APPENDIX B

Laboratory Testing of Alternate Methanol Catalyst

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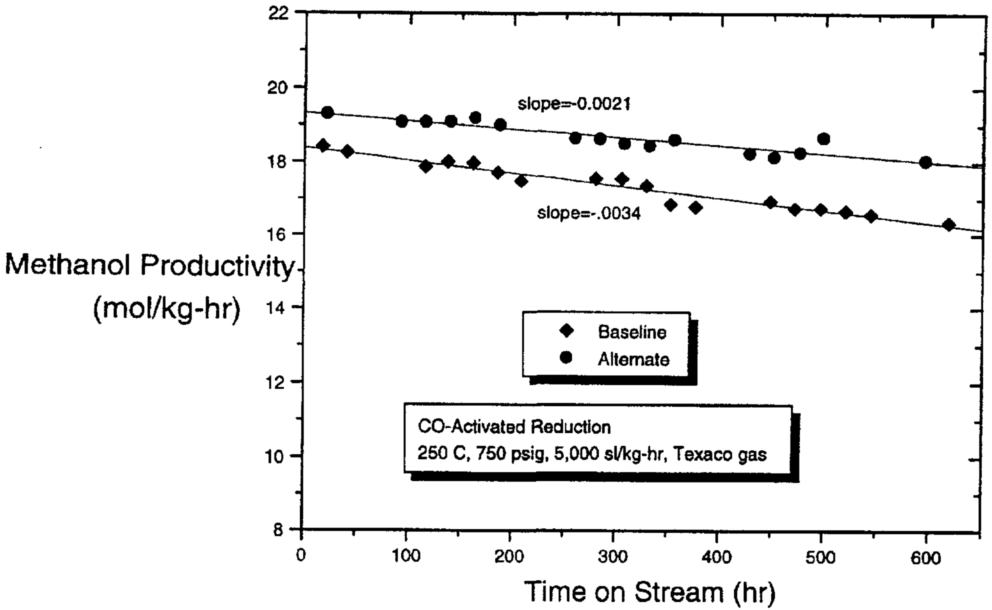
Establishment of a tested, alternate catalyst supply is part of any process development. For the LPMEOH™ process, demonstration must be made at the LaPorte scale. One of the objectives of the methanol/fluid dynamic run in the AFDU at LaPorte was to demonstrate the performance of an alternate catalyst.

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 catalyst is compared to the LPMEOH Baseline catalyst in Figure B.1. The catalyst performed well, showing slightly higher activity than the Baseline catalyst. Also, the Alternate catalyst aged slightly slower than the Baseline catalyst.

Figure B.1 Life Test Results



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Reduction of the catalyst was accomplished by the new CO reduction procedure discussed in Appendix A. The reduction temperature profile is shown in Figure B.2, and the off-gas profiles for the catalyst are shown in Figure B.3. Both CO uptake and CO_2 generation were lower for the Alternate catalyst than for the Baseline catalyst, possibly because of a different copper content, and with less water being generated in this reduction, it is possible that the water gas shift reaction, which can occur at a late stage of the activation, was less important for the Alternate catalyst.

Figure B.2 Reduction Temperature Profiles

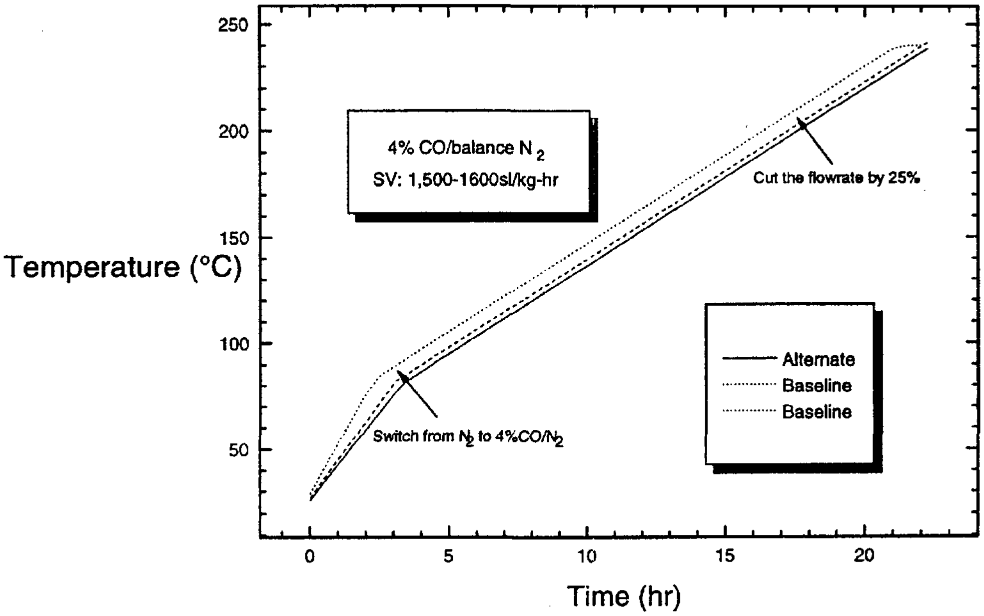


Figure B.3 Off-Gas Profiles for Two Catalysts

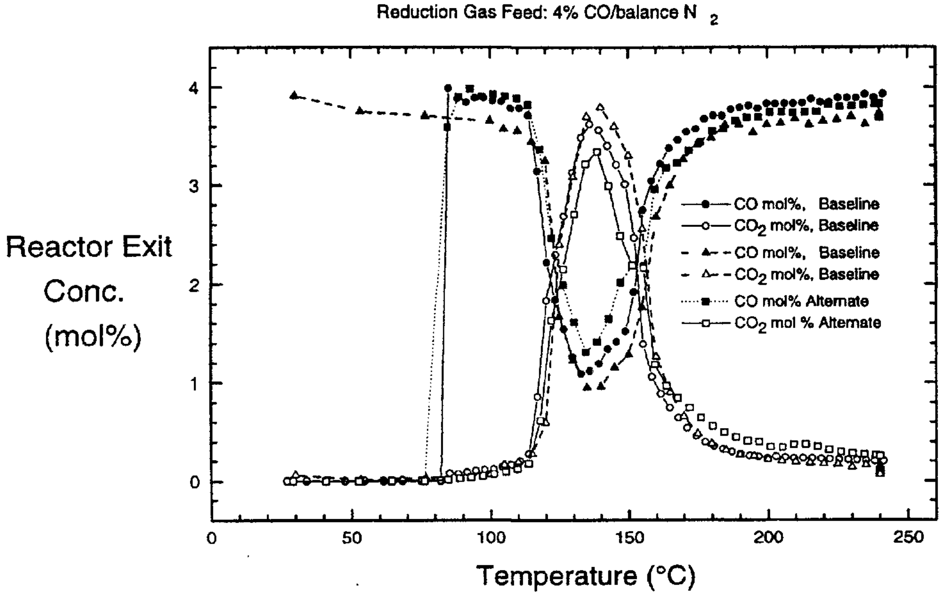
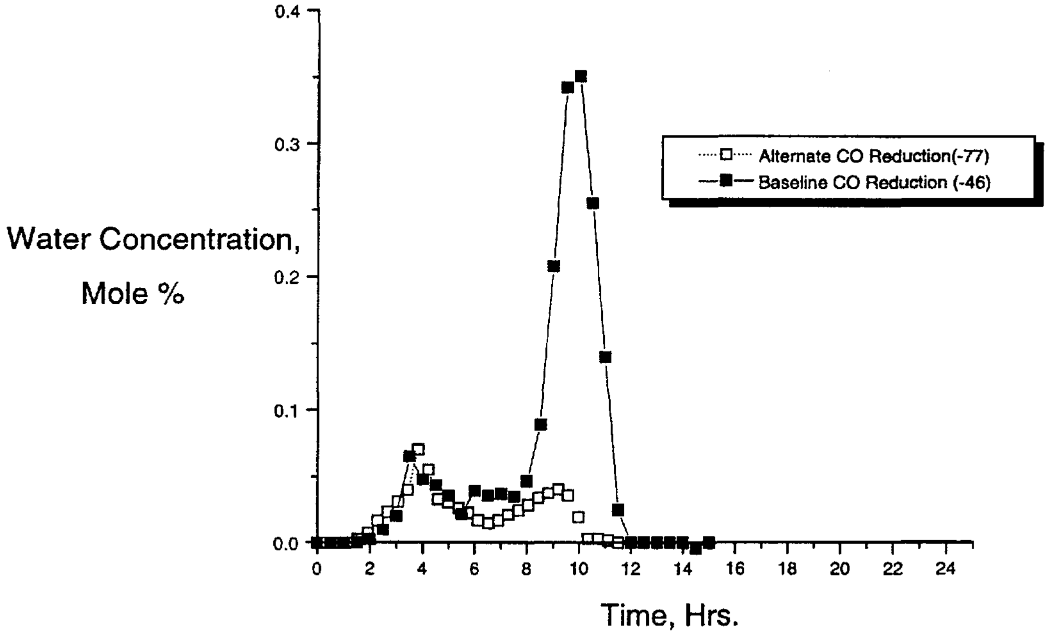


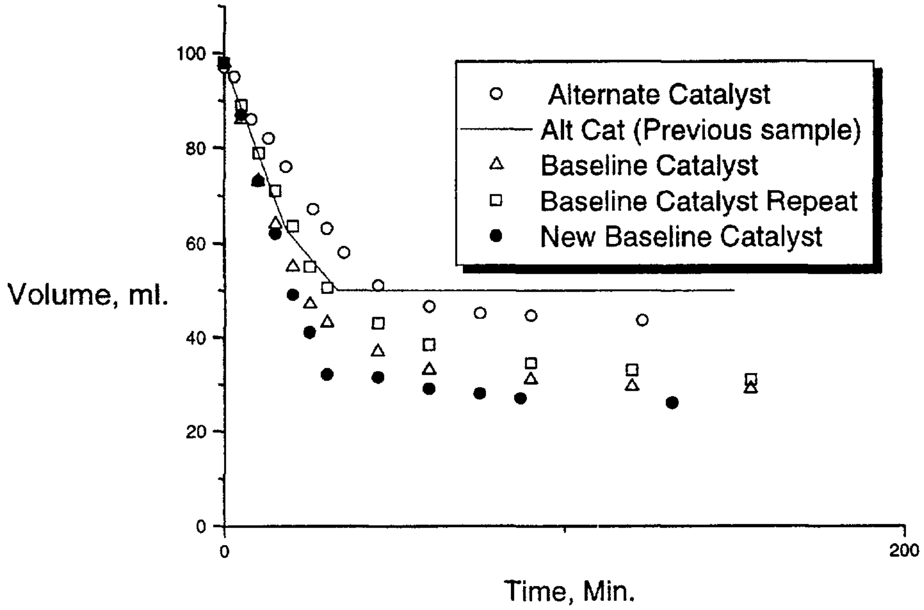
Figure B.4 shows water evolution, which was much lower for the Alternate catalyst than for the Baseline catalyst. At low temperatures, the sorbed water driven off both catalysts was similar. However, the difference was pronounced during the higher temperature portion of the reduction. Water evolution is attributed to the breakdown of hydroxycarbonates in this higher temperature region. The previous sample of the Alternate catalyst, which was taken from a different place in the production line, showed higher water evolution and therefore possibly a higher level of hydroxycarbonates. (In fact, the level was higher than for the typical Baseline catalyst.)

Figure B.4 Comparison of Water Concentration 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 the 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 B.5). The candidate catalyst showed a satisfactory settling rate, and should perform well in the slurry reactor.

Figure B.5 Results of Slurrification Test



Summary and Recommendation

All recent data on the activation of the Baseline catalyst and the Alternate catalyst are summarized in Table B.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 B.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. Also, the catalyst ages slightly slower than 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.

Table B.1 Catalyst Activation on Texaco Gas

Catalyst	$K(R=K f_{H2}^{2/3} f_{CO}^{1/3})$ [1-appr]		Productivity (5,000 GHSV, 250°C)	
Source	Alcohols*	Bulk**	Alcohols	Bulk
Process Model for Baseline	2.86		17.4	
Historic Data (Hsiung)			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_2, 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.