Section 1

EXECUTIVE SUMMARY

INTRODUCTION

Air Products and Chemicals, Inc. and Chem Systems Inc. have completed a 40-day run in the LaPorte LPMEOH Process Development Unit (PDU) with R71/OF12-26 catalyst. This work was part of the LaPorte experimental program in Task 6 of contract No. DE-AC22-81PC30019 with the U.S. Department of Energy. The objective of this run was to demonstrate short-term activity maintenance of the Liquid Phase Methanol Process with unbalanced (CO-rich) synthesis gas at the LaPorte PDU scale of operation. A secondary objective was to verify the feasibility of sustained operation in the liquid-entrained mode at the LaPorte PDU.

The operability of the LaPorte unit has been demonstrated during a 10-day shakedown run in March 1984.(3) Liquid-fluidized catalyst R71/OF12-26 completely attrited during this run as predicted from earlier tests in the Lab PDU at Fairfield.(4,5,6) Thus, the LaPorte PDU was proven reliable in both the liquid-fluidized mode and the liquid-entrained mode in a single run.

Catalyst R71/OF12-26, also designated EPJ-19LR, was developed by United Catalyst, Inc. Specifically for the Liquid Phase Methanol Process in the liquid-fluidized mode of operation. Earlier Lab PDU tests proved this methanol synthesis catalyst to be the best available candidate for liquid-fluidized operations although its attrition resistance was still inadequate for commercialization. However, once completely attrited, the resulting catalyst slurry became a productive material for liquid-entrained mode testing. It was thus decided to proceed to short-term activity maintenance testing at LaPorte using a slurry formed by attriting R71/OF12-26.

A run was planned with enough R71/OF12-26 catalyst reduced in the vapor phase such that a 30 weight percent slurry would result after full attrition of the catalyst extrudates. The initial part of the test was to be dedicated to obtaining conversion data on balanced gas at high space velocities. The remainder of the run (approximately 35 days) was to involve activity maintenance testing with CO-rich synthesis gas at constant operating conditions.

RUN SUMMARY

A total of 613.5 kilograms of catalyst was charged to the reactor on April 5-6, 1984. Reduction was completed by April 9 and circulation of Freezene-100 oil began on April 10. Balanced synthesis gas was introduced to the reactor on April 11. Catalyst attrition was extremely rapid. After 25 hours on synthesis gas, the fluidized bed had broken up and overflowed the reactor and, by 30 hours on stream, a slurry of approximately 29 weight percent oxide was obtained. The first 102.5 hours on synthesis gas involved balanced gas tests at high gas superficial velocities. On April 15, unbalanced synthesis gas containing 35 percent hydrogen, 51 percent carbon monoxide, 13 percent carbon dioxide and one percent inerts was introduced into the reactor and the activity maintenance period began. The nominal conditions for this period were as follows:

Reactor temperature, ^{o}C	250
Reactor pressure, kPa	5,400
Catalyst concentration, weight percent	27.5-23.3
Space velocity, liters/hr-kg catalyst	10,000-12,500

These conditions were maintained until May 21 when the unit was voluntarily shut down after accumulating 964.5 hours on synthesis gas. A brief summary of the major events during this 40-day run is presented in Table 1-1.

Table 1-2 summarizes the on-line time-averaged results obtained during this 40-day run. Four process variable data points were investigated during the early part of this test 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)

These variables scan results are summarized in Table 1-3.

Table 1-1

40-DAY LAPORTE RUN MAJOR EVENT SUMMARY

Date	Total Hours	Hours on Synthesis Gas	Event
4/05/85	0	0	409.1 kg R71/OF12-26 loaded
4/06/84	26.00	0	Add'l 204.5 kg R71/OF12-26 loaded
4/07/84	51.00	0	Began reduction with hydrogen
4/10/84	106.75	0	Reduction complete
	117.50	0	Freezene oil introduced
4/11/84	130.50	0	Introduced balanced gas
4/13/84	176.00	45.5	Condition at 5,400 kPa and Ug = 6 cm/sec complete
4/14/84	208.75	78.3	Condition at 5,400 kPa and Ug = 11 cm/sec complete
4/15/84	233.00	102.5	Condition at 5,400 kPa and Ug = 17 cm/sec complete; begin CO-rich gas
5/21/84	1,095.00	964.5	Run completed
	1,101.00	964.5	End of gas holdup study

The activity maintenance period with CO-rich gas can be summarized as follows:

	Initial		Final
Date	4/16	4/20	5/21
Hours on synthesis gas	100	236.5	964.5
CO conversion, percent	(10.7)*	9.5	4.8
Productivity, gmol/kg-hr	(23.5)	21.8	14.3
Equilibrium approach, °C	(29)	35	59

*Numbers in parenthesis are back-extrapolated projected to 100 hours on syngas.

In linear terms, if the decline in catalyst activity is measured with respect to time, the data show a 1.4 percent (relative) decrease in CO conversion per day. However, in order to evaluate the intrinsic performance of the catalyst the catalyst loss from the system has to be taken into consideration and the methanol production per unit weight of catalyst in the reactor should be utilized instead of CO conversion. In this manner, a decline in methanol productivity of one percent per day is obtained.

Results of catalyst analyses together with cumulative feed gas flows and cumulative methanol production are summarized in Table 1-4.

Table 1-2

LAPORTE PDU AVERAGED DATA SUMMARY FOR 40-DAY RUN

Date	Balance Period (hours)	Synthesis Hours on Stream	Feed Gas Type	Reactor Temp. (°C)	Reactor Press. (kPa)	Gas Velocity (cm/sec)	Space Velocity (l/kg-hr)	Slurry Conc. (wt. %)	CO Conv. (%)	MeOH Prod. (gmol/kg-hr)
4/11/84	5	10.5	B	250	5,380	5.7	2,400	1.0	40.0	7.0
4/11	4	14.5	B	250	5,380	6.0	2,770	5.9	39.2	8.8
4/12	10	25.5	B	250	5,370	5.4	3,210	15.0	40.5	10.9
4/14	22	76.5	B	250	6,430	11.6	11,000	29.4	28.8	30.0
4/15	21	101.5	B	250	5,480	17.0	14,400	28.7	19.5	27.0
4/16	11	129.5	U	250	5,420	10.3	9,390	26.9	10.4	23.5
4/16	7	140.5	U	250	5,420	10.6	8,910	27.2	11.3	21.7
4/17	8	148.5	U	250	5,410	10.7	10,000	27.5	9.9	23.6
4/18	5	186.5	U	250	5,380	10.6	11,100	25.1	9.3	22.5
4/20	24	236.5	U	250	5,370	10.5	10,200	26.3	9.5	21.8
4/21	24	260.5	U	250	5,380	10.3	10,300	26.4	9.6	22.1
4/22	19	279.5	U	250	5,400	10.5	9,710	26.3	9.4	21.3
4/25	27	340.5	U	250	5,400	10.3	10,300	26.1	9.1	20.4
4/27	33	389.5	U	250	5,400	10.5	10,900	25.8	8.7	21.0
4/28	24	428.5	U	249	5,400	10.5	10,400	26.1	8.6	20.4
5/01	25	485.5	U	250	5,400	10.6	10,800	25.9	8.0	19.4
5/02	24	524.5	U	250	5,400	10.5	10,900	25.6	7.7	19.3
5/03	24	548.5	U	249	5,400	10.5	11,000	25.1	7.8	19.6
5/04	24	572.5	U	249	5,400	10.6	10,900	25.2	7.5	19.0
5/05	23	596.5	U	249	5,400	10.6	11,100	25.1	7.7	19.2
5/06	24	620.5	U	249	5,410	10.6	11,200	25.0	7.4	18.9
5/07	24	644.5	U	250	5,410	10.6	11,400	24.9	7.2	18.7
5/08	14	658.5	U	250	5,400	10.7	11,400	24.8	7.1	18.4
5/09	14	692.5	U	250	5,410	10.7	11,600	24.6	6.7	18.1
5/10	24	716.5	U	250	5,400	10.6	11,500	24.4	6.5	17.8
5/11	24	740.5	U	250	5,400	10.5	11,600	24.4	6.6	17.5
5/12	24	764.5	U	250	5,400	10.5	11,900	24.2	6.4	17.6
5/13	24	788.5	U	250	5,400	10.5	11,900	24.2	6.3	17.4
5/14	24	812.5	U	250	5,400	10.4	12,000	24.0	5.9	16.3
5/15	24	836.5	U	250	5,410	10.4	12,100	23.9	5.7	15.9
5/16	24	860.5	U	250	5,400	10.5	12,200	23.9	5.5	15.6
5/17	24	884.5	U	250	5,400	10.5	12,300	23.7	5.4	15.3
5/18	24	908.5	U	249	5,400	10.6	12,500	23.6	5.2	15.0
5/19	24	932.5	U	249	5,400	10.5	12,600	23.4	4.8	14.7
5/20	24	956.5	U	250	5,400	10.5	12,500	23.3	4.6	14.3
5/21	8	964.5	U	251	5,400	10.5	12,400	23.3	4.8	14.3

Table 1-3

PROCESS VARIABLE SCAN SUMMARY
BALANCED GAS

Run No.	Synthesis Hours On Stream	Temperature (°C)	Pressure (kPa)	Space Velocity (Nl/kg-hr)	Gas Velocity (cm/sec)	Slurry Conc. (wt. %)	Fines In Reactor (%)	CO Conversion (%)	Approach to MeOH Equil. (°C)	MeOH Productivity (gmol/hr kg)
E-1A1	10.5	250	5,380	2,400	5.7	1.0	1.0	40.0	22.4	7.0
E-1A2	14.5	250	5,380	2,770	6.0	5.9	3.9	39.2	19.3	8.8
E-1A3	25.5	250	5,370	3,210	5.4	15.0	20.0	40.5	15.2	10.9
E-1C	101.5	250	5,480	14,400	17.0	28.7	100.0	19.5	41.1	27.0
E-1B	76.5	250	6,430	11,000	11.6	29.4	100.0	28.8	39.1	30.0
					UNBALANCED GAS					
E-1D	236.5	250	5,370	10,200	10.5	26.3	100.0	9.5	35.0	21.8

DISCUSSION AND CONCLUSIONS

The completion of the 40-day run in the LaPorte LPMEOH PDU was an important milestone in this program. From a mechanical point-of-view, this process development unit functioned excellently, not only in the liquid-fluidized and the liquid-entrained modes, but also in a period of rapid transition between the two modes of operation. Prior nearly flawless operation of the slurry pump and its mechanical seal system is particularly noteworthy.

Initial catalyst activity in the liquid entrained mode with both balanced and unbalanced gas was nearly as good as expected based on earlier Lab PDU and autoclave tests as well as model predictions. Prior experience with attrited R71/OF12-26 catalyst is limited and it is difficult at this point to explain the slight differences observed.

The rapid attrition of the catalyst experienced at the initiation of operations was a consequence of the high superficial gas velocities and was probably aggravated by the low bed expansions. The fouling of the slurry heat exchanger when the bed had attrited completely was likely a consequence of small catalyst pellets that elutriated from the reactor and settled at the exchanger surfaces. The heat exchanger thermowells were particularly fouled and gave erroneous low temperature readings. Higher superficial liquid velocities (more than 5 cm/sec in the reactor) completely eliminated the fouling problem.

The major issue in this test was catalyst activity maintenance with unbalanced gas and the resulting performance was not quite as good as anticipated. The buildup of metal poisons in the catalyst such as nickel explain the catalyst deactivation to a limited extent. Changes in copper valence states and crystal size were observed with time on stream. The relationship of these changes to catalyst activity, if any, cannot be fully determined at this time. The steeper decline in catalyst activity experienced at the LaPorte PDU when compared with earlier Lab PDU or autoclave runs may be explained at least partly, by the higher throughput and severity at which the LaPorte PDU was operated. Other factors in addition to catalyst poisoning or operating conditions, that may have influenced the deactivation rate include:

- Use of an attrited catalyst actually intended for liquid-fluidized operation.

- Unknown effect of external environment of the slurry recirculation loop.

Table 1-4

SUMMARY OF CATALYST ANALYSES AND CUMULATIVE FLOWS

HOURS ON SYNTHESIS GAS	IRON IN CATALYST (ppm)		NICKEL IN CATALYST (ppm)		CRYSTAL SIZE BY XRD (A)	Cumulative Space Velocity Nm3/Kg	Cumulative Methanol Productivity Kg/Kg cat.	Methanol Productivity * gmol/hr Kg
	XRF	AAS	XRF	AAS				
0.0	258	165	45	42	96	—	—	—
10.5	—		—		—	25.2	2.36	—
13.0	582	540	—	56	165	—	—	—
14.5	—		—		—	36.4	3.49	—
25.5	—		—		—	71.7	7.33	—
34.0	—		—		146	—	—	—
37.0	375		70		171	—	—	—
76.5	—		—		—	631.9	56.30	—
81.0	384		52		215	—	—	—
101.5	—		—		—	990.9	77.93	—
129.0	553		65		231	—	—	—
129.5	—		—		—	1240.9	98.98	23.5
140.5	—		—		—	1345.0	106.63	21.7
148.5	—		—		—	1423.2	112.67	23.6
179.0	633		69		249	—	134.83	(22.6)
186.5	—		—		—	1844.4	140.28	(22.5)
203.0	446	310	65	44	320	—	151.81	(22.3)
236.5	—		—		—	2356.2	175.22	21.8
260.5	—		—		—	2603.7	192.23	22.1
279.5	—		—		—	2795.6	205.20	21.3
296.0	482		67		357	—	215.99	(21.1)
340.5	—		—		—	3426.6	245.07	20.4
344.0	553		86	51	371	—	247.43	(20.4)
389.5	—		—		—	3959.1	278.04	21.0
392.0	916	650	75	60	267	—	279.67	(21.0)
428.5	—		—		—	4364.5	303.49	20.4
485.5	—		—		—	4982.5	338.88	19.4
486.0	517		70		357	—	339.19	(19.4)
524.5	—		—		—	5400.9	363.03	19.3
533.0	510		87	83	361	—	368.37	(19.4)
548.5	—		—		—	5673.0	370.12	19.6
572.5	—		—		—	5935.0	392.73	19.0
580.0	606		110		371	—	397.35	(19.1)
596.5	—		—		—	6200.3	407.53	19.2
620.5	—		—		—	6468.7	422.02	18.9
644.5	—		—		—	6741.5	436.41	18.7
656.0	576	302	120	94	342	—	443.20	(18.5)
658.5	—		—		—	6901.8	444.68	18.4
692.5	—		—		—	7297.2	464.35	18.1
704.0	572		128		342	—	470.92	(18.0)
716.5	—		—		—	7574.0	478.87	17.8
740.5	—		—		—	7852.8	491.54	17.5
750.0	584	401	130	112	362	—	496.88	(17.5)

Table 1-4 (Continued)

HOURS ON SYNTHESIS GAS	IRON IN CATALYST (ppm) XRF	IRON IN CATALYST (ppm) AAS	NICKEL IN CATALYST (ppm) XRF	NICKEL IN CATALYST (ppm) AAS	CRYSTAL SIZE BY XRD (A)	Cumulative Space Velocity Nm3/Kg	Cumulative Methanol Productivity Kg/Kg cat.	Methanol Productivity * gmol/hr Kg
764.5	—		—		—	8137.2	505.04	17.6
788.5	—		—		—	8422.2	518.41	17.4
812.5	—		—		—	8709.3	530.94	16.3
822.0	597		150		368	—	535.79	(16.2)
836.5	—		—		—	9000.5	543.20	15.9
860.5	—		—		—	9293.6	555.24	15.6
870.0	646	397	—		368	—	359.91	(15.5)
884.5	—		—		—	9588.4	567.04	15.3
908.5	—		—		—	9887.9	578.59	15.0
920.0	615		157		348	—	583.41	(14.9)
932.5	—		—		—	10190.0	589.91	14.7
956.5	—		—		—	10440.5	600.90	14.3
964.0	649	394	180	137	362	—	604.33	(14.3)
964.5	—		—		—	10588.7	604.56	14.3

* Parenthesis Indicate Interpolated Data

- Effect of the liquid media on the catalyst surface properties.
- A less than perfect catalyst reduction.

It is not known at this time whether any of these postulations actually influenced activity maintenance.

RECOMMENDATIONS

Another activity maintenance run should be conducted in the LaPorte LPMEOH PDU, but only after several metallurgical changes are made to the unit to minimize the opportunity to form iron and nickel carbonyls. Furthermore, a series of tests should be performed in smaller laboratory units to verify optimal operating conditions and procedures prior to initiating another LaPorte PDU run. Among the points which require investigation are the following:

- Determining whether operating at high methanol productivity conditions causes rapid catalyst deactivation.

- Simulating the slurry recirculation loop conditions for possible deactivation effects.

- Optimizing reduction procedures at reasonable catalyst loadings when starting with powdered catalyst.

- Determining which of the several available catalyst candidates is best suited for liquid-entrained operation at reasonable slurry concentrations.

Since the 40-day run conducted during April-May 1984 has demonstrated the feasibility of operating with 25-30 weight percent catalyst concentrations in the liquid-entrained mode and has achieved acceptable methanol productivities during the early portion of the run, the main objective during the next stage of development must be to sustain catalyst activity over a reasonable catalyst lifetime. The steps outlined above should help to achieve this goal.