

"STATUS OF THE DEVELOPMENT OF METHANOL
SYNTHESIS BY THE LPMEOH* PROCESS"

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DOE Indirect Liquefaction Contractors' Review Meeting

Pittsburgh, PA
13-15 November 1989

ABSTRACT

The Liquid Phase Methanol Project is a viable alternative to traditional gas phase methanol processes and is well suited to coal-derived synthesis gas which is rich in carbon monoxide. This paper describes the progress that has been made at the LaPorte LPMEOH process facility and in the supporting research programs over the last twelve months.

The primary purpose of the Process Development Unit (PDU) operating program is to obtain sufficient data to evaluate the LPMEOH technology and allow for a confident move to the next scale of operation. Several process improvements, including elimination of the liquid circulation loop and operating at high slurry concentrations, have simplified and improved the economics of the process.

The productivity of the modified LaPorte PDU was near or above the productivity predicted by a laboratory scale autoclave, and record production rates of 12 tons per day were achieved using a CO-rich (35% H_2 , 51% CO, 13% CO_2 , 1% N_2) feed gas with a H_2 /CO ratio of 0.7 to 1. A number of other coal-derived syngas feedstocks were also evaluated for their methanol potential. Slurry concentrations of up to 50 wt% were activated and operated successfully, and gave higher productivities than previous attempts. Catalyst deactivation rates of less than 0.2%/day were seen over a 120 day life test. Catalyst addition and withdrawal was demonstrated successfully and the PDU's ability to load-follow, useful in the co-production of power and methanol, was investigated.

This progress represents another step towards commercialization of the LPMEOH process.

INTRODUCTION

Methanol is a versatile commodity chemical with applications ranging from synthetic fuels to feedstocks for higher valued chemicals such as methyl methacrylate and methyl t-butyl ether (MTBE—an octane booster). Many applications have evolved for methanol as a fuel including methanol as a gasoline extender, the methanol to gasoline process, and integrated gasification-combined cycle (IGCC) technology for the coproduction of methanol and electricity.

The Liquid Phase Methanol (LPMEOH^{*}) process represents a major departure from traditional gas-phase routes to methanol in the method of removing the heat of reaction. The reactions of hydrogen and carbon oxides to form methanol are highly exothermic. One of the most difficult design problems of the methanol synthesis process is removing the heat of reaction while maintaining close temperature control to achieve optimum catalyst life and reaction rate. Catalyst life is seriously reduced by excessive temperatures. In conventional gas-phase reactors, either cool unreacted gas, injected at stages in the catalyst bed, or internal cooling surfaces are used to provide temperature control. These schemes, however, were developed for diluted syngas which yields low conversion per pass. The LPMEOH process uses a solid catalyst entrained in an inert hydrocarbon liquid, usually a mineral oil. The presence of this liquid adsorbs the reaction heat, effectively controlling the reaction temperature, thereby allowing a higher conversion per pass than in gas-phase processes. In addition, LPMEOH process technology is particularly well suited to coal-derived synthesis gas which is rich in carbon monoxide. These capabilities make the LPMEOH process a potentially lower-cost conversion route to methanol, especially when methanol coproduction is added to a coal-based IGCC power plant. For a modest increase in complexity of an IGCC plant, the methanol coproduction scheme produces a storable liquid fuel in parallel with electric power production, providing a significant turndown and peak-load capability for the IGCC plant.

*LPMEOH is a trademark of Chem Systems Inc.

This continuous development of the LPMEOH technology from 1975 to the present is shown in Table 1. Chem Systems conceived the concept of liquid-phase methanol synthesis in the mid-1970s. Early research was done with an ebullated-bed reactor, using relatively large (3-5 mm) catalyst particles fluidized by gas and liquid flow. Slurry reactor development began at Chem Systems in 1979 with the initial bench-scale work being done in stirred autoclave reactors.

In September 1981, the United States Department of Energy (DOE) awarded Air Products and Chemicals, Inc. (Air Products) a contract which was the first phase of a program aimed at further developing the LPMEOH process in a representative engineering-scale Process Development Unit (PDU). A second contract was awarded in July 1985. The third, currently active contract (DE-AC22-85PC80007) entitled "Liquid Phase Methanol LaPorte PDU: Modification, Operation, and Support Studies" began on 9 April 1987 to complete the final phase of the development work. Air Products is the prime contractor providing overall program management and is responsible for engineering design, procurement, construction, and operation of the PDU. Chem Systems acts as the key subcontractor in the program. Cost-sharing is being provided by Air Products and the Electric Power Research Institute (EPRI).

In the previous programs, a DOE-owned skid-mounted pilot plant was disassembled and equipment components renovated. The unit was transferred from Chicago, Illinois, to Air Products' LaPorte, Texas, facility, refurbished, and rebuilt for service as the PDU for LPMEOH process development. Synthesized feed gas from the adjacent Air Products facility was used to test the unit. A total of ten major PDU synthesis runs and numerous hydrodynamic and analytical tests have been conducted at LaPorte since commissioning of the PDU in March 1984.

The development of the LPMEOH process has been supported by extensive laboratory programs funded by both DOE and EPRI, which included catalyst screening, bench-scale tests, fundamental modeling, catalyst poisons studies, CO₂ effect on methanol productivity, alternate liquid screening, slurry

TABLE 1

<u>Date</u>	<u>Development Scale and Key Results</u>
1975	LPMEOH concept patented by Chem Systems
1979 - 1981	2 Liter bench scale stirred autoclave Concept Verification Catalyst/Oil Screening Initiated Catalyst Activation Methods Demonstrated
1981 - 1989	300 cc/1 Liter laboratory scale stirred autoclaves Method to Activate Conc. Slurries Developed Catalyst Poisons Studied Feed Gas Compositional Effects Determined Syngas Activation Developed
1983	4.5" ID x 7' tall Lab. PDU (up to 0.14 TPD MeOH) Reactor Productivity Defined Hydrodynamic Behavior Identified Reactor Modeling Begun
1984 - 1985	2' ID x 18' tall LaPorte PDU (up to 8 TPD MeOH) Reactor Performance Demonstrated Catalyst Life Demonstrated Materials of Construction Defined Operating Experience Base
1988 - 1989	2' ID x 20' tall LaPorte PDU (up to 13 TPD MeOH) Isolated Reactor Design Proven Catalyst Addition/Withdrawal Demonstrated Load Following Demonstrated Improved Reactor Productivity Improved Catalyst Life Improved Oil Recovery

criteria study, and the effect of in-situ reduction conditions on catalyst activity. The results of the LaPorte runs and the laboratory research have been reported by Chem Systems and Air Products in the project final reports and at the 1982-1988 annual DOE Indirect Liquefaction Contractors' Review Meetings (1-11). This paper briefly summarizes the previous activities (1981-1988) but focuses primarily on the objectives and results for both the PDU and laboratory programs achieved since the previous Review Meeting (Nov 1988).

PROGRAM DESCRIPTION

Previous LaPorte PDU operations, conducted during the first five major runs, successfully demonstrated LPMEOH process technology at a representative engineering scale. A summary of these campaigns is included in Table 2. The PDU accumulated over 2,500 hours of methanol synthesis operation (over 2200 hours with CO-rich gas) with an on-stream factor of 96-100 percent. Identification of catalyst poisons (iron and nickel carbonyl) and subsequent application of new metallurgy contributed to superior performance. Low catalyst deactivation while operating the liquid-entrained system with a 25 wt% catalyst slurry for 40 days on CO-rich synthesis gas and matching laboratory predictions for catalyst life and activity were notable achievements. Methanol production levels as high as 8 TPD for balanced gas feed and 7 TPD for CO-rich gas feed were achieved; the purity of the methanol product from CO-rich gas was consistently higher than 96 wt%, a good quality for use as a fuel.

Activation of the methanol synthesis catalyst powders in an inert liquid at high concentrations and operation at a 45 wt% slurry concentration were also successful. High operability was maintained during the 45 wt% slurry run for 10 days and the reactor performance was close to 7 tons per day; however, the catalyst productivity was lower than laboratory predictions. This deficiency was attributed to a mass transfer limitation and/or inadequate gas/slurry mixing at the high solids loading.

The PDU operations, laboratory activities, and commercial studies conducted under the two previous DOE contracts helped to prove the viability of the LPMEOH process. Further requirements needed to be met, however, to scale to a larger demonstration plant or a small commercial unit.

The primary focus of the latest PDU operating program was to allow for a confident move to the next scale of operation with an optimized and simplified process. Although the PDU had been very reliable in prior campaigns, several new design options of merit were identified. These options were thoroughly evaluated in a subsequent process engineering study which became the basis for the new PDU modification/operating program.

TABLE 2

LAPORTE PDU OPERATIONS SUMMARY

DOE Run Cont. #	Date	Objective	Operation Mode	Catalyst Type	Hours On Syngas	Principle Results
LP-1 E-1	Mar 84	Shakedown	Hybrid Fluidized /Slurry Loop	Extrudates	248	Mech. operation of PDU demonstrated Catalyst activation successful Catalyst resilience poor
LP-1 E-1	Apr 84/ May 84	Activity Maintenance	Hybrid Fluidized /Slurry Loop	Extrudates	964	Catalyst activation successful Catalyst resilience and life poor
LP-1 E-2	Jun 84	High Slurry Conc., High Throughput	Slurry Loop	Powder	145	PDU operation with high slurry conc. Catalyst activity poor
LP-1 E-3	May 85/ Jun 85	Activity Maintenance	Slurry Loop	Powder	948	PDU materials of constr. proven Catalyst activity and life good
LP-2 E-4	Jul 85	High Slurry Conc., High Throughput	Slurry Loop	Powder	231	Activation of conc slurry successful PDU operation with high slurry conc.
LP-3 E-5	Jul 88	Equipment Evaluation	Hybrid Slurry Loop/Isolated	Powder	259	Simplified process demonstrated Improved product quality
LP-3 E-6	Aug 88	Alternate Catalyst	Isolated	Powder	161	Alternate/improved catalyst demo.
LP-3 E-7	Sep 88/ Jan 89	Activity Maintenance	Isolated	Powder	286	Improved catalyst life Excel. process resilience/response
LP-3 E-8	Jan 89/ Feb 89	Process Variable Scans	Isolated	Powder	1138	Wide operating range demonstrated Good operation with high slurry conc Record 12.8 TPD production
LP-3 E-9	Mar 89	Simplified Catalyst Activation	Isolated	Powder	329	Simplified reduction process Syngas reduction successful
Total hours					7404	

DOE CONTRACTS

LP-1 DE-AC22-81PC30019
 LP-2 DE-AC22-85PC80007
 LP-3 DE-AC22-87PC90005

These process simplifications and operating options, which were described at the previous DOE Contractors' Review Meeting (9), were incorporated into a flexible process design which allowed for the individual evaluation of each specific process modification. The various options were tested in an operating program (Run E-5) in June and July of 1988. This initial run under the current contract was a complete success and was a major milestone in moving the LPMEOH technology forward. This test program resulted in the much simplified reactor internal design shown in Figure 1. In addition, a series of planned and unscheduled shutdowns during the run demonstrated that the new reactor configuration was not only simpler, but much more resilient to major process upsets.

In the preferred configuration, vapor/liquid disengagement is accomplished in a new, longer, all-stainless steel reactor by incorporating a freeboard section followed by a small-diameter external cyclone to knock out small slurry droplets. Recovered slurry droplets are returned to the reactor via a positive displacement pump.

The heat of reaction is controlled by an internal heat exchanger consisting of parallel 1-inch diameter tubes manifolded at each end by a 16-inch diameter header ring. The heat exchanger occupies only 3.5% of the reactor cross-sectional area and does not interfere with the reactor hydrodynamics.

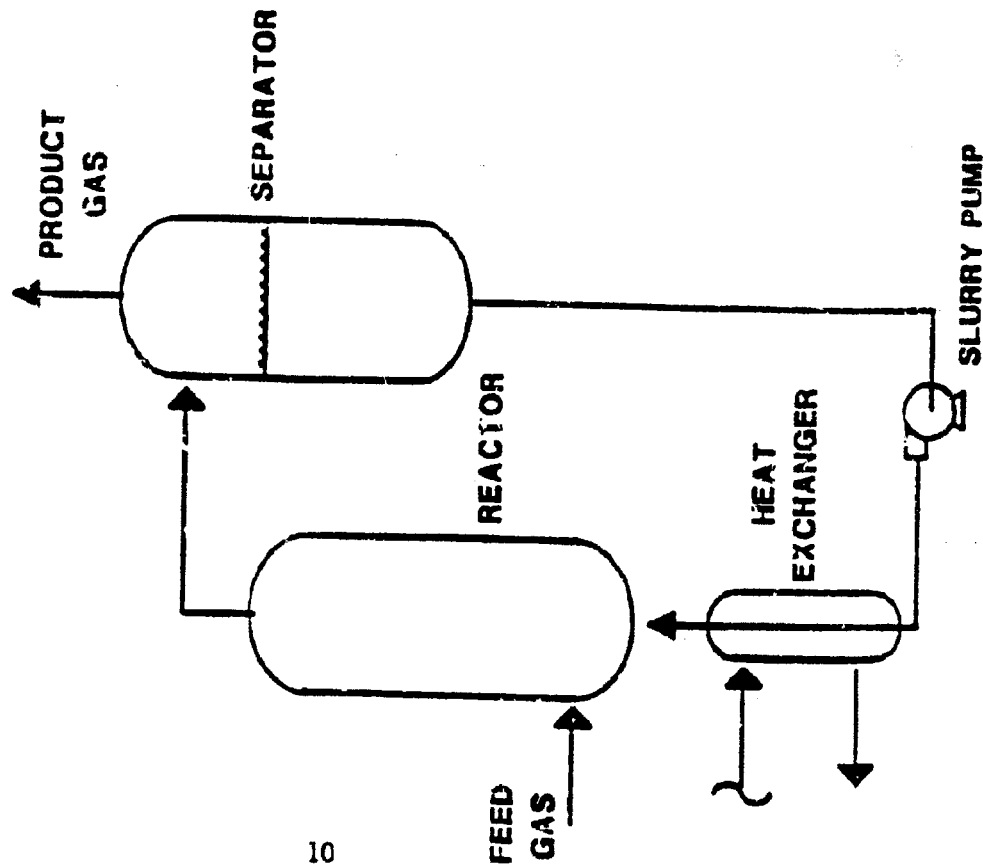
Feed synthesis gas is introduced to the reactor using a circular gas sparger. The slurry circulation rate resulting from the feed gas flow is sufficient to suspend the catalyst particles. The newly designed gas sparger suspends high concentration catalyst slurries while providing intimate gas/slurry mixing and improved mass transfer.

Strategically, this process design eliminates the separate slurry/product gas separator, the large slurry pump, the external slurry heat exchanger, a large external catalyst inventory and the associated operating concerns. This preferred internal configuration was used in all of the subsequent campaigns.

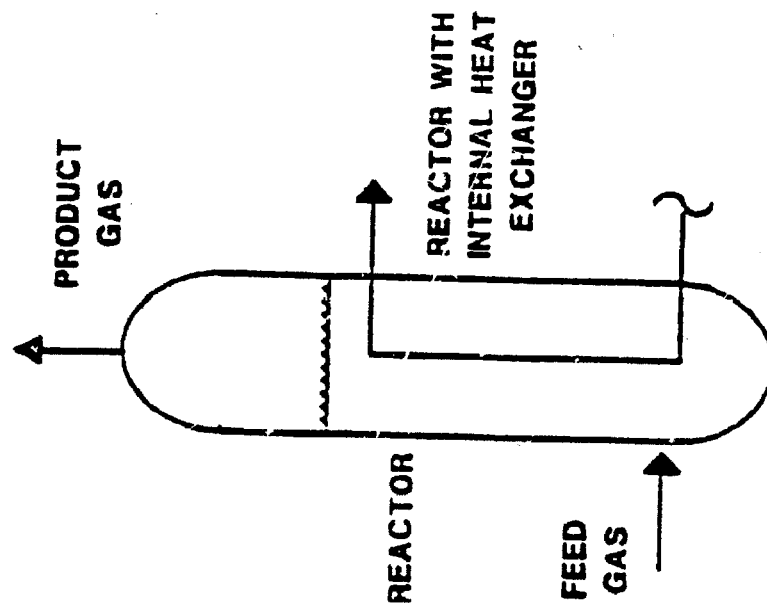
LPMEOH REACTOR/SLURRY LOOP SIMPLIFICATION

FIGURE 1

LP I, II CONTRACTS
OLD, PROVEN CONFIGURATION



LP III CONTRACT
NEW TEST CONFIGURATION



In addition to the reactor simplification, other process modifications resulted in reducing the contained oil in the condensed crude methanol product to 0.1-0.2%. This represents a 95% reduction in the slurry oil losses, a significant improvement in both product purity and process economics.

Run E-6 was started in late August for the purpose of studying an alternate commercial catalyst. A comparison of the baseline and alternate catalysts at equal feed rates and reactor volumes showed that the alternate catalyst produces 9% more methanol at 35 wt% than the previous catalyst at 40 wt%. The alternate catalyst run was therefore continued as run E-7 for a 120 day catalyst life study at nominal conditions of 10,000 sl/kg-hr, 250°C, 750 psi and 35 wt% oxide catalyst. The PDU produced a record 10.1 tons per day of methanol during the first 2 weeks of Run E-7.

Recent PDU Results

The recent PDU operations include the Activity Maintenance Run (Run E-7), the Process Variable Scan (PVS) Run (Run E-8) and Simplified Catalyst Activation Run (Run E-9).

The Activity Maintenance Run was the keystone of the operating program consisting of a steady-state continuous run of approximately 120 days to establish the baseline catalyst deactivation rate. The final portion of this task was a demonstration of catalyst slurry withdrawal followed by the addition of catalyst slurry that was activated at the beginning of the operating program. The PVS Run examined PDU performance under various operating conditions and feedstocks in order to expand the operating data base. The Simplified Catalyst Activation Run tested the ability of the system to reduce the catalyst using syngas in place of hydrogen, without the use of a slurry pump.

As stated before, Run E-7, the Activity Maintenance Run, was a continuation of the Alternate Catalyst Run. After 120 days of operation, the methanol

production rate was still in excess of 8 TPD, indicating a baseline (poison-free) deactivation rate of no more than 0.2%/day. This was half the rate of that in Run E-3 in 1985. These results are shown in Figure 2. The differences in deactivation rate between Run E-1 and E-3 are attributable to the effects of metal carbonyl poisoning. The differences between Run E-7 and E-3 are much less, but are probably the result of an improved catalyst and removal of the last of the carbon steel in the PDU system (new stainless reactor). Improvements to the reactor gas distribution system may also have had an effect.

Although the Activity Maintenance Run was only 4 months in duration, the high productivity resulted in a cumulative methanol production of over 2500 lb of MeOH per lb of catalyst. This corresponds to approximately 30-40% of the typical gas phase catalyst life. Therefore, on a catalyst consumption basis, an expected commercial life of the LPMEOH catalyst of 1 yr is equivalent to a 3 yr gas-phase catalyst life.

While the improvement in catalyst productivity is indicative of improved catalyst activity and stability, the improvement in reactor volumetric productivity, as illustrated by the total production rate, demonstrates the improvements achieved by the new reactor design. The two-fold increase in the methanol production rate, as shown in Figure 3, was largely accomplished by the ability to operate with a more concentrated catalyst slurry.

At the end of the catalyst life-run a series of tests were carried out aimed at defining the response of the LPMEOH unit to fast and major changes in the feed rate. These tests parallel what would be expected in load-following of commercial gasification systems. The results are presented in Figure 4 and Table 3. In short, the unit responded exceptionally well to all changes. Cuts of 80% in the feed flow were accommodated easily and resulted in process fluctuations lasting only a few minutes. In every case the temperature response of the reactor was very good--the maximum difference seen being 3°C.

FIGURE 2

LAPORTE PDU PRODUCTIVITY vs TIME

CO-Rich gas, 482 deg F, 750 psig

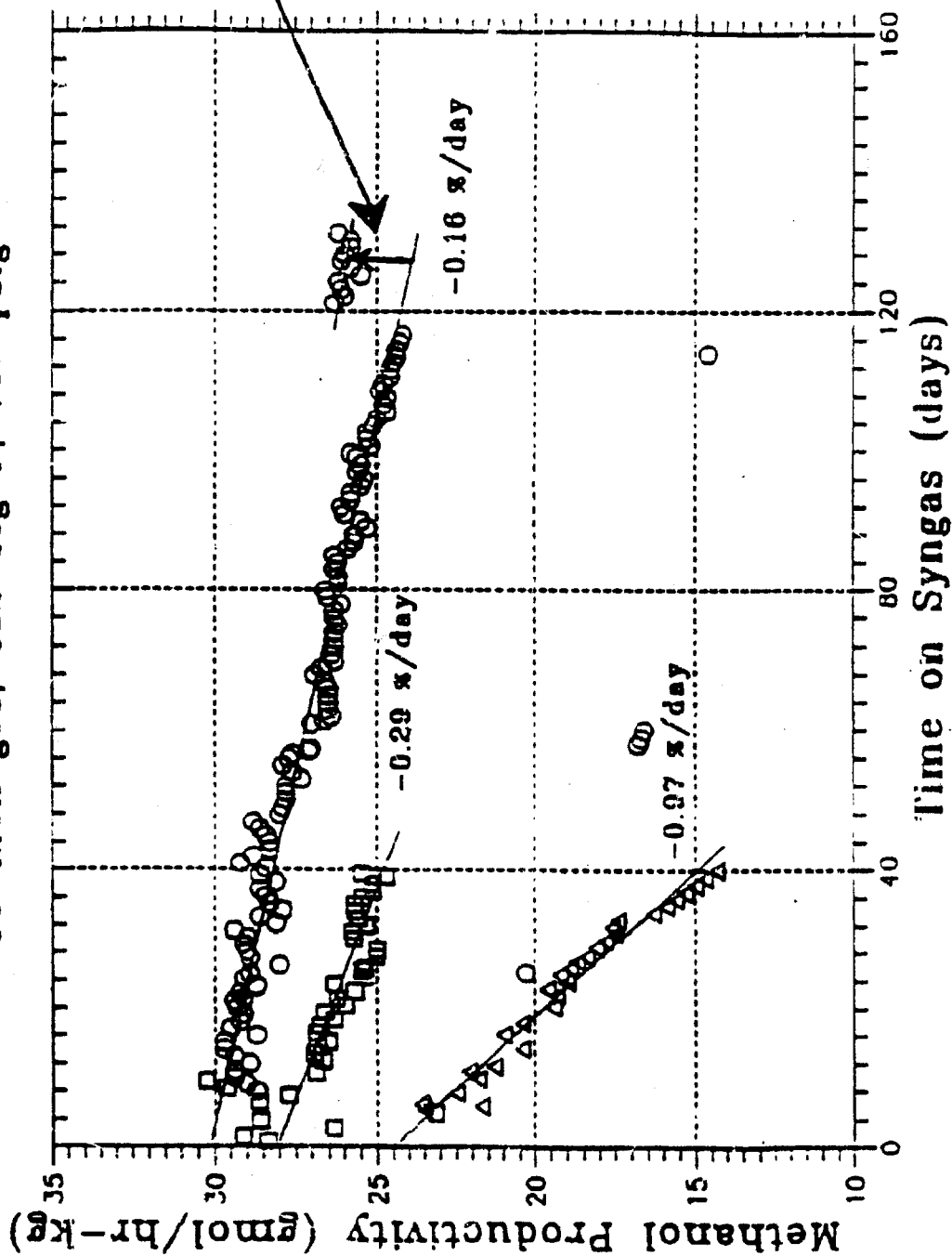


FIGURE 3

LAPORTE PDU METHANOL PRODUCTION VS TIME
CO-Rich gas, 482 deg F, 750 psig

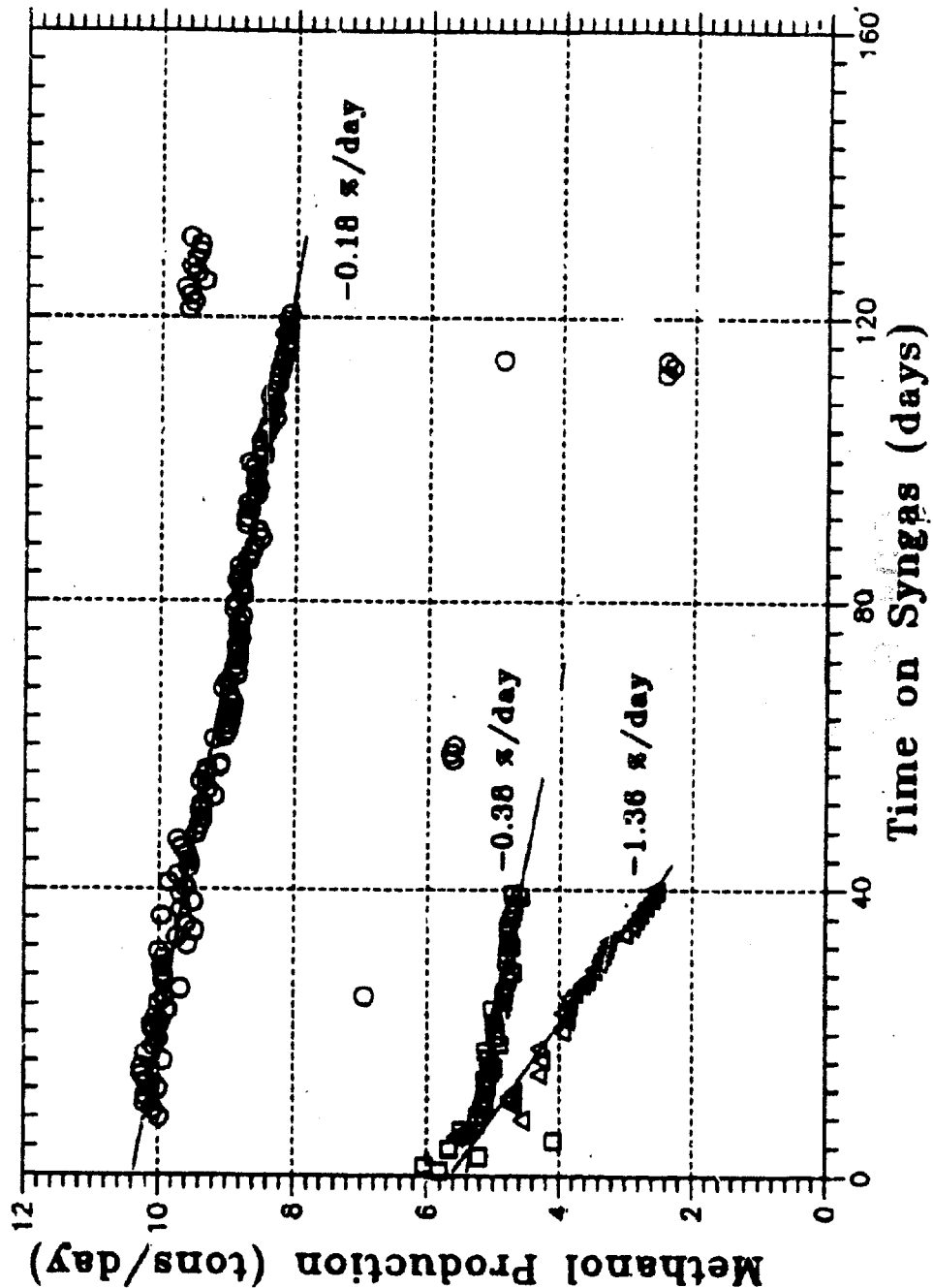


FIGURE 4

LaPorte PDU RUN E-7 LOAD FOLLOWING TESTS Methanol Concentration in Reactor Outlet Stream

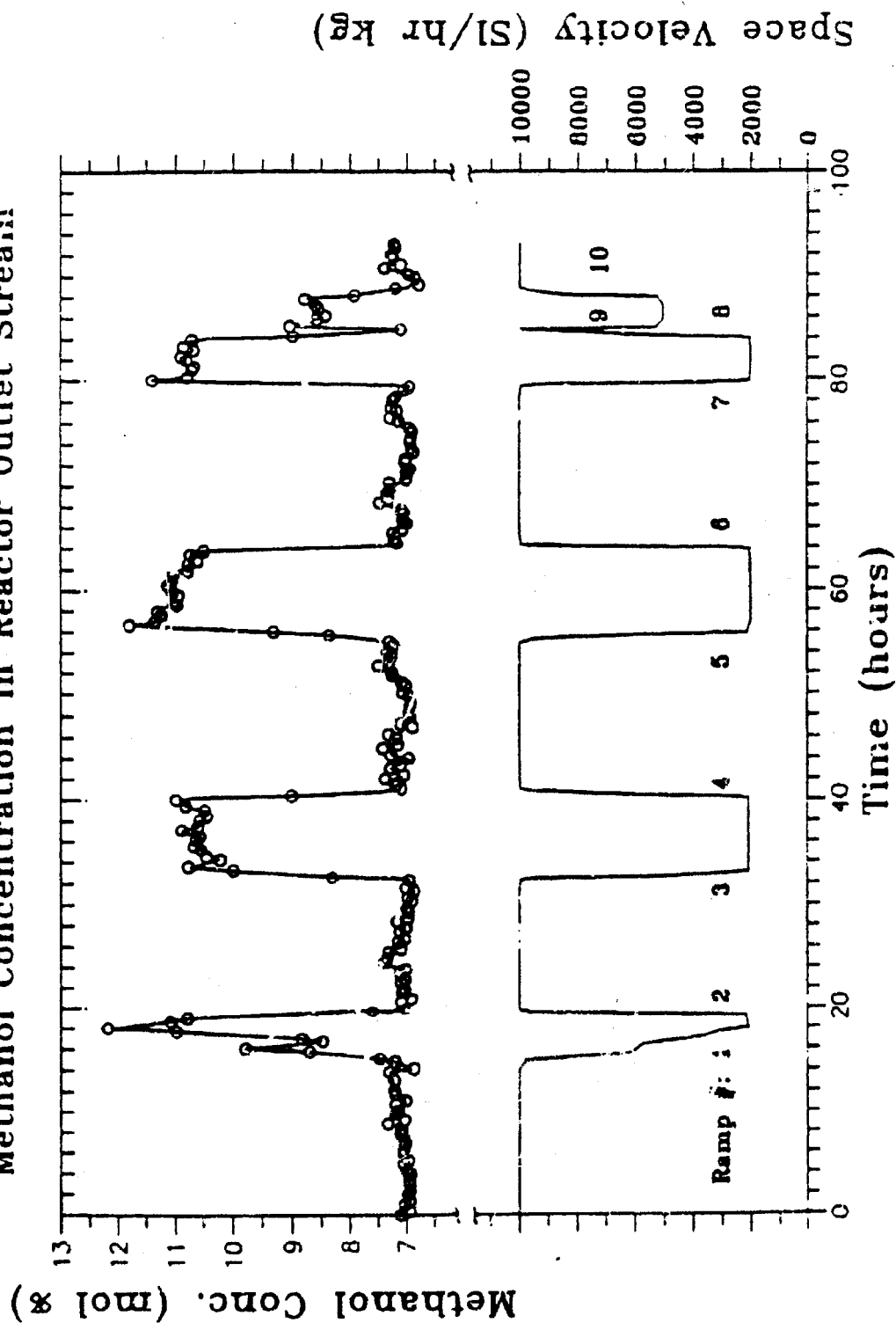


TABLE 3

RAMPING TEST SUMMARY - LaPORTE PDU RUN E-7

Ramp #	Date	Time		FT-187 Flow (MSCFH)		Rate %/min.
		Initial	Final	Initial	Final	
1	12/19	2:55	6:00	145	30	- 0.4
2	12/19	19:10	19:33	30	145	+ 3.4
3	12/20	8:15	3:55	145	29	- 2.0
4	12/20	16:05	16:45	29	145	+ 2.0
5	12/21	7:20	8:00	145	29	- 2.0
6	12/21	16:00	16:08	29	145	+ 10.0
7	12/22	7:30	7:39	145	29	- 8.9
8	12/22	12:00	12:40	29	145	+ 2.0
9	12/22	13:00	13:02:30	145	73	- 16.0
10	12/22	16:00	16:15	73	145	+ 3.3

TEMPERATURE RESPONSE OF SLURRY REACTOR

Ramp #	Temperature Range (°C)			Maximum Error (°C)
	Minimum	Target	Maximum	
1	247	250	253	3
2	248	250	252	2
3	248	250	251	2
4	249	250	252	2
5	249	250	252	2
6	249	250	251	1
7	247	250	251	3
8	247	250	252	3
9	247	250	252	3
10	248	250	253	3

Following these tests, the potential for catalyst addition and withdrawal was investigated. Approximately half of the aged catalyst slurry was removed from the reactor and replaced by fresh catalyst which had been held in the slurry preparation vessel--where it had been activated 120 days previously as part of the original batch (for Run E-6). The result is shown in Figure 2 & 3. The new production level was within 5% of that predicted assuming the added catalyst had the same activity as that used initially in Run E-6. This significant result answered two key questions. One, it is possible to store activated catalyst for long periods of time and two, catalyst addition/withdrawal seems a viable means of maintaining catalyst "activity" (production rate).

Overall, Run E-7 was tremendously successful. Over 1,000 tons of methanol were produced at high purity (see Table 6) and the unit responded superbly to the ups and downs of normal everyday operation. Total lost time was 137 out of 3,100 hours, of which 130 hours were the result of electrical or gas supply outages unrelated to the LPMEOH PDU.

The next run in the PDU was the matrix of Process Variable Scans. The intention here was to define the limits of performance of the slurry system, in an effort to provide data for commercialization activities. Pressure, temperature and space-velocity effects on a variety of feedstocks were studied. The latter included those from commercial gasifiers (Shell, Dow, Great Plains), and one with an "optimal" CO_2 content (using data from Research Subtask 3.2). Particularly important to improved process economics were runs aimed at maximizing gas linear velocity and catalyst concentration.

The full matrix of operating conditions for Run E-8 is shown in Table 4. Highlights include: stable operation of 50 wt% slurry, throughputs exceeding 0.6 ft/sec superficial velocity, and methanol production rates in excess of 12 TPD. In addition, the CO_2 enhancement of methanol productivity was confirmed. Throughout the run, operating conditions were returned to a standard baseline condition to check on changes in catalyst activity. The results suggest healthy catalyst throughout with perhaps some loss being seen following the high temperature (285°C) condition.

TABLE 4

MATRIX OF PVS RUN CONDITIONS FOR RUN E-3; ACTUAL PDU CONDITIONS

Run No.	Start Date	Gas Type	Temp °C	Pres. PSIG	Space Velocity L/hr-kg	Slurry Conc. wt%	Slurry Height %	Productivity Mole/hr-kg	Production TPD	Gas Velocity Ft/S	Comments
1	Jan 10	CO-Rich	250.3	753.2	6729	45.3	100	20.5	10.04	0.50	
2	Jan 12	CO-Rich	249.8	753.3	6767	49.6	83	18.5	9.06	0.51	
3	Jan 13	CO-Rich	249.9	753.3	3081	50.0	72	9.7	4.74	0.23	
4	Jan 15	CO-Rich	249.9	753.3	3112	45.6	87	11.0	5.40	0.23	
5	Jan 16	CO-Rich	250.2	893.0	4914	42.1	100	19.0	8.78	0.29	
6	Jan 18	CO-Rich	250.0	753.3	6525	41.1	100	24.9	9.99	0.52	
7	Jan 20	CO-Rich	250.8	893.6	9151	41.1	100	30.3	12.03	0.47	Baseline RECORD
8	Jan 21	CO-Rich	250.1	752.9	4331	40.4	98	15.3	6.08	0.24	
9	Jan 23	CO-Rich	250.0	502.3	6819	37.5	100	14.8	5.14	0.53	Maximum Flow
10		CO-Rich	250.0	500.0	12600	40.0	THIS CONDITION WAS UNATTAINABLE				
11	Jan 25	CO-Rich	250.2	752.4	10841	36.5	100	29.9	9.28	0.52	Baseline
12	Jan 26	CO-Rich	250.0	753.0	6168	36.5	100	20.7	6.42	0.30	
13	Jan 28	CO-Rich	250.1	763.6	13684	37.0	100	34.1	10.48	0.64	Max Gas Vel
14	Jan 29	CO-Rich	250.2	752.6	2985	36.5	77	11.6	3.50	0.14	
15	Jan 31	H ₂ -Rich	250.2	503.0	6819	33.2	100	19.5	6.04	0.48	
16	Feb 01	H ₂ -Rich	250.5	753.0	6600	32.2	100	29.2	9.07	0.31	
17	Feb 03	H ₂ -Rich	250.1	753.0	11066	33.7	100	38.3	11.91	0.52	
18	Feb 05	Balanced	249.7	753.2	6634	36.8	88	20.0	6.20	0.33	
19	Feb 06	Dow Gas	250.0	753.2	6573	36.4	87	25.6	7.77	0.31	
20	Feb 07	Dow Gas	250.4	893.0	6557	36.8	85	28.6	6.71	0.26	
21	Feb 08	CO-Rich	249.8	752.9	11006	35.8	100	30.0	9.14	0.52	Baseline
22	Feb 10	Balanced	250.2	752.9	11024	34.8	100	28.3	8.59	0.52	
23	Feb 11	Balanced	249.7	893.5	11085	35.8	95	31.1	9.34	0.44	
24	Feb 13	CO-Rich*	250.1	752.9	11022	35.8	100	31.9	9.59	0.52	Optim CO
25	Feb 14	CO-Rich*	249.9	893.8	11156	37.0	95	36.1	10.95	0.44	Optim CO
26	Feb 16	Shell Gas	249.8	753.3	11039	36.2	100	22.3	6.78	0.52	
27	Feb 17	Shell Gas	250.0	893.6	11114	37.3	95	25.7	7.89	0.44	
28	Feb 19	CO-Rich	249.6	752.7	10962	35.5	100	29.4	8.98	0.51	Baseline
29	Feb 20	CO-Rich	235.2	753.0	10958	35.9	99	24.1	7.27	0.50	
30	Feb 21	G. Plains	249.7	893.3	6711	36.3	85	23.9	7.20	0.27	
31	Feb 23	CO-Rich	270.1	753.3	10959	35.2	101	28.6	8.58	0.53	
32	Feb 24	CO-Rich	251.1	752.9	Var.	36.4	N/A	25.4	7.81	0.43	
33	Feb 25	CO-Rich	285.0	753.0	2076	36.6	100	4.6	1.40	0.13	
34	Feb 26	CO-Rich	249.8	752.7	11024	35.6	100	28.6	8.78	0.52	Baseline
35	Feb 27	CO-Rich	249.6	753.0	10327	37.6	65	26.4	5.76	0.35	L/D Effe
36	Feb 28	CO-Rich	250.0	750.0	Var.	35.0					

The final run of the current program (E-9) used a fresh batch of the new, alternative catalyst and in a short 10-day run investigated operating conditions which could significantly impact capital and operating costs. A 35 wt% catalyst slurry was activated using raw syngas following successful development of the procedure in the laboratory (Subtask 3.3). Use of syngas avoids the necessity for having separate hydrogen available for activation purposes. The catalyst was activated successfully in-situ without the use of the slurry pump for recirculation/mixing (the pump had been used in the activation of catalyst for Runs E-6/7/8). In fact, as shown in Figure 5 and Table 5, this reduction procedure resulted in the most active catalyst slurry ever produced in the PDU. Elimination of the slurry pump with the associated savings is now confirmed. Finally, having made some modifications to the gas recycle compressor, an operating condition on CO-rich gas was achieved which gave a superficial gas velocity of 0.72 ft/sec and a record production rate of 12.8 tons per day. Little catalyst carryover was observed. This quite remarkable result was a fitting culmination to a very successful PDU operating program.

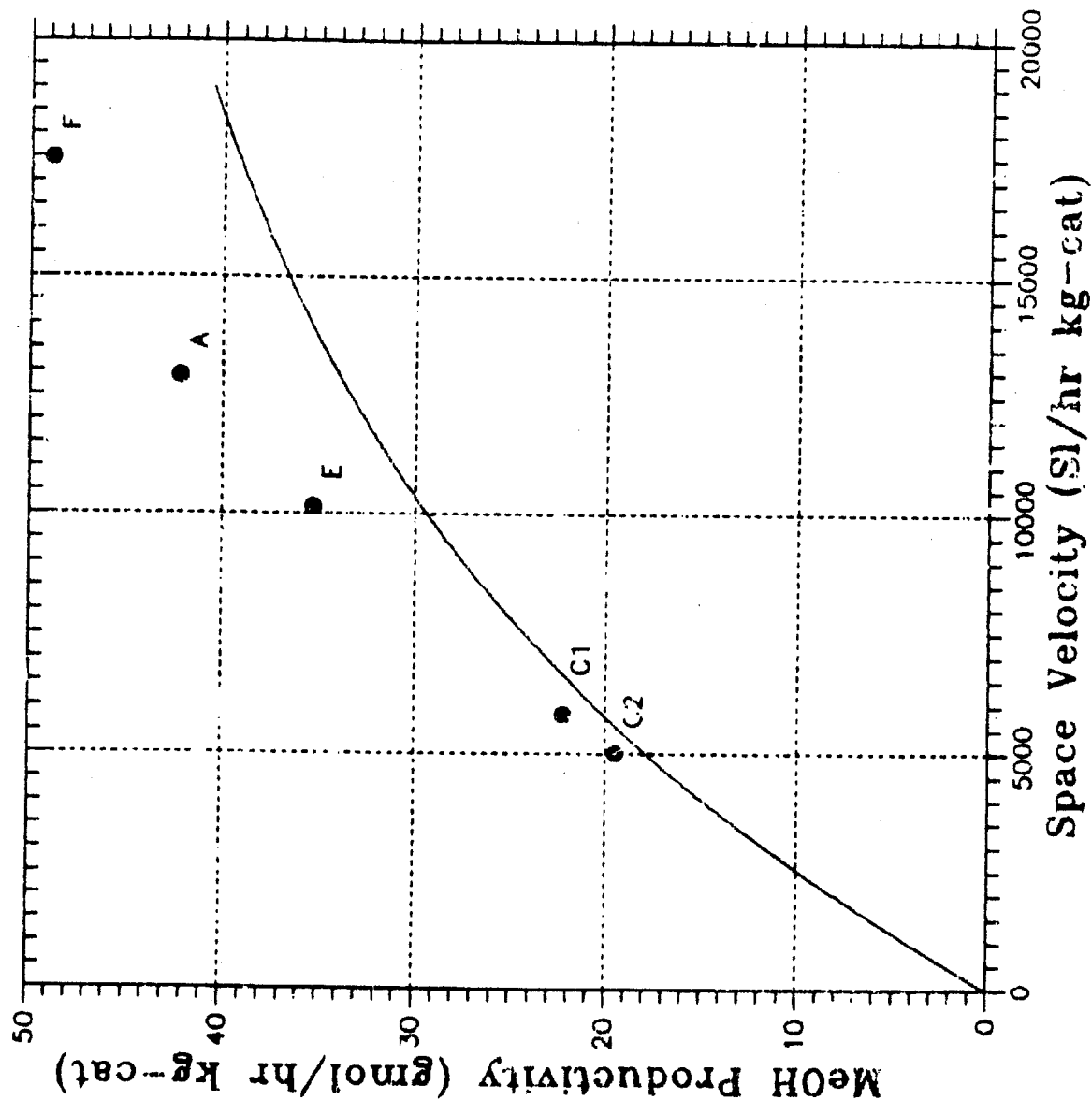
The typical "as condensed" methanol purity produced during these recent campaigns is listed in Table 6. This material, without further upgrading, appears to be an excellent full grade product and is a substantial improvement over previous material produced in the PDU.

Operating Data Analysis

As an additional test during the PVS runs, a two-day study to determine the gas mixing characteristics was carried out using an argon⁴¹ radioactive tracer. During these tests the reactor was fitted with 20 radioactive detectors at various heights and positions. Eighteen argon⁴¹ injections were done. A typical detector response curve for a tracer injection is shown in Figure 6.

FIGURE 5

LAPORTE LPMEOH PDU REACTOR PERFORMANCE Run E-9: CG-Rich Gas, 750 psig, 482°F



LEGEND

Autoclave Data

• Run E-9

TABLE 5

MATRIX OF PVS RUN CONDITIONS FOR RUN E-9; ACTUAL POU CONDITIONS

Run No.	Start Date	Gas Type	Temp °C	Pres. PSIG	Space Velocity L/hr-kg	Slurry Conc. wt%	Slurry Height %	Productivity Mole/hr-kg	Production TPD	Gas Velocity Ft/S	Comments
9A	Mar 23	CO-Rich	249.9	752.6	12914	34.9	100	42.2	11.05	0.52	Baseline
9B	Mar 24	G. Plains	250.0	753.0	12953	33.1	100	39.6	10.17	0.52	
9C1	Mar 25	CO-Rich	299.8	753.0	5833	35.2	93	22.3	5.94	0.23	
9C2	Mar 26	CO-Rich	249.8	753.0	5018	35.0	93	19.5	5.18	0.20	
9D1	Mar 27	CO-Rich	250.1	753.0	5126	35.4	100	20.6	5.47	0.20	Steam Inject.
9D2	Mar 28	CO-Rich	250.0	753.0	10220	34.4	100	36.0	9.39	0.40	Steam Inject.
9E	Mar 29	CO-Rich	250.1	753.0	10148	34.4	100	35.3	9.21	0.40	
9F	Mar 31	CO-Rich	241.6	728.1	17483	34.4	100	48.9	12.84	0.72	Max Gas Vel. RECORD PRODUCTION

TABLE 6

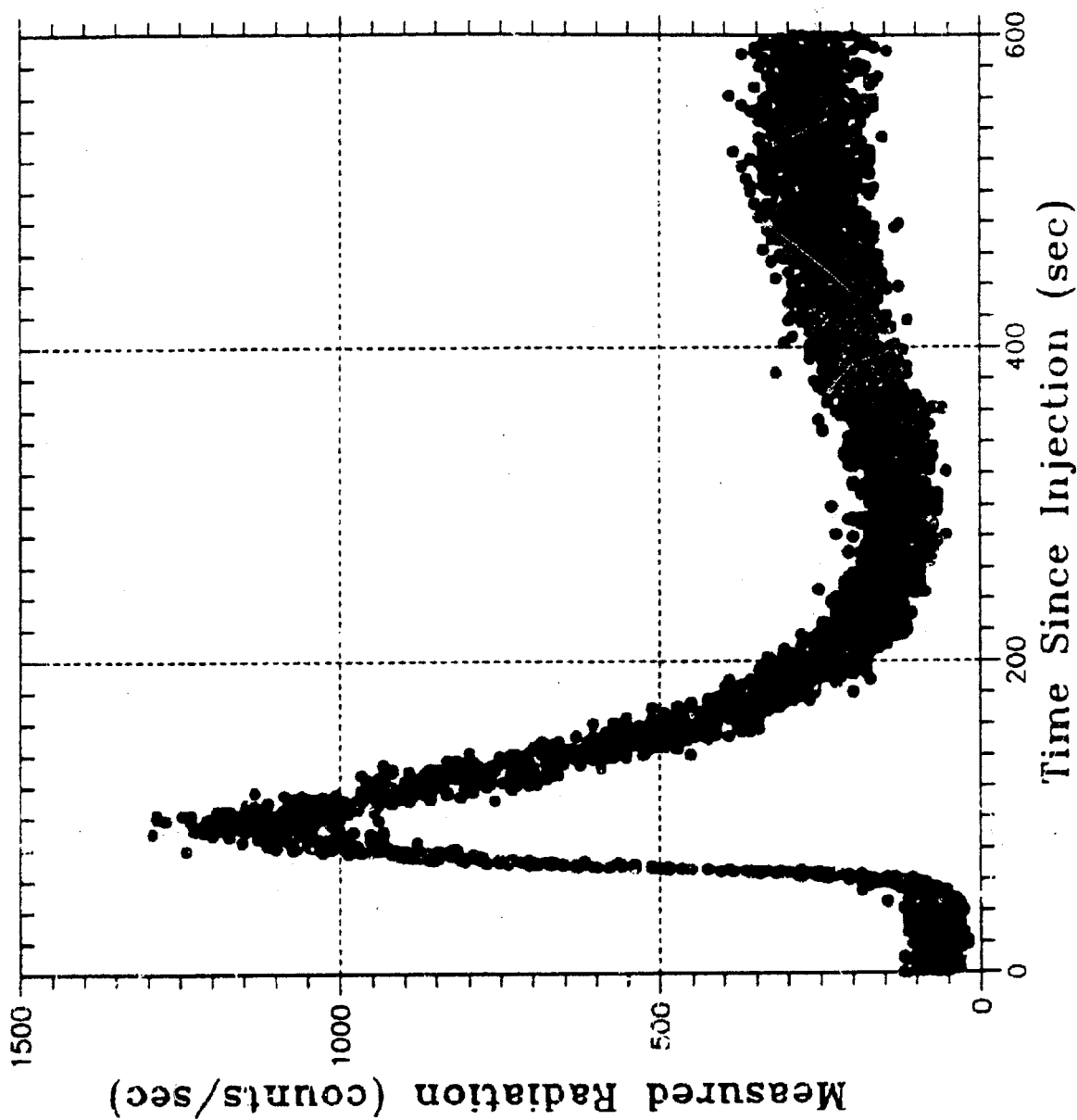
TYPICAL "AS CONDENSED" METHANOL PRODUCT PURITY

<u>COMPONENT</u>	<u>WEIGHT % RANGE</u>	
	<u>H₂ RICH</u>	<u>CO RICH</u>
METHANOL	98.5	97.7
WATER	3.4	0.9
ETHANOL	0.1	0.0
PROPANOL	0.04	0.2
OTHERS	0.01	0.15
OIL	0.08 - 0.2	

FIGURE 6

LAPORTE LPMEOH RADIOACTIVE TRACER STUDY

Typical Detector Response Curve



The detector data from these injections was smoothed and fit to a "tanks-in-series" mixing model. As can be seen in the results from this analysis in Figure 7, backmixing clearly decreases with increasing gas linear velocity. At moderate superficial gas velocities of 0.4 ft/sec, the slurry reactor behaves as essentially 1 CSTR per 3 reactor L/D's. This data is currently being reevaluated using a dispersion modeling approach. The conclusions obtained from the radioactive tracer studies will be an essential element of future scale-up activities.

The performance of the internal slurry heat exchanger has also been evaluated. The internal exchanger was originally designed using the Deckwer correlation (12). In this correlation the Stanton Number is equal to a constant, beta, times the product of the Reynolds, Froude and Prandtl Number squared, raised to the negative one quarter power.

The data from the five runs (E5-E9) has been analyzed and compared to the predicted values. The calculated overall and external heat transfer coefficients agree very well with the predicted values. The average absolute error is 5.8% for the overall coefficient and 17.3% for the external coefficient. A parity plot of the calculated shell-side heat transfer coefficient versus the Deckwer correlation is shown in Figure 8. The data are centered around and fall within 40% of the predicted value. This can be compared to the original data presented in the Deckwer paper which were correlated to within 30% using this correlation.

The level of scatter in the calculated coefficients is a result of the constraints imposed by the PDU. The external coefficients were determined from the calculated overall coefficients. In the PDU, a utility oil system is used on the tube-side of the heat exchanger to control the reactor temperature. The heat exchanger design minimized the contribution of the tube-side heat transfer resistance, however, this resistance was still a major contribution to the overall heat transfer resistance. As a consequence, small instrument errors, inaccuracies in the physical property estimation of the utility oil and uncertainty in the tube-side heat transfer coefficient correlation, result

FIGURE 7

LAPORTE LPMEOH RADIOACTIVE TRACER STUDY CSTRs IN SERIES PER L/D vs GAS SUPERFICIAL VELOCITY

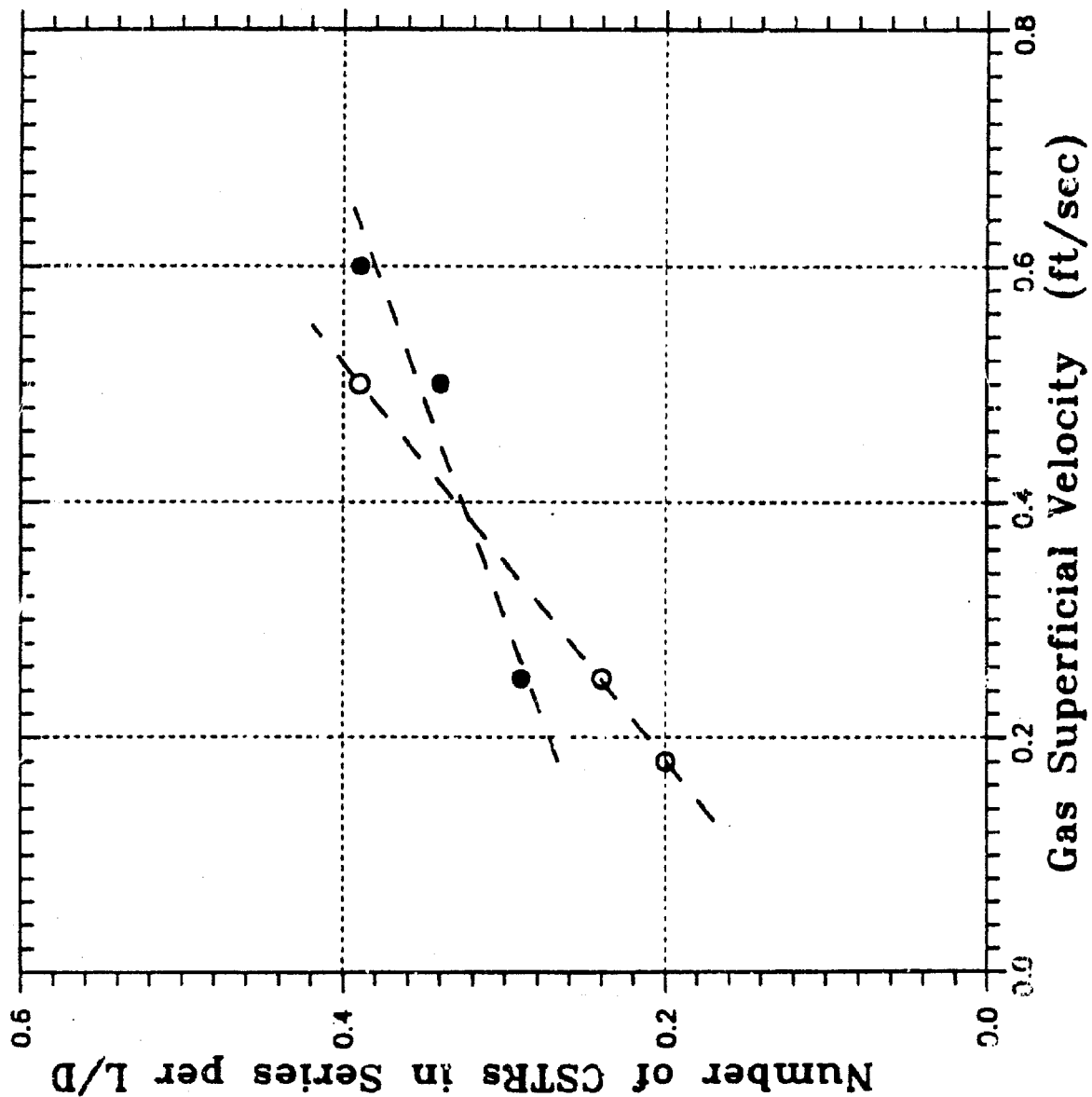
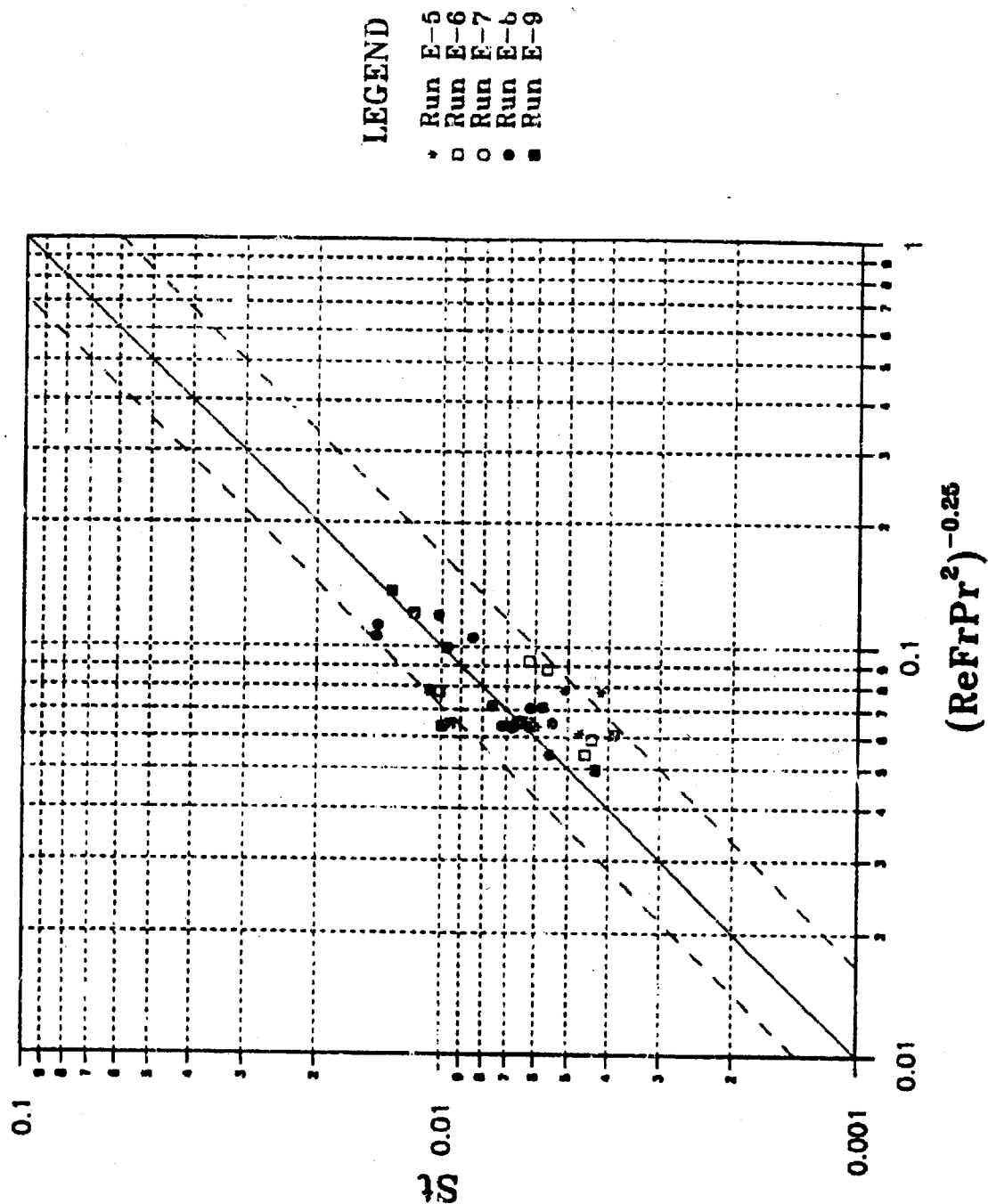


FIGURE 8

DECKWER CORRELATION PARITY PLOT 27.10B Shell-side Heat Transfer Coefficient



in a significant loss of accuracy in the calculated shell-side heat transfer coefficient. This is illustrated in Figure 9 which shows the predicted uncertainty in the data from Run E-9, as calculated by a propagation of error analysis. The conclusion from this study is that the Deckwer correlation is a reasonable method to predict the slurry heat transfer coefficients in the LPMEOH reactor.

Research Program

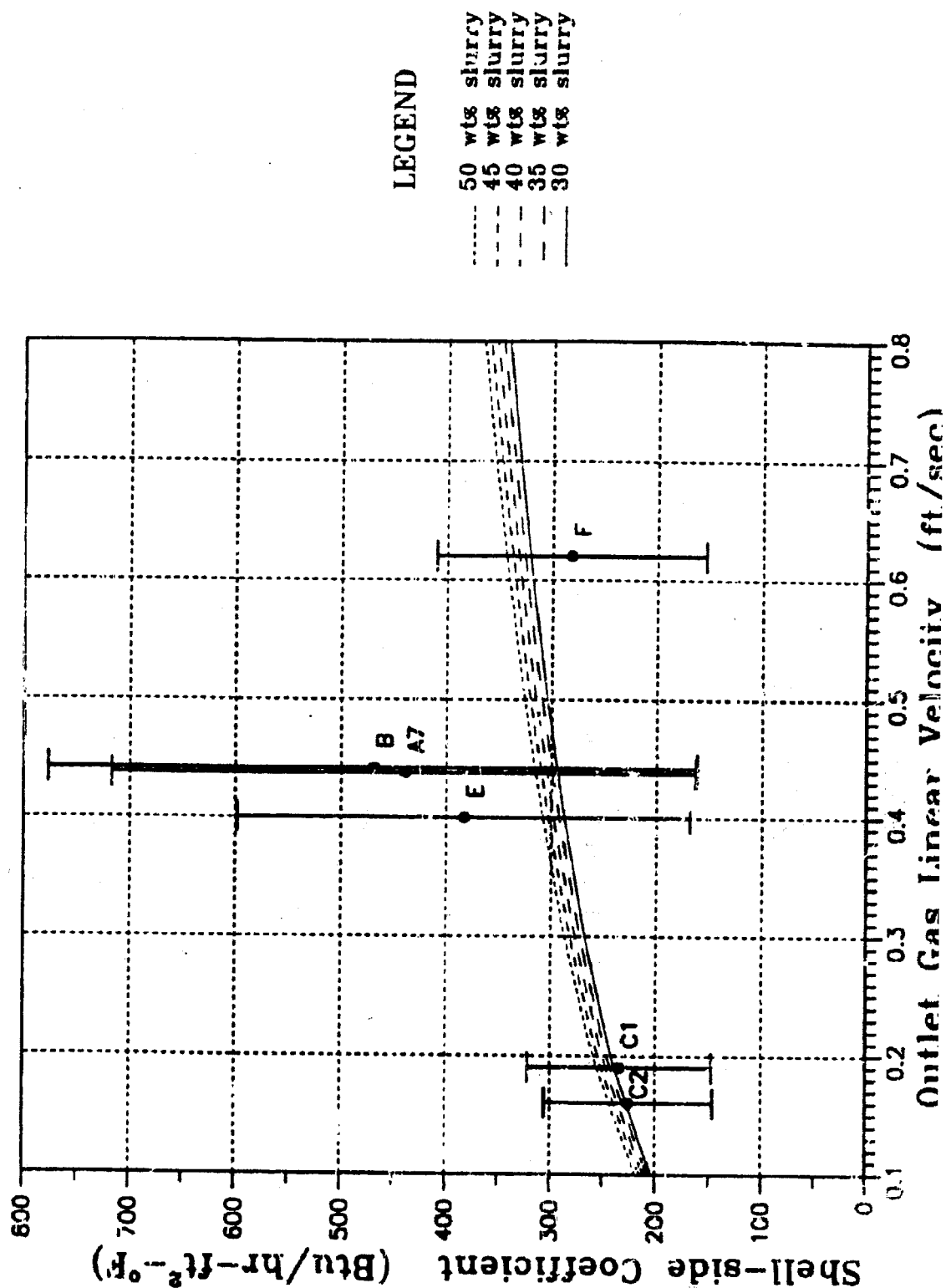
In the above description of the PDU operations, several references were made to contributions originating from the research program. Catalyst activation with syngas, the ability to store activated catalyst, and the certification of an alternative catalyst and liquid were critical to the success of PDU operations and were developed initially as part of the laboratory research program.

The research program is comprised of eight subtasks which are listed in Table 7. With the exception of subtasks 3.3.2 Improving the Reduction Procedure, 3.5 Fundamental Modeling, and 3.8 Catalyst Poisons Field Tests, the completed status of each of these efforts was reported in the previous DOE Contractors' Review Meeting (10). As in the PDU operations, the following discussion therefore focuses on the results obtained since that time.

The success of the subtask to Improve the Reduction Procedure is best illustrated with the results obtained in the PDU Run E-9. Laboratory screening experiments lead to a procedure to activate the catalyst slurry using a dilute syngas stream. Guidelines to monitor and control the progress of the reduction procedure were also defined in this program. The syngas reduction procedure employed in Run E-9 resulted in a fully active catalyst slurry. The apparent performance of the catalyst above the autoclave prediction, as seen in Figure 5, is due to the partial plug flow nature of the LPMEOH reactor. Subsequent laboratory testing confirmed that this activation procedure resulted most active catalyst slurry obtained in the PDU operating program.

FIGURE 9

SHELL-SIDE COEFFICIENT vs. LINEAR GAS VELOCITY Run E-9, 27.10B Internal Heat Exchanger



these assumptions regarding the adsorption behavior of the reacting species. The form of the numerator depends on the assumption of the rate-limiting steps in the sequences for CO and CO₂ hydrogenation. The best fit was obtained for the rate expression assuming that the addition of the third hydrogen atom to CO is rate-limiting in the CO hydrogenation pathway, while the addition of the second hydrogen atom to CO₂ is rate-limiting in the CO₂ pathway. The resulting rate expression is shown in Table 8.

Figure 10 is a parity plot of the predicted versus measured methanol production rates. This model does an adequate job of predicting rates with an average absolute error of 13% for the entire database. Figure 11 shows a comparison of the predicted effect of CO₂ concentration in the CO-rich gas matrix with actual data at a space velocity of 5,000 SL/hr-kg. As can be seen in this example, there is reasonably good accuracy in both the trend and absolute value of the predicted rates.

When this rate model was applied to the database obtained on the new alternate catalyst, F21/OE75-43, the average error increased to 37%. This was a surprising result since both catalysts are similar copper/zinc based catalysts. New rate expressions are therefore being investigated which will successfully describe both catalyst databases.

The Catalyst Poisons Field Test is a followup to the Catalyst Poison Laboratory Studies. In this initial program, several adsorbents were screened for the individual removal of Fe(CO)₅, Ni(CO)₄, COS, H₂S, and HCl. The concentration targets of these process impurities, and the equilibrium capacities of the preferred adsorbents and their regenerability was presented at the previous Contractors' Meeting.

The results of the above study were incorporated into the design and assembly of a gas clean-up test rig. This rig, complete with a "proof of concept" serial autoclave, is housed in a self-contained trailer capable of being taken to gasification sites as needed. The operability of the unit was demonstrated

MODEL A3-C2

Key Assumptions:

- Langmuir-Hinshelwood Kinetics.
- CO and CO₂ hydrogenation occur in parallel.
(Graaf et al., Chem. Eng. Sci. Vol. 43, No. 12, pp 3185-3195)
- Two adsorption sites: CO and CO₂ adsorb competitively on site 1, H₂ and H₂O adsorb competitively on site 2.
- Water-gas shift reaction is always at equilibrium.

Derived rate expression:

$$\text{rate} = \frac{b_0(f_{\text{CO}}f_{\text{H}_2} - f_{\text{CH}_3\text{OH}}/K_{\text{eq}}f_{\text{H}_2}) + b_1(f_{\text{CO}_2}f_{\text{H}_2}^{1/2} - f_{\text{CH}_3\text{OH}}f_{\text{CO}_2}/K_{\text{eq}}f_{\text{CO}}f_{\text{H}_2}^{3/2})}{(f_{\text{CO}} + b_2f_{\text{CO}_2})(1 + b_3f_{\text{CO}_2}f_{\text{H}_2}^{1/2}/f_{\text{CO}})}$$

FIGURE 10

PARITY PLOT FOR F21/OE75-44 CATALYST DATABASE

Model A3-C2

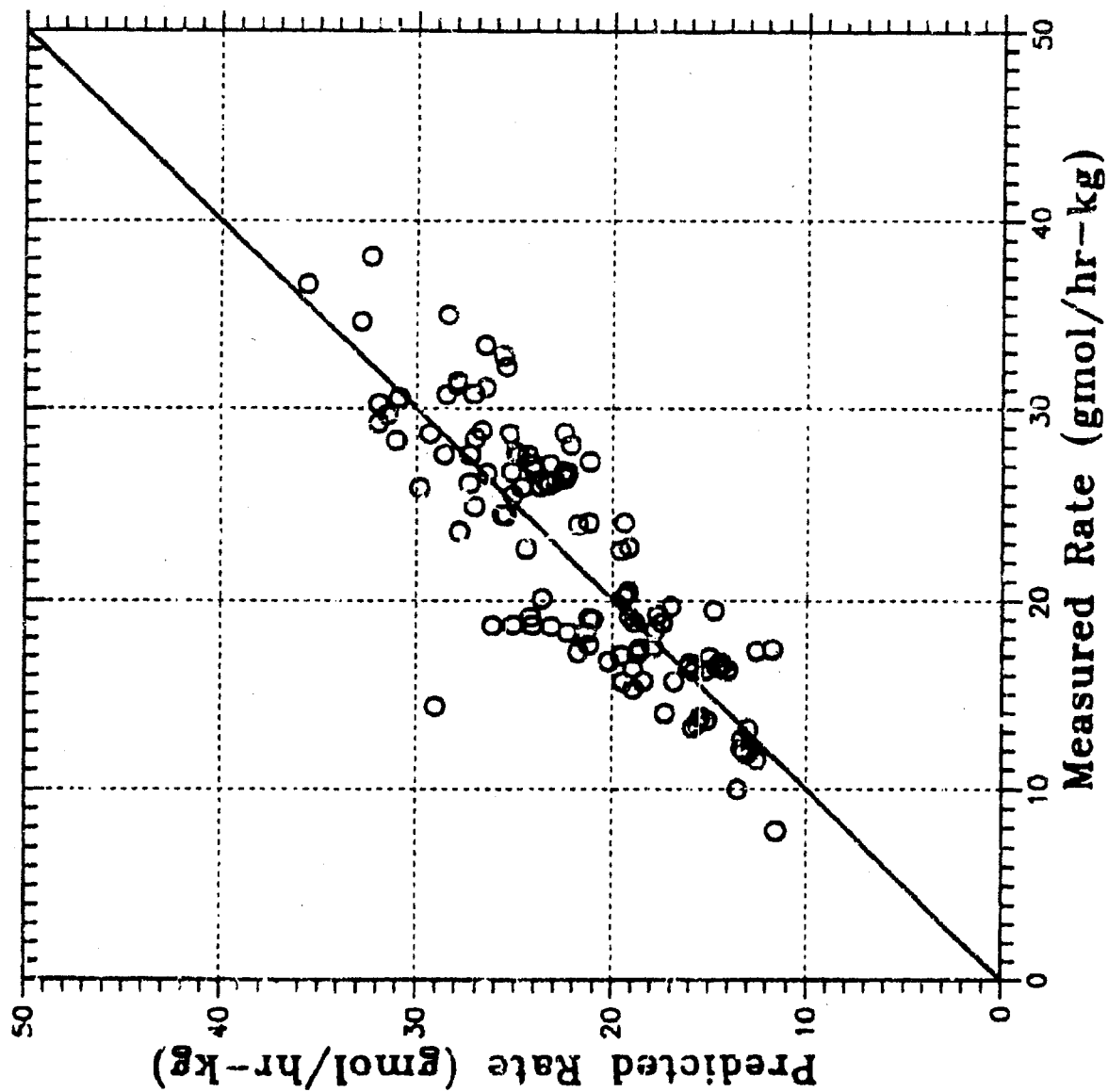
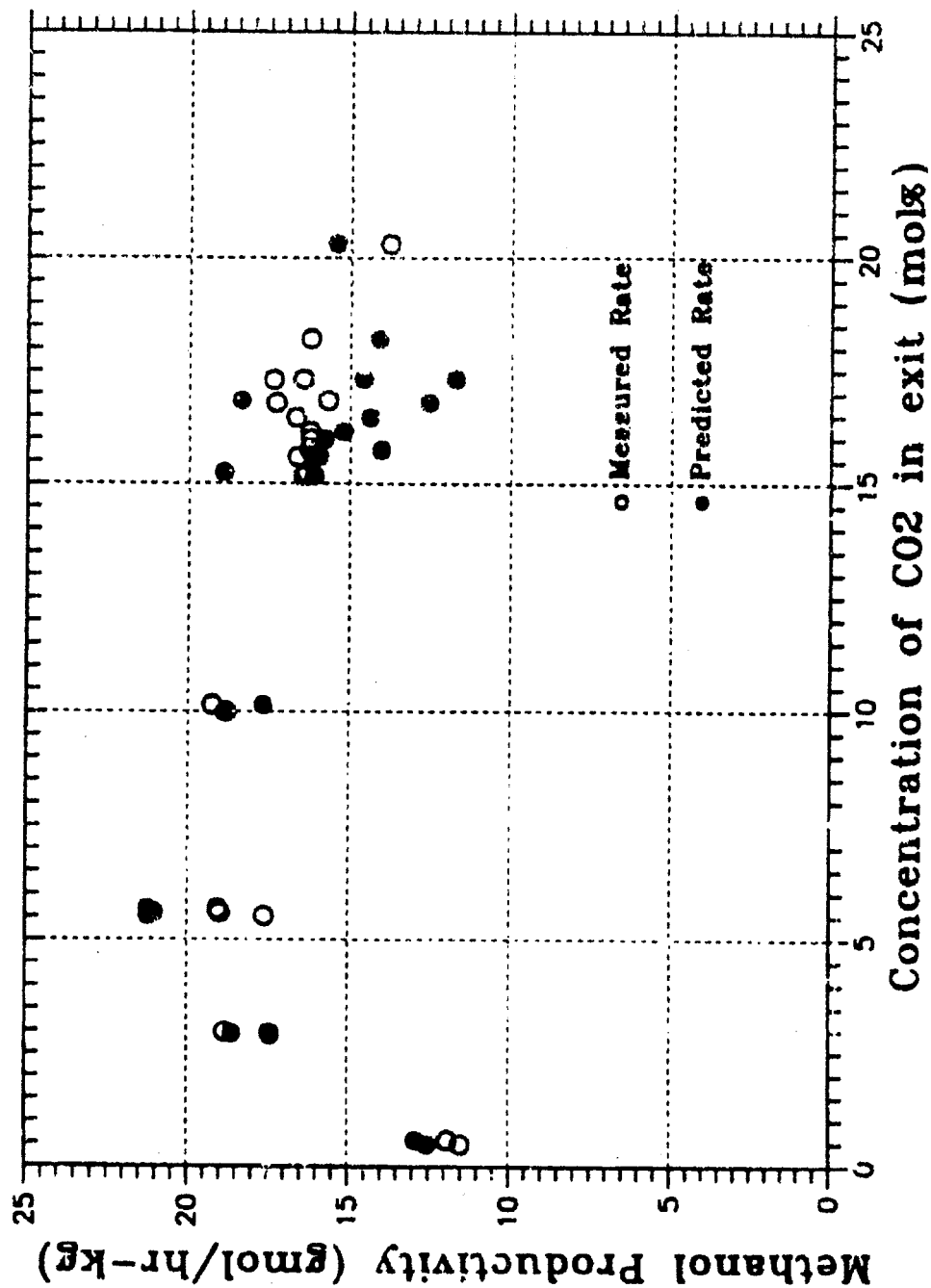


FIGURE 11

EFFECT OF CARBON DIOXIDE CONCENTRATION ON METHANOL RATE

CO-Rich gas, 482 °F, 750 psig, 5000 SI/hr-kg



on stored CO-rich gas from Cool-Water's Texaco gasifier. The gas clean-up rig is currently being tested at Dakota Gasification's Great Plains facility in Beulah, ND. The ability of the absorber unit to efficiently remove potential catalyst poisons, resulting in acceptable activity maintenance, will be a key program result.

Summary

The past eighteen months has seen significant achievements in the path to commercializing LPMEOH technology. Strong interaction between research and PDU operating programs has led to several notable "first's", each having an impact on capital and operating costs.

The key results are summarized below:

- commercial catalysts and slurry liquids proved successful
- simple reactor design confirmed
- catalyst activation with syngas and operation with highly concentrated slurries (up to 50 wt%) successfully demonstrated
- catalyst "life" excellent (less than 0.2% per day deactivation)
- continuous catalyst addition/withdrawal demonstrated
- productivity high, quality good
- operations excellent; over 1,000 tons of methanol produced; shutdowns/restarts/load-following easily accommodated

The technology is now developed. Once the field-test on catalyst poisons removal is satisfactorily completed we have all the necessary information to take LPMEOH to the next step of commercialization.

Air Products and Dakota Gasification have jointly proposed to design, construct and operate a demonstration LPMEOH plant at the Great Plains Facility under the DOE CCT-III program. This will be a 500 TPD facility operating on real coal gas produced from Lurgi gasifiers. If selected in December 1989, this demonstration plant will be the final hurdle in the joint 10-year DOE/EPRI/Air Products/Chem Systems effort to commercialize the LPMEOH technology.

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