ALTERNATIVE FUELS AND CHEMICALS
FROM SYNTHESIS GAS

DOE/PC/93052--72

Quarterly Status Report No. 2

For the Period 1 January - 31 March 1995

Contractor

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Alternative Fuels and Chemicals from Synthesis Gas

Quarterly Technical Progress Report

1 January - 31 March 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

- Several meetings were held between Process, Operations, and R&D to come up with a run plan for the hydrodynamic/methanol run scheduled in June 1995. Some changes were made in previously agreed objectives. It was decided not to start up the old reactor (F-T) system. Modifications and associated expenditure needed to operate the F-T train for methanol synthesis are significant. In view of the current budgetary constraints, it was decided to defer the "cleanup" and hydrodynamic study in the F-T reactor until the next F-T campaign. In order to take advantage of availability of the new reactor (methanol) system, an additional objective to evaluate an alternate methanol catalyst was added to the new reactor run plan. This objective was originally deferred until 1996. Certainly, it is more cost-effective to address several objectives in one reactor system than to study fewer objectives in two systems. Centrifugal testing of the spent slurry to separate spent catalyst and oil was dropped as it appears that this method is not commercially viable because of high capital costs. The run will last nominally 3 weeks, with a 1-week operation on BASF S3-86 catalyst and a 2-week operation on Haldor-Topsoe MK-101 catalyst. A table of the current run plan is attached. The target start-up date is June 1.

  CO reduced BASF S3-86 methanol catalyst showed about the same level of initial activity and subsequent deactivation in the laboratory compared to using H_2 as the reduction gas.

  A preliminary hazards review was conducted on March 2 for the modifications needed for this run. Facility Change Notice (FCN) forms will be filled out and reviewed next month.

- Radian Corporation completed its evaluation of the air permit issues for the next LaPorte run scheduled for June 1995. After discussions with TNRCC personnel, Radian proposed several options. Air Products has decided to follow the alternative to the exemption option by reverting the old reactor configuration to the one originally permitted by TNRCC. By physically disconnecting the high pressure reactor feed system, we will eliminate the

possibility of increasing production or emission rates. We will not remove the new internal heat exchanger, as the heat exchanger alone does not increase production or emissions rates. As suggested by Radian, we will internally document this and other modifications for Air Products' files.

- In DME studies, work has focused on use of the new Robinson-Mahoney reactor. Since the Robinson-Mahoney (RM) internals immobilize the catalyst, it is valuable to develop samples for further analysis; however, this immobility also causes a mass transfer limit which makes interpretation of the life studies difficult unless a long run is carried out. The last life run using the RM internals was carried out long enough to show that deactivation of the catalyst system was significantly reduced by the immobilization of the catalyst particles. Subsequent testing of the catalyst particles from the RM experiment showed that the dehydration catalyst had been deactivated, but to a lesser extent than if the reaction had been carried out in a standard slurry reactor. The methanol catalyst had not deactivated. Thus we conclude that the intimate contact between particles is necessary for the level of deactivation experienced in the slurry reactor. This surprising result will be followed up and exploited in the next few months.

- A follow-up thorough analysis of the data from all dehydration catalyst screening runs, along with the results from the LPDME run using Robinson-Mahoney basket internals and pelletized catalysts, shows that the deactivation of both methanol and dehydration catalysts is not correlated with the activity of dehydration catalysts, at least for the long-term deactivation. *If one could reduce the intimate physical interaction* (e.g., collisions, intimate contact among fine powders) between the two catalysts, a stable catalyst system might be achievable.

- Following up on the lead provided by silica not affecting aging, a Condea silica alumina containing 15% alumina and 85% silica was tested as a MeOH dehydration catalyst. The catalyst system for DME using this material aged rapidly.

- In February four more dehydration catalysts were screened, including fumed alumina, zirconia, zirconia-modified silica gel, and WO_3-modified Catapal alumina. None exhibited better activity and stability than Catapal B alumina. We have been able to identify several distinct modes of deactivation, e.g., deactivation of both catalysts or deactivation of one component only. This understanding suggests new directions in the search for alternate dehydration catalysts.

- Three more dehydration catalysts were screened in March, including a silica alumina containing 95% of SiO_2, a calcium phosphate catalyst (hydroxyapatite), and a silica sample doped with phosphoric acid. None exhibited attractive performance.

- The University of Aachen reports that they have been able to reproduce the isobutanol productivity of Falter's best catalyst. Methanol formation rate is higher than the original catalyst. Unfortunately, this increased productivity is accompanied by a high rate of formation of unwanted methane.

- At Lehigh, the Cs-doped Cu/ZnO/Cr$_2$O$_3$) catalyst has been tested at 325°C for HAS under two reaction pressures (7.6 and 6.5 MPa) and five contact times with a syngas of H$_2$/CO of 0.75. At longer contact times (low space velocities), HAS seems to be enhanced by the lower reaction pressure. In addition the lower pressure decreases methanol formation.

- Professor Foley reports continued work on testing of alkali-doped catalysts precipitated with KOH. Temperatures necessary for isobutanol formation are still higher than desired for slurry operation, but progress over the initial set of catalysts is apparent.

- In early January, a literature search was conducted on heterogeneous carbonylation catalysts, and based on this a plan was generated for our goal of converting DME to EDA using a heterogeneous catalyst. The plan calls for the preparation of several rhodium catalysts. In particular, we will prepare [Rh(diphos$_2$)]$^+$ complexes and support them on different types of alumina, prepare supported Rh complexes on Reillex polymers, and also prepare a supported Li[Rh(CO)$_2$X$_2$]. We will also attempt to intercalate an anionic Rh complex within the layers of a double hydroxide.

- During February, a first attempt was made to prepare a heterogeneous rhodium catalyst for the conversion of dimethyl ether to ethylidene diacetate (EDA). A sample of Reillex 425 polymer was loaded with a solution of Rh$_2$(CO)$_4$Cl$_2$ in toluene (2% by weight Rh). During March, we tested this material as a heterogeneous catalyst for the conversion of dimethyl ether (DME) to ethylidene diacetate (EDA). The catalytic performance of the heterogeneous catalyst was compared with the analogous homogeneous system using similar experimental conditions (syngas, 190°C, 1500 psi). In the absence of lithium iodide, the heterogeneous catalyst worked much better than the homogeneous analog forming acetic anhydride, acetaldehyde and EDA. Adding lithium iodide did not improve the performance of the heterogeneous system, but it did help the homogeneous system produce EDA, although the productivity was still less than that of the heterogeneous system.

- Various previously tested catalysts for isobutanol synthesis from methanol (Ag/K on SrO and Ag/Cs on SrO) were retested to determine reactor reproducibility. In addition, the best catalyst was prepared again, tested, and identical results were obtained. By varying the mol ratio of Ag/Cs on SrO, it was determined that an Ag/Cs mol ratio of 1 favors higher selectivity to oxygenates. This suggests Ag/Cs ratios of less than 1 should be screened. An IR of used Ag/Cs on SrO catalyst shows carbonate bands. However, Ag on SrCO$_3$ is inactive as a catalyst.

- Final details were made to the subcontract with Bechtel. This subcontract was officially in place at the end of March. Bechtel's first priority is in defining isobutanol catalyst performance targets to achieve a final MTBE product at 70¢/gal.

RESULTS AND DISCUSSION

TASK 1: ENGINEERING AND MODIFICATIONS

1.1 Liquid Phase Hydrodynamic Run

Radian Corporation completed its evaluation of the air permit issues for the hydrodynamic/methanol run scheduled for June 1995. No permit/exemption action is needed for the new reactor as its operation is covered by the 1994 exemption. The key question for the old reactor was whether disconnecting an additional feed source (high pressure hydrogen) to limit methanol production would be acceptable to TNRCC. Radian worked with TNRCC to resolve this issue. After discussions with TNRCC personnel, Radian proposed several options. While most options required an exemption application, Air Products decided to follow an alternative to the exemption options by reverting the old reactor configuration to the one originally permitted by TNRCC. By physically disconnecting the high pressure reactor feed system, the possibility of increasing production or emission rates will be eliminated. However, the new internal heat exchanger will not be removed, as the heat exchanger alone does not increase production or emission rates. As suggested by Radian, we will internally document these and other modifications for Air Products' files.

Several meetings were held between Process, Operations and R&D to come up with a run plan. Some changes were made in previously agreed-to objectives. It was decided not to start up the old reactor (F-T) system. Modifications and associated expenditure needed to operate the F-T train for methanol synthesis are significant. In view of the current budgetary constraints, it was decided to defer the "cleanup" and hydrodynamic study in the F-T reactor until the next F-T campaign. In order to take advantage of availability of the new reactor (methanol) system, an additional objective to evaluate an alternate methanol catalyst was added to the new reactor run plan. This objective was originally deferred until 1996. Certainly, it is more cost-effective to address several objectives in one reactor system than to study fewer objectives in two systems. Centrifuge testing of the spent slurry was dropped as it appears that this method is not commercially viable because of high capital costs. During the design of Tennessee Eastman's Kingsport LPMEOH™ plant, it was determined that incineration of spent slurry was more economical then separating catalyst and oil using a centrifuge. The run will last nominally three weeks, with a one-week operation on BASF S3-86 catalyst and a two-week operation on Haldor-Topsoe MK-101 catalyst. The current run plan is summarized in Table 1.1.1. The target start-up date is June 1.

A preliminary hazards review was conducted on March 2 for the modifications needed for this run. Facility Change Notice (FCN) forms will be filled out and reviewed in April. Catalyst orders were placed for LaPorte: 3000 lbs of BASF S3-86 catalyst (1 + 1 spare charge) and 1500 lbs of Haldor-Topsoe MK-101 catalyst (1 charge).

1.2 and **1.3** No progress to report this quarter.

Table 1.1.1. 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	Lb Cat. oxide	Approx. MeOH Prodtn, GPD
NEW REACTOR (27.20) / BASF CATALYST											
	3	Carbonyl Burnout, Dephlegmator Testing	Texaco								
AF-A9	1	Kingsport Reduction	4% CO in N2	60		1500				1177	
AF-R13.1	2	Base Case	Texaco	765	482	7000	367.5	0.83	42	1177	3790
AF-R13.2	3		Kingsport	750	482	4000	210	0.47	40	1177	3320
AF-R13.3	2		Texaco	765	482	10000	525	1.2	43	1177	4850
Total	11										27240
NEW REACTOR (27.20) / HALDOR-TOPSOE CAT											
AF-A10	1	Kingsport Reduction	4% CO in N2	60		1500				1177	
AF-R14.1	2	Base Case	Texaco	765	482	7000	367.5	0.83	42	1177	3790
AF-R14.2	3		Kingsport	750	482	4000	210	0.48	40	1177	3320
AF-R14.3	1.5		Texaco	765	482	10000	525	1.2	43	1177	4850
AF-R14.4	1.5		Texaco	765	482	4000	210	0.47	41	1177	2340
AF-R14.5	1	Base Case	Texaco	765	482	7000	367.5	0.83	42	1177	3790
AF-R14.6	3	Tracer Study	Texaco	765	482	4000-10000	210-525	0.47-1.2	40-43	1177	3790
Total	13										43485
GRAND TOTAL	24										

5

1.4 AFDU R&D Support

1.4.1 Catalyst Activation With CO

One of the objectives of the methanol/hydrodynamics run in the AFDU at LaPorte will be to demonstrate new technology proposed for Kingsport. To simplify the process equipment and procedure for catalyst reduction in the Liquid Phase Methanol plant design for Eastman, a new reduction procedure for BASF S3-86 was investigated in the lab. The goal of the new reduction procedure was to eliminate H_2O production during reduction by using H_2-free reduction feed gas, decrease the time required for reduction, and simplify the temperature ramping procedure. To this end, reduction of S3-86 was carried out in the lab autoclave using CO in N_2 feed gas (H_2-free). The activity and life of the catalyst were also tested.

Background

The current design for the Liquid Phase Methanol plant at the Eastman Chemical Company complex includes a catalyst reduction vessel from which slurry containing fresh, reduced catalyst will be supplied to the process. The heretofore established reduction procedure for the BASF S3-86 catalyst involves an empirically established temperature ramping protocol and the use of H_2-containing reduction gases (either 2% H_2 in N_2 or 4% Texaco syngas in N_2). The use of H_2 as a reductant results in the production of H_2O via CuO reduction:

$$H_2 + CuO \rightarrow Cu + H_2O.$$
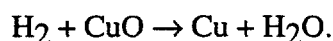
However, H_2O production during reduction complicates downstream processing since slurry mineral oil vaporized during reduction and H_2O may form two phases and the H_2O produced must be processed as waste water.

To investigate the possibility of simplifying the process equipment and operating procedure for catalyst reduction, a new reduction procedure was investigated in the 300 cc lab autoclave. The goal of the new reduction procedure is to minimize water production during reduction, decrease the time required for reduction, and simplify the temperature ramping procedure. In this experiment, a nominal 2% CO in N_2 reduction gas was used. Thus, CuO is reduced by CO:

$$CO + CuO \rightarrow Cu + CO_2,$$
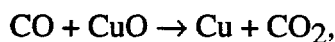
which eliminates H_2O as a direct product of reduction.

Experimental

The time-temperature ramp was simplified. The previously established procedure involved a 12 hr temperature hold at 200°C during the overall increase from 100°C to 240°C. For the present experiment, the temperature was increased from 100°C to 240°C at 10°C/hr continuously, thereby saving 12 hr in the reduction procedure. A feed flow rate of 1500 std.lit./kg-hr and a pressure of 50 psig were chosen.

Reduction with 2% CO-98% N_2

Figure 1.4.1 shows the time temperature profile used for this experiment.

Figure 1.4.1. Temperature Ramp Used for Catalyst Reduction

Run 13458-90
BASF S3-86 - 91/14638
Reduction Gas Feed: 1.88% CO/balance N_2
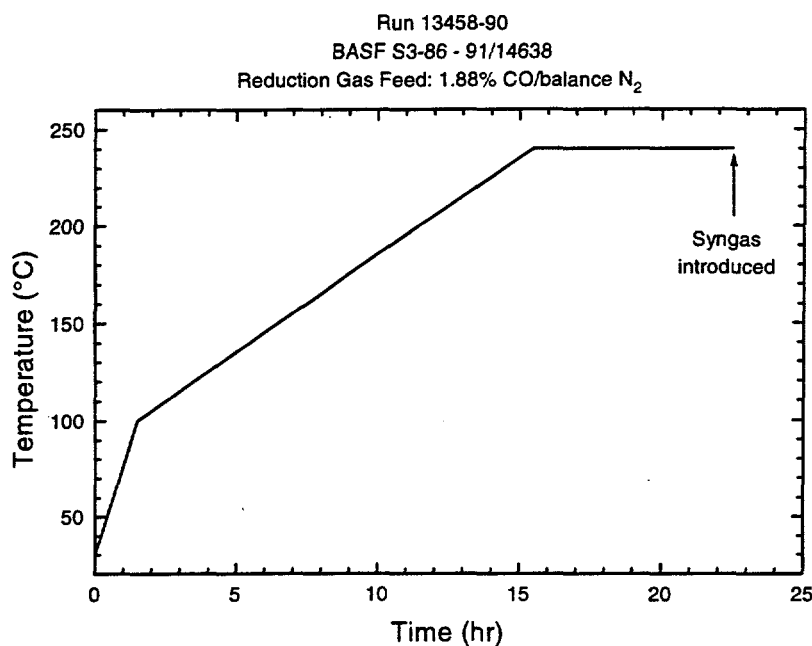
Syngas introduction was delayed for several hours after 240°C was reached so that the feed could be switched during normal working hours. As shown below, very little occurs during the 240°C hold. In practice, the feed could be switched as soon as the reactor temperature reaches 240°C.

The reactor effluent concentrations of CO, CO_2, H_2O, and H_2 during reduction were obtained by GC. The GC was calibrated for H_2O using a controlled temperature and pressure H_2O saturator. For low concentrations, a sub-0°C condenser (freezer) was used downstream of the H_2O saturator. Water concentration was calculated from the vapor pressure of liquid or solid H_2O at the saturator or freezer temperature. The GC response was slightly non-linear, necessitating the use of a calibration curve. Quantitation accuracy for H_2O was ±10% (relative) for H_2O concentrations greater than 0.1 mol%, but the detection limit was about 0.025 mol%.

Figure 1.4.2 shows the reactor effluent concentrations of CO, CO_2, H_2O, and H_2 during reduction plotted as a function of the reduction temperature.
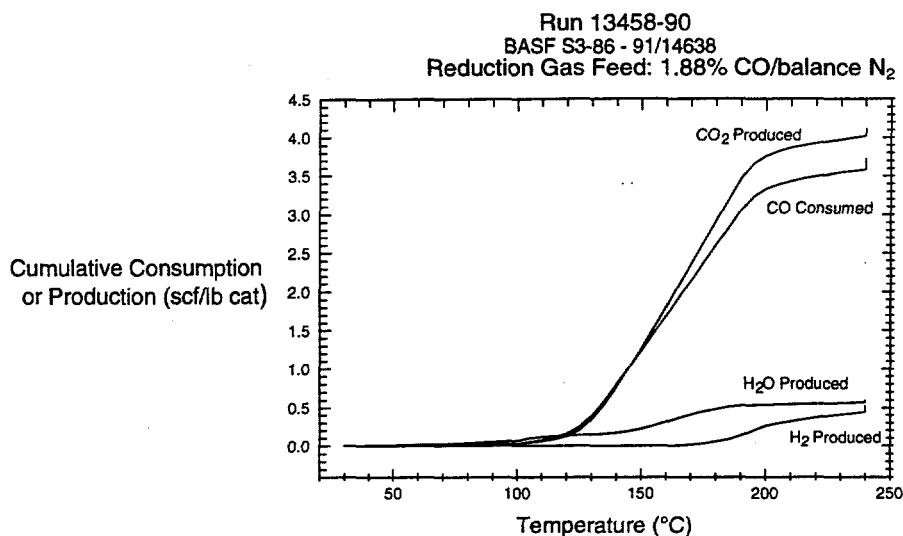
Figure 1.4.2. Reactor Exit Concentration versus Reduction Temperature

Run 13458-90

Reduction Gas Feed: 1.88% CO/balance N
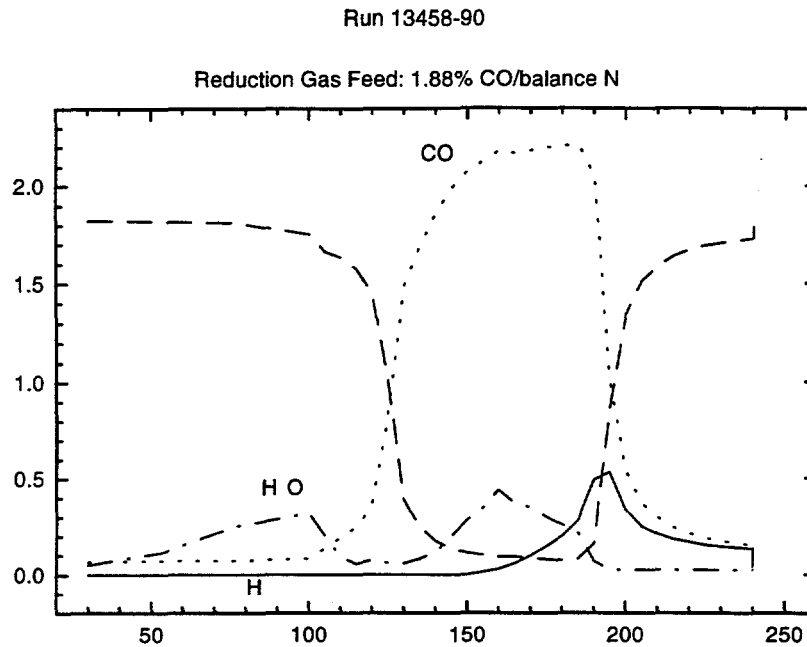
Clearly, CO is consumed, while CO_2, H_2O, and H_2 are produced during reduction.

Figure 1.4.3 shows the cumulative consumption of CO and the cumulative production of CO_2, H_2O, and H_2 versus reduction temperature.

Figure 1.4.3. Cumulative Consumption/Production versus Reduction Temperature

Run 13458-90
BASF S3-86 - 91/14638
Reduction Gas Feed: 1.88% CO/balance N_2

Cumulative Consumption or Production (scf/lb cat)

CO$_2$ Produced

CO Consumed

H$_2$O Produced

H$_2$ Produced

Temperature (°C)

The use of the CO/N_2 feed gas did not completely eliminate H_2O production during reduction. Approximately 0.55 scf of H_2O/lb of as-received catalyst was produced during reduction. This detection of unexpected H_2O was examined in detail.

The presence of two peaks in the water concentration profile in Figure 1.4.2 suggests that H_2O is derived from two different sources during reduction. The low temperature peak probably corresponds to the loss of physically adsorbed H_2O that has been retained after calcination or adsorbed during handling after calcination. The second peak is probably produced from decomposition of the "hydroxy-carbonate" precursor that constitutes the as-received catalyst. This hydroxy-carbonate precursor eliminates hydroxide groups as H_2O during heat-up.
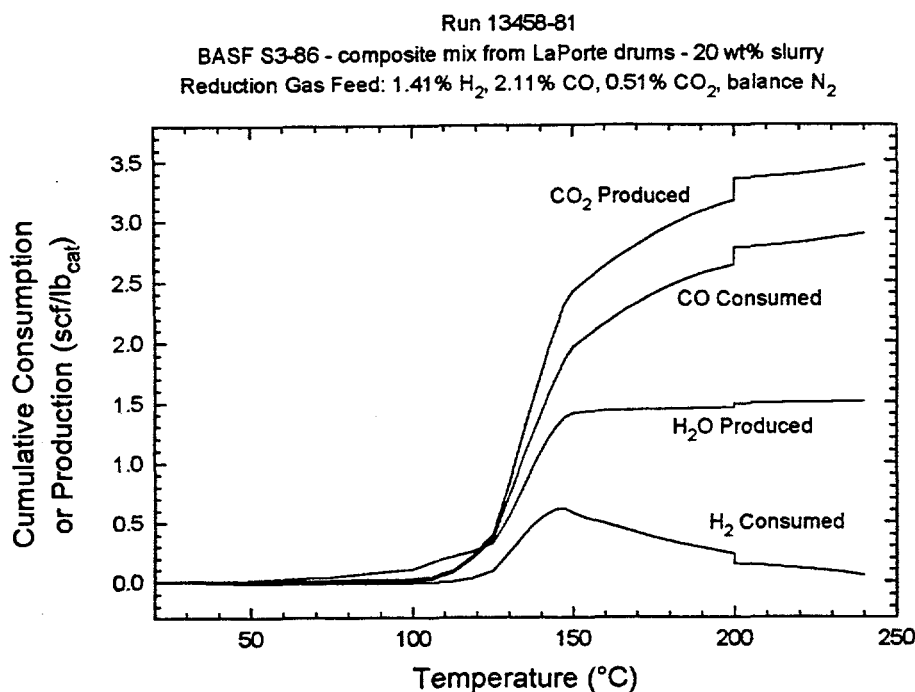
The H_2 produced in the later stage of reduction results from H_2O reacting with CO via the water-gas shift reaction:

$$CO + H_2O \leftrightarrow H_2 + CO_2.$$
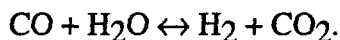
Thermodynamic equilibrium for the exothermic shift reaction lies very far to the right for the temperature range of reduction, thereby representing a possible "sink" for H_2O during reduction. The equilibrium constant, Kp, ranges from 3600 at 100°C to 105 at 240°C. However, the data show that the shift reaction was far from equilibrium at any point during reduction up to 190°C. At temperatures greater than 190°C, the H_2O concentration was below the detection limit, so it was impossible to determine whether the shift reaction was close to equilibrium.

Comparison of the present results with results from a "standard" reduction using 4% syngas in N_2, for which a slower temperature ramp was also used, reveals corroborating evidence. Figure 1.4.4 shows the cumulative consumption of CO and H_2 (H_2 is first consumed and then produced during reduction with syngas) and the cumulative production of CO_2 and H_2O.

Figure 1.4.4. Cumulative Consumption/Production versus Temperature for Reduction Using 4% Syngas in N_2


Run 13458-81
BASF S3-86 - composite mix from LaPorte drums - 20 wt% slurry
Reduction Gas Feed: 1.41% H_2, 2.11% CO, 0.51% CO_2, balance N_2

As expected, the H_2O produced for the H_2-containing reduction feed gas is higher: 1.5 scf of H_2O/lb versus 0.55 scf of H_2O/lb for the 2% CO/N_2 reduction gas. Again, the shift reaction is far from equilibrium for data points where the H_2O concentration was above the detection limit.

Activity of CO-Reduced (2% CO in N_2)

The catalyst activity after reduction using 2% CO/N_2 was measured at 250°C and 750 psig using Texaco syngas feed (35% H_2/51% CO/13% CO_2/1% N_2) at GHSVs of 5,000 and 10,000 std.lit./kg-hr. The expected performance and the results for the activity tests after reduction using 2% CO/N_2 are shown in Figure 1.4.5.

Figure 1.4.5. Performance of Catalyst After Reduction Using 2% CO in N$_2$

Run 13458-90
250°C, 750 psig, Texaco Gas
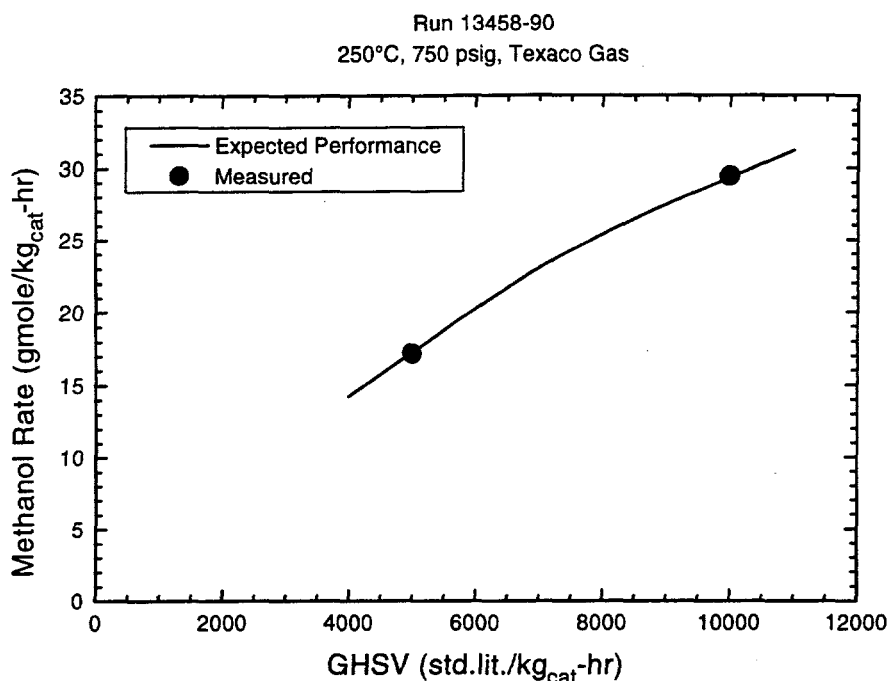
The expected performance curve was established by previous lab data for S3-86 after reduction in 4% syngas in N$_2$ or 2% H$_2$ in N$_2$ using slower temperature ramps. Clearly, reduction using 2% CO/N$_2$ and the faster temperature ramp produced a catalyst with the same performance as that obtained using the H$_2$-containing reduction gases.

**Reduction and Performance Using 4% CO(Balance N$_2$)**

H$_2$O production during reduction was not entirely eliminated but reduced by 63% compared to reduction by 4% syngas in N$_2$ (contains H$_2$). Even though the 2% CO reduction gas was H$_2$-free, H$_2$O was still produced from thermal desorption of physically adsorbed H$_2$O and dehydroxylation of the hydroxy-carbonate catalyst precursor. Also evident in this experiment was that the CO concentration was nearly zero during a portion of the temperature ramp, indicating almost complete consumption of the reductant.

In an attempt to avoid the complete consumption of reductant and to further reduce the production of H$_2$O during reduction, in situ reduction was done in the lab autoclave using a feed gas with a higher CO content (4% CO in N$_2$). The hypothesis was that the higher CO concentration may drive the water-gas shift reaction, $CO + H_2O = CO_2 + H_2$, to the right, thereby reducing H$_2$O production during reduction. Moreover, the use of higher CO concentration may avoid complete consumption of reductant, a situation that has an unknown, but possibly deleterious, effect on catalyst activation.

In situ reduction of S3-86 was carried out using the 300 cc autoclave system. The temperature ramp, pressure, and feed flow rate were the same as those used for the 2% CO in N$_2$ reduction experiment. Figure 1.4.6 compares the CO uptake and reactor exit CO concentration as a

function of temperature for reduction using 2% CO and 4% CO. The final consumption of CO is slightly higher for the 4% CO case, but probably not significantly different within the accuracy of the measurements. Also, the rate of CO consumption is faster for the 4% CO case, indicating a positive dependence of reduction rate on CO concentration. Note also that the lowest reactor exit CO concentration for the 4% CO feed case dropped to a minimum of 1 mol%, in contrast to the 2% CO feed case in which the reactor exit CO concentration fell nearly to zero.

Figure 1.4.6. The Effect of CO Feed Concentration on CO Consumption and Reactor Exit CO Concentration
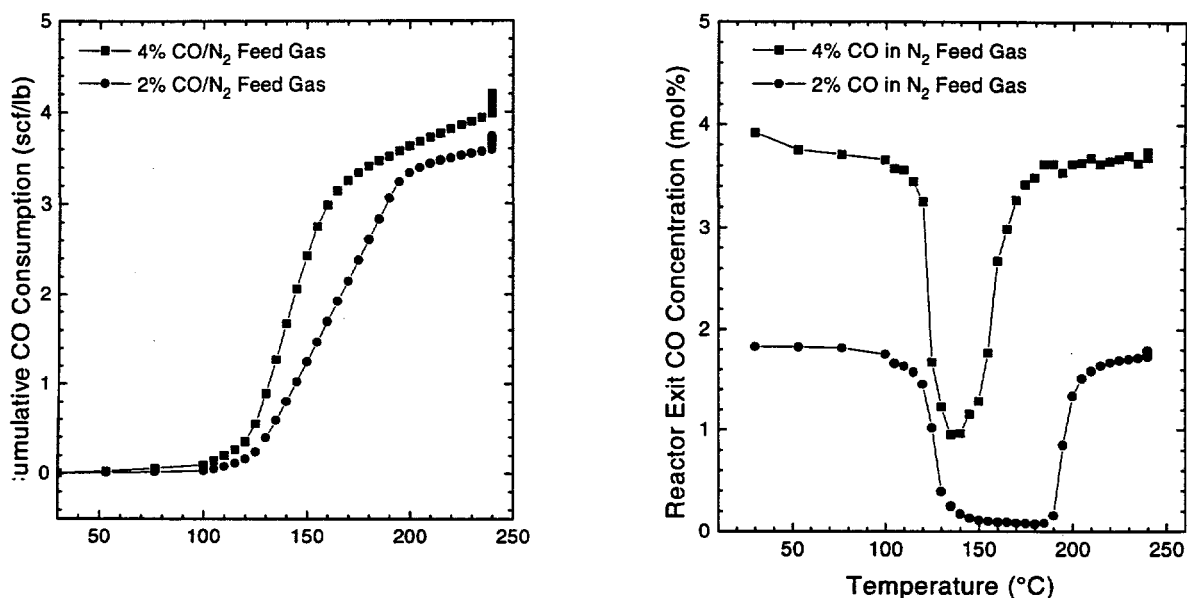
The fact that the CO concentration in the reactor was higher for 4% CO reduction apparently had no effect on the H_2O produced. The cumulative H_2O produced for the 4% CO reduction was estimated to be 0.65 scf/lb, which is comparable (within the experimental accuracy of the GC measurements) to the 0.55 scf/lb measured for the 2% CO reduction. Of course, these values are much lower than the 1.5 scf/lb measured for reduction using 4% Texaco gas in N_2. Evidently, the higher reactor CO concentration did not have a measurable effect on H_2O conversion via the water-gas shift reaction.

Reduction with 4% CO resulted in a catalyst with the same methanol synthesis activity as that obtained after reduction using the standard H_2-containing reduction gases. Figure 1.4.7 shows the measured performance after reduction with 4% CO and the expected performance curve after reduction using previously established reduction procedures and H_2-containing reduction gases. Clearly, the performance of the catalyst after the new reduction procedure equals that obtained for the previously established reduction procedure. Thus, in situ reduction of S3-86 with 4% CO in N_2 is a viable way of activating the catalyst.

Figure 1.4.7 Methanol Synthesis Rate after 4% CO Reduction
250°C, 750 psig, Texaco Gas
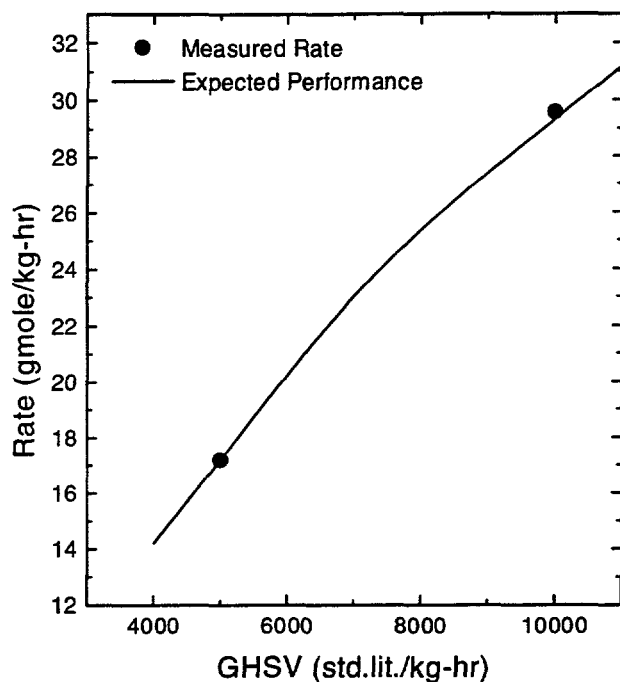
A new procedure that was changed slightly from the initial procedure to conserve CO was implemented. The data for the run are summarized in Figures 1.4.8-1.4.11. The heating rate and gas flow rate have been slightly modified from the initial run (Run 8--Figure 1.4.8). Gas uptake rate and product generation (Figs. 1.4.9-11) were satisfactory for all runs. The new procedure is substantially similar to the old procedure.
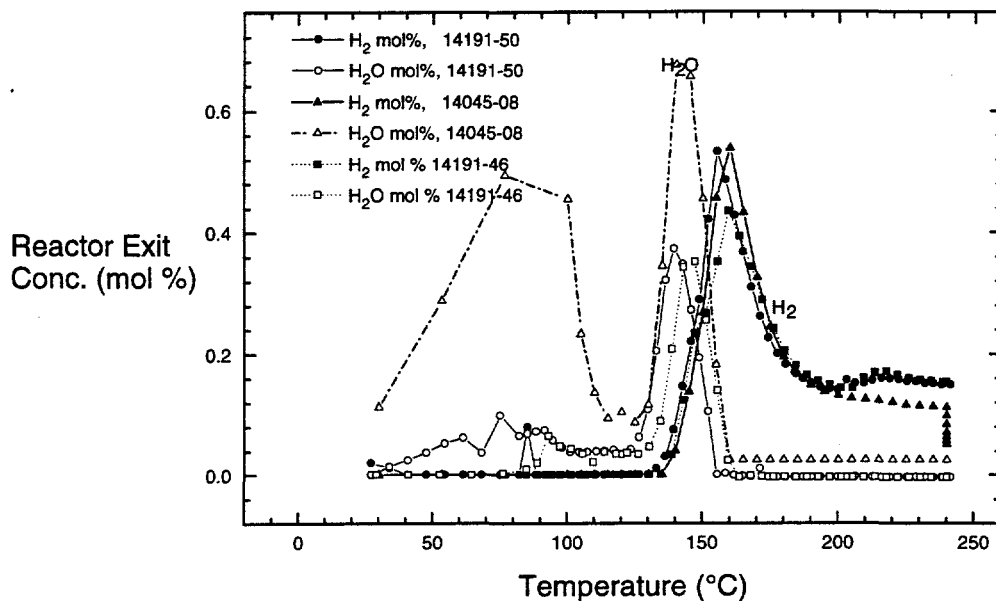
Figure 1.4.8 Reduction Temperature Profiles

4% Co/Balance N_2;
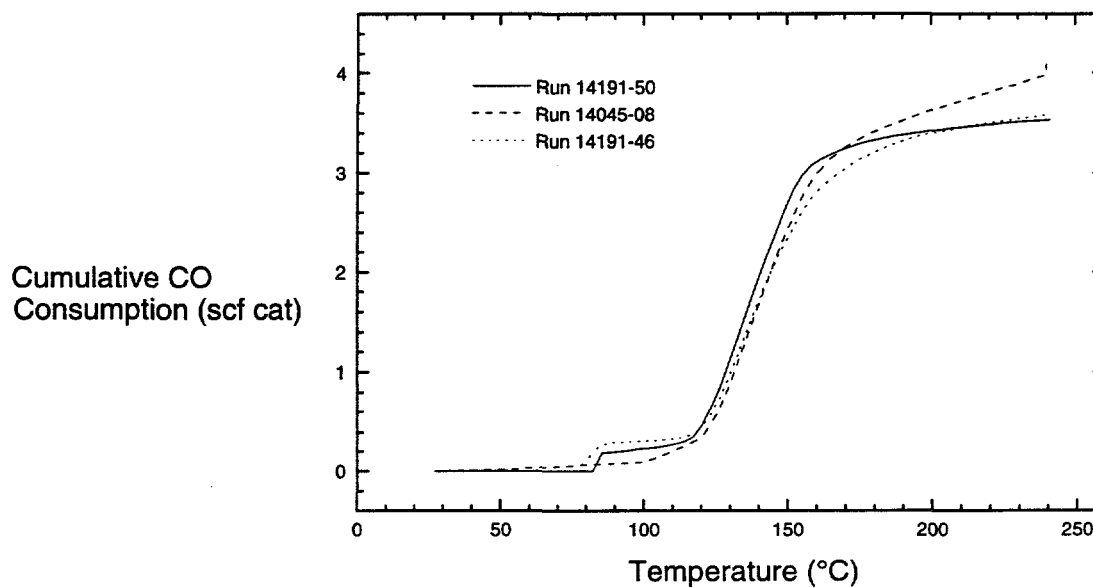
SV: 1,500 sl/kg-hr for 14191-50, 1,600 for 14045-08

Time (hr)
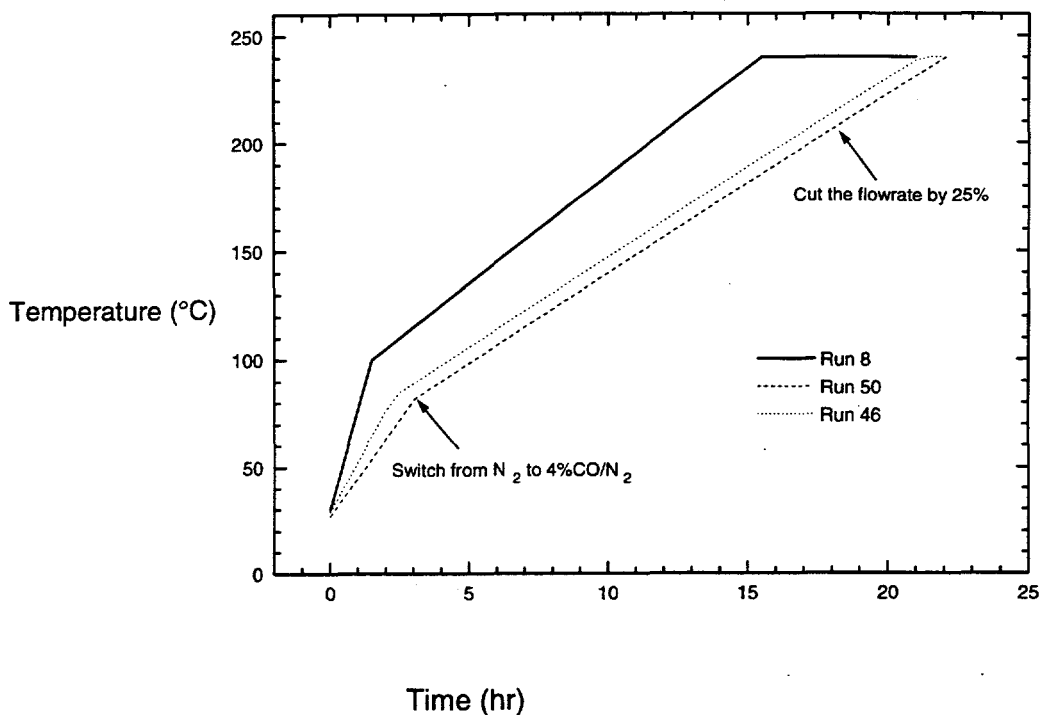
Figure 1.4.9 Runs 14191-50 and 14045-08

Reduction Gas Feed: 4% Co/Balance N_2;
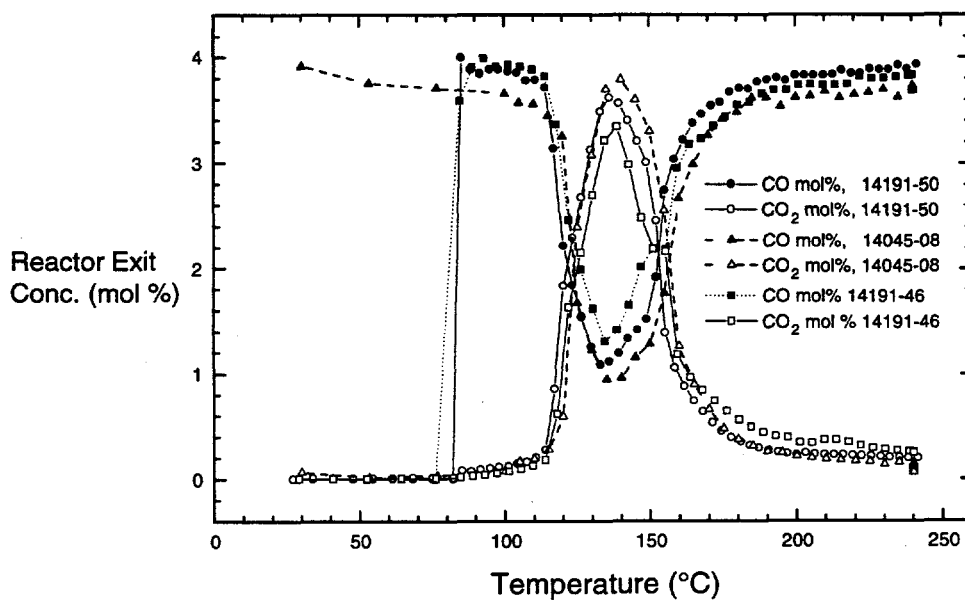
Figure 1.4.10 Runs 14191-50, 14191-46, anbd 14045-08
Reduction Gas Feed: 4% Co/Balance N_2

Figure 1.4.11 Comparison of Different Procedures
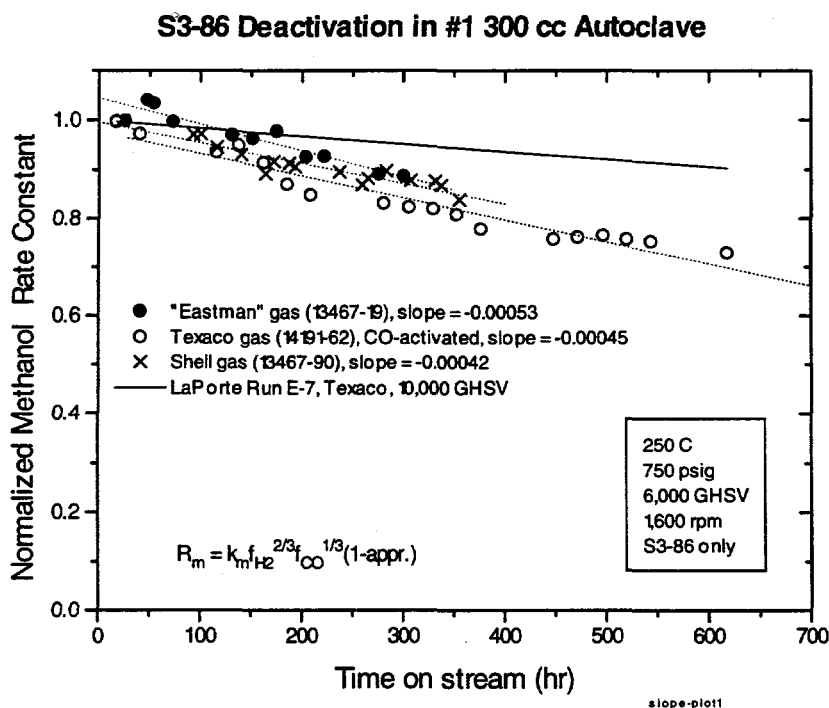Runs 14191-50 and 14045-8 14191-46
BASF S3-886 - 91/14638

Life Test of Catalyst Activated Using CO

The final check on the CO activation procedure was to test the life of a CO-activated catalyst. Test results were analyzed by noting the change in specific rate constant with time. A decrease in rate constant translates to catalyst aging. To account for small differences in initial activity, aging is expressed as a % of the initial activity/unit time.

While the best kinetic expression available for methanol formation is not perfect, the correlation is good enough so that aging data can be compared. Since a CSTR is used for the rate measurement, the reaction conditions depend upon the activity of the catalyst. Using the rate expression allows comparison with experiments done at other conditions and accounts for small changes in operating conditions and catalyst activity.

Figure 1.4.12 shows historical data of activation with H_2 taken for the S3-86 catalyst. The slope of the line is a direct measurement of aging. The laboratory tests always show a higher aging rate than measured in the LaPorte test. The reasons for this difference are not clear. The laboratory test gives a fairly constant value for aging and thus, may be used as an indication of the relative stability of the catalysts.

Figure 1.4.12. S3-86 Deactivation in #1 300 cc Autoclave

S3-86 Deactivation in #1 300 cc Autoclave

- ● "Eastman" gas (13467-19), slope = -0.00053
- ○ Texaco gas (14191-62), CO-activated, slope = -0.00045
- ✕ Shell gas (13467-90), slope = -0.00042
- —— LaPorte Run E-7, Texaco, 10,000 GHSV

250 C
750 psig
6,000 GHSV
1,600 rpm
S3-86 only

$$R_m = k_m f_{H_2}^{2/3} f_{CO}^{1/3}(1\text{-appr.})$$

The data for CO activated catalyst are shown in Figure 1.4.13. The slope of the line from the laboratory data is about the same as for the laboratory data using the standard activation method. Therefore, we conclude that CO activation does not adversely affect the performance of the catalyst.