	Seal flush filter changed
	21:00	388.00	270.50	257.50	Began to optimize feed/recycle, but abandoned per CSI request
4/22/84	13:30	404.50	287.00	274.00	Feed gas rate trimmed slightly from 2,950 to 2,830 M^3/hr
4/23/84	07:15	422.25	304.75	291.75	Seal flush filter changed
4/24/84	12:00	451.00	333.50	320.50	Seal flush filter changed
4/25/84	01:30	464.50	347.00	334.00	Recycle flow increased from 2,730 to 2,830 M^3/hr
	12:00	475.00	357.50	344.50	Slurry sample taken
4/26/84	03:15	490.25	372.75	359.75	Utility oil high alarm TE-555 was reading 246°C all night and then alarmed at 280°C, reactor temperature during heater outage dropped to 244°C
	19:45	506.75	389.25	376.25	Seal flush filter changed
4/27/84	10:15	521.25	403.75	390.75	Slurry sample taken
	17:45	528.75	411.25	398.25	Seal flush filter changed

Table 3-5 (Continued)

Date	Time	Total Hours	Hours with Liquid	Hours on Synthesis Gas	Event
4/28/84	05:00	540.00	422.50	409.50	Bottom of primary V/L agitated by pumping 500 L/min slurry through reactor by-pass into V/L bottom
	05:15	540.25	422.75	409.75	Slurry pump sped up to 100% for 1/2 hour, 600 L/min slurry to pump
	07:00	542.00	424.50	411.50	Pump flow to reactor to be reduced to 897 L/min
	07:45	542.75	425.25	412.25	Slurry flow at 850 L/min
4/29/84	08:15	567.25	449.75	436.75	Barrier fluid DP lowered from 510 to 450 kPa, seal should be clean after washing by several gallons of fluid
	10:00	569.00	451.50	438.50	Seal DP lowered to 405 kPa
4/30/84	21:00	604.00	486.50	473.50	Packing leak on feed gas valve to feed/product exchanger. Extinguished fire and tried to tighten packing. Did some good but still weeping.
5/02/84	16:45	647.75	530.25	517.25	Problems with oil condensate pump suction screen plugged with caked-on catalyst.
5/03/84	13:30	668.50	551.00	538.00	Changed seal flush filters in order to have clean filters for weekend.
5/03/84	14:15	669.25	551.75	538.75	Problem with seal flush flow after swapping filters. First a low flow then a sudden surge as if something was plugging the line. Sudden increase in primary V/L separator level, no change in reactor gas flow or oil condensation pump flow. Density gauge reading dropped.
5/06/84	03:15	730.25	612.75	599.75	Reactor temp. holding @ 249°C, utility up to 253°C, pump to full output to try to clear slurry exchanger (if plugged).
	04:00	731.00	613.50	600.50	Returned pump flow to normal.
5/07/84	23:00	774.00	656.50	643.50	Slight upset in process, signal lost to compressor recycle valve, flow to reactor manually increased to 3,700 M^3/hr and opened valve for cleaning.
	23:15	774.25	656.75	6543.75	Plant back to normal, everything on automatic as before upset.

Table 3-5 (Continued)

Date	Time	Total Hours	Hours with Liquid	Hours on Synthesis Gas	Event
5/08/84	04:45	779.75	662.25	649.25	There is an interface in intermediate oil separator, looks like oil on bottom and methanol on top.
5/12/84	19:30	880.50	763.00	750.00	Slurry sample taken.
5/17/84	09:30	1000.50	883.00	870.00	Slurry sample taken.
5/19/84	2:30	1041.50	924.00	911.00	Utility oil at maximum temp. of 260°C to maintain reactor at 250° during rainstorm.
	12:15	1051.25	933.75	920.75	Slurry sample taken.
5/21/84	07:30	1094.50	977.00	964.00	Slurry sample taken.
	08:00	1095.00	979.50	964.50	Begin system shutdown.
	08:30	1095.50	978.00	964.50	Nitrogen purge to plant begun while starting to cool reactor.
	11:30	1098.50	981.00	964.50	Gas holdup measurements starts using nirogen.
	14:00	1101.00	983.50	964.50	End of gas holdup study.

distributor plate with an oil circulation of 600 liters/min (158 gpm). Syngas was introduced at 0330 hours on April 11, and flow was stabilized at about 1,300 NM^3/hr (50,000 SCFH). Six hours later the first nuclear density gauge (NDG) scan took place. A second scan ten hours after syngas introduction showed that the location of the bed interface had not changed and remained at 333 cm (131 in). However, the third NDG scan at 23 hours on syngas revealed a uniform density indicating that the bed had already disappeared. Although the unchanging bed height between the first two bed profile determinations seemed to indicate a stable system, the NDG readings at the freeboard showed an extremely rapid attrition rate and densification of the oil that started shortly after the second NDG bed scan. Calculations show that the attrited catalyst extrudates of the second bed profile determination were being fluidized by an oil slurry of about 10 weight percent catalyst fines.

In the period between the first and second bed profile determinations, the attrition rate was on the order of 2 percent per hour or about 10 kg of catalyst fines were being generated every hour. At this rate it would have taken about two

days to fully attrite the bed. However, the transition to fully entrained mode took only about 24 hours, probably owing to elutriation of the smaller catalyst particles to the slurry piping and pump.

As the catalyst particles became smaller or more buoyant during the rapid bed weight loss, the bed continued expanding to near the upper limit of the NDG at 447 cm mark (176 in). Shortly before the uniform density profile was obtained, the catalyst bed began to overflow rapidly, as shown by a step change in the NDG recording chart, thus accelerating the attrition of the remaining catalyst extrudates. A slurry concentration of about 30 weight percent (oxide) was reached shortly after the bed overflowed (see Figure 3-1).

About 26 hours after syngas was introduced, indications of fouling in the process side of the slurry heat exchanger became evident. Cooling on the slurry side was occurring even though the utility oil heating load had been increased. This problem was first diagnosed as being concentration- related since it was associated with an earlier drop in slurry pump circulation rate coupled with an increase in pump amps. As a first preventive measure, an additional 378 liters of fresh oil were added to dilute the slurry and give a more workable level in the primary V/L separator. The pump circulation rate was also increased from 35 to 43.6 M^3/hr but it was subsequently dropped to 36.3 M^3/hr.

Since the problem with the heat exchanger continued, a process diagnosis plot was prepared revealing a close correlation of the problem with the liquid superficial velocity. In Figure 3-2 it could be seen that the increase in pump circulation at 28.5 hours on synthesis gas initiated a recovery in heat exchanger temperatures as well as methanol concentration in the reactor effluent. At 30.5 hours on synthesis gas it was decided to increase the pump speed and flow to the maximum. During this period the slurry pump ran smoothly without problems and signs of exchanger fouling gradually disappeared. The operation was back to normal at 44 hours on synthesis gas.

As can be seen in Table 3-6, at the initiation of operation there were recurrent problems with the on-line chromatograph valve switching modules. However, due to the inherent redundancy of the system coupled with the material balance and stoichiometric considerations, it was possible to analyze the data and obtain conclusions. For the first 80 hours on balanced gas four "steady-state" periods totaling 41 hours of operation were examined.

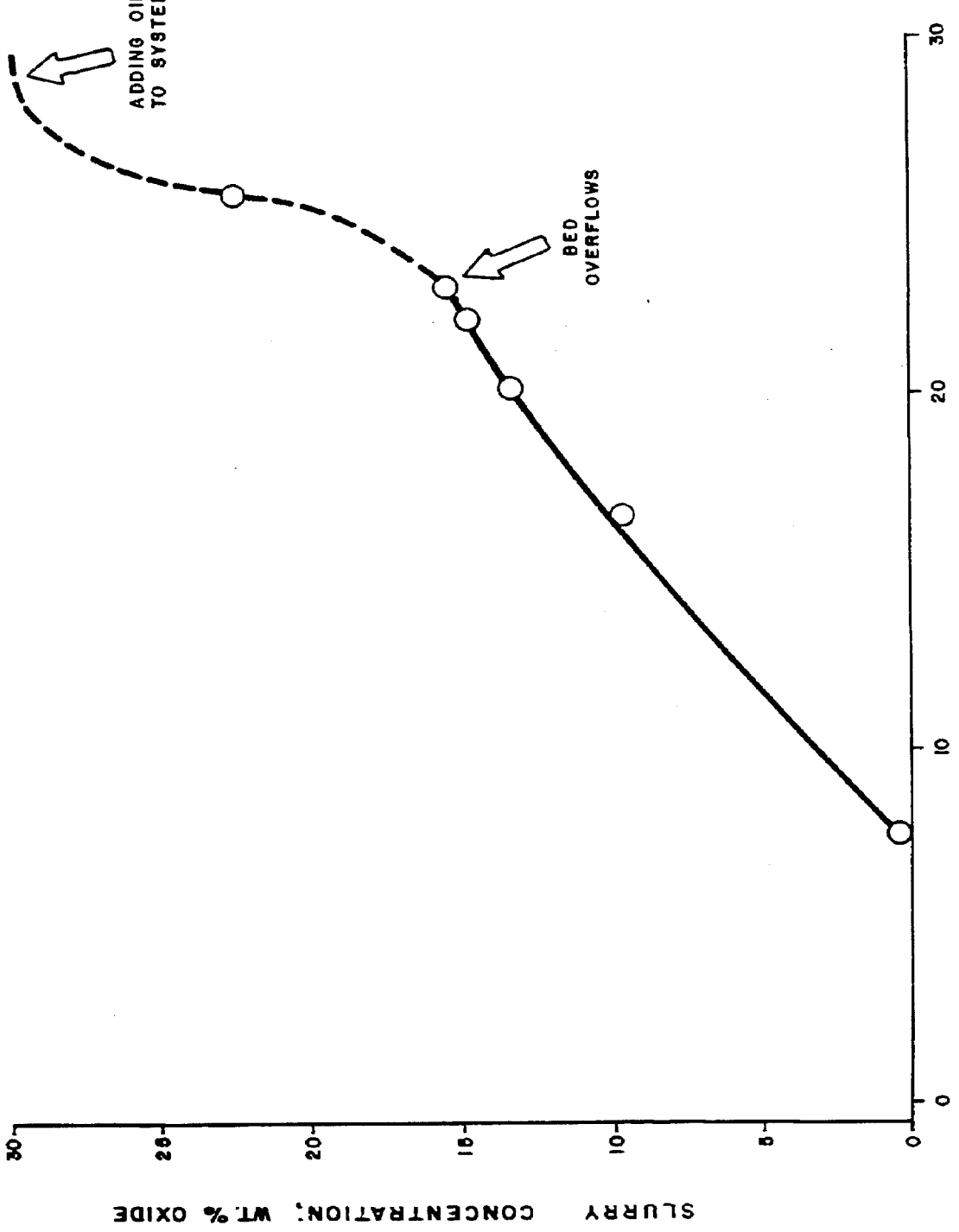

Figure 3-1. Transition to Entrained Mode - Slurry Concentration

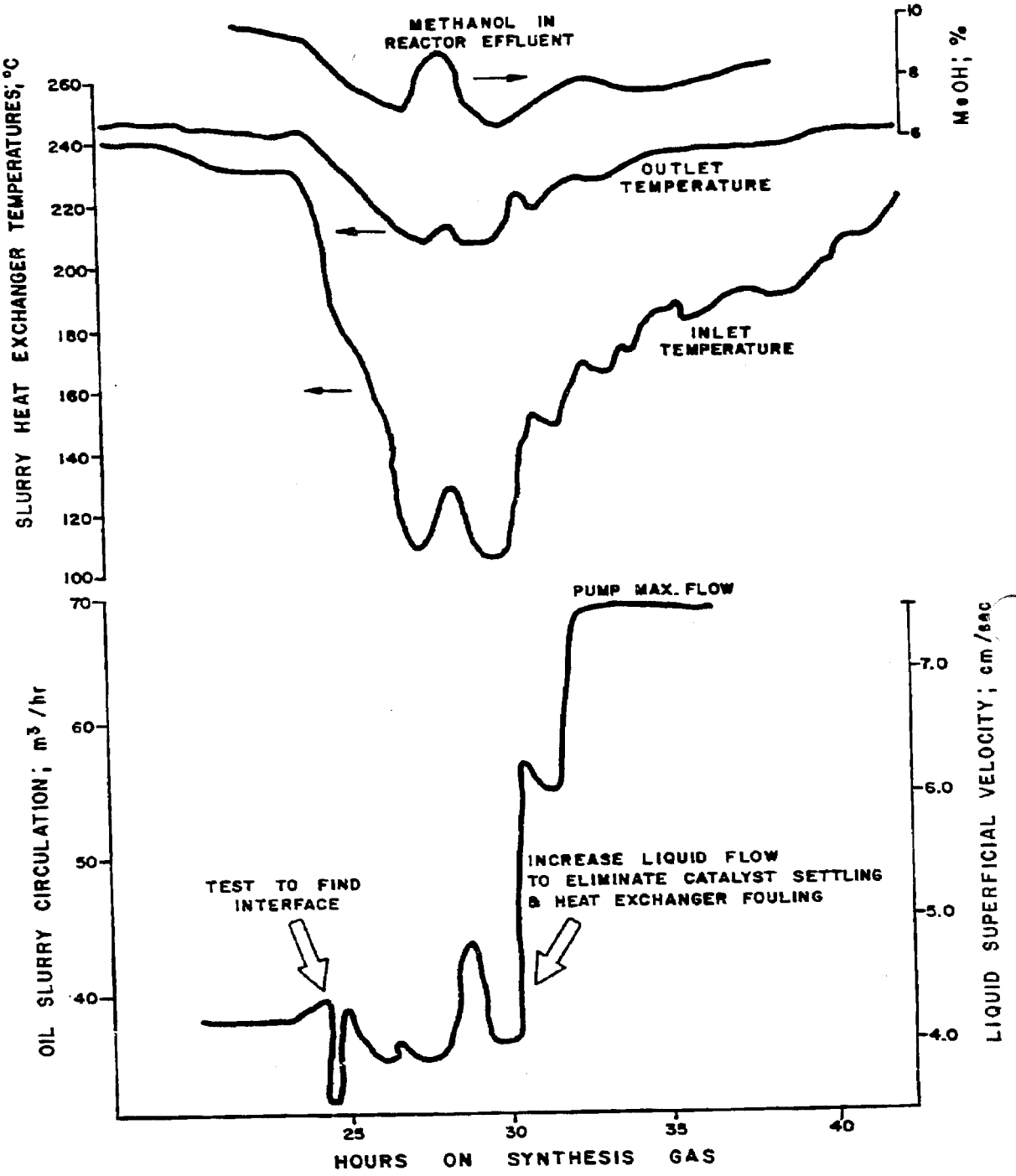

Figure 3-2. Diagnosis of Fouling Problem

At 103 hours on syngas with the objectives of run conditions E-1A through E-1C completed, transition to the CO-rich gas activity maintenance condition E-1D began. The plant operating conditions were stabilized by 22:00 hours on April 15, and the following day both on-line chromatographs were operating with new calibrations.

Table 3-6

DATA ACQUISITION SYSTEM EVENT SUMMARY
INITIAL PLANT PERFORMANCE

Date	Time	Event
		--- Catalyst Reduction ---
4/07/84	14:00	GC#1 switching module not operating correctly - changed module.
	16:00	GC#2 series 400 switching module programming problems.
4/08/84	07:40	GC#1 operating correctly. Results reliable for reduction operation. GC#2 results are reported in wrong streams.
	09:30	Verifying GC#1 H_2 concentration using peak heights (standard's H_2 conc. 2.1%, actual about 1.0%).
	14:15	Both GC's operating correctly; GC#1 appears to be more accurate.
4/09/84	12:15	Decide to order a new series 400 switching module for GC#1.
4/10/84	07:30	Verifying transmission of GC data to DAS computer. FORTRAN program does not update concentrations greater than 100% (one-component streams).
		--- Balanced Gas Operation ---
4/11/84	04:00	GC#2 switching module locks-up.
	05:40	H_2, N_2 and CO not detected during analysis of Guard Bed Feed stream.
	06:00	Steam to reactor effluent sample line turned off.
	09:00	Start of run E-1A-1 balance period.
	14:00	End of run E-1A-1 balance period. Start of run E-1A-2 balance period.
	18:00	End of run E-1A-2 balance period.
	19:00	Start of run E-1A-3 balance period.
4/12/84	05:00	End of run E-1A-3 balance period.
	09:00	Specialist from CSRI (Fairfield) begins to disassemble GC#1.
	10:40	Spare parts with new Series 400 module from Carle Instruments arrive. Start assembly.
	14:00	GC#1 back on-line.
	23:00	Problems with GC#2 H_2 concentration. Integration of H_2 peak owing to an electrical power supply disturbance on the valve switching mechanism.

Table 3-6 (Continued)

Date	Time	Event
4/13/84	10:00	Start of run E-1B balance period.
	20:00	CO analysis in reactor effluent seems low when CO calculated conversion is compared to MeOH make (period 0500-1600, 4/13). Decide to improve heat tracing in the reactor effluent. Switch flash gas analysis to reactor effluent on GC#2.
4/14/84	02:00	Started "forced" integration of H_2 peak on GC#2.
	04:40	MeOH product meter calibrated (correction factor: 0.83).
	08:00	End of run E-1B balance period. Small errors in CO concentrations coupled to inaccuracies in reactor flows lead to inconsistencies in the mass balances.

Operations Analysis

The performance of the plant and its critical equipment items, such as the slurry pump, was outstanding for the duration of this run.

Catalyst carryover. During the high flow operation on balanced gas on April 14, slurry entrainment from the primary V/L separator was detected. The problem was probably aggravated by momentary high gas flows encountered during the depressurization following the change from 6,300 kPa to 5,300 kPa (900 to 750 psig).

Since catalyst carryover to the intermediate oil separator appeared to continue during CO-rich operation, several corrective measures were taken. First, the slurry concentration was decreased from 27 weight percent to about 25 weight percent by addition of fresh oil during April 17 and April 18. This also eliminated a pump control problem caused by low liquid level in the primary V/L separator. Secondly, since it was consideredthat the high liquid velocities were aggravating the entrainment problem through splashing at the primary V/L separator, the slurry rate was reduced from 950 liters/min (250 gpm) to 850 liters/min (225 gpm) on April 17. However, some carryover from the primary V/L separator prevailed but at a reduced rate. The impact of catalyst loss from the system through filters was minimized by decreasing the oil seal flush flow to the minimum and recycling the remainder of the condensed oil to the primary V/L separator directly.

All oil additions and withdrawals were recorded from the initiation of the run in order that slurry concentrations and catalyst losses could be estimated from inventory considerations in addition to NDG or analytical determinations.

Heat exchangers. During the operation at high flows, no sign of fouling of the feed/product exchanger was detected. However, the slurry heat exchanger apparently experienced some fouling in addition to the fouling during the transition to entrained-mode operation. During April 15, the slurry flow began to drop and plugging was suspected. The flow was increased to 950 liters/min (250 gpm) and the problem did not recur.

Plant upsets. A minor plant upset occurred at approximately 14:00 hours on April 15. A brief seal flush flow surge, created while working on the oil condensate pumps, caused a trip of the slurry pump. The pump was restarted within several minutes. A second pump trip occurred when switching barrier fluid pumps. The slurry pump was again restarted quickly. This upset resulted in a brief "clouding" of the methanolproduct. During April 16 and April 20, two brief reactor feed flow upsets occurred. These upsets originated when the compressor recycle flow controller malfunctioned. During the second flow upset the reactor gas flow peaked at 3,800 Nm^3/hr (145,000 SCFH). As a result of the rapidly changing flow, which was initially noticed by the increased noise at the flare, the methanol product became slightly cloudy.

Catalyst Performance

Operation at 2,600 Nm^3/hr (100,000 SCFH) with CO-rich gas had a duration of approximately 36 days. The performance indices at the beginning and at the end of the run were as follows:

	Start*	End
Date	4/16	5/21
CO conversion, %	10.7	4.8
Productivity, gmol/kg-hr	23.5	14.3
Equilibrium approach, ^oC	29	59

*Projected with linearized data to beginning of CO-rich run.

The rate of decline in catalyst activity during this run was steeper than experienced in the autoclaves or Lab PDU runs with CO-rich gas (see Section V).

However, the average methanol productivity over the 36-day period was approximately 19 g mol/hr - kg catalyst, resulting in an average production rate of 3.5 metric tons of methanol per day. The cumulative methanol production during the activity maintenance period was 125 metric tons.

Carbonyl and catalyst analyses. Analyses for carbonyls were conducted first when the plant reached steady state with CO-rich gas. Measurements made during April 17 and 18 indicated concentrations of carbonyls below the detectable limit. A second carbonyl survey was performed during May 7 with longer sampling periods to improve the detectable limits. Samples of methanol product and oil were also taken to check for iron contamination.

Slurry samples taken every other day were regularly shipped to APCI headquarters for preparation and analysis. The analyses determined the oxidation state of the catalyst (Cu^{+1}/Cu^{0}), crystal size, chemical composition (Cu^{+}/Zn), and different poisons (Fe, Ni, Cl^{-}, and S^{-}).

Temperature control. The slurry heat exchanger temperatures were closely monitored during the run to prevent high localized temperatures which could be detrimental to the catalyst activity. Early in the CO-rich run when conversions were high, the heat of reaction exceeded the overall heat loss from the slurry loop and the utility oil system operated in the cooling mode with inlet temperatures around 240°C. However, at the lower conversions experienced towards the end of the run, it was necessary to increase the utility oil temperature to maintain the reactor temperatures at 250°C (482°F). A maximum allowable temperature of 260°C (500°F) was established for the utility oil inlet, which limited the amount of heat input to the system.

Plant Shutdown and Final Inspection

The PDU completed the scheduled 40 days of syngas operation at 03:30 hours on May 21, and the planned shutdown of the plant commenced at 08:25 hours. The plant was brought down in a controlled manner, and final measurements of gas holdup under nitrogen and slurry density were then completed.

Following completion of the 40-day run the major equipment was opened and inspected. Unlike the shakedown run, an oil wash was not used following draining of the slurry to the prep tank. Therefore, the evidence left behind reflected residue in place during the run plus material deposited during the stop-flow/drain operation. The inspection was performed during the May 22-24, 1984 period.

The general appearance of the equipment and piping was good. Wet slurry sludge had settled in certain areas, and thin and uneven slurry films coated equipment and piping. However, there were no hard blockages or massive deposits.

It had been planned to try to recover and weigh all of the accumulated slurry, but this proved impractical. The deposits were too spread out, uneven, and often inaccessible. Therefore, estimates were made of the thickness of films and the volumes of sludge. Individual volumes were converted to solids using a nominal wet sludge density of 1.4 kg/liter (measured) and a solids content of 50 weight percent (measured 47.6 percent reduced = 52.8 percent oxide). From the examination and assessment, it was estimated that some 108 kg of reduced catalyst was deposited in the equipment and piping (19 percent of the original reduced charge). Another 22 kg of reduced catalyst was estimated to have been lost in slurry sampling (4.5 kg), filtering (16.3 kg), and in the product (0.9 kg.). This gave a total catalyst accountability of 129.4 kg reduced. This estimate is probably $\pm$ 25 percent, although it does compare well to an expected loss of 123.8 kg derived from the final nuclear density gauge reading and liquid inventory measurement. The breakdown of the residual catalyst inventory and losses is given in Table 3-7.

Table 3-7

LAPORTE INVENTORY SUMMARY - CATALYST "LOSS" ESTIMATES*

		Reduced Catalyst, Kilograms	
Loss in slurry filter changes (12 changes)		16.3	
Loss in slurry samples (41 samples)		4.5	
Reactor:	Bottom head	3.2	
	Tray bottom	0.2	
	Tray top	10.4	
	Walls	0.2	
	Top fill nozzle	0.9	
	Top head	0.9	
Primary separator:	Manway	0.9	
	Walls	36.3	
Slurry piping & dead volumes		4.5	
Intermediate separator:	Bottom flange	0.9	
	Walls	4.5	
Feed/product exchanger:	Inlet head	1.8	
	Outlet head	0.9	
	Tubes	40.0	
Product separator		0.2	
Liquid-liquid separator		0.5	
Slurry heat exchanger:	Inlet spool piece	0.9	
	Tubes	0.5	
Loss in MeOH product		0.9	
		129.4	± 25%

*Nearly all inspection estimates were based on estimated volume of sludge, bulk wet density of 1.4 kg/liter, and assumed solids content of 50 weight percent.