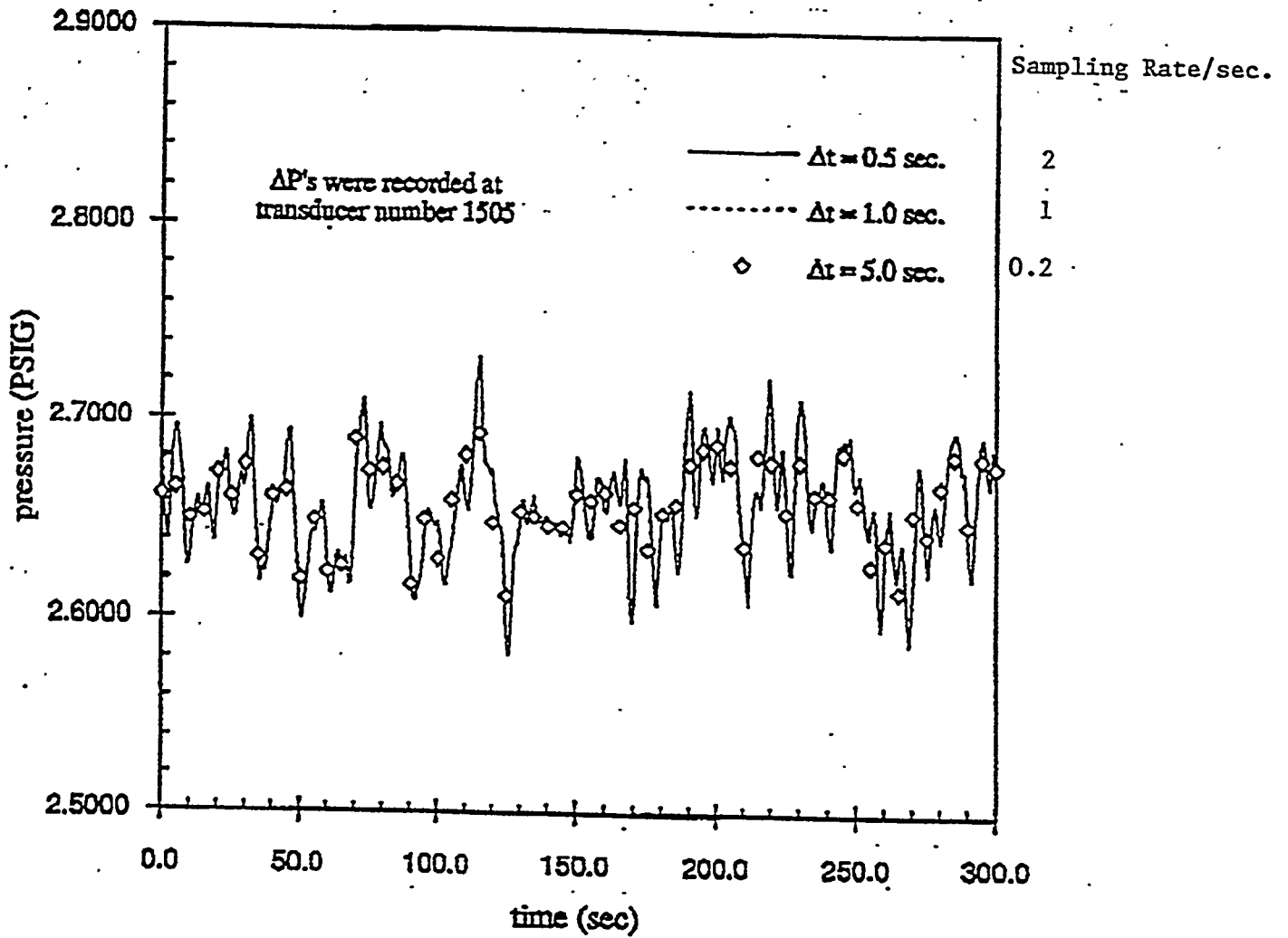# Figure 2.3 Pressure Signal versus Time for Different Sampling Rates

condensation was observed in the 27.14 oil separator. With almost 17 mole% methanol in the reactor effluent, the methanol dew point was 268°F. Hence, the temperature of the 27.14 was increased from 280 to 295°F to avoid methanol condensation.

The differential pressure (DP) measurements appeared to be working well. The DP measurement locations on the reactor are shown in Figure 2.4. Preliminary estimates of gas holdups from the DP readings indicated holdups showing similar trends, but lower in magnitude than those derived from nuclear density readings:

Run No.	Gas Holdup from DP vol%	Gas Holdup from NDG vol%
13.1A	43.8	50.5
13.1B	48.0	54.7
13.2A	36.3	42.3
13.2B	36.5	43.1

As observed with the NDG measurements, a holdup profile was also observed along the length of the reactor with the DP measurements. DP and gas holdups for different sections of the reactor are shown below for Run No. 13.2A. Holdup was higher at the top.

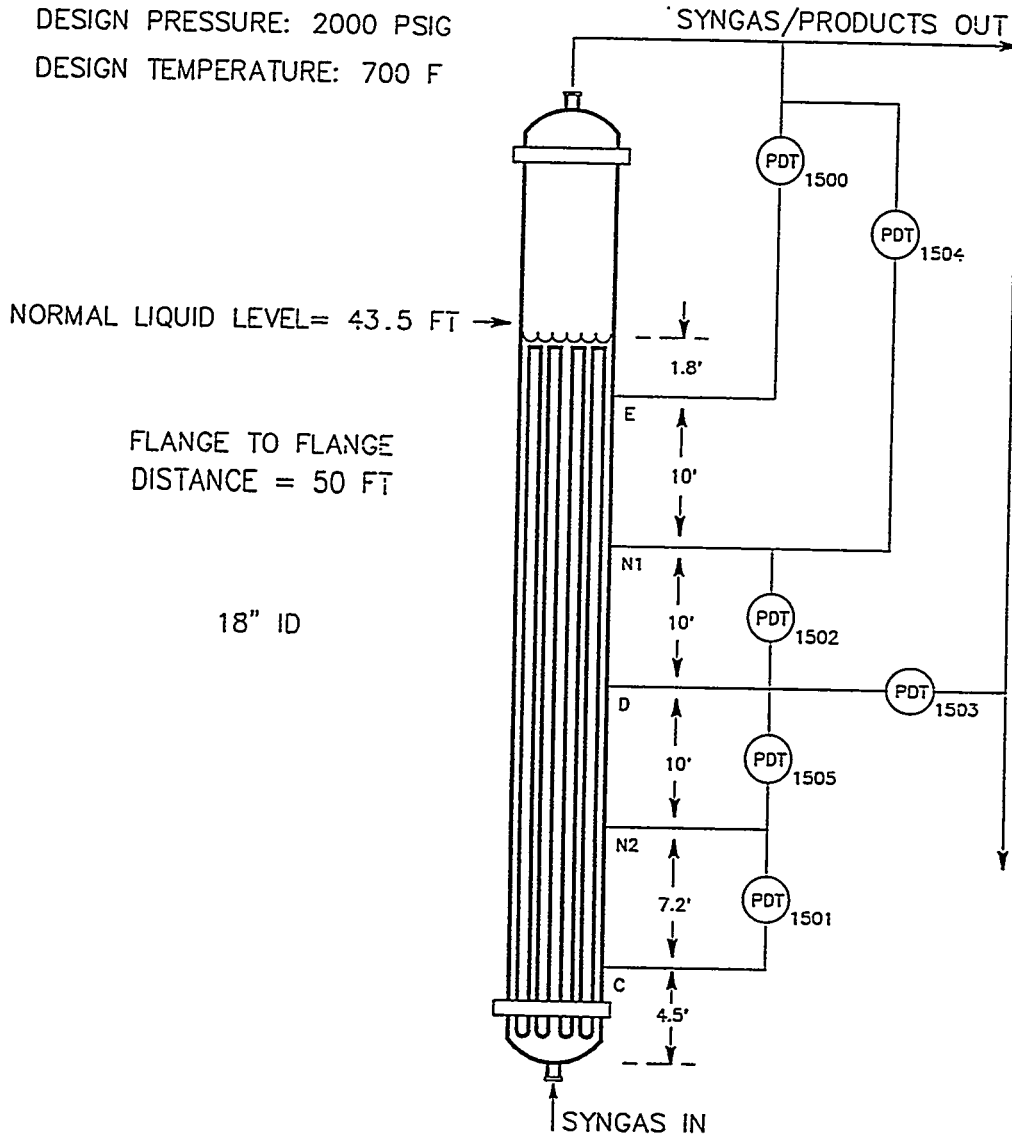| Nozzles	Transmitters PDT	Differential Pressure, psi	Gas Holdup, vol%
C-N2	1501	1.95	37.4
N2-D	1505	2.96	31.2
D-N1	1502	2.84	34.0
N1-E	1504 - 1500	2.49	42.5

A shutdown test was conducted at the end of Run AF-R13.2 to obtain a more accurate holdup estimate. Based on liquid level measurement with flow shutdown, gas holdup was calculated at 32.9 vol%. This compares with an estimate of 43.1 vol% based on NDG measurements and 36.5 vol% based on DP measurements. An attempt was made to measure the rate of drop of liquid level immediately after the gas was shut down using the NDG. However, this drop was too fast compared to the response of the NDG as well as the speed at which the NDG can be moved. DP data were collected during the shutdown test with the Sandia data acquisition system. These data may help sort out distribution of large bubbles vs. small bubbles. Kim Shollenberger (Sandia) conducted a preliminary analysis of the data. Smooth curves were obtained when gas holdup was plotted as a function of time during the shutdown test (Figure 2.5), indicating only a single normal bubble size distribution in the column. Further analysis is ongoing.

Figure 2.4 LaPorte AFDU Oxygenates High Pressure Reactor

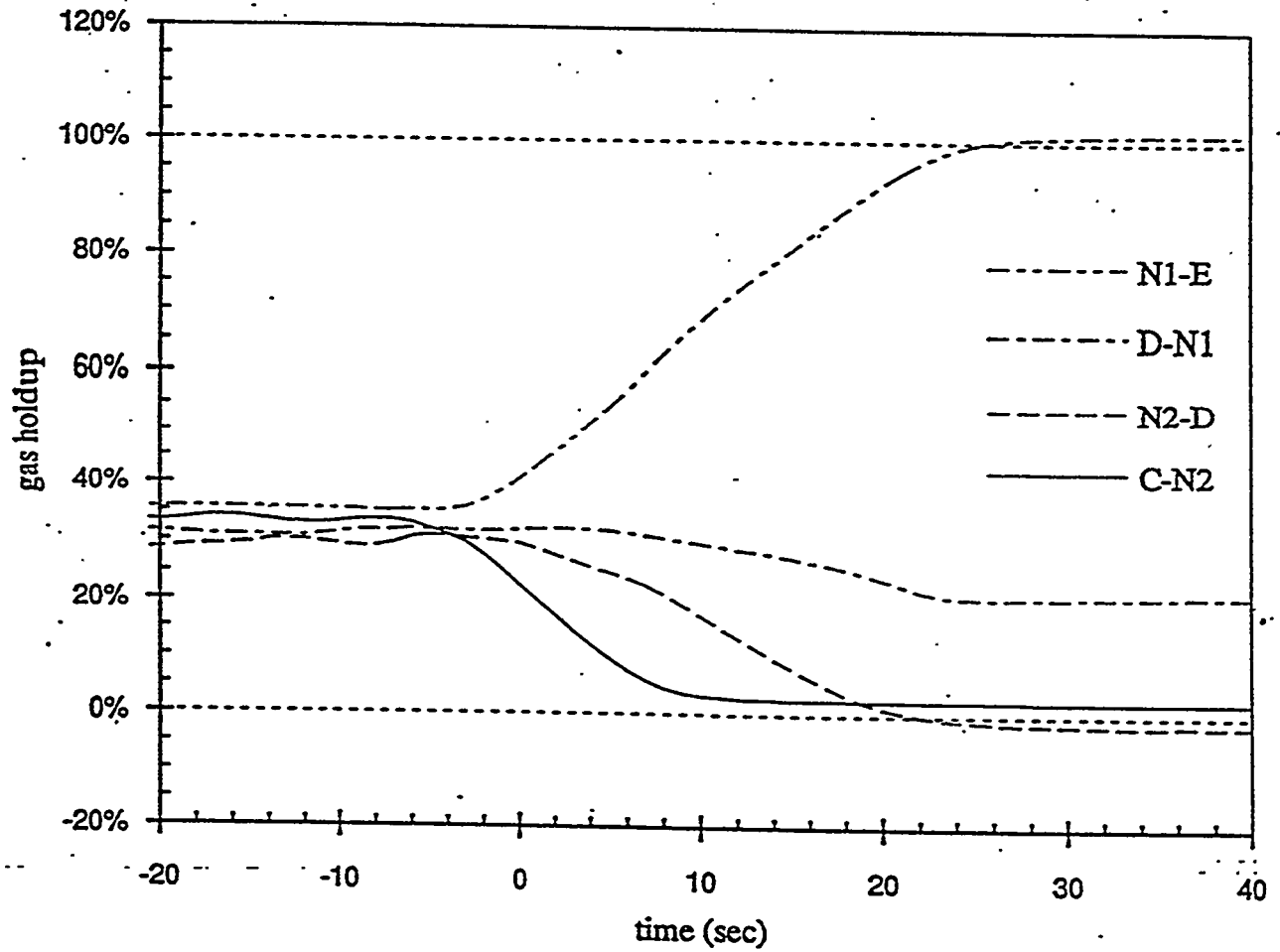DIFFERENTIAL PRESSURE TRANSMITTER POSITIONS

DESIGN PRESSURE: 2000 PSIG

DESIGN TEMPERATURE: 700 F

SYNGAS/PRODUCTS OUT

NORMAL LIQUID LEVEL= 43.5 FT →

PDT 1500

PDT 1504

1.8'

E

10'

N1

10'

FLANGE TO FLANGE
DISTANCE = 50 FT

18" ID

PDT 1502

PDT 1503

D

10'

PDT 1505

N2

7.2'

PDT 1501

C

4.5'

SYNGAS IN

DPT2720.SKD

BL3   9/20/95

19

Figure 2.5 Run No. R13.2B
Gas Holdup During Shutdown

After the shutdown test, the unit was brought on-stream with Texaco gas in an attempt to reach the conditions of Run AF-R13.3: 10,000 sl/hr-kg, 750 psig, 482°F, 1.2 ft/sec gas inlet velocity. With Texaco gas, the 01.20 recycle compressor reached its limit at 0.95 ft/sec. Operating at lower pressure helped little as pressure drop through the plant increased. In order to achieve higher gas velocity, the feed composition was changed from Texaco gas to Kingsport gas. Higher methanol production was expected with Kingsport gas, which would lower the pressure drop in the back end. A linear velocity of 1.13 ft/sec was achieved with this gas, and stable operation was obtained at this condition. Reactor performance was stable with a production rate of about 18 TPD. The NDG readings showed higher fluctuations compared to those typically observed at lower velocities. A gas holdup of 55.8 vol% with a catalyst concentration of 48.7 wt% was estimated from the NDG readings. The DP measurements indicated a holdup of 44.9 vol% and a catalyst concentration of 39.2 wt%. Oil loss rate from the reactor was measured at this velocity. A modest loss rate of about 10 gph was estimated from level rises in vessels downstream of the reactor (21.11 & 27.14).

At 00:45 hours on 11 June, the plant experienced a shutdown due to loss of compression. Belts on the motor for the two compressors broke, shutting down the plant 6 hours earlier than scheduled. Since there were enough data at this last condition with the Baseline catalyst, it was decided to cool down the reactor in preparation for a turnaround to the Alternate catalyst run. The slurry was drained directly from the reactor.

2.2 LPMEOH with Alternate Catalyst

2.2.1 Slurry Preparation
A 40 wt% oxide catalyst slurry was mixed in the 28.30 Prep Tank. The Prep Tank was charged with 1766 lbs of Drakeol-10 oil at 08:00 on 10 June and 1178 lbs of Alternate catalyst at 08:00 on 12 June. Catalyst was taken from eleven drums of lot # 022811. The slurry was heated and agitated in the Prep Tank for two hours prior to transfer to the reactor.

2.2.2 Catalyst Reduction
Catalyst reduction began at 14:30 on 12 June. The reduction gas (4% CO in N_2) was set at 12,500 scfh with the reactor pressure at 67 psig (Run # A10). The heat up commenced at 14:45 and proceeded from 193°F to 464°F at a rate of 15°F/hr.

Initially, the Alternate catalyst reduction seemed a little slower than the previous Baseline catalyst reduction. The reduction rate increased later, and most of the uptake was complete by about 360°F (12-13 hours on-stream, same as Baseline). The total uptake peaked out close to the theoretical maximum value of 2.68 SCF/lb oxide (see Figure 2.6). Reduction in the bubble column was a little slower compared to that in the autoclave. The 27.20 internal heat exchanger was easily able to control temperature, and the ramp rate proceeded on schedule with no evidence of an exotherm. At 392°F, the reduction gas flow was reduced to 9,375 scfh as planned to reduce oil loss from the reactor and conserve on nitrogen usage. When the flow was reduced, the slow adjustment of CO concentration in the reduction gas caused the calculated uptake value to drift. Gas holdup during the reduction was slightly higher than expected: 29-34 vol% at 12,500 scfh. Catalyst concentration was in the 41-42 wt% range.

Figure 2.6 Hydrodynamic Run at LaPorte

CO Reduction of Haldor—Topsoe   Alternate P

LEGEND

H2 Uplk	
CO Uplk	
Tot Uplk.	
Lab Uplk	

22
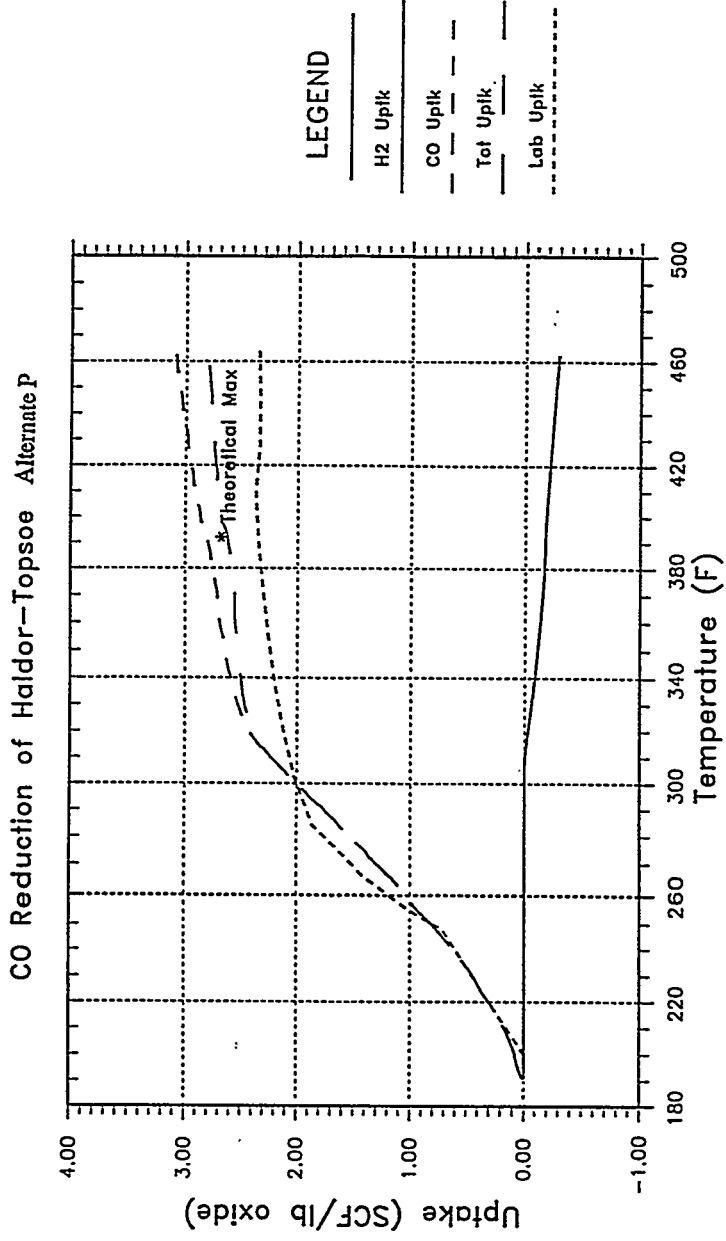
2.2.3 Process Variable/Hydrodynamic Study

Syngas flow to the reactor began at 11:00 on 13 June. The unit was fully lined out at the conditions of Run No. AF-R14.1 (Texaco gas, 7200 sl/hr-kg, 750 psig, 482°F, 0.84 ft/sec) by 18:00. The initial data indicated typical hyperactivity of the catalyst. The operational results were very similar to those seen previously during AF-R13.1 with the Baseline catalyst. The production rate was 12.0 TPD of methanol, and the CO conversion was 16.4%. The mass balance around the plant was excellent. Liquid analysis showed typical methanol product composition with some very slight variations in the impurity mix. Nuclear density gauge readings indicated a gas holdup of 49.6 vol%, and a catalyst concentration estimated at 45.4 wt%. Steady operations continued for another day at conditions of Run No. AF-R14.1. Compared to the Baseline catalyst, the Alternate catalyst showed even less decline in activity over its initial 24 hours of operation. The production rate decreased to 11.7 TPD of methanol, and the CO conversion dropped to 16.2%. Nuclear density gauge readings were identical to the previous data period. A shutdown test immediately following this run indicated 38.9 vol% gas holdup.

Conditions were changed to Run No. AF-R14.2 (Kingsport gas, 4000 sl/hr-kg, 735 psig, 482°F, 0.48 ft/sec) shortly after noon on 15 June. The plant ran smoothly at this condition for three days with stable catalyst performance. The Alternate catalyst continued to perform very similarly to the Baseline catalyst. The production rate was about 10 TPD methanol. Nuclear density gauge readings indicated a gas holdup of 37.8 vol%, and catalyst concentration was estimated at 39.6 wt%.

Due to the lack of an adequate CO supply, the originally planned condition of Run No. 14.3 (Kingsport gas, 10,000 sl/hr-kg, 735 psig, 482°F, 1.2 ft/sec inlet gas velocity) could not be achieved. Instead, it was decided to operate at another high velocity condition that would consume less CO. Conditions were changed to 7,100 sl/hr-kg, 520 psig, 482°F and 1.18 ft/sec inlet gas velocity with Kingsport gas. The plant performed steadily at this condition. Catalyst performance was close to expected. CO conversion was about 33% compared to a modeled 2-CSTR expectation of 32.5%. Nuclear density readings had some fluctuations similar to those observed with the Baseline catalyst at high velocity. A gas holdup of 50.4 vol% and catalyst concentration of 45.6 wt% were estimated based on the nuclear density readings. DP measurements on the reactor indicated a holdup of 36.6 vol%. A shutdown test was conducted at the end of the mass balance period. Gas holdup of 36.6 vol% was measured during the shutdown test.

After the shutdown test, the unit was brought to conditions of Run 14.4 (Texaco gas, 4,100 sl/hr-kg, 750 psig, 482°F, and 0.47 ft/sec inlet gas velocity). The plant performed steadily at this condition. Catalyst activity was close to expected. CO conversion was 17.5% compared to the modeled 2-CSTR expectation of 17.7%. Increased levels of higher alcohols, methyl formate and methyl acetate were observed at this low space velocity condition. Nuclear density readings had no fluctuations, as the linear velocity at this condition was low as well. A gas holdup of 42.9 vol% and catalyst concentration of 42.2 wt% were estimated based on the nuclear density readings. DP measurements on the reactor indicated a holdup of 33.3 vol%.

The operating conditions of the unit were changed to baseline conditions (Run No. AF-R14.5: Texaco gas, 7,200 sl/hr-kg, 750 psig, 482°F, and 0.83 ft/sec inlet gas velocity) on the morning of 21 June. The plant performed steadily at this condition. Catalyst activity was very close to that observed initially at the same condition (Run No. AF-R14.1). CO conversion dropped only slightly from 16.2% to 15.9%, and by-product formation was down to the same level as Run 14.1 A gas holdup of 50.8 vol% and catalyst concentration of 46.5 wt% were estimated based on the nuclear density readings.

Further measurements were made on the 21.11 dephlegmator at the baseline condition. Although flooding was ruled out as a reason for less-than-design performance, variability in oil capture was still apparent. A large amount of AFDU data is in need of analysis before a final decision is made on possible inclusion of dephlegmators in commercial flowsheets.

2.2.4 Catalyst Performance Comparison

The Alternate catalyst performance is compared with the Baseline catalyst performance in Table 2.3. The comparison can be made at two different conditions. Very similar CO conversion and methanol production rates are evident. Lower gas holdup was obtained with the Alternate catalyst. Results obtained with the two catalysts at high velocity are presented in Table 2.4. A direct comparison cannot be made because the two conditions were different. However, some similarities are notable. During both runs, the NDG readings had high fluctuations but a stable average. Also, the oil loss rate from the reactor was moderate. CO conversion obtained with both catalysts at different conditions is shown in Figure 2.7. In addition to the similarity of the two catalysts, the plot shows stable operation with the Alternate catalyst, when conversion for R14.5 is compared with that for R14.1.

By-product data were analyzed more closely because increased levels of higher alcohols, methyl formate and methyl acetate were observed with the Alternate catalyst at low space velocity condition (Run No. AF-R14.4). The Baseline catalyst was not operated at this condition in the previous run; however, comparison of the two catalysts is available at two other conditions: Run Nos. 13.1/14.1 and 13.2/14.2 (see Table 2.5). By-product formation was very similar for the two catalysts at these conditions.

2.2.5 Reactor Tracer Study

On 21 June, ICI Tracerco personnel started preparing for a 3-day tracer study of the reactor unit. The study was started on 22 June at the baseline conditions (Run AF-R14.6: 0.83 ft/sec inlet velocity, 7200 sl/hr-kg, 750 psig, 482°F, Texaco gas). Detectors were set up at various locations outside the reactor as shown in Figure 2.8. Sets of four detectors at 90° angles were set up at seven different heights. In addition, detectors were installed at the reactor inlet, reactor outlet, vapor space near the reactor top and recycle feed line. During the liquid injection, the detector at the reactor inlet was moved to the liquid injection nozzle.

Table 2.3 Catalyst Performance Comparison for LPMEOH

Catalyst Run No.	Baseline AF-R13.1B	Alternate AF-R14.1B	Baseline AF-R13.2B	Alternate AF-R14.2B
Syngas Composition	Texaco	Texaco	Kingsport	Kingsport
Space Vel., sL/hr-kg	7130	7200	4000	4030
Pressure, psig	751	754	735	735
Temperature, deg. F	484	482	483	483
Inlet Linear Velocity (ft/s)	0.85	0.84	0.49	0.48
CO Conversion to MEOH (%)	15.5	16.2	49.6	48.6
Methanol Production (TPD)	11.6	11.7	9.9	9.8
Slurry Concentration Based on NDG (wt %)	48.2	45.3	42	39.7
Gas Holdup Based on NDG (Vol %)	54.7	49.9	43.1	38.1

Table 2.4 LPMEOH Results at High Velocity

Catalyst	Baseline	Alternate
Run No.	AF-R13.3B	AF-R14.3
Syngas Composition	Kingsport	Kingsport
Space Vel., sL/hr-kg	9110	7090
Pressure, psig	720	521
Temperature, deg. F	482	482
Inlet Linear Velocity (ft/s)	1.13	1.18
CO Conversion to MEOH (%)	39.9	33
Methanol Production (TPD)	18.3	11.1
Slurry Concentration (wt %)	48.9	45.6
Gas Holdup (vol. %)	55.8	50.4
Limitation	Recycle Compressor	CO Supply
NDG Readings	High Fluctuations Stable Average	High Fluctuations Stable Average
Oil Loss Rate from Reactor	Moderate	Moderate
Reactor Design Basis	Kingsport:	0.64 ft/sec
	Recent Commercial Designs:	0.80-0.85 ft/sec
	New Commercial Design:	~1.0 ft/sec

Figure 2.7 Hydrodynamic/Methanol Run at LaPorte

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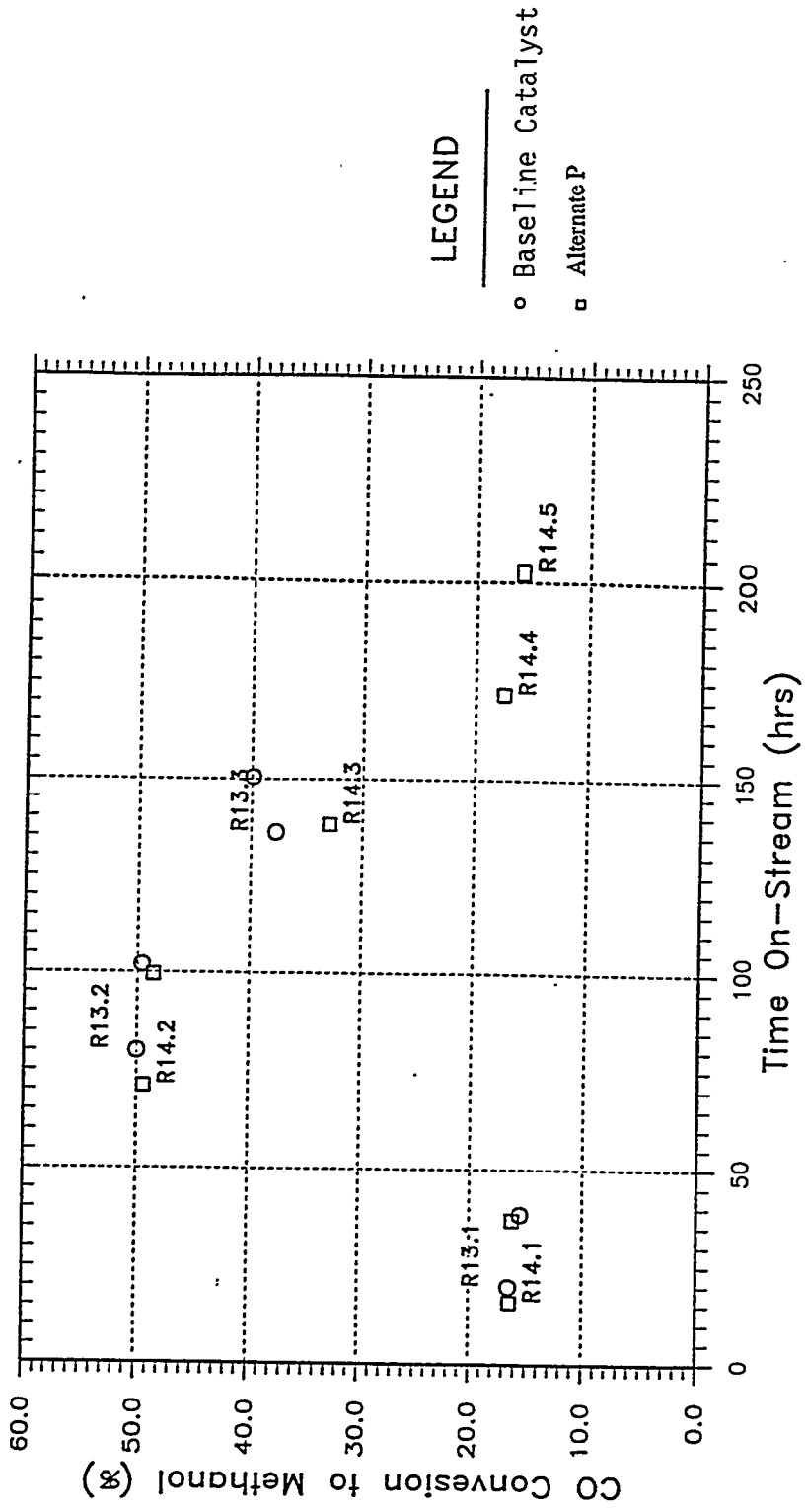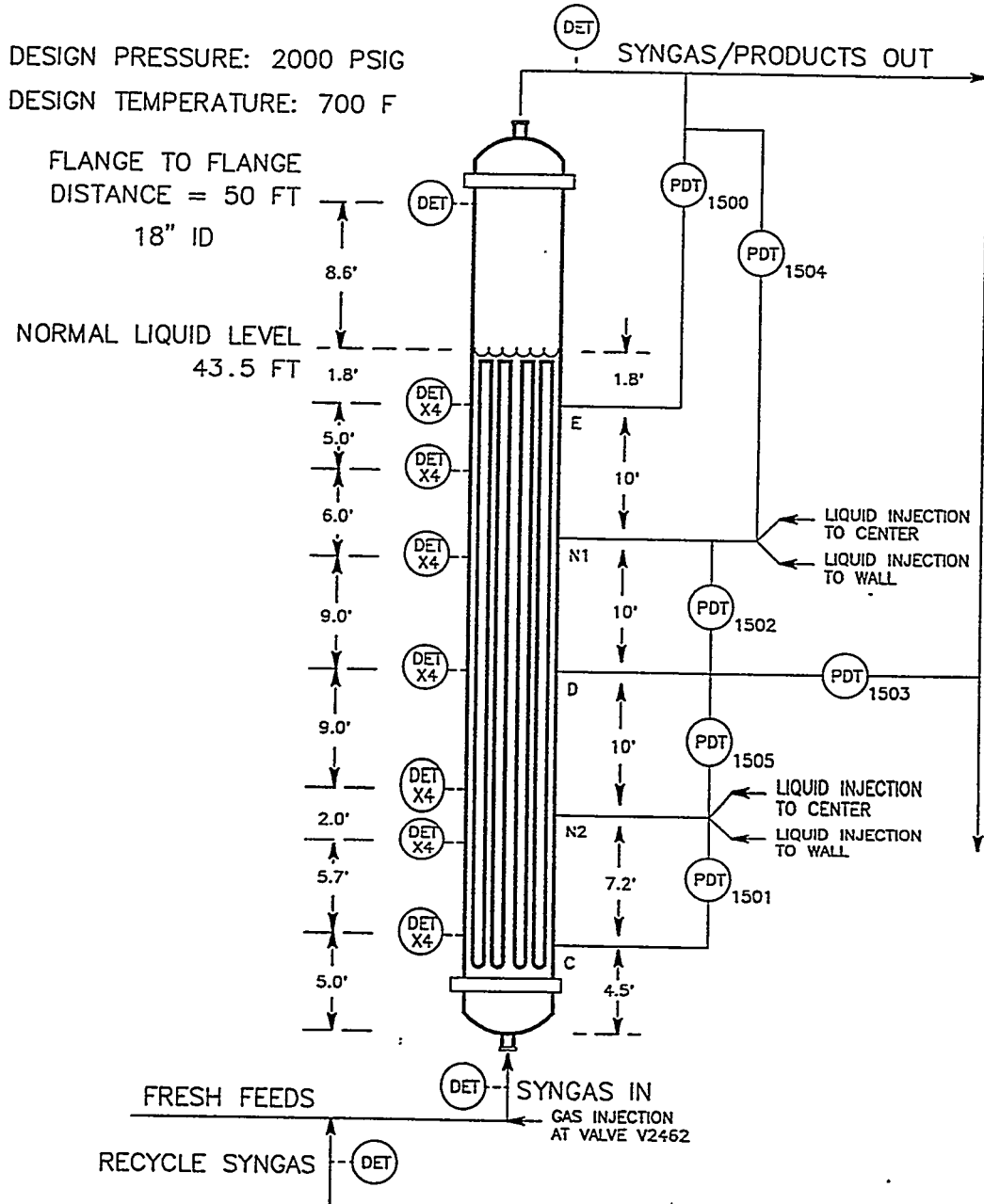o Baseline Catalyst

□ Alternate P

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Table 2.5 By-Product Analysis Comparison for LPMEOH

Catalyst Run No.	Baseline AF-R13.1B	Alternate AF-R14.1B	Baseline AF-R13.2B	Alternate AF-R14.2B
Syngas Composition	Texaco	Texaco	Kingsport	Kingsport
Space Vel., sL/hr-kg	7000	7000	4000	4000
Pressure, psig	750	750	735	735
Temperature, deg. F	482	482	482	482
Product Analysis, wt %				
Methanol	96.72	96.73	97.31	97.42
Ethanol	0.89	0.91	0.32	0.35
1-propanol	0.25	0.26	0.08	0.10
isopropanol	0.02	0.02	0.01	0.00
1-butanol	0.17	0.17	0.09	0.08
2-butanol	0.06	0.05	0.03	0.03
isobutanol	0.06	0.05	0.01	0.02
2-Methyl 1-Buoh	0.00	0.00	0.00	0.00
1-pentanol	0.08	0.08	0.03	0.03
2-Methyl 1-Peoh	0.00	0.00	0.00	0.00
1-hexanol	0.04	0.04	0.00	0.00
2-Methyl 1-Isobutyrate	0.00	0.00	0.00	0.00
meAc	0.20	0.22	0.06	0.07
etAc	0.00	0.00	0.00	0.00
meFm	0.91	0.99	0.42	0.44
DME	0.00	0.00	0.00	0.00
CO2	0.00	0.00	0.00	0.00
Water	0.43	0.42	1.46	1.30
Oil	0.19	0.06	0.19	0.16
Total	100.00	100.00	100.00	100.00

Figure 2.8 LaPorte AFDU Oxygenates High Pressure Reactor

DIFFERENTIAL PRESSURE TRANSMITTER
& TRACER STUDY DETECTOR POSITIONS

DESIGN PRESSURE: 2000 PSIG

DESIGN TEMPERATURE: 700 F

FLANGE TO FLANGE
DISTANCE = 50 FT
18" ID

SYNGAS/PRODUCTS OUT

DET

PDT 1500

PDT 1504

8.6'

NORMAL LIQUID LEVEL
43.5 FT

1.8'

DET X4

1.8'

E

5.0'

DET X4

10'

6.0'

DET X4

N1

LIQUID INJECTION TO CENTER

LIQUID INJECTION TO WALL

9.0'

DET X4

10'

PDT 1502

DET X4

D

PDT 1503

9.0'

10'

PDT 1505

DET X4

LIQUID INJECTION TO CENTER

2.0'

DET X4

N2

LIQUID INJECTION TO WALL

5.7'

7.2'

PDT 1501

DET X4

C

5.0'

4.5'

FRESH FEEDS

DET SYNGAS IN

GAS INJECTION AT VALVE V2462

RECYCLE SYNGAS

DET

TRAC2720.SKD

BLB 9/20/95

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A vapor residence time distribution study was initiated by injecting Argon-41 into the inlet gas line and monitoring its progress through the reactor. Excellent pulses were obtained at the inlet and sharp responses were observed at other locations. It appeared that the pulse moved through the reactor at a velocity equivalent to the superficial gas velocity. This was in contrast to the previous study during the 1993 isobutylene run when the pulse appeared to move up more slowly.

Four injections of radioactive manganese oxide (Mn_2O_3) were made in the reactor slurry to study liquid phase mixing. Portions of radioactive Mn_2O_3 mixed in Drakeol-10 were injected at: (1) nozzle N2-4.5" from wall, (2) nozzle N2-wall, (3) nozzle N1-4.5" from wall, and (4) nozzle N1-wall. The data showed some of the tracer flowing in both an upward as well as downward direction. There appeared to be more downward movement at the wall.

Both gas and liquid injections were made at the two other conditions: low velocity condition (Run AF-R14.7: 0.47 ft/sec, 4100 sl/hr-kg, 750 psig, 482°F, Texaco gas) and high velocity condition (Run AF-R14.8: 1.18 ft/sec, 7100 sl/hr-kg, 520 psig, 482°F, Kingsport gas). Detailed analysis on data collected is necessary before any conclusions can be made on the mixing in the reactor. The data will take several months for workup.

Following the tracer study, a very low velocity condition (Run No. AF-R14.9: 0.15 ft/sec, 1270 sl/hr-kg, 750 psig, 482°F, Texaco gas) was operated briefly to evaluate the bed stability at the expected minimum velocity. Hydrodynamic information was gathered at this condition to ensure the same turndown capability with this catalyst as with the Baseline catalyst. All hydrodynamic data such as nuclear density readings, differential pressure readings and reactor temperature appeared uniform and extremely stable, suggesting acceptable turndown capability. Following this test, the unit was shut down at 23:10 hours on 24 June. The plant was cooled overnight and liquid drained on 25 June.

2.3 Summary and Future Work

The hydrodynamic study was successfully completed in the bubble column reactor at pilot scale. Significant hydrodynamic information was gathered during three weeks of liquid phase methanol operations. In addition to the usual nuclear density gauge and temperature measurements, differential pressure measurements (DP) were made to better understand the hydrodynamics of the system. The DP measurements worked very well mechanically, without the anticipated plugging problems, throughout the run. Gas holdup estimates based on DP measurements followed the same trends as those indicated by NDG readings. Interesting DP data were collected using Sandia's high speed data acquisition system, which could provide insight on bubble size distribution. Responses to radioactive pulses were studied for both the gas and liquid phase at three different operating conditions to evaluate mixing in the reactor. A large effort will be required to understand and interpret the hydrodynamic data collected during this run. Help from Washington University in St. Louis and Ohio State University is expected for this analysis.

High gas velocity conditions were demonstrated during this run. Operation with a linear velocity of 1.2 ft/sec was achieved with stable hydrodynamics and catalyst performance. The magnitude of the velocity was limited only by the recycle compressor capacity as the plant was designed for 1 ft/sec maximum velocity). Acceptable (i.e., low) oil carry-over from the reactor was observed at this velocity.

Improvements included in the Kingsport design for catalyst activation were also demonstrated. Successful catalyst activations were achieved using dilute CO as reductant, a faster temperature ramp, and smaller gas flow, compared to previous "standard" activation procedures.

An Alternate catalyst was demonstrated for the LPMEOH™ process. Expected catalyst activity, by-product formation, and stability were obtained with the Alternate catalyst. Overall, the catalyst appeared very comparable to the Baseline catalyst. Stable performance was obtained at both high and very low (turndown) velocity.

Dephlegmator testing was conducted at various conditions during the run. During the carbonyl burnout period, testing was conducted with a two-phase system to eliminate fouling considerations. While detailed analysis is pending, it appeared that heat transfer performance of the dephlegmator was satisfactory. However, there was significant oil carry-over. Although flooding was ruled out, variability in oil capture was still apparent throughout the run. A large amount of data requires analysis before a final decision is made on possible inclusion in commercial flowsheets.

Approximately 64,300 gallons of methanol were produced during this demonstration which will be used for product testing both in support of the Kingsport demonstration and other independent DOE studies.

TASK 3: RESEARCH AND DEVELOPMENT

3.1 New Processes for DME

3.1.1 DME Catalyst Activity and Maintenance

The progress made in this quarter features more advanced understanding of the mechanism of catalyst deactivation under LPDME conditions. This understanding was obtained by analyzing the results from 1) screening runs using different dehydration catalysts, and 2) the experiments using Robinson-Mahoney basket internals and pelletized catalysts. This understanding provides new directions in solving the catalyst stability problem. The details of the analysis and the work conducted based on the new understanding are given below.

Analysis of the Trends in Catalyst Deactivation
We have reported previously that an interaction between the methanol synthesis and dehydration catalysts is responsible for catalyst deactivation under LPDME conditions. Since then, we have been screening for alternative dehydration catalysts that could be compatible with a standard methanol catalyst (e.g., BASF S3-86). One need for efficient screening is an idea of the properties required in a dehydration catalyst. Part of the answer to this question has been

obtained by analyzing the results from the previous screening runs, including 14 samples described in the last two quarterly reports.

One of the key ideas developed during this analysis is that the catalyst deactivation is divided into four modes: the initial and long term deactivation of the methanol catalyst, and the initial and long term deactivation of the dehydration catalysts.

Major conclusions so far include:

1. The initial deactivation of the methanol catalyst is caused by the strong acid sites on the dehydration catalyst.

2. The initial deactivation of the dehydration catalyst is related to the type as well as the strength of the acid sites. Both strong acid sites and sites of Bronsted acid nature appear to deactivate rapidly.

3. The long term deactivation of both methanol and dehydration catalysts is not directly correlated to the acidity (e.g., the dehydration activity) of dehydration catalysts. Most dual catalyst systems show a similar rate of long term deactivation for the methanol catalyst. This rate is about a factor of 2 greater than that of the methanol catalyst-only system.

The following are the details of the analysis.

a. Observations of Deactivation of the Methanol Catalyst

Observations were made according to groups consisting of different dehydration catalysts. All systems used BASF S3-86 methanol catalyst as the other catalyst in the dual system.

Catalyst systems based on Catapal B g-alumina. Figures 3.1.1 and 3.1.2 display the activity of methanol catalyst and dehydration catalyst, respectively, as a function of time on stream for Catapal B-based catalyst systems, namely S3-86 plus virgin Catapal B or Catapal B modified by Si, WO_3, and ZnO. (Activity is measured by the rate constants of the methanol synthesis and dehydration reactions. The rate expressions for these rate constants and the adjustment performed to make the comparison between the different catalysts possible are given in the Appendix.) All data were obtained under standard conditions (i.e., 250°C, 750 psig, 6000 GHSV, Shell gas, and a methanol-to-dehydration catalyst ratio of 80:20).

As shown in Figure 3.1.1, the deactivation of the methanol catalyst can be divided into two stages: an *initial*, fast deactivation followed by a stage of slower but continuous, *long-term* deactivation. The division between the initial and long-term deactivation is the point at which the deactivation starts to slow down and the deactivation rate becomes almost constant. For example, for the catalyst system containing virgin alumina, the initial deactivation period stops at ca. 80 hr on stream. For the system containing ZnO-modified alumina, it stops at ca. 40 hr. The first observation from these two figures is that *the methanol catalyst deactivates at a similar rate in the second stage, regardless of the activity of the dehydration catalysts*. The deactivation in this stage is referred to as *long-term deactivation* hereafter.

Figure 3.1.1 "Normalized" Methanol Synthesis Rate
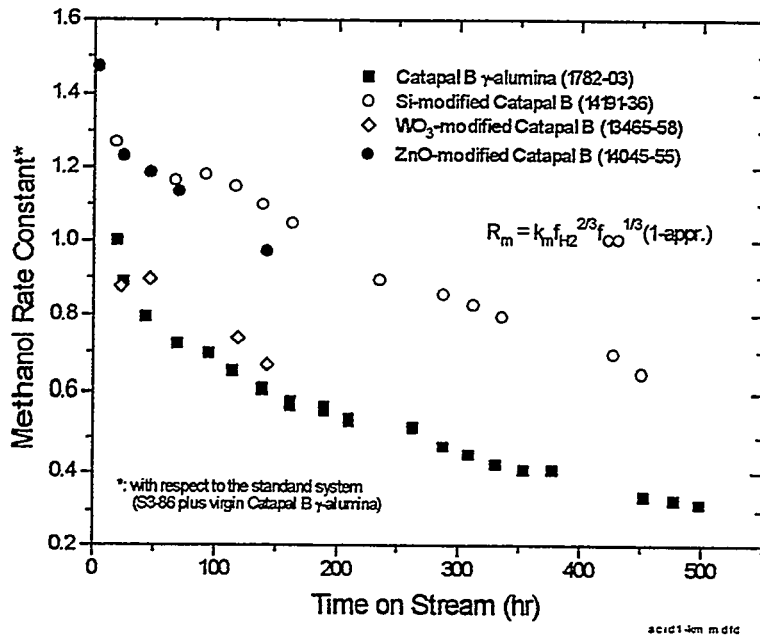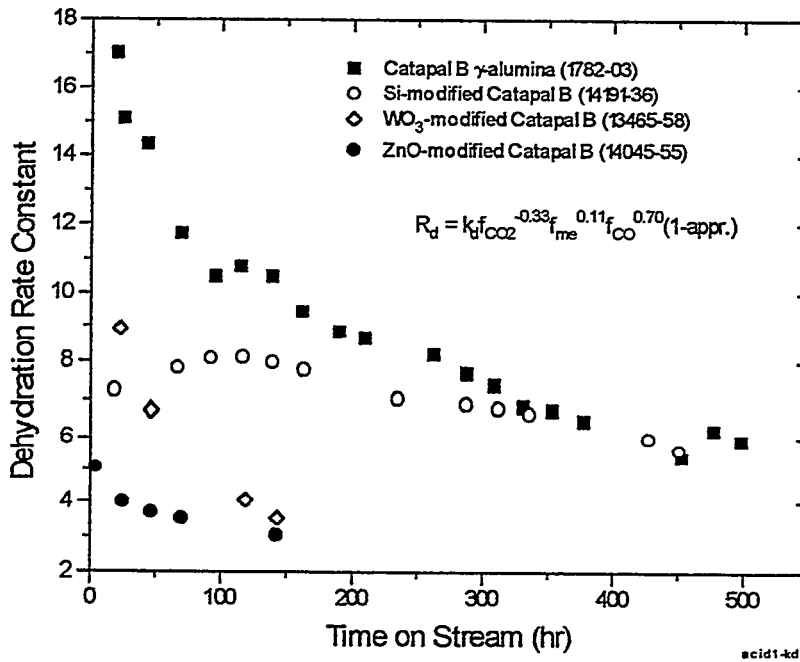## Constant as a Function of Time on Stream for Different Catalyst Systems

$$R_m = k_m f_{H2}^{2/3} f_{CO}^{1/3}(1\text{-appr.})$$

*: with respect to the standard system
(S3-86 plus virgin Catapal B γ-alumina)

Legend:
- ■ Catapal B γ-alumina (1782-03)
- ○ Si-modified Catapal B (14191-36)
- ◇ WO₃-modified Catapal B (13465-58)
- ● ZnO-modified Catapal B (14045-55)

Figure 3.1.2 Dehydration Rate Constant as a Function of Time on Stream for
Different Catalysts

$$R_d = k_d f_{CO2}^{-0.33} f_{me}^{0.11} f_{CO}^{0.70}(1\text{-appr.})$$

Legend:
- ■ Catapal B γ-alumina (1782-03)
- ○ Si-modified Catapal B (14191-36)
- ◇ WO₃-modified Catapal B (13465-58)
- ● ZnO-modified Catapal B (14045-55)

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The second observation is that *deactivation of the methanol catalyst can occur during reduction*, as suggested by the different initial activities of the same methanol catalysts in different catalyst systems. Rapid deactivation continues into the early period when the system is switched to syngas. The deactivation in this stage is referred to as *initial deactivation,* hereafter. In the standard catalyst system (S3-86 plus virgin Catapal B alumina), the methanol catalyst loses 20-30% of its activity in the initial stage.

Systems of other traditional solid acids. The deactivation patterns of the catalyst systems consisting of S3-86 and silica alumina or zeolites are shown in Figures 3.1.3 and 3.1.4, along with that of the standard catalyst system. Again, all the data were collected under the standard reaction conditions. The two observations mentioned above hold true for these four additional systems, that is, the rate of the long-term deactivation of the methanol catalyst is similar among different systems, and the initial deactivation of the methanol catalyst varies from one system to another.

Systems of inert materials. A number of metal oxides we have tested, including silica gel, titania, zirconia, and, zirconia-doped silica gel, exhibited nil or negligibly small dehydration activity. The most important observation from these runs, as shown in Figure 3.1.5, is that *there is no significant initial deactivation of the methanol catalyst when the dehydration component is inert.* The system containing the silica gel shows a long-term methanol catalyst deactivation similar to that of S3-86 in a LPMEOH run (no dehydration catalyst). The experiments using other systems are too short to establish a trend in the long-term deactivation.

Figure 3.1.3 "Normalized" Methanol Synthesis Rate Constant as a Function of Time On-Stream for Different Catalyst Systems
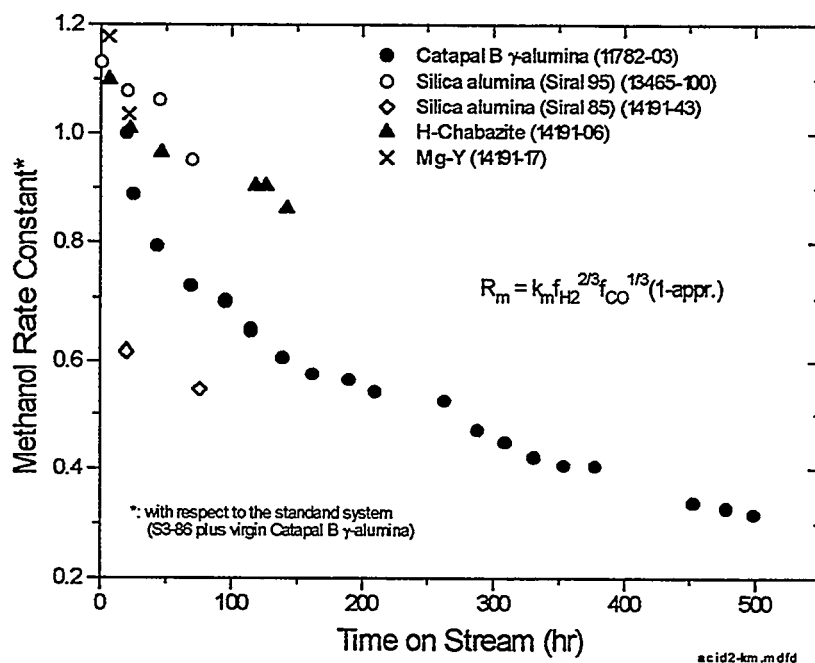

● Catapal B γ-alumina (11782-03)
○ Silica alumina (Siral 95) (13465-100)
◇ Silica alumina (Siral 85) (14191-43)
▲ H-Chabazite (14191-06)
✕ Mg-Y (14191-17)

$$R_m = k_m f_{H2}^{2/3} f_{CO}^{1/3}(1\text{-appr.})$$

*: with respect to the standard system
(S3-86 plus virgin Catapal B γ-alumina)

Methanol Rate Constant*

Time on Stream (hr)

acid2-km.mdfd

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Figure 3.1.4 Dehydration Rate Constant as a Function of Time On-Stream for Different Catalysts

Legend:
- ● Catapal B γ-alumina (11782-03)
- ○ Silica alumina (Siral 95) (13465-100)
- ◇ Silica alumina (Siral 85) (14191-43)
- ▲ H-Chabazite (14191-06)
- ✕ Mg-Y (14191-17)

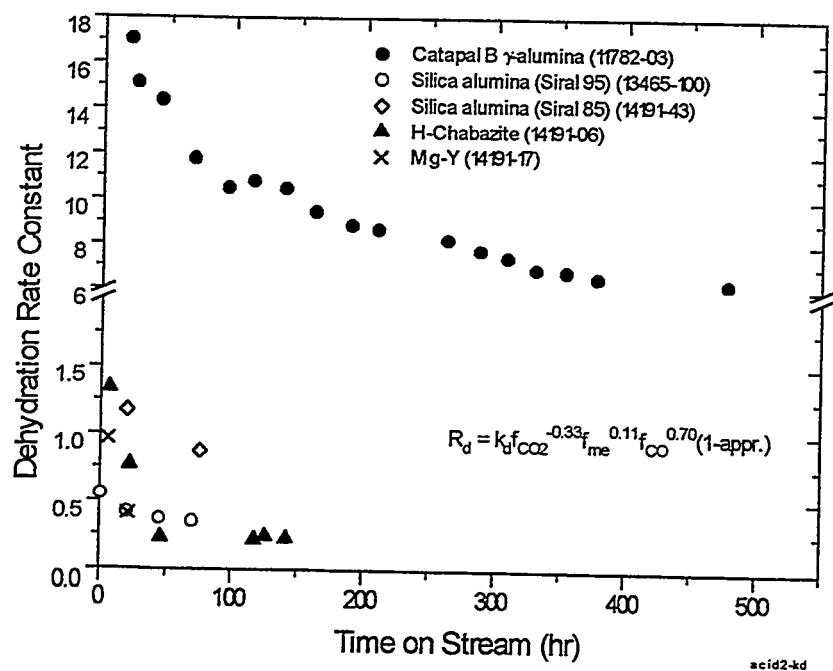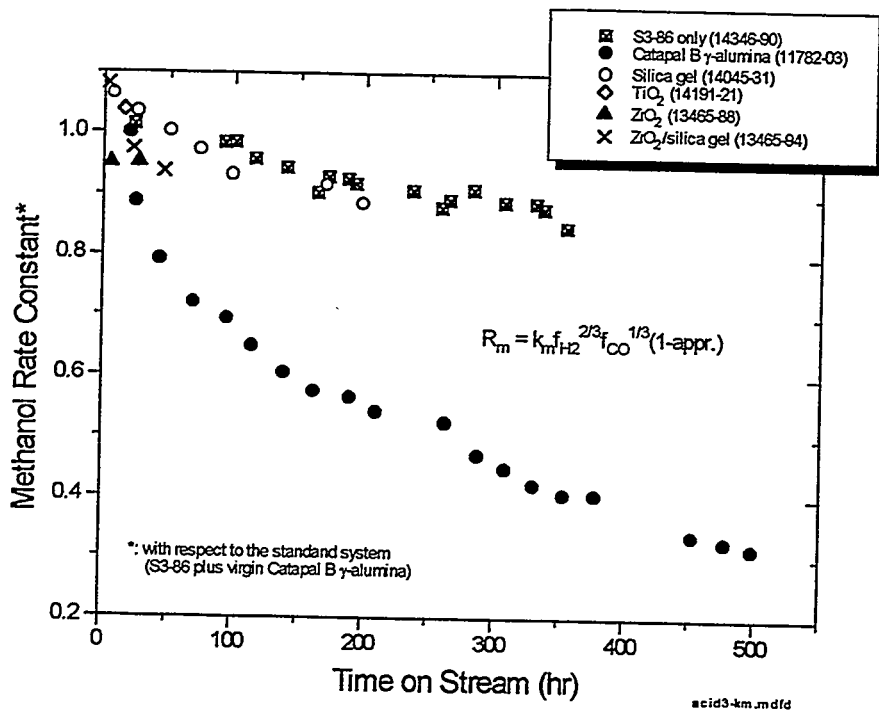$$R_d = k_d f_{CO2}^{-0.33} f_{me}^{0.11} f_{CO}^{0.70}(1\text{-appr.})$$

acid2-kd

Figure 3.1.5 "Normalized" Methanol Synthesis Rate Constant as a Function of Time On-Stream for Different Catalyst Systems

Legend:
- ⊠ S3-86 only (14346-90)
- ● Catapal B γ-alumina (11782-03)
- ○ Silica gel (14045-31)
- ◇ TiO₂ (14191-21)
- ▲ ZrO₂ (13465-88)
- ✕ ZrO₂/silica gel (13465-94)

$$R_m = k_m f_{H2}^{2/3} f_{CO}^{1/3}(1\text{-appr.})$$

*: with respect to the standard system
(S3-86 plus virgin Catapal B γ-alumina)

acid3-km.mdfd

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b. Trends in Deactivation of the Methanol Catalyst

With the exception of the system containing silica gel, *long-term deactivation* of the methanol catalyst is observed in all dual systems, and does not depend on the activity of dehydration catalysts. The methanol catalyst deactivates at a rate of ~ 0.082% hr^{-1}, which is about a factor of 2 greater than that of the S3-86-only system (0.045% hr^{-1}).

It is not straightforward to correlate the initial deactivation of the methanol catalyst to the activity of dehydration catalysts, because the dehydration catalysts may also have deactivated during reduction. Thus, the dehydration activity shown by the first data point in Figures 3.1.2 and 3.1.4 may not be a fair indication of the initial or intrinsic activity of a dehydration catalyst. The best way to determine the activity of a dehydration catalyst is to conduct a measurement using only the dehydration catalyst with methanol as feed gas. Since few measurements have been made in this regard, we have to use literature and general principles to estimate the initial dehydration activity.

Figure 3.1.6 displays the *initial deactivation* of the methanol catalyst against different dehydration catalysts. Dehydration catalysts are arranged in increasing dehydration activity order with the least active catalyst at the bottom. The initial deactivation of the methanol catalyst is measured approximately by methanol synthesis activity at 80 hours on syngas stream. Although we do not have direct measurements of the initial or intrinsic activity of these dehydration catalysts as mentioned above, a correlation can be established based on the following discussion.

First, silylation (i.e., Si-modification) has been known in the literature as a means to passivate strong acid sites on metal oxides. Modification of Catapal B by ZnO was also aimed at passivating the catalyst through acid-base reaction between ZnO (a base) and acid sites on Catapal B. Therefore, these two catalysts should have less dehydration activity than virgin Catapal B g-alumina. Second, WO$_3$ has been reported in the literature to have greater or similar dehydration activity compared to g-alumina. Third, silica alumina is generally more acidic than g-alumina. Siral 85, a silica alumina containing 85 wt % of SiO$_2$, has shown higher isobutanol dehydration activity in this lab than a g-alumina comparable to Catapal B. While the dehydration activity of the Chabazite and Siral 95 samples remains to be determined, the available data indicate that the initial deactivation of the methanol catalyst is correlated to the activity of dehydration catalysts. The greater the dehydration activity is, the larger is the initial deactivation of the methanol catalyst.