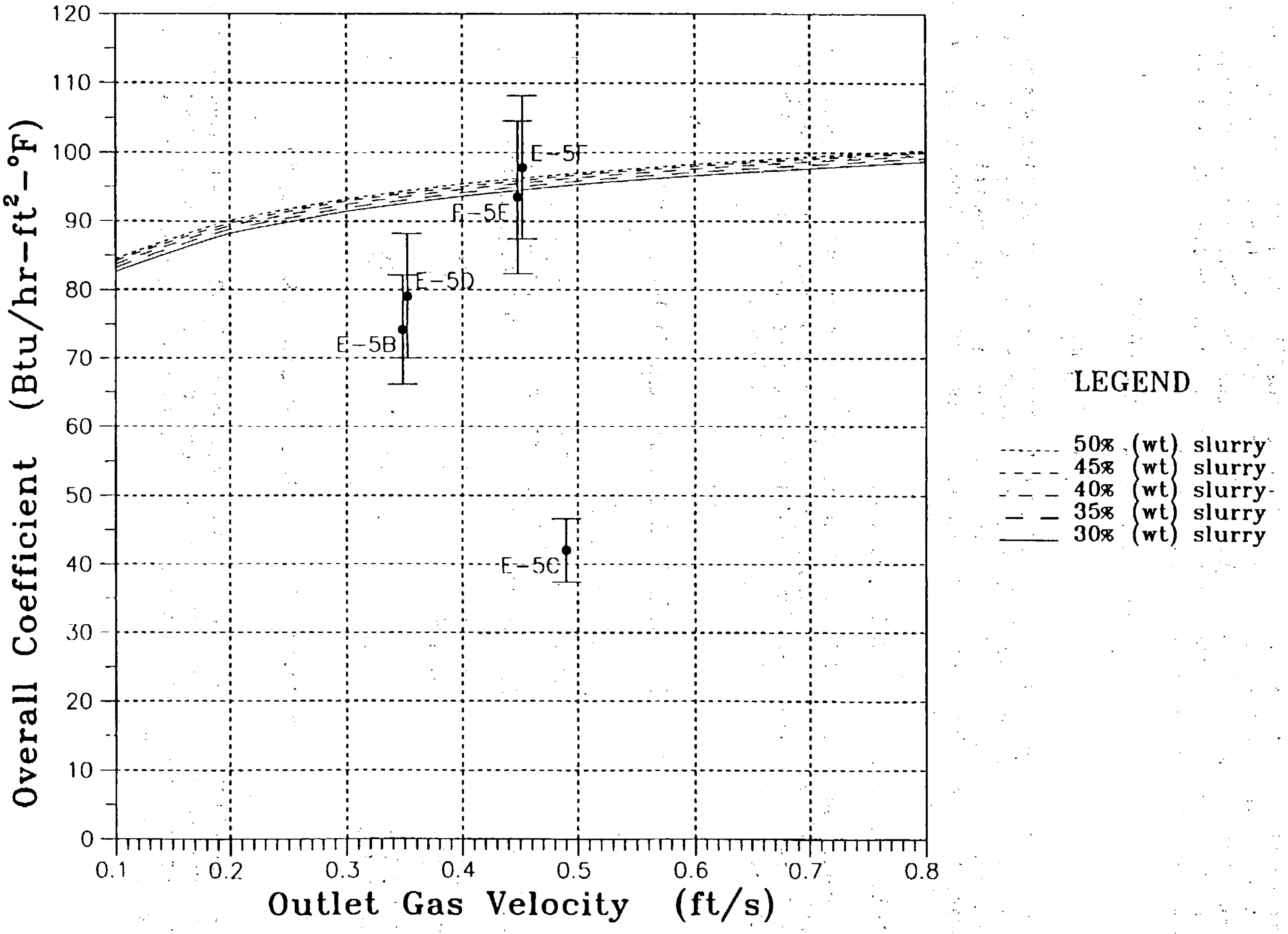
FIGURE V.5

OVERALL COEFFICIENT vs. SUPERFICIAL GAS VELOCITY

Run E-5, 27.10B Internal Heat Exchanger



The shell-side (slurry-side) heat transfer coefficient was backed out from the overall coefficient using the predicted tube-side heat transfer coefficient, which was calculated from the Sieder-Tate equation. The predicted shell-side heat transfer coefficients were calculated using the Deckwer correlation for heat transfer in slurries (Deckwer 1980).

$$St = beta * (ReFrPr^2)^{-0.25}$$

$$\text{where } St = h_o/(rho*c_p*u_g)$$

The slope of the line (beta) predicted by the Deckwer correlation was 0.10; however, except for Case E-5F, the data from Run E-5 was beneath this line (Figure V.6). This result indicates that the shell-side coefficient is being overestimated. The scatter of data was greater than that found by Deckwer in his experiments with organic slurries.

Analytical Results and Activity Testing

As stated before, the activation period cumulative H_2 and CO consumption curves indicate that the catalyst was only 85% reduced. Average autoclave performance on samples of freshly reduced catalyst indicated only 87% activation as shown below in Table V.5 and in Figure V.7.

TABLE V.5

AUTOCLAVE TESTS OF POST-REDUCTION CATALYST SAMPLES

Sample #	Space Velocity (Sl/hr-kg cat)	CO Conversion (%)	Methanol Productivity (gmol/hr-kg cat)	Approach to Autoclave Curve (%)
ER-4-EOR-A-1	5,000	13.4	14.5	83.8
ER-4-EOR-A-2	10,200	10.2	24.0	88.0
ER-4-EOR-B-1	5,200	13.2	15.5	87.0
ER-4-EOR-B-2	9,600	11.3	24.0	90.8

Conditions: CO-Rich Gas, 765 psia, 250°C (482°F)

The crystallite size of the catalyst grew only slightly over the course of the run, the change being generally within the accuracy of the measurement techniques. Table V.6 summarizes the crystallite size and surface area data available from Run E-5.

Figure V.6

DECKWER CORRELATION

27.10B Shell-side Heat Transfer Coefficient, Run E-5

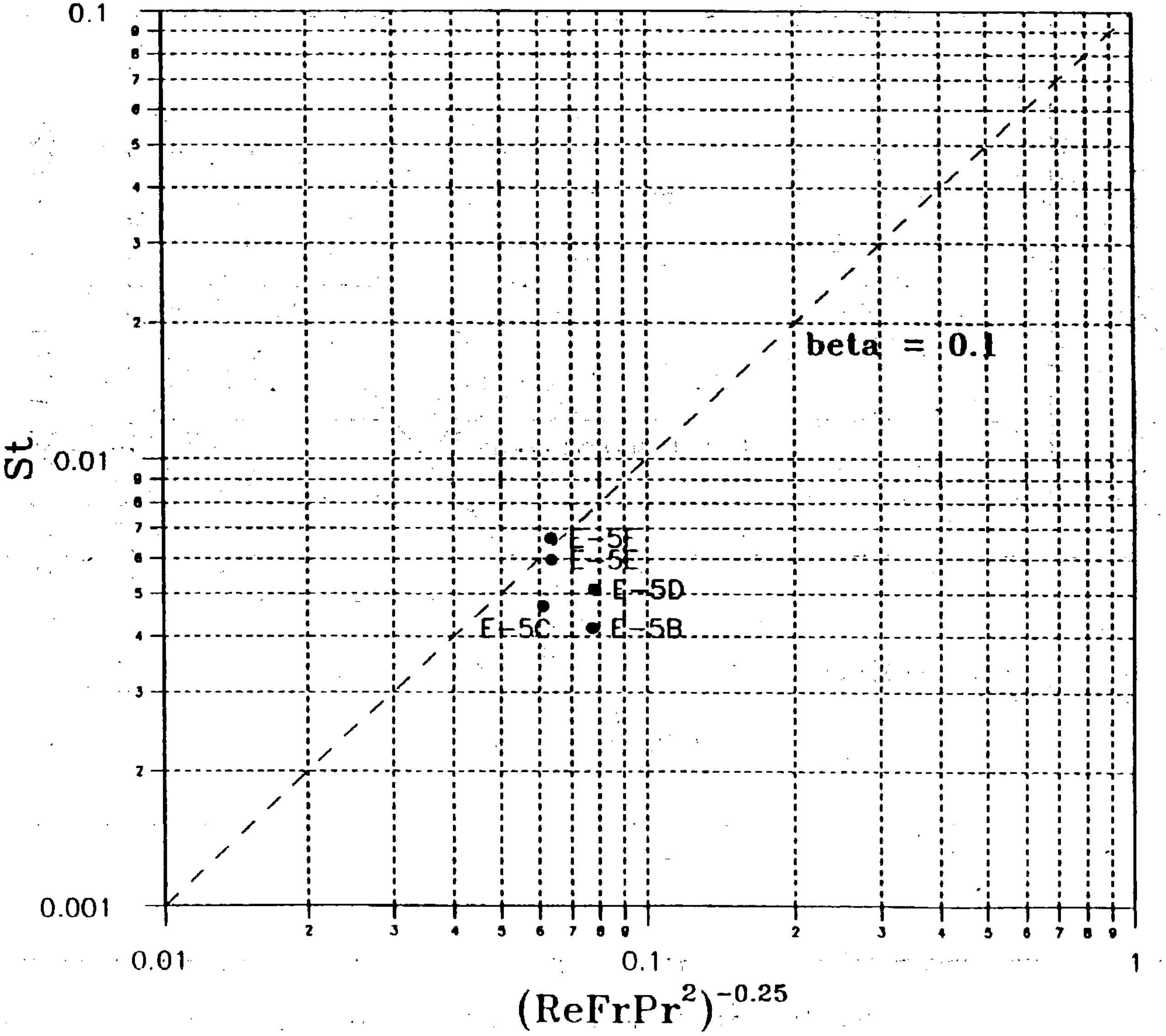


Figure V.7

LAPORTE LPMEOH PDU RUN E-5 SLURRY SAMPLE

Autoclave Catalyst Activity Check

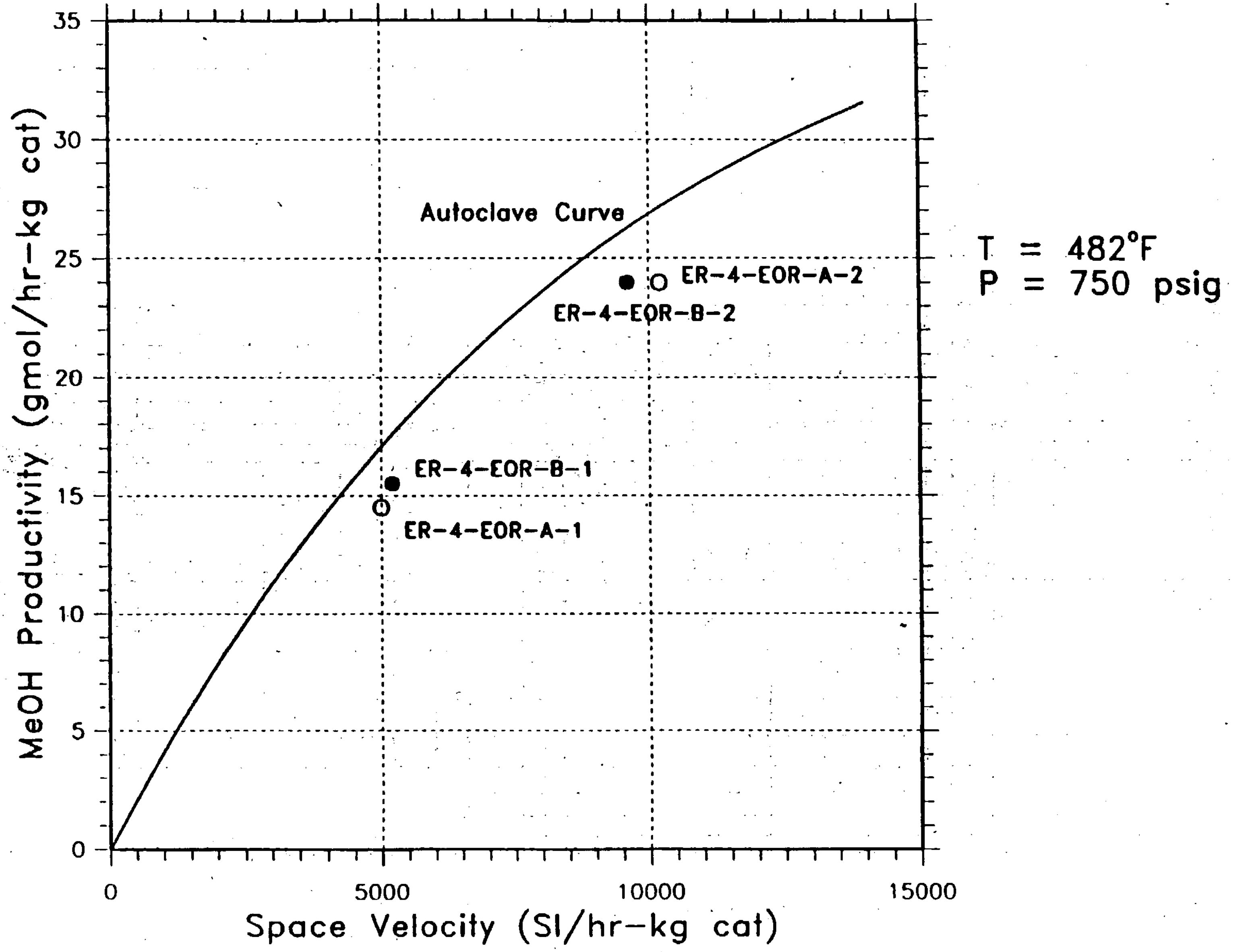


TABLE V.6

CATALYST ANALYSIS FOR RUN E-5

Sample #	Hours on Syngas	Crystallite Size by XRD (angstroms) Cu	ZnO	BET Surface Area (m^2/gm)
ER4-05	0.0	83.1	70.4	
ER4-06B	0.0	105	79.6	102.9
E5-01	4.4	109	79.1	
E5-02	9.9	119	73.0	
E5-03	24.4	109	81.8	
E5-04	120.0	135	83.5	
E5-05	172.9	118	86.2	85.2

Product Methanol Composition

Typical product methanol composition is shown for Run E-5 in Table V.7. Methanol purity averaged 96 wt%. The repiping of the feed/product heat exchanger from concurrent to countercurrent allowed the intermediate oil separator to be operated at 270°F instead of the 350°F used in the previous runs, thus allowing more oil to be removed from the reactor effluent gas stream. The presence of an oil phase seen in the methanol in previous runs was eliminated, and the weight percent of dissolved oil methanol was reduced from the 1.3 wt% to 0.6 wt%.

During Case E of this run free oil was again found in the methanol, even though the oil dissolved in the methanol was only 0.55 wt%. This indicated the possibility of oil droplet carryover from the 27.14 Intermediate Oil Separator. As a result, it was recommended that a demister be installed in the top of the 27.14 vessel to prevent future oil droplet carryover.

Carbonyls

Throughout Run E-5 the production of catalyst poisons, particularly iron and nickel carbonyls, were monitored. Table V.8 shows the levels of $Fe(CO)_5$ and $Ni(CO)_4$ in parts per billion in the reactor feed gas and in the intermediate vapor/liquid separator over the entire Run E-5. From available laboratory and literature data, the low carbonyl levels found indicate that the problem of the formation of catalyst poisons has been eliminated with the changing of the material of construction.

Alternate Oil Evaluation

The observable hydrodynamic performance during the gas holdup tests, the catalyst activation and the methanol synthesis run was nearly identical to the previous results. On this basis, the Drakeol-10 oil appeared to perform as an acceptable substitute for the Freezene-100 oil previously used in the catalyst

TABLE V.7
LaPorte LPMeOH PDU
Typical Methanol Product Compositions for Run E-5

CASE	E-5A	E-5B	E-5C	E-5D	E-5E	E-5F
GAS TYPE	CO-Rich	CO-Rich	CO-Rich	CO-Rich	CO-Rich	CO-Rich
SLURRY CONC. (WT% OX.)	45.0	44.9	45.9	45.0	34.1	33.9
SPACE VELOCITY(Sl/hr-kg)	5,297	5,313	7,084	5,445	11,356	11,444
METHANOL PRODUCT COMPOSITION:						
WT % OIL	0.660	0.670	0.627	0.527	0.550	0.564
WT % WATER	0.702	0.700	0.734	0.446	0.683	0.697
WT % METHANOL	94.540	94.400	95.610	96.350	96.400	96.770
WT % METHYL FORMATE	0.700	0.830	0.680	0.704	0.745	0.786
WT % ETHANOL	1.370	1.425	1.025	0.843	0.455	0.552
WT % ISO-PROPANOL	0.030	0.025	0.020	0.020	0.012	0.015
WT % METHYL ACETATE	0.370	0.417	0.240	0.251	0.083	0.103
WT % N-PROPANOL	0.698	0.596	0.413	0.329	0.163	0.207
WT % SEC-BUTANOL	0.070	0.083	0.070	0.050	0.040	0.042
WT % ETHYL ACETATE	0.024	0.024	0.017	0.020	0.023	0.000
WT % ISOBUTANOL	0.120	0.117	0.080	0.054	0.024	0.040
WT % N-BUTANOL	0.290	0.283	0.200	0.163	0.700	0.110
WT % T-AMYL ALCOHOL	0.030	0.030	0.020	0.016	0.022	0.000
WT % 2&3-PENTANOL	0.040	0.061	0.030	0.024	0.000	0.000
WT % ISOPENTANOL	0.110	0.099	0.066	0.047	0.026	0.030
WT % 1-PENTANOL	0.170	0.170	0.123	0.102	0.052	0.060
WT % ETHYL BUTYRATE	0.080	0.080	0.055	0.045	0.025	0.030
MOL WT OF PRODUCT(lb/mol)	32.990	32.670	32.460	32.580	32.850	32.790

TABLE V.8

RUN E-5 CARBONYL CONCENTRATIONS

Time On Syngas (hr)	27.10 Feed Gas Concentration $Fe(CO)_5$ (ppb)	$Ni(CO)_4$ (ppb)	21.10 Off Gas Concentration $Fe(CO)_5$ (ppb)	$Ni(CO)_4$ (ppb)
6.23			0.5	8.4
6.37			0.4	6.3
6.60			0.3	6.1
6.72			0.4	5.6
9.48	2.1	4.9		
9.58	2.0	2.1		
9.67	2.1	3.0		
9.76	1.6	5.1		
20.47			0.3	6.7
20.62			0.3	6.0
21.15			0.3	5.1
21.50	1.8	2.5		
21.92	1.8	2.0		
22.10			0.3	4.1
22.20			0.4	4.4
22.38	1.7	1.3		
22.50	1.7	1.0		
23.08	2.0	4.0		
23.27	1.9	3.8		
23.35			0.5	8.2
23.45			0.5	7.4
31.13			0.5	7.2
31.22			0.5	7.5
31.37	1.4	2.9		
31.45	1.6	2.7		
45.95	1.4	2.4		
46.05	1.5	1.0		
46.18			0.5	6.0
46.28			0.5	7.0
50.82			0.7	5.3
50.92			0.7	4.9
51.37	1.5	2.3		
51.47	1.5	4.1		
51.60	1.5	1.2		
105.23	1.0	7.3		
105.32	0.9	2.6		
105.42			0.9	2.3
105.52			0.6	2.9
105.65	1.1	2.2		
116.65	1.0	8.5		
116.80	0.8	4.6		
116.90			0.5	5.1
116.98			0.4	4.7
117.08	0.9	3.4		

TABLE V.8

RUN E-5 CARBONYL CONCENTRATIONS

(continued)

Time On Syngas (hr)	27.10 Feed Gas Concentration		21.10 Off Gas Concentration	
	$Fe(CO)_5$ (ppb)	$Ni(CO)_4$ (ppb)	$Fe(CO)_5$ (ppb)	$Ni(CO)_4$ (ppb)
127.82	0.8	3.8		
127.98			0.6	
128.07			0.4	3.0
128.19			0.3	3.0
128.32	0.6	0.6		
128.43	0.6	0.9		
128.63	0.9	2.8		
141.57	0.7	3.6		
142.05	1.0	5.3		
142.24	1.2	5.8		
142.48			0.4	3.1
142.63			0.5	4.2
148.30	1.0	11.4		
148.68	0.9	5.7		
148.98			0.5	4.2
149.08			0.5	5.1
149.22	1.0	3.0		
165.08	1.1	7.1		
165.18	0.9	3.2		
165.27	1.0	3.9		
165.37			0.4	3.9
165.92			0.2	2.7
166.02			0.4	3.9
175.28	0.5	0.3		
175.72	0.7	0.4		
175.83			0.1	0.4
175.92			0.1	0.4
195.83	0.9	4.1		
196.03	0.8	2.3		
196.15	0.8	1.6		
196.22		1.4		
196.65			0.4	3.0
196.78			0.5	3.2
197.03			0.4	3.0
197.20			0.4	3.1
213.65	0.7	3.3		
213.77	0.8	4.0		
213.85	0.8	2.8		
213.95	0.7	2.1		
214.05			0.3	2.9
214.13			0.3	2.9
214.25			0.3	3.2
214.35			0.3	4.0
214.92			0.4	2.4

slurry. Either oil would be an acceptable candidate for future commercialization. The physical properties of both the Freezene-100 and Drakeol-10 oils are listed in Table V.9.

Post Run Inspection

Run E-5 was concluded on July 28, 1988 after approximately 12 days of operation. During the post run inspection the process equipment was opened and found to be in good condition. There was no evidence of catalyst blocking or plugging. This was a significant improvement over the previous 45 wt% run which showed a substantial catalyst build-up on the bubble cap tray. All other major pieces of equipment were also found to be much cleaner than in previous runs.

The demister was the only piece of equipment not in good shape. It was dislodged and pushed past the top support bracket. The demister was also plugged with about 25 pounds of slurried catalyst.

During this inspection period, the internal heat exchanger was equipped with an expansion loop to relieve thermal stresses caused by high heat loads experienced during periods of high methanol production. This modification was made so that operation at high catalyst loadings and high gas velocities would be possible. In addition, the 27.14 Oil Separator was retrofit with a demister to eliminate the possibility of oil carryover into the product methanol.

Table V.9

Properties of Oils Used for Catalyst Slurry

	Freezene-100	Drakeol-10
Average Mol. Wt.	340	366
Distillation by ASTM D1160, (°F)		
Initial Boiling Point	505	541
10%	603	667
50%	696	765
90%	802	898
End Point	883	
Hydocarbon Type		
% Paraffinic	100	65
% Naphthenic	0	35
Specific Gravity at 77°F	0.868	0.849
Surface Tension at 77°C, (lb/ft)	0.0021	0.0021
Viscosity at 77°F, (lb/ft-hr)	82	76
Pour Point, °F	-35	19
Flash Point, °F	>230	365

VI. CONCLUSIONS AND RECOMMENDATIONS

A detailed Process Engineering Study, Two-Phase Gas Holdup Study, and Equipment Evaluation Run E-5 were performed under Tasks 2.1 and 2.2 of the new modification/operating program. The process simplifications to the slurry loop, which were identified and examined in the Process Engineering Study, resulted in a new flexible process design of the LaPorte PDU. The aim of the process simplifications was the elimination of the entire loop (vapor/slurry separation vessel, slurry circulating pump, and external heat exchanger) from outside the reactor. The subsequent Two-Phase Gas Holdup studies and Equipment Evaluation Run E-5 demonstrated the improvements to the PDU operation attributable to the implemented process simplifications. The major accomplishments of these tasks are summarized as follows:

- The performance of the new reactor with the new sparger and the new internal heat exchanger exceeds the performance of the old reactor.
- There is sufficient slurry circulation and turbulence induced by the high synthesis gas velocities to suspend the catalyst particles homogeneously within the slurry without bulk slurry circulation.
- The required internal heat transfer area to remove the heat of reaction is small enough such that a sufficient heat exchanger area can be installed with little effect on reactor bubble column hydrodynamics.
- Reactor effluent vapor/liquid disengagement can be achieved with a reactor freeboard section in combination with an external cyclone. The short operating period limited a thorough cyclone evaluation.
- The repiping of the feed/product heat exchanger from cocurrent to countercurrent allowed the intermediate oil separator temperature to be reduced from 350°F to 270°F, thus allowing more oil to be removed from the reactor effluent gas stream. The oil phase seen in the methanol product in previous runs was eliminated and the weight percent oil in the methanol product was reduced from the 1.3 wt% seen in previous runs to 0.6 wt%.
- The new slurrying oil, Drakeol-10, recommended from the laboratory program was acceptable for the PDU operation.
- Catalyst powder was successfully activated with the in-situ activation technique at 45 wt% slurry loading.
- From available laboratory and literature data, the low carbonyl levels found indicate the problem of the formation of these catalyst poisons has been eliminated with the changing of the materials of construction.
- The ability to maintain catalyst activity and the resilience of the newly simplified process after extended shutdown periods in Run E-5 were demonstrated. Four unplanned power outages during the month of July also demonstrated the reliability of this process after unscheduled shutdowns.

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