Copper and zinc oxide crystallite size grew with time but at a much slower rate than in earlier PDU operations. As mentioned earlier, crystallite growth is conventionally associated with thermal effects. Performance comparison to autoclave suggests convincingly that there is good heat removed in the PDU reactor, so that the crystal growth seen in earlier PDU runs could be the result of other effects. Poisons were absent in Run E-3. Chemical analyses show essentially no pickup of any of Fe, Ni, Cℓ and S. The lack of poisons may have resulted in the slow crystal growth.

The BET surface area analyses have a substantial scatter due to difficulties experienced in washing the samples absolutely clean. A general decline in BET surface area is obvious. At the end of the run the surface area was decreased to 70 m^2/gm range from a starting surface area about 120 m^2/gm.

In summary, the catalyst analyses confirm that there were no poisons such as carbonyls, Cl and S entering the system as was also indicated by the wet chemical analyses of the reactor feed. The slow increase in crystal sizes and slow decrease in BET surface area observed in this run appear to be the characteristics of a successful run with a slow deactivation rate.

A catalyst trap was installed upstream of the suction snubber on the 01.10 feed compressor to provide further information on trace contaminants in the fresh makeup feed gas in addition to the wet chemistry analyses. The trap consisted of 114.3 gm (0.25 lb) of reduced catalyst (R71/0F12-26) loaded into a short length of 1-in. schedule 40 stainless steel pipe and installed off the fresh feed piping using 1/4-in. stainless steel tubing for inlet and outlet nozzles. Approximately 2.0 Nm^3/hr (70 SCFH) were bled from the fresh feed piping to the inlet nozzle of the catalyst trap. High-pressure steam (615 psia) was used to maintain the trap at an elevated temperature. Gas flow through the trap was maintained for the entire 948 hours of operation under synthesis gas.

The catalyst trap provided valuable information on the quality of the makeup feed gas. Postrun analysis of the trap yielded an indication of the type and quantity of impurities from the makeup feed to which the catalyst in the slurry loop was exposed during the run. The information from the postrun analysis of the trap provided a check on the wet chemistry analyses performed on the synthesis gas feedstock to the PDU.

Table VI-7 displays the results from the analyses on the catalyst in the trap. The small accumulation of Fe and Ni on the catalyst is consistent with the results of wet chemistry analyses and the analyses of catalyst samples from the slurry loop (Table VI-7). The increase of approximately 250 ppmw of chloride on the catalyst in the trap appears high, but it corresponds to an average chloride concentration of only 10 ppbv in the makeup feed during the entire run. This result confirmed the low or undetectable chloride levels on the slurry samples taken throughout the run. In view of the high catalyst activity and the good activity maintenance achieved in Run E-3, it is believed that the poisons in the makeup feed were either absent or well below the threshold concentrations that would impede the performance of the catalyst.

TABLE VI-7

LAPORTE LPMEOH PDU
CATALYST TRAP ANALYSES FOR RUN E-3

CATALYST TYPE	:	114.3 gm (0.25 lb) of reduced R71/OF12-26
TEMPERATURE	:	200°C (392°F)
PRESSURE	:	930 kPa (135 psia)
GAS FLOW	:	2.0 Nm^3/hr (70 SCFH)
ON-STREAM TIME	:	948 Hrs.

Sample Location	XRD, Å		Quantitative Analysis, ppmw			
	Cu	ZnO	Fe	Ni	S	Cl
Fresh Oxide	-	-	178	31.0	<0.1%	<13
Gas Inlet	115	86.7	161	<17.5	<0.2%	245
Gas Outlet	-	-	256	40.9	<0.1%	256

	Fe, ppbv	Ni, ppbv	Cl, ppbv
Equivalent Concentration In Makeup Feed	2	-	10

Figure VI-6 compares the boiling point distribution curve for fresh Freezene-100 oil and the 'used' oil at the end of Run E-3. The shift of the curve to the right indicates that some of the lighter components of the oil were removed during PDU operation. The effect, if any, of this change in oil properties is still under investigation.

Postrun Inspection

Postrun inspection showed that all process equipment was in good condition and free of blockage. The bottom head and tray of the 27.10 reactor were dropped for inspection. The bottom head, reactor wall, gas and liquid spargers, and bubble caps were coated with only a thin film of slurry. The primary and intermediate vapor/liquid separators were inspected and found to be in good condition. Tubes in the feed/product exchanger had an accumulation of slurry approximately 0.16 cm (0.06 in.) thick at the inlet to the exchanger. The buildup had deposited only through the first 90 to 120 cm (3 to 4 ft) on the tubeside of the feed/product exchanger.

Table VI-8 gives the catalyst inventory summary and carry-over estimate from the postrun inspection. During the run, an estimate of 0.45 kg/day (1 lb/day) catalyst loss as carry-over from the primary separator was used in tracking the catalyst and oil inventory. The estimated 14.1 kg (31 lb) of catalyst (oxide-based) found downstream of the primary V/L separator agrees very well with the initial estimate of 0.45 kg/day (1 lb/day) carry-over loss over the 40 days of operation.

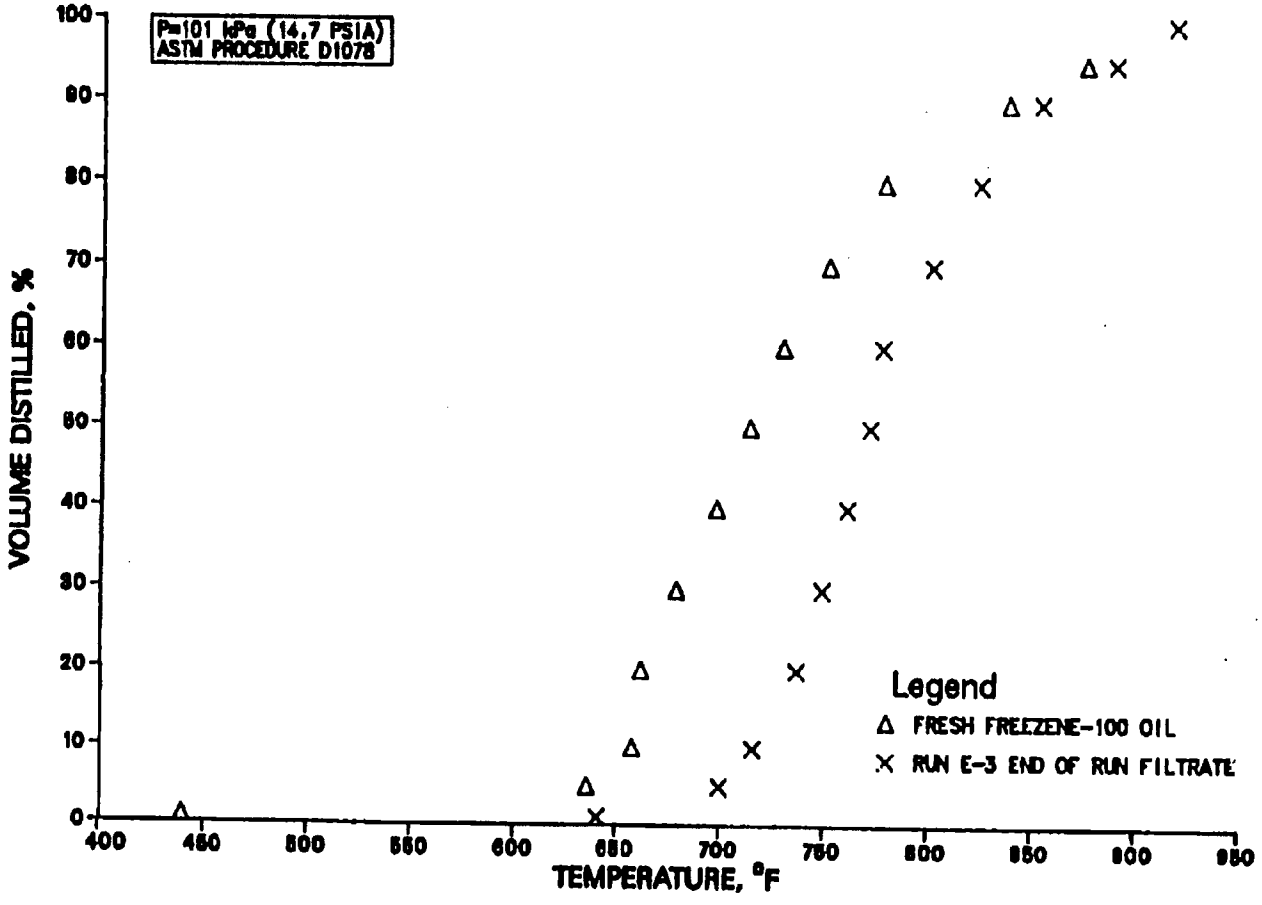

Figure VI-6. LaPorte LPMEOH PDU Change in Boiling Point Distribution for Freezene-100 Oil

TABLE VI-8

LAPORTE LPMEOH PDU

CATALYST INVENTORY SUMMARY AND CARRY-OVER ESTIMATE

	Catalyst Found During Postrun Inspection		Estimated Catalyst Carry-over from 27.13
	Kg (lb) of Black Catalyst	Kg (lb) of Red Catalyst	Kg (lb) of Red Catalyst
Reactor			
Bottom Head	1.13 (2.5)		
Walls & Tray	0.45 (1)		
Primary V/L Separator			
Manway	0.45 (1)		
Walls	3.63 (8)	3.63 (8)	
Interm. V/L Separator			
Bottom Head	1.13 (2.5)		1.13 (2.5)
Oil			
Feed/Prod. Heat Exch.	3.63 (8)		3.63 (8)
Condensed Oil Filter			
Filter A (5/23/85)			4.54 (10)
Filter B (6/15/85)	2.49 (5.5)		2.49 (5.5)
Total	13.0 (28.5)	3.63 (8)	11.80 (26) => 13.90 kg oxide (31 lb* oxide)

*Estimate based on 190 liters (50 gal) oil and 0.1 wt% solid concentration. This number agrees with the 0.45 kg/day (1 lb/day) catalyst loss used in the catalyst inventory estimate.

VII. CONCLUSIONS AND RECOMMENDATIONS

Two runs, E-2 and E-3, were made in the LaPorte LPMEOH PDU under Task 10 of this program, Liquid-Entrained (slurry) Operation. A commercially available catalyst powder was used in both runs. The liquid-entrained operations have provided valuable experience for the operations and engineering staff on handling catalyst slurry and have contributed significantly toward demonstrating LPMEOH technology at the LaPorte PDU scale. The major accomplishments of this task are summarized as follows:

- Slurry preparation and handling methods were demonstrated at slurry concentrations above 40 wt%.

- The mechanical performance of the LaPorte LPMEOH PDU was excellent, achieving 96 to 100% on-stream factors with slurry concentrations ranging from 25 to 49 wt%.

- Catalyst powder was successfully activated with the in-situ reduction technique at 25 wt% slurry loading.

- As the result of selective metallurgical upgrades and chemical cleaning, catalyst poisons were reduced to the level at which the intrinsic catalyst deactivation rate could be measured.

- A slow rate of catalyst deactivation was achieved with CO-rich gas over the 40-day operation of Run E-3. The 0.28%/day decline in methanol productivity observed in Run E-3 was a significant improvement over the 1.1%/day decline observed during the earlier activity maintenance run (Run E-1) and is comparable to the best results achieved in autoclave reactors.

- The ability to maintain catalyst activity after an extended outage was demonstrated during Run E-3.

- A liquid product with a methanol purity of 96 wt% was produced using both balanced feed gas and CO-rich feed gas.

Although a great deal of progress was made in demonstrating the liquid-entrained mode of operation, the runs also revealed that more research must be conducted if the LaPorte LPMEOH reactor is to achieve the performance of the bench-scale reactors at high slurry loadings. A laboratory program conducted following Run E-2 found that inadequate catalyst activation at LaPorte was a contributor to the lower than predicted performance at the high solids loading. Changes in the reduction procedure were identified to remedy this problem. Mass transfer limitations may also have contributed to the reduced catalyst performance during Run E-2, but its existence would have been masked by the inadequate catalyst activation. A second high slurry concentration run at the LaPorte LPMEOH PDU will be necessary to isolate this effect after the catalyst activation procedure is modified.

Hydrodynamics of a bubble column reactor deserve further study to understand the cause of the axial solid density profile observed in the bottom section of the reactor while operating with high slurry concentrations. Slurry properties such as viscosity and surface tension, which may affect the reactor performance and hydrodynamics, should be determined at operating conditions.

The catalyst deactivation rate measured during the 40-day activity maintenance run (E-3) reflected only early life trends in view of the 2 to 3 years of expected catalyst life. It is anticipated that the deactivation rate will decrease with time. Longer-term runs are necessary in order to measure this effect accurately.

Removal of trace poisons in the reactor feed is critical to the catalyst life. Research efforts should be continued to identify effective adsorbants for various poisons removal. In addition, the relationship(s) between the concentrations of poisons and the catalyst life need to be determined for process optimization.

VIII. REFERENCES

1. Topical Report "LaPorte LPMEOH PDU Renovation, Installation, and Shakedown (Run F-2)," prepared by Air Products and Chemicals, Inc. for the U.S. DOE under Contract No. DE-AC22-81PC30019, October 1985.

2. Topical Report "LaPorte LPMEOH™ PDU 40-Day Run with R71/OF12-26 Catalyst," prepared by Chem Systems Inc. for the U.S. DOE under Control No. DE-4622-81PC30018, December 1984.

3. Akita K. and Yoshida, I&EC Process Design Development, 7B (1973).

4. Shah, A.M. et al., "Thermal Hydrocracking of Athabasca Bitumen: Correlation of Reactor Voidage in Vertical Two-Phase Flow," CANMET Report 77-48, December 1976.

5. "Catalyst Activity and Life in Liquid Phase Methanol," presented by D. M. Brown, P. Rao, T. H. Hsiung, and M. I. Greene at the 10th Annual EPRI Clean Liquid and Solid Fuels Contractors' Conference, Palo Alto, California, 23-25 April 1985.

APPENDIX A

CHEMICAL WASH OF LAPORTE LPMEOH PDU

The wash sequence was divided into seven sections, each section corresponding to a piping/equipment circuit in the LaPorte LPMEOH PDU. Listed below are the equipment/piping involved and the associated wash solution(s) used. A listing of the wash solutions is given in Table A-1.

Wash I-A -- Selected Areas of 01.10/01.20 Compressor

Equipment/Piping Involved:

- 01.10 1st-Stage Suction Bottle
- 01.10 Intercooler and Piping up to and including 2nd-Stage Suction Bottle
- 01.22 Outlet Piping up to and including 01.20 Suction Bottle
- 01.14 & 01.24 Compressor Recycle Coolers

Wash Performed:

1. Metex Wash

2. Flush with demineralized water until conductance < 60 micromhos

Wash I-B -- Selected Areas of 01.10/01.20 Compressor

Equipment/Piping Involved:

- 01.10 1st-Stage Suction Bottle
- Piping from 01.10 Intercooler up to and including 2nd-Stage Suction Bottle
- 01.22 Outlet Piping up to and including 01.20 Suction Bottle
- 01.14 & 01.24 Compressor Recycle Coolers
- 01.10 1st-Stage Discharge Bottle

TABLE A-1

LAPORTE LPMEOH PDU
CHEMICAL WASH SOLUTIONS

Detergent Wash (Oil/Catalyst Removal)

3 wt% Caustic, 1 wt% Trisodium Phosphate,
1 wt% Sodium Metasilicate, 0.1 wt% Triton X-100
Non-ionic Detergent in Demineralized Water
(6 hr. circulation)

Demineralized Water Flush

Citric Acid Wash (Rust Removal)

Acid Step - 3 wt% Citric Acid with Inhibitor
pH Adjusted to 3.0-3.5 with Ammonia
(4 hr. minimum circulation at 150°F)

Chelating Step - 0.5 wt% Citric Acid Addition
pH Adjusted to 8.5-9.5 with Ammonia
0.5 wt% Sodium Nitrite Addition
(4 hr. minimum circulation at 150°F)

Demineralized Water Flush

Metex Wash (Nickel Removal)

Demineralized Water with Metex Solid and Liquid Component
pH Adjusted with Caustic
(1/2 hr. circulation)
Demineralized Water Flush

Passivation Flush

1 wt% Caustic, 0.5 wt% Sodium Nitrite (2 hr. circulation)

Wash Performed:

1. Citric Acid Wash with Sodium Tolytriazol used as inhibitor

2. Passivation Flush

Notes:

- Inspection of the piping on the inlet to the 01.20 suction showed a black coating which could be removed by rubbing the surface.
- 01.10 Intercooler not included due to concerns over compatibility of ammonia (in Metex) with Admiralty brass materials.
- 01.10 1st-stage discharge bottle washed in mix tank.

Wash II-A -- Utility Oil System

Equipment/Piping Involved:

- Utility Oil System

Wash Performed:

1. Detergent Wash

Wash II-B -- Utility Oil System

Equipment/Piping Involved:

- Utility Oil System

Wash Performed:

1. Metex Wash

2. Flush with demineralized water

Notes:

- Metex solution from Wash I-A used to provide sufficient inventory for circulation.

Wash III-A -- Compressor Discharge Circuit

Equipment/Piping Involved:

- 01.10 2nd-Stage Discharge Bottle through 01.13 Surge Tank, overhead through 21.10 Shellside to HV-150
- 01.20 Discharge Bottle
- 01.14 & 01.24 Compressor Recycle Coolers and associated piping

Wash Performed:

1. Citric Acid Wash with 0.4 wt% Rodine 31-A used as inhibitor.

2. Passivation Flush

Notes:

- Coating found in bottom of 01.13 (stagnant flow area).

Wash IV-A -- Feed Gas/Reduction Gas/Back End of Plant

Equipment/Piping Involved:

- Feed Gas from Paymeter Area and CO_2 System to 01.10 Suction
- Reduction Gas Circuit
- 21.30 Cooler through 22.10 Product Separator to 22.12 Demister and 01.22 Filter
- 22.11 Degasser through 22.15 Separator, 10.56 & 10.52 Pumps, 22.15 Filters to Seal Flush Connection at 10.50 Pump

Wash Performed:

1. Citric Acid Wash with 0.4 wt% Rodine 31-A used as inhibitor.

2. Passivation Flush

Notes:

- Debris found in suction to 01.10, 22.10, 22.15, 22.51 A&B.
- 22.10 and 22.15 sandblasted and wiped with oil to protect surface.

Wash V-A -- Slurry Loop/Prep Tank Circuit

Equipment/Piping Involved:

- Slurry Loop (27.10, 10.50, 21.20, 27.13)
- Overhead from 27.13 through 21.10 Tubeside to 27.14
- 28.30 Slurry Prep Tank and Associated Transfer Lines to/from Slurry Loop

Wash Performed:

1. Detergent Wash

2. Flush with demineralized water

Notes:

- Detergent from this circuit transferred to 28.20 Oil Storage Tank (Wash VI-A).

Wash V-B -- Slurry Loop/Prep Tank Circuit

Equipment/Piping Involved: Same as Wash V-A

Wash Performed:

1. Citric Acid Wash with 0.3 wt% Rodine 31-A used as inhibitor. (4 hr. circulation at 150°F)

2. 0.25 pH wt% sodium nitrite added at low pH (4 hr. circulation at 150°F)

3. Neutralized with liquid caustic until pH > 6.0, then drained

4. Citric Acid Wash with 0.4 wt% Rodine 31-A used as inhibitor

Notes:

- Debris in bottom of 28.30, 27.14, 21.10 heads.
- Coating on 27.13 manway.
- 28.30 hydroblasted with demineralized water, sandblasted, wiped with oil to protect surface.

Wash VI-A -- Oil Storage Tank Circuit

Equipment/Piping Involved:

- 28.20 Storage Tank
- Line from 10.52 to 27.13

Wash Performed:

1. Detergent Wash

2. Flush with demineralized water

Notes:

- Detergent for this circuit transferred from Slurry Loop Circuit (Wash V-A).

Wash VI-B -- Oil Storage Tank Circuit

Equipment/Piping Involved:

- 28.20 Storage Tank
- Line from 10.52 to 27.13

Wash Performed:

1. Citric Acid Wash with 0.4 wt% Rodine 31-A used as inhibitor

Notes:

- Debris in bottom of 28.20.
- 28.20 hydroblasted with demineralized water, sandblasted, wiped with oil to protect surface.

Wash VII-A -- Solvent Wash of PDU

Equipment/Piping Involved:

- Equipment involved in Wash III, IV, V, VI except:

- 28.30 Slurry Prep Tank
- 28.20 Process Oil Storage
- 22.10 Product Separator
- 22.11 MeOH Degasser (filled and drained separately)
- 22.15 Low-Pressure Liquid-Liquid Separator

Wash Performed:

1. Solvent wash with ethylene glycol n-butyl ether (filled, soaked overnight, 1/2 hour circulation through isolated circuits)

2. Flush with demineralized water

APPENDIX B

APRIL 1985 METALLURGICAL CHANGE-OUT

Following the March 1985 carbonyl survey operation, a decision was made to upgrade the metallurgy of the slurry loop of the LaPorte LPMEOH PDU to minimize metal carbonyl generation during operation on CO-rich gas.

Previous laboratory experience under this program indicated success using Type 316 stainless steel material. Literature was also available indicating comparative resistance among various alloys to carbon monoxide attack. The conclusion drawn from this information was that steel alloys display increasing resistance to carbon monoxide attack as the chromium content is increased. On this basis, Type 304 stainless steel was viewed to be superior to Type 316 stainless steel in this application. Further, Type 310 stainless steel would be most preferred; however, limitations on the availability of this material were recognized.

Each component of the slurry loop was evaluated for upgrade, and the following scope of work was established and implemented:

Piping

For straight length piping, pipe elbows and forged fittings, Type 304 stainless steel was selected. In replacing the ANSI flanges it was necessary to upgrade the pressure rating class from 600 to 900 psi due to the change in metallurgy. All of these new stainless steel components were immersed in a 50% nitric acid solution and rinsed with demineralized water to enhance the protective chrome oxide surface layer.

Valves

Type 316 stainless steel was found to be the most prevalent upgrade material for all valve manufacturers. All replacement valves as indicated below were fabricated of this material.

The Mogas ball valves in critical shutoff service on the slurry pump suction and discharge could not be replaced in exact duplicate; however, similar valves with interchangeable 316 stainless steel internals were acquired from Ashland Petroleum Company. The original 1-1/4% Cr - 1/2% Mo body components were used to house the newly acquired valve internals. Internal surfaces of the body components were coated with 310 stainless steel material applied by a plasma-arc metal spray process.

A less critical shutoff service on the slurry inlet to the reactor (valve #340-S) was satisfied by replacement with a readily available gate valve of more standard construction. A hard facing of Stellite #6 alloy was applied to the disc and seat of this valve as a protection against galling in service and for resistance to potential abrasive action of slurries.

Smaller manual block valves required for tight shutoff service in the slurry sampling area were replaced with globe valves of standard manufacture. Operating experience with this slurry and refinements to the slurry sampling layout gained through 1984 operations supported this change from the plug valve design originally specified in this service.

The original low-point drain valves for transferring slurry out of the system were isolated from the operating system by modifying their positions to being just downstream of the new gate valves. In this way, the desirable features of the plug valve were retained, while the process was normally isolated from plug valve material of construction.

Equipment Details

A plasma arc spray process using 310 stainless steel was employed to coat the process-wetted surfaces of several carbon or low-alloy steel components, which could not be reasonably replaced. The items in this category include:

- The 10.50 Slurry Pump casing and hub disc. Although a full liner insert of a 28% chrome alloy steel is assembled into this casing, a process wetted surface behind this liner experiences minimal flow.

- The heads and tubesheet of the 21.20 Slurry Heat Exchanger.

- The body components of Mogas valves, NV-161 and NV-330.