APPENDIX A

EXOTHERM PROBLEM AND SOLUTION

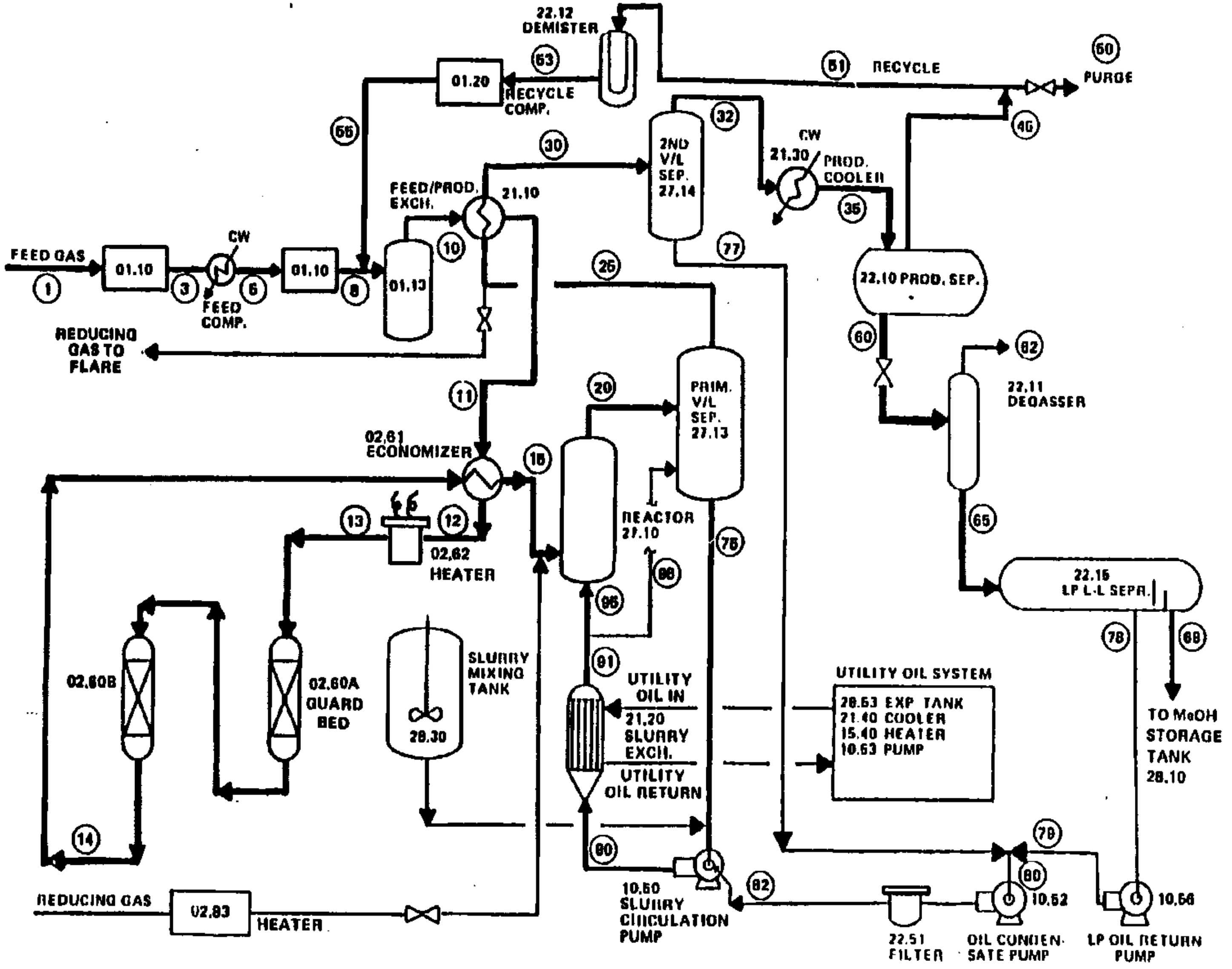
During December 1983, precommissioning of the LaPorte LPMEOH PDU progressed to the point where the unit was ready for fully integrated test operation with synthesis gas. At that time it was necessary to prove the feed gas blending capabilities and the analytical functions of the data acquisition system, as well as perform a final check for circuit-to-circuit leakage that would not have been apparent during previous pressure testing on nitrogen alone. The experimental program also called for a set of two-phase gas holdup data on the reactor system, without catalyst in place. These needs were consolidated in tests conducted before methanol synthesis operation was begun.

Exotherm Event #1

On 10-11 December 1983, the PDU was heated up with a recycling flow of nitrogen. During this test, the ability of the utility oil system to compensate for heat leak was marginal. (During normal methanol synthesis operation, the heat of reaction assists in overcoming heat leak.) To facilitate the commissioning test activities, additional heat input was provided by bypassing the economizer exchanger in the carbonyl removal system and providing a higher temperature gas feed to the reactor. A simplified process flowsheet of the LaPorte LPMEOH PDU at this time is given by Figure A-1. The additional heat input required the electric preheaters in the carbonyl removal system to operate hotter than normal.

Hydrogen was introduced into the unit on 10 December as the recycling nitrogen was slowly purged off. After 2 days of successful checkout with an 80% hydrogen, 20% nitrogen mixture, full synthesis gas (hydrogen, carbon monoxide, carbon dioxide) was blended for the first time, and added to the recycling hydrogen-nitrogen stream. During the initial hours of this feed gas transfusion process, the carbon monoxide took longer than expected to be indicated on the process analyzer sample point located at the exit of the carbonyl removal beds. When the carbon monoxide was detected, the apparent concentration was low.

FIGURE A-1
SIMPLIFIED PROCESS FLOWSHEET FOR LAPORTE LPMEOH PDU – ORIGINAL CONFIGURATION



At that time, the accuracy of the process analyzers was questioned. It was decided to modify the transfusion procedure by shutting off the recycle gas flow and allowing the freshly blended feed gas stream to pass through the system on a once-through basis. This would introduce a more definitive syngas composition to the reactor.

The results of this action were sharp and unexpected. There was a change in the temperature profile across the carbonyl guard beds. This area had previously exhibited a temperature drop due to heat leak. Under the new flow condition, the temperature at the outlet of the two beds increased in relation to the inlet bed temperature. The temperature at the mid-point of the two-bed system subsequently exceeded the temperature of the first bed. It was apparent that an exothermic reaction was occurring. The feed gas flow was subsequently stopped and the system was depressurized. The thermal inertia of the guard beds, however, caused a high temperature gas wave to proceed through the beds. The dial gauges on the bimetallic thermometers installed in this area exceeded their 550°C (1,000°F) range.

The operating conditions around the carbonyl removal system and a summary of observations are provided in Tables A-1 and A-2. In the initial review, it was concluded that the hot alumina adsorbent material in the carbonyl guard beds had allowed reactive conditions to occur. One theory was that rust particles from the newly assembled PDU had accumulated on the alumina and had been effectively reduced by the hydrogen to produce an active catalyst for the Fischer-Tropsch and/or Boudouard reactions. A second theory was that Freezene-100 oil, which had earlier entered this area by error, had remained absorbed by the alumina and cracked to lighter components upon exposure to higher process temperatures.

A visual inspection of the carbonyl guard bed system showed no evidence of damage from the temperature excursion; this was confirmed by the results of dimensional checks and metallurgical analyses performed on the vessels. After the alumina adsorbent material was emptied from the

TABLE A-1

EXOTHERM EVENT #1 - 12 DECEMBER 1983

Operating Conditions of Front End Preheat Train

Temperature: 382 to 388°C (720 to 730°F) (321-stainless steel heater sheath temperatures are estimated to have reached 482 to 538°C (900 to 1,000°F) at this time)

CO Partial Pressure: 1,830 kPa (265 psia) (system pressure was approximately 6,310 kPa (915 psia))

Immediate Effects Noted

- An exotherm caused gas temperatures to rise significantly above 538°C (1,000°F). Gas temperatures of 649 to 760°C (1,200 to 1,400°F) were estimated.
- Liquid hydrocarbon products were collected in downstream product recovery equipment.

Follow-up Evidence Collected

- Carbon powder was found throughout the alumina in the carbonyl removal beds.
- Analysis of the carbon powder revealed significant magnetite (Fe_3O_4).
- Metallurgical examinations of coupons taken from the carbonyl removal bed vessels revealed the vessels had not exceeded 649°C (1,200°F).
- The liquid hydrocarbon products collected during the event were analyzed and characterized as hydrocracked oil rather than Fischer-Tropsch products.

TABLE A-2

CHRONOLOGY OF EVENTS OF 12-13 DECEMBER 1983

Time	Guard Bed Temp. In/Out °C (°F)	Guard Bed Inlet Flow Nm^3/h (SCFH)	Make-Up Analyzer H_2/CO Mol%	Recycle/ Purge H_2/CO Mol%	Comments
1730	313/~413 (720/~650)	1,580 (60,000)	58/21	66/0	CO-rich make-up gas (35 mol% H_2, 51 mol% CO, 13 mol% CO_2, 1 mol% N_2) first brought into PDU @ 265 Nm^3/h (10,000 SCFH). Remained relatively constant unless noted.
2000	384/ - (724/ -)	1,580 (60,000)	56/28	45/tr	First CO indication on recycle/purge analyzer sample point.
2145	385/ - (725/ -)	1,580 (60,000)	60/0	43/10	CO make-up shut off for ~5 minutes to check make-up process analyzer.
2215	385/ - (725/ -)	1,580 (60,000)	0/75	43/15	H_2 make-up shut off for ~5 minutes to check make-up process analyzer.
0005	388/ - (730/ -)	265 (10,000)	42/58	43/19	Recycle flow shut off. Only CO-rich make-up. Gas heaters off.
0025	- / - (- / -)	265 (10,000)	42/58	41/24	Guard bed feed 42 mol% H_2, 55 mol% CO. Guard bed exit 27 mol% H_2, 40 mol% CO. Evidence of liquids in guard bed exit sample line.
0040	<316/ - (<600/ -)	265 (10,000)	-/-	-/-	
0100	- / - (- / -)	265 (10,000)	-/-	-/-	Guard bed exit 14 mol% H_2, 38 mol% CO.
0115	333/399 (632/750)	265 (10,000)	-/-	-/-	Temperature between guard beds ~427°C (~800°F). Make-up gas stopped. Plant depressurization begun. Compressor shut off.
0200	- /460 (- /860)	- (-)	0/0	-/-	Plant pressure 3,550 kPa (515 psia). Compressor restarted, N_2 brought into hold pressure. Upon notice of heat wave, depressurization resumed.
0215	- />538 (- />1000)	- (-)	0/0	-/-	Plant pressure 2,170 kPa (315 psia). 10.50 pump off.

beds and a hydroblast of these vessels was completed, the commissioning program resumed.

Exotherm Event #2

During the week of 12 December, final calibration was completed on the nuclear density gauge, enabling two-phase gas holdup studies to be conducted in a pure nitrogen mode by 17 December. These tests were uneventful. A CO-rich make-up feed gas was blended and gradually introduced into recycling nitrogen during the early morning hours of 18 December. During the initial hour of this syngas operation, hydrogen was the first new feed component to appear on the process analyzer. Again, the temperature profile across the carbonyl removal beds (now empty) began to show a temperature increase. The unit was immediately shut down, before the exotherm could establish any momentum. Depressurization was slowed by a blockage of carbon powder, causing a high pressure differential between the feed and reactor circuits. The operating conditions and a summary of observations made of this second exotherm event are presented in Tables A-3 and A-4.

The shutdown inspection revealed the presence of light carbon powder within the empty guard bed vessels and excessive carbon deposition upstream in the electric heater. This suggested that high temperature, not alumina, was the prime cause of the exothermic reaction. Expert opinion was solicited from various sources to obtain industry experience with similar process conditions. This review identified a series of potential reactions that could be occurring in this system. A list of these reactions is given in Table A-5. In particular, the information available at this time indicated that metal dusting, or carburization of the 321-stainless steel heater sheaths in the presence of carbon monoxide, could provide a catalytic surface for several of the exothermic reactions.

TABLE A-3

EXOTHERM EVENT #2 - 18 DECEMBER 1983

Operating Conditions of Front End Preheat Train

Temperature:	404°C (760°F) (Heater sheath temperature approximately 482°C (900°F))
CO Partial Pressure:	3,000 kPa (435 psia) (system pressure was 6,310 kPa (915 psia))

Immediate Effects Noted

- A mild exotherm was detected early; gas temperatures did not exceed 416°C (780°F).
- Pressure drop between the empty carbonyl removal beds and the reactor rose rapidly to over 2,170 kPa (315 psi).
- Gas analyses indicated increasing CO_2 and CH_4 concentrations in the recycling gas over the period of the event.

Follow-up Evidence Collected

- Carbon powder was found caked on elements of the carbonyl removal system electric heater.
- Analysis of the carbon powder revealed the presence of iron; small amounts of nickel and chrome were also detected in samples taken around the heater elements.
- No obvious evidence of pitting was noted on the 321-stainless steel heater sheaths.

TABLE A-4

CHRONOLOGY OF EVENTS OF 18 DECEMBER 1983

Time	Guard Bed Temp. In/Out °C (°F)	Guard Bed Inlet Flow Nm^3/h (SCFH)	Make-Up Analyzer H_2/CO Mol%	Recycle/ Purge H_2/CO Mol%	Comments
0445	404/327 (760/620)	1,845 (70,000)	-/-	-/-	CO-rich make-up gas (35 mol% H_2, 51 mol% CO, 13 mol% CO_2, 1 mol% N_2) first brought into PDU. Temperature between guard beds 343°C (650°F).
0530	406/332 (762/630)	1,055 (40,000)	38/64	6.5/10	First CO indication on recycle/purge analyzer sample point about 15 minutes after H_2. Temperature between guard beds 332°C (630°F). Pressure drop across carbonyl system and reactor 550 kPa (80 psi).
0550	- /332 (- /630)	1,055 (40,000)	-/-	14/28	
0615	- / - (- / -)	1,055 (40,000)	36/66	22/46	Pressure drop across carbonyl system and reactor 835 kPa (121 psi).
0625	- / - (- / -)	660 (25,000)	37/65	22/48	
0630	399/366 (750/690)	1,066 (40,000)	-/-	-/-	Temperature between guard beds 371°C (700°F). Reduced firing on gas heaters.
0635	386/385 (727/725)	530 (20,000)	-/-	-/-	Temperature between guard beds 399°C (750°F). Make-up gas shut off. Purge N_2 in @ 27 Nm^3/h (1,000 SCFH). Pressure drop across carbonyl system and reactor 1,075 kPa (156 psi).
0637	382/402 (720/755)	- (-)	-/-	-/-	Temperature between guard beds 410°C (770°F). Reduced firing on gas heaters.
0640	- /416 (- /780)	1,320 (50,000)	-/-	-/-	Maximum temperature achieved.
0645	368/416 (695/780)	1,590 (60,000)	-/-	-/-	
0650	- / - (- / -)	1,590 (60,000)	-/-	-/-	Gas heater inlet pressure 6,480 kPa (940 psia), local reactor inlet pressure 5,340 kPa (775 psia), primary separator pressure 5,240 kPa (760 psia); total pressure drop 1,240 kPa (180 psi).
0658	371/416 (700/780)	- (-)	-/-	19/49	Gas heaters shut off.
0659	337/ - (639/ -)	- (-)	-/-	-/-	

TABLE A-4
CHRONOLOGY OF EVENTS OF 18 DECEMBER 1983
(continued)

Time	Guard Bed Temp. In/Out °C (°F)	Guard Bed Inlet Flow Nm^3/h (SCFH)	Make-Up Analyzer H_2/CO Mol%	Recycle/ Purge H_2/CO Mol%	Comments
0700	313/413 (595/775)	2,120 (80,000)	-/-	-/-	Pressure drop across carbonyl system and reactor 1,970 kPa (286 psi).
0710	263/385 (595/725)	1,855 (70,000)	-/-	-/-	Gas heater inlet pressure 6,380 kPa (925 psia), local reactor inlet pressure 5,340 kPa (775 psia), primary separator pressure 4,960 kPa (720 psia); total pressure drop 1,420 kPa (205 psi). Temperature between guard beds 324°C (615°F).
0715	- / - (- / -)	1,590 (60,000)	-/-	15/46	Make-up N_2 @ 30 Nm^3/h (1,200 SCFH). Pressure holding steady.
0725	260/316 (500/600)	1,990 (75,000)	-/-	-/-	Pressure drop across carbonyl system and reactor 2,340 kPa (340 psi).

TABLE A-5

POTENTIAL REACTIONS IN LAPORTE LPMEOH PDU EXOTHERM EVENTS

LAPORTE OBSERVATIONS	POSSIBLE REACTIONS		NECESSARY CONDITIONS
Metallic Fe, Ni, Cr and Magnetite (Fe_3O_4) Found in Carbonyl Preheaters and through Guard Beds.	1. Steel + CO ---> Fe, Cr, Ni? Fe_3O_4	Metal Dusting	T >371°C (700°F)
	2. Fe_2O_3/Rust + H_2 ---> Fe* + H_2O		T >450°C (450°F), High p.p. H_2
	3. $\text{Fe/Steel} + 5CO \overset{\substack{149\text{-}260°C \\ (300\text{-}500°F)}}{\rightleftarrows} Fe(CO)_5 \overset{\substack{>316°C \\ (600°F)}}{\rightleftarrows} Fe^{*} + 5CO$		Reportedly insignificant over over stainless steels
	4. $\text{Ni/Steel} + 4CO \overset{\substack{149\text{-}260°C \\ (300\text{-}500°F)}}{\rightleftarrows} Ni(CO)_4 \overset{\substack{>316°C \\ (600°F)}}{\rightleftarrows} Ni^{*} + 4CO$		
Prolific Carbon: SEM Confirms Boudouard-type Growth	5. $2CO \rightleftarrows CO_2 + C^{*} + \text{HEAT}$	Boudouard	T >316°C (600°F), Fe or Ni
Methane Formed	6. $C^{*} + 2H_2 \rightleftarrows CH_4 + \text{HEAT}$	Methanation	T >316°C (600°F), Fe or Ni
Significant Loss of CO + H_2	7. $CO + 3H_2 \rightleftarrows CH_4 + \text{HEAT}$	Methanation	T >204°C (400°F), Ni (Fe)
Liquid Hydrocarbon Product Formed	8. $CO + H_2 \rightleftarrows (CH_2\text{-}) + H_2O + \text{HEAT}$	Fischer-Tropsch	T >204°C (400°F), Fe
Water Formed	9. $CO + H_2 + \text{HEAT} \rightleftarrows CO + H_2O$	Shift	T >204°C (400°F), Fe
Freezene-100 Oil in Guard Beds	10. $C_{15}\text{-}C_{31}$ ---> CH_4 + Cn + HEAT Freezene-100	Cracking	T >343°C (650°F)

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Exotherm Solution

A review of the reactivity potential in this system determined that the most effective way to eliminate any future exothermic reactions in the feed circuit would be to limit process temperatures to below 204°C (400°F). This was accomplished by removing the high temperature preheat equipment upstream of the carbonyl removal beds. The economizer and electric heater were eliminated, and the 21.10 feed/product heat exchanger was repiped to a cocurrent configuration. It was recognized that additional electric heat input would be required in the utility oil system to compensate for preheat that would no longer enter via the feed gas stream. This was accomplished by rearranging the location of process heater units already on hand. The resultant process flowsheet is depicted in Figure III-1.

A detailed process hazards review was conducted on the overall modified process flowsheet. The most notable recommendation was the addition of several temperature monitoring devices that would automatically initiate a safe depressurization and nitrogen purge upon sensing process temperatures in the potentially hazardous range above 204°C (400°F).

After the review and physical modifications to the PDU during January 1984, the unit was restarted to complete the two-phase gas holdup studies. On 3 February 1984, close temperature monitoring was provided as the balanced syngas feed was introduced into the PDU. Operation was smooth and there were no further exothermic events.

Nickel Contamination Finding

Although the elimination of high temperature preheat solved the exotherm problem, further relevant information resulted from measurements made during the gas holdup test series. During the gas holdup tests with balanced gas feed, a nickel carbonyl survey was performed. The nickel carbonyl concentration was measured in the recycling gas stream, and reached 20 ppmv at the end of the gas hold up tests. The PDU was intentionally shut down after completion of the gas holdup tests to determine the source of this nickel carbonyl. A specific carbonyl test and survey was planned. The PDU was first purged with nitrogen after which balanced gas was run in a single-pass (i.e., no recycle flow) operation. Drager tubes were used to survey the plant to isolate the problem; wet chemistry was then employed to better quantify the carbonyl concentration. Single-pass flow was limited to 530-660 Nm^3/h (20,000-25,000 SCFH), but loop temperatures largely resembled those in earlier gas holdup tests. The results showed that nickel carbonyl was being generated between the 21.10 feed/product exchanger (return side) and the outlet of the 27.14 intermediate V/L separator.

Upon shutdown of the PDU, equipment was dismantled and approximately 18 kg (40 lb) of dense nickel catalyst material (gray fines) was found in the 22.10 product separator, as well as a residual amount in a lower nozzle on the intermediate V/L separator. This catalyst had been used in the Chicago LPM Pilot Plant, and preconstruction cleaning procedures in this program had not removed all of this material. Although sources of nickel contamination were identified, these deposits did not exactly correspond to the locations indicated by the carbonyl survey. It was therefore concluded that there was a likelihood of a pervasive nickel contamination throughout the PDU. For this reason, a chemical wash solution was sought that would be selective in removing residual nickel without attacking the materials of construction for the PDU.

Suggestions were solicited from research contacts at the International Nickel Company. From these discussions, technical leads were established with chemical manufacturers serving the electroplating industry. A proprietary aqueous solution (Metex SCB, supplied by MacDermid, Inc.) containing an oxidizing agent, suitable for use at high pH, was chosen for further examination. Samples of this solution were tested for effectiveness on the nickel material found in the PDU, as well as for its passiveness on materials of PDU construction. On the basis of these confirming tests, the solution was approved for use in cleaning operations.

The main process vessels and interconnecting piping in the PDU were thus solvent-cleaned, beginning with the 01.13 feed surge tank, through to the 22.15 low-pressure liquid-liquid separator and the 01.22 recycle filter. The criterion used to determine completion of the chemical wash was to establish analytically that there was no longer an increase in nickel content in the circulating wash solution. This chemical wash was followed by a deionized water wash, a dilute citric acid wash, and a final flush with deionized water.

The discovery of nickel contamination and nickel carbonyl generation lead to renewed thinking about the prior exotherm events. It is now believed that nickel carbonyl which was formed at the back end of the PDU was recycled to the front end, and then thermally decomposed in the electric heater operating at high temperature. It is postulated that the carbonyl decomposition produced highly active metallic nickel, which triggered the exothermic syngas reaction(s). While there remain several potential reactions, it is now suspected that the methanation reaction was the dominant one. It is concluded that the removal of the high temperature preheat equipment effectively eliminated the potential for any exothermic reactions, while the later removal of nickel contamination probably eliminated the catalyst required for key potential reactions.