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# Alternative Fuels and Chemicals From Synthesis Gas


## Quarterly Report April 1 - June 30, 1995

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For  
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# Alternative Fuels and Chemicals from Synthesis Gas

## Quarterly Technical Progress Report

1 April- 30 June 1995

### Contract Objectives

The overall objectives of this program are to investigate potential technologies for the conversion of synthesis gas to oxygenated and hydrocarbon fuels and industrial chemicals, and to demonstrate the most promising technologies at DOE's LaPorte, Texas, Slurry Phase Alternative Fuels Development Unit (AFDU). The program will involve a continuation of the work performed under the Alternative Fuels from Coal-Derived Synthesis Gas Program and will draw upon information and technologies generated in parallel current and future DOE-funded contracts.

### Summary of Activity

- A Hydrodynamic study was successfully completed in the LaPorte 18" bubble column during June. Significant information on fluid dynamics 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. However, there appeared to be a systematic difference between gas holdup estimates from the two methods. Calibration of the DP readings by filling the reactor with a known-density fluid is planned to increase their accuracy. Interesting DP data that could provide insight on bubble size distribution were collected using Sandia's high speed data acquisition system. Responses to radioactive pulses were studied for both gas and liquid phase at three different operating conditions to evaluate the mixing in the reactor. A large effort will be required to understand and interpret the hydrodynamic data collected during this run.
- High velocity conditions were demonstrated during the Hydrodynamic run. Operation with a linear velocity of 1.2 ft/sec was achieved with stable bubble column 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 oil carry-over from the reactor was observed at this velocity.
- Improvements included in the Kingsport design for catalyst activation were also demonstrated in the June operation. Successful activations were achieved using dilute CO as reductant, a quicker 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 LPMEOH™ catalyst. Stable performance was obtained at both high and very low (turndown) velocity.

- In addition, dephlegmator testing was conducted at various conditions during the run. During the carbonyl burnout period, testing was conducted with the 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 inclusion in commercial flowsheets.
- Approximately 64,300 gallons of methanol were produced during the June demonstration, which will be used for testing in fuel and chemical (MTBE) applications.
- A meeting was held with Shell personnel on May 22 to discuss a proprietary run with Shell at LaPorte. Shell proposed a two month campaign with its own cobalt catalyst for October-November 1996. This schedule is significant, as the start-up date for Kingsport is December 1996, and this run is expected to monopolize resources for 4-6 months. Confidentiality, funding, and technical issues must be worked out before the project is kicked off.
- Deactivation of the DME catalyst systems is associated with some physical features of a slurry phase reactor, since both methanol and dehydration catalysts do not suffer long term deactivation in the LPDME run with Robinson-Mahoney basket internals and pelletized catalysts. Most likely, the intimate contact between the two catalysts is necessary for catalyst deactivation of our two component system. This suggests new directions in our future research to better understand the deactivation mechanism and develop solutions.
- A repeat of the LPDME run in the Robinson-Mahoney reactor confirmed the result that the methanol catalyst does not age significantly when only a small amount of physical contact is allowed by the catalysts. In addition, the long term deactivation of the dehydration catalyst is eliminated. The only deactivation of this catalyst was the initial drop discussed last month.
- Si modification of the alumina catalyst surface again reduced the initial steep deactivation seen in LPDME synthesis. However, the deactivation rate was still relatively high due to long term deactivation. In another LPDME approach, a Si-based dispersion aid gave the desired dispersion of the mixed catalysts in the slurry reactor, but the material polymerized during the run. More stable dispersants will be tried. A Si-modified Catapal B g-alumina sample with a very high SiO<sub>2</sub> content (35 wt%) was prepared using a polymeric Si-containing material. However, the modification resulted in little improvement in the long-term stability of the methanol catalyst.

- In LPDME studies BASF S3-86 methanol catalyst exhibited a better long-term stability when used with a potassium (k) doped Catapal B g-alumina. This is the first time that an improved **long-term** stability has been observed. However, the dehydration activity of this alumina was low due to high K loading. K-doped alumina samples of lower loading, and therefore higher dehydration activity, will be tested in the coming month to see if a similar stability can still be obtained.
- A *one-component* catalyst was made according to a Shell patent by impregnating Catapal B g-alumina with zinc and copper. This catalyst performs both methanol synthesis and dehydration functions. However, it has very low activity and poor stability. A recheck may be in order.
- At Lehigh, a Cu-free ZnO/Cr<sub>2</sub>O<sub>3</sub> catalyst was doped with Cs and tested at 405°C and 7.6 MPa with H<sub>2</sub>/CO = 0.75 at two different GHSV. At a GHSV of 5450 l/kg cat./hr., the space time yields (g/kg cat./hr.) for the major products were 52.8, 39.5, 51.6 and 11.1 for methanol, isobutanol, C<sub>7</sub> + oxygenates and C<sub>2</sub>-C<sub>4</sub> hydrocarbons, respectively, at 8.1% CO conversion.
- A two step route to isobutanol was tested at Lehigh University, where a double bed catalyst configuration was operated with two different catalysts, each at different temperatures. The 3% Cs/Cu, ZnO, Cr<sub>2</sub>O<sub>3</sub> (325°C) bed was followed by a 4% Cs/Zn, Cr<sub>2</sub>O<sub>3</sub> (405°C) bed, and this configuration improved the isobutanol/methanol molar ratio from 1/11.8 (single Cs/Cu/ZnO/Cr<sub>2</sub>O<sub>3</sub>) to 1/1.7.
- The capability of producing a high isobutanol yield catalyst has been demonstrated (414 g/l-hr @ 20000 GHSV, 441°C, 25 KPa). Results show higher methanol production than previously measured by Falter. The big improvement was that five-fold reduction in methane formation has been achieved. Catalyst preparation continues to concentrate on the alkalinity of the catalyst surface using the sol gel technique.
- Professor Foley at Delaware reports continued work on testing of alkali-doped catalysts. He has determined that catalysts precipitated with lithium nitrate are more active than those precipitated with lithium hydroxide. A variable study showed that the catalyst activity is still far from the target, even at optimized conditions.
- Cobalt enhances the catalyst activity to produce alcohols at high temperature. Thus far, trials at the University of Delaware using IR and Rh as dopants have shown little improvement.
- Thermodynamic calculation of model syngas to alcohol reactions suggests that CO<sub>2</sub> rejection should be considered as a favored mode of oxygen rejection for maximizing isobutanol concentration.
- In previous months catalytic tests converting DME to ethylidene diacetate (EDDA) were restricted to 45 min. In order to improve yield of EDDA, the reaction time was increased to 180 min. Though the yield of EDDA was observed to improve up to the 100 min mark, it was found to decrease slowly thereafter due to hydrogenation to produce ethyl acetate and

acetic acid. It was also found that the product distribution was different for two different runs using the same batch of catalyst. Based on the results obtained thus far, it appears that in a reactor, partial conversion with recycle is better than complete conversion.

- A single batch of a rhodium complex supported on a Reillex polymer was tested in three consecutive catalytic runs using fresh charges of DME, methyl iodide and acetic acid. The catalytic activity for the conversion of DME to ethylidene diacetate did not decrease from run to run, showing that the catalyst was not leaching out. An elemental analysis of the catalyst revealed a 23% decrease in rhodium content, and we feel that this decrease is due to the increase in the weight of polymer from methyl iodide incorporation.
- During June, several new catalysts were prepared in APCI Corporate laboratories. One was an alumina (methanol dehydration catalyst) that was treated with t-butyl-diphenylchlorosilane in order to provide a sterically hindered blocking group. It is hoped that this treatment will mitigate the stability problems experienced in the liquid phase DME process. In addition, two other rhodium containing materials were prepared for testing as catalysts for the conversion of DME to EDDA.
- In screening catalysts for the cracking of ethylidene diacetate (EDDA), temperature studies indicate that at temperatures of 200°C and above, EDDA is unstable and leads to a polymeric decomposition product and plugging of sample lines. Several catalysts were examined, but at too high a temperature. VAM and acetic acid were observed prior to plugging.
- Initial design of the mobile Catalyst Poisons Test Lab was completed. The trailer has been selected, and reactor plans and the control system have been reviewed. This project is still on time and within budget. The trailer is being modified to separate the office from the lab area, and add insulation and steps. It is expected to be on site and ready for internal installation by the end of July.
- In the new Hydrodynamics Program, statements of work from both Ohio State University and Washington University were received, reviewed, and accepted. Work on the subcontracts is almost completed.
- B. Bhatt presented a paper entitled "Productivity Improvements for Fischer-Tropsch Synthesis" at the 14<sup>th</sup> North American Meeting of the Catalysis Society. The paper, which was co-authored by Shell and DOE personnel, was well received.

## **RESULTS AND DISCUSSION**

### **TASK 1: ENGINEERING AND MODIFICATIONS**

#### **1.1 Liquid Phase Methanol/Hydrodynamic Run**

Changes were incorporated into the AFDU process flow diagrams to reflect the ongoing modifications. A hazards review was conducted on April 10 to review Facility Change Notices (FCNs) for AFDU modifications. FCNs on reactor differential pressure (DP) taps, flow totalizers, local hand-operated valves, trailer pad/sump and trailer overfill protection were approved.

Final preparations were completed during May for the June run. The DEC workstation data acquisition system was set up on-site, and modifications were included. The analytical system was set up for methanol synthesis. Both the Baseline and Alternate methanol catalyst lots were received. A stronger source (8 curie - Cs) for the nuclear density gauge (NDG) was installed for the high-pressure reactor to achieve better resolution, and the NDG was calibrated with N<sub>2</sub>.

#### **1.2 Liquid Phase Fischer-Tropsch Demonstration**

A meeting was held with Shell personnel on May 22 to discuss a Fischer-Tropsch run with Shell's participation at LaPorte. Shell proposed a two month campaign with their own cobalt catalyst for October-November 1996. This schedule is significant, as the start-up date for Kingsport is December 1996, and the Kingsport demonstration start-up is expected to utilize resources for 4-6 months. Confidentiality, funding, and technical issues must be worked out before the project can be kicked off.

#### **1.3 Fischer-Tropsch Support**

No progress to report this quarter.

#### **1.4 AFDU R&D Support**

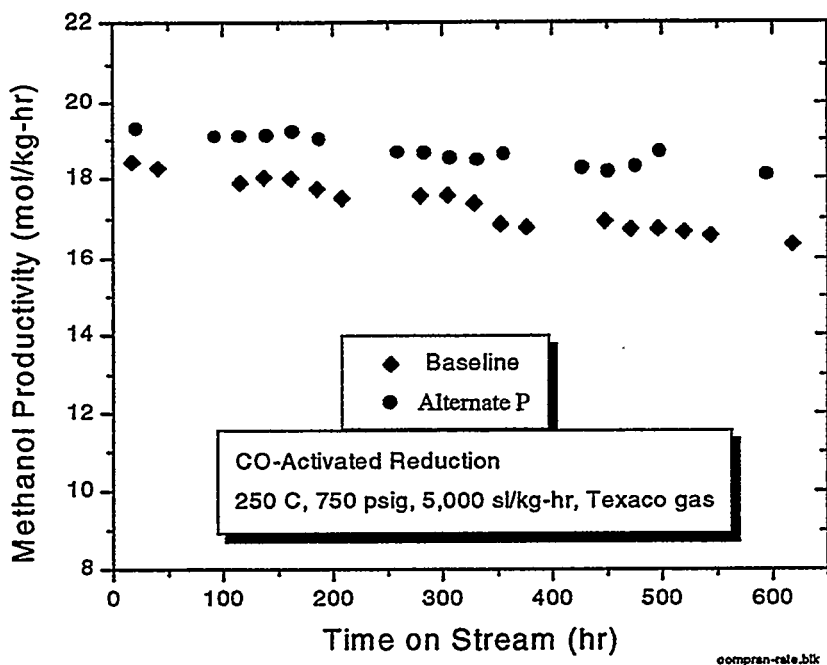
##### **1.4.1 Laboratory Testing of Alternate Methanol Catalyst**

Establishment of a tested, alternate catalyst supply is part of any process development. For the LPMEOH™ process, demonstration must be made at the LaPorte scale. One of the objectives of the methanol/hydrodynamics run in the AFDU at LaPorte is to demonstrate the performance of an alternate catalyst.

After initial testing of old samples of this catalyst showed good performance, a new sample was obtained for LaPorte. The laboratory life data for this Alternate P (P for powder) catalyst is compared to the LPMEOH Baseline catalyst in Figure 1.4.1. The catalyst performed well, showing slightly higher activity than the Baseline catalyst. The Alternate catalyst aged slightly faster, but the activity of the Alternate catalyst was always higher than that of the LPMEOH Baseline catalyst.



Figure 1.4.1 Life Test Results



Reduction of the catalyst was accomplished by the new CO reduction procedure discussed in the last quarterly report. The reduction temperature profile is shown in Figure 1.4.2, and the off-gas profiles for the catalyst are shown in Figure 1.4.3. (NOTE: "Baseline" is the name of a catalyst type. The two lines are repeat runs for a catalyst type to show reproducibility. Also, all reductions were done at a lower flow rate.)

Figure 1.4.2 Reduction Temperature Profiles

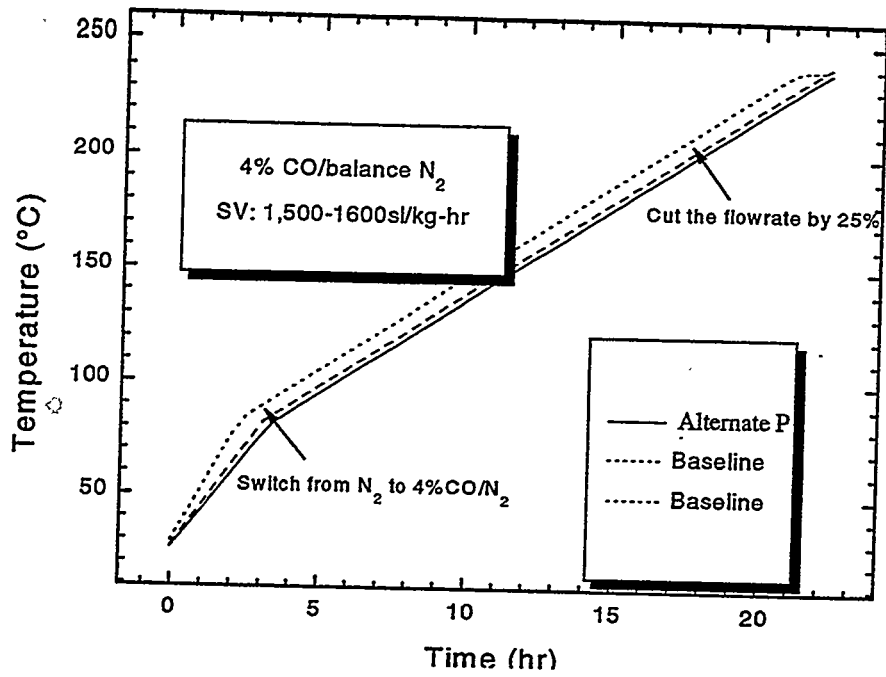
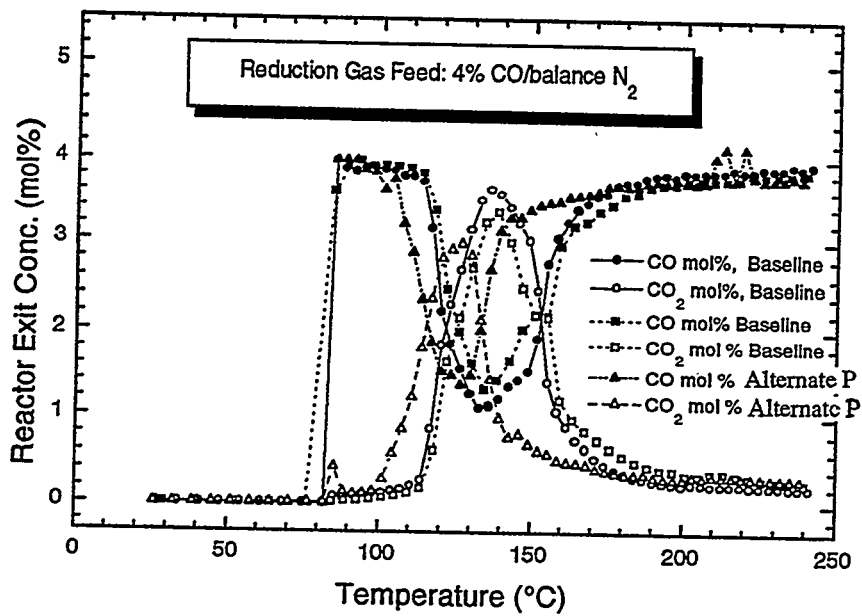


Figure 1.4.3 Off-Gas Profiles for Two Catalysts



In addition to activity and life considerations, a candidate catalyst must pass the previously developed slurrification test, which indicates the suitability of a catalyst for use in a slurry bubble-column reactor. The rate of settling of the catalyst is compared to settling rates of standard catalysts. In this case the settling characteristics of the previous sample of Alternate catalyst, as well as the one representative of the current production, were tested and are compared to the results from the standard (see Figure 1.4.5). The candidate catalyst showed a satisfactory settling rate, and should perform well in the slurry reactor.

#### **1.4.2 Summary and Recommendation**

All recent data on the activation of the Baseline and Alternate catalysts are summarized in Table 1.4.1 and compared to historic data. The data are presented as the value of the specific rate constant for the methanol formation reaction and the productivity of the catalyst.

Based on the productivity of the initial two runs (14045-8 and 13458-90), we concluded that the CO activation leads to a catalyst with the same activity as does the standard activation procedure with hydrogen.

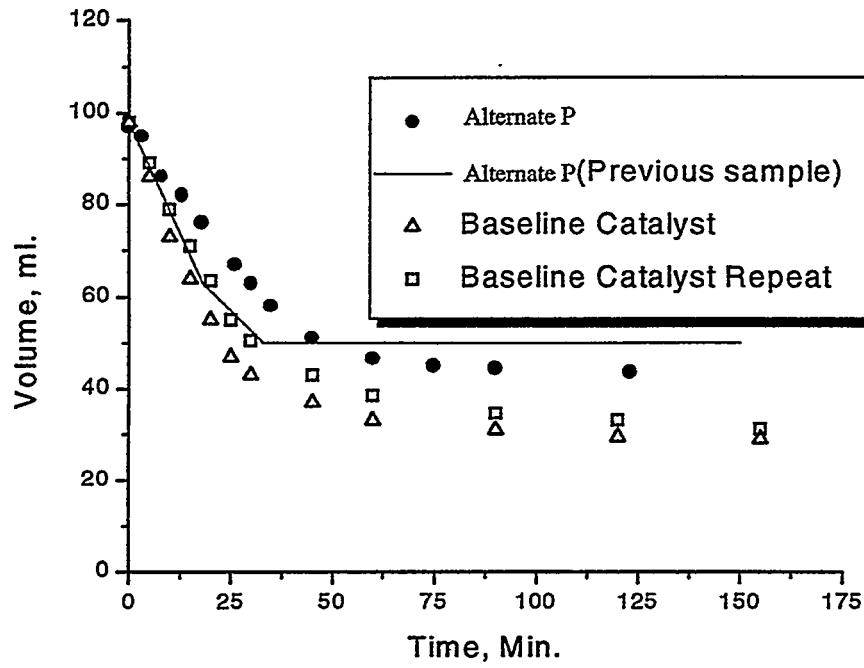
The life runs show some periodic difficulty in analytical measurement as described in the footnote to Table 1.4.1. However, as there is only a small difference in results, the CO activation is considered to be essentially the same as the standard. In addition, based on this run, catalyst life is adequate.

The Alternate catalyst exhibits at least as good an initial activity as the Baseline catalyst. Deactivation is a little higher, but even after 600 hours, the activity of the Alternate catalyst is higher than that of the Baseline catalyst.

The variation in the calculated value of the rate constant is interesting. We calculate rate constant from the concentration data. There may be a difference in water-gas shift activity for CO activated catalysts and, perhaps, between the various catalysts.

The Alternate catalyst showed adequate activity, life and slurriability in the laboratory tests and was considered suitable for testing in the AFDU in the upcoming trial.

Figure 1.4.5 Results of Slurrification Test



**Table 1.4.1 Catalyst Activation on Texaco Gas**

Catalyst Source	K(R=K f <sub>H<sub>2</sub></sub> <sup>2/3</sup> f <sub>CO</sub> <sup>1/3</sup> ) [1-appr] gmol/hr/atm		Productivity (5,000 GHSV, 250°C) gmol/kg cat/hr		
	Alcohols*	Bulk**	Alcohols	Bulk	
Process Model for Baseline		2.86		17.4	
Historic Data (Hsuing)				17.4	
Plant Run-E-7 (after 7 days)		2.32			
Baseline, CO Activated					
Run 14045-8	2.29		17.2		
13458-90	2.55		17.3		
14191-62	2.18	2.8	16.5		18.4
Alternate, H <sub>2</sub> , Activated	3.02	3.67	17.5		19.3
Alternate, CO Activated	2.87	4.29	17.5		19.7

\*, \*\* Data after Run 62 are shown for both Alcohols and Bulk GC. This is indicative of our analytical problem. The Bulk GC data gives good material balances and shows low variation with time. The Bulk GC is the method that has been used to gather historical data.

Halfway into Run 62 the Alcohol GC calibration factor changed significantly and the day to day variability of the results became less steady. It is suspected that there is a leak that we have not yet been able to find.

Complicating the issue is that our calibration mixtures have only 5% MEOH, while MEOH concentrations in the reaction product are as high as 9%. We suspect the Bulk GC is not linear. We will soon receive a new calibration standard, at which time, the linearity of both GCs will be checked and we will use CRSD analytical help to find the GC stability problem in the Alcohols GC.

## **TASK 2: AFDU SHAKEDOWN, OPERATIONS, DEACTIVATION AND DISPOSAL**

### **2.1 Liquid Phase Methanol/Hydrodynamic Run**

#### **2.1.1 Carbonyl Burnout**

The reactor was loaded with Drakeol-10 oil and heated up on 30 May to start normal carbonyl burnout and, in parallel, the two-phase dephlegmator testing. Carbonyl levels were extremely low during the entire burnout: 2-10 ppb iron carbonyl and undetectable (< 10 ppb) nickel carbonyl. A summary of the carbonyl data is shown in Table 2.1.

The carbonyl burnout was completed at 19:00 on 2 June. At the end of the burnout, with sufficient data to permit a thorough analysis of the dephlegmator problem, the plant was cooled and drained in preparation for catalyst loading and reduction.

#### **2.1.2 LPMEOH with Baseline Catalyst**

##### ***Slurry Preparation***

A 40 wt% oxide catalyst slurry was mixed in the 28.30 Prep Tank, which was charged with 1767 lbs of Drakeol-10 oil at 09:00 on 2 June and 1179 lbs of Baseline methanol catalyst at 08:00 on 3 June. Catalyst was taken from four drums of lot # 94/15730. The slurry was heated and agitated in the Prep Tank for two hours before it was transferred to the reactor.

**Table 2.1 Metal Carbonyl Analysis Results**

Nickel Tetracarbonyl: not detected in any samples (lower detection limit is 10 ppbv).

Iron Pentacarbonyl (ppbv): Averages of 2 injections

Reactor Temp = 482°F Reactor Pressure = 750 psig	Sample Point 3A Economizer Product Outlet	Sample Point 4 Combined Fresh Feed + Recycle	Sample Point 15 Inlet to Reactor
5/31/95 16:30-17:30 Once-through syngas (12 KSCFH)	4	8	8
5/31/95 21:30-22:30 Once-through syngas (12 KSCFH)	2	3	3
6/1/95 08:30-09:30 Once-through syngas (12 KSCFH)	3	2	3
6/1/95 11:30-12:00 Recycle syngas (84 KSCFH)	4	3	5
6/1/95 15:30-16:00 Recycle syngas (84 KSCFH)	6	4	7
6/1/95 20:30-21:00 Recycle syngas (84 KSCFH)	7	6	8
6/2/95 08:30-09:00 Recycle syngas (132 KSCFH)	9	7	10
6/2/95 11:30-12:00 Recycle syngas (132 KSCFH)	10	6	10

### *Catalyst Reduction*

Catalyst reduction began at 14:30 on 3 June. The reduction gas (4% CO in N<sub>2</sub>) was set at 12,500 scfh with the reactor pressure at 67 psig (Run # A9). The heat up commenced at 15:45 and proceeded from 197°F to 464°F at a rate of 15°F/hr, as shown in Figure 2.1. The temperature ramp was significantly faster than the previous "standard" ramp as this, in lab tests, had successfully saved time in the activation procedure.

The reduction under CO was quite rapid, as shown in Figure 2.2, and the total uptake peaked very close to the theoretical maximum value of 2.82 scf/lb oxide. This condition was obtained by about 360°F or 12-13 hours on-stream, which is an encouraging result for the Kingsport project. Reduction in the bubble column was faster than in the autoclave. Despite the rapid uptake, 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. Gas holdup during the reduction was close to expected: 27-30 vol% at 12,500 scfh and 24 vol% at 9375 scfh. The catalyst concentration was in the 39-41 wt% range.

### *Process Variable / Hydrodynamic Study*

Reduction was completed at 10:00 hours on 4 June, and synthesis gas was brought into the reactor at 11:45. A run plan table corresponding to actual operating conditions during the campaign is given in Table 2.2. The initial data indicated typical hyperactivity of the catalyst. Problems were experienced with analytical communication boxes during the evening of 4 June. The problems were resolved and data were collected at the conditions of Run No. AF-R13.1 (Texaco gas, 7100 sl/hr-kg, 750 psig, 482°F, 0.85 ft/sec). A production rate of 12.1 TPD methanol was achieved which was close to expected for fresh catalyst. Mass balance around the plant was excellent. Liquid analysis showed typical methanol product composition. Nuclear density gauge readings indicated a gas holdup of 50.5 vol%, higher than the expected holdup of 43 vol%. The catalyst concentration was estimated at 45.8 wt%. Data were taken for an additional mass balance period to examine initial catalyst aging. Steady operations continued, and conversion to methanol showed an expected drop from 16.5% to 15.5%. Nuclear density gauge readings indicated a gas holdup of 54.7 vol% and a catalyst concentration of 48.2 wt%. These results were very steady during this period, in contrast to the previous data period when both showed measurable increases throughout the operation.

A high speed data acquisition system installed by Sandia National Laboratories personnel to monitor differential pressures on the reactor column was started up. Initial results indicated that a sampling rate of 1 hertz (1 sample/second) was optimum (see Figure 2.3). Also, the fluctuations being recorded were much above the noise in the signal.

Conditions were changed to Run No. AF-R13.2 (Kingsport gas, 4000 sl/hr-kg, 735 psig, 482°F, 0.49 ft/sec) shortly after noon on 6 June. The plant operated very steadily for three days at expected performance. CO conversion of 49.6% and methanol production of 9.9 TPD were achieved. Liquid analysis showed stable methanol product composition comparable to last year's Kingsport test period. Nuclear density gauge readings indicated a gas holdup of 42.7 vol% and a catalyst concentration of 41.9 wt%. During the operation at this condition, some methanol



Figure 2.1 Hydrodynamic Run at LaPorte

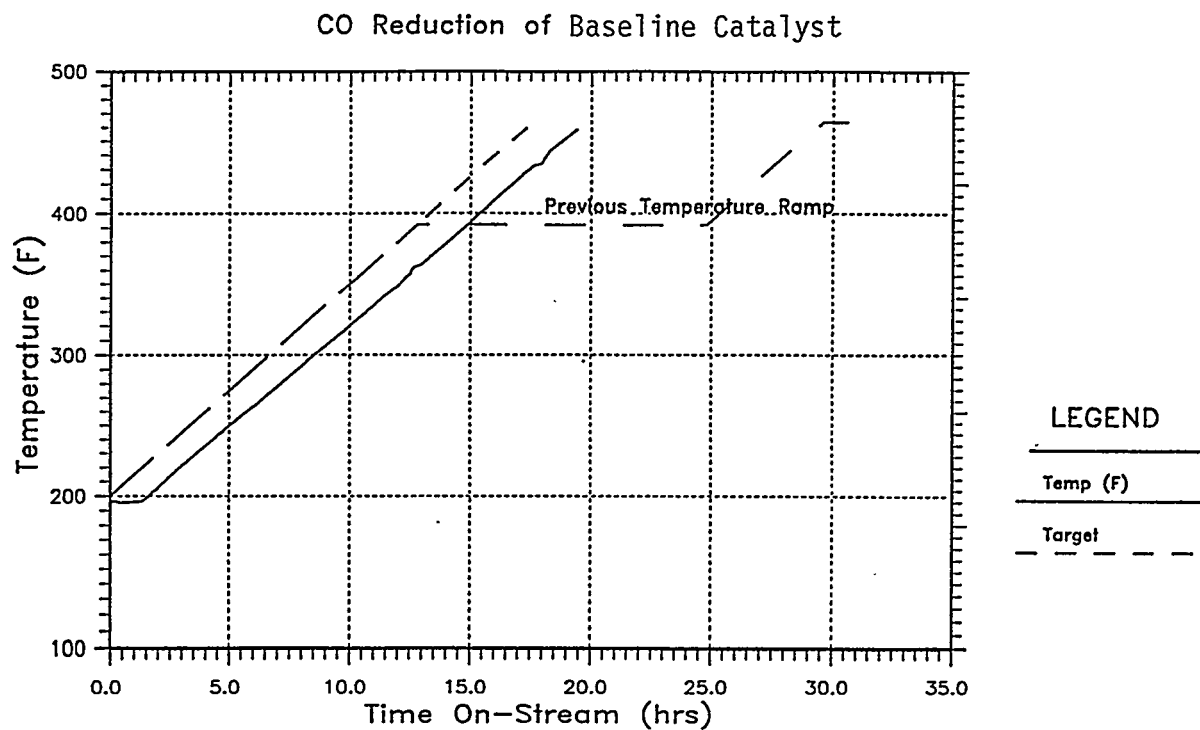


Figure 2.2 Hydrodynamic Run at LaPorte

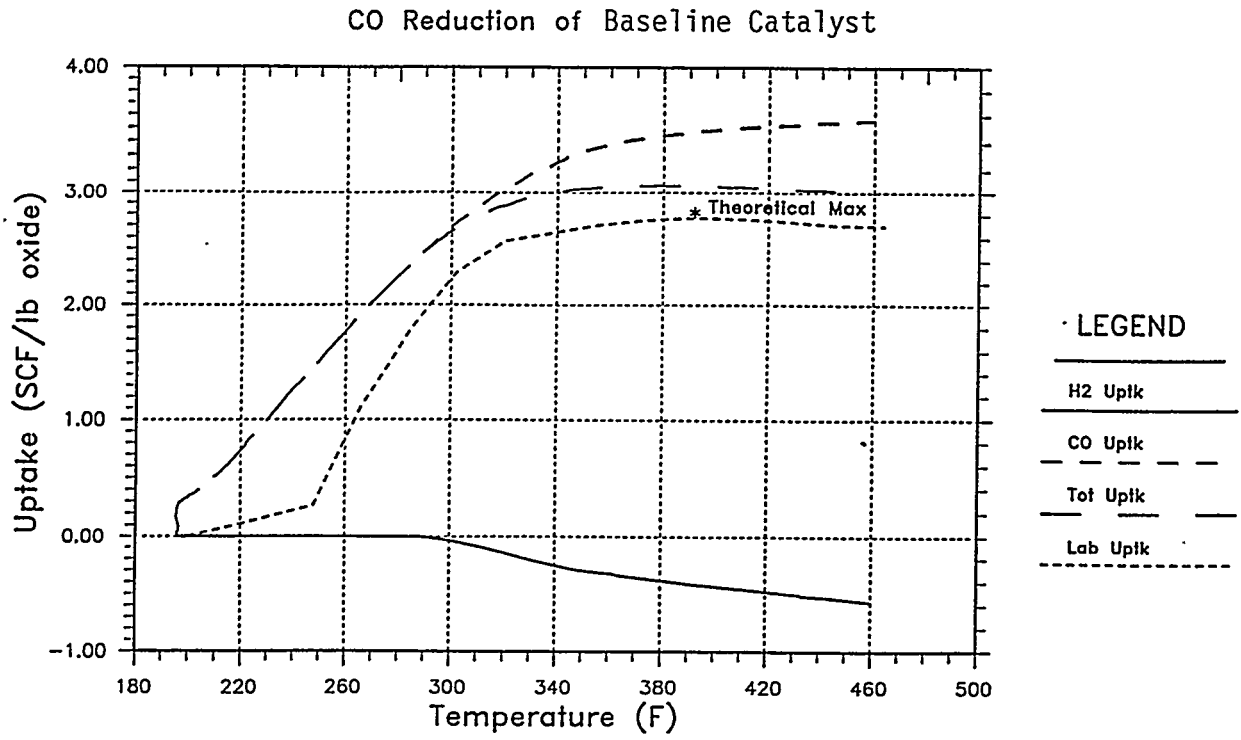


Table 2.2 LaPorte AFDU LPMEOH/Hydrodynamics Run - June 1995

Run No.	No. of Days	Comment	Gas Type	Reactor Pressure psia	Reactor Temp. deg F	Space Vel. sL/kg-hr	React. Fd. lbmol/hr	Inlet Sup. Vel. ft/sec	Slurry wt% oxide
<b>NEW REACTOR (27.20) / BASELINE CATALYST</b>									
	3	Dephlegmator Testing, Carbonyl Burnout	Nitrogen, Texaco						
AF-A9	1	Kingsport Reduction	4% CO in N2	67		615	32.3	0.62	40
AF-R13.1	2	Base Case	Texaco	765	482	7100	375	0.85	46
AF-R13.2	3	Kingsport Design	Kingsport	750	482	4000	210	0.49	41
AF-R13.3	2	High Velocity	Kingsport	735	482	9100	480	1.13	48
Subtotal	11								
<b>NEW REACTOR (27.20) / ALTERNATE CATALYST</b>									
AF-A10	1	Kingsport Reduction	4% CO in N2	67		615	32.3	0.62	40
AF-R14.1	2	Base Case	Texaco	765	482	7200	370	0.84	44
AF-R14.2	3	Kingsport Design	Kingsport	750	482	4000	210	0.48	39
AF-R14.3	1.5	High Velocity	Kingsport	535	482	7100	365	1.18	44
AF-R14.4	1.5		Texaco	765	482	4100	210	0.47	41
AF-R14.5	1	Base Case	Texaco	765	482	7200	370	0.83	45
AF-R14.6	0.8	Tracer Study	Texaco	765	482	7200	370	0.83	45
AF-R14.7	1	Tracer Study	Texaco	765	482	4100	210	0.47	41
AF-R14.8	1	Tracer Study	Kingsport	535	482	7100	365	1.18	44
AF-R14.9	0.2	Turn-down	Kingsport	765	482	1300	67	0.15	44
Subtotal	13								
GRAND TOTAL	24								