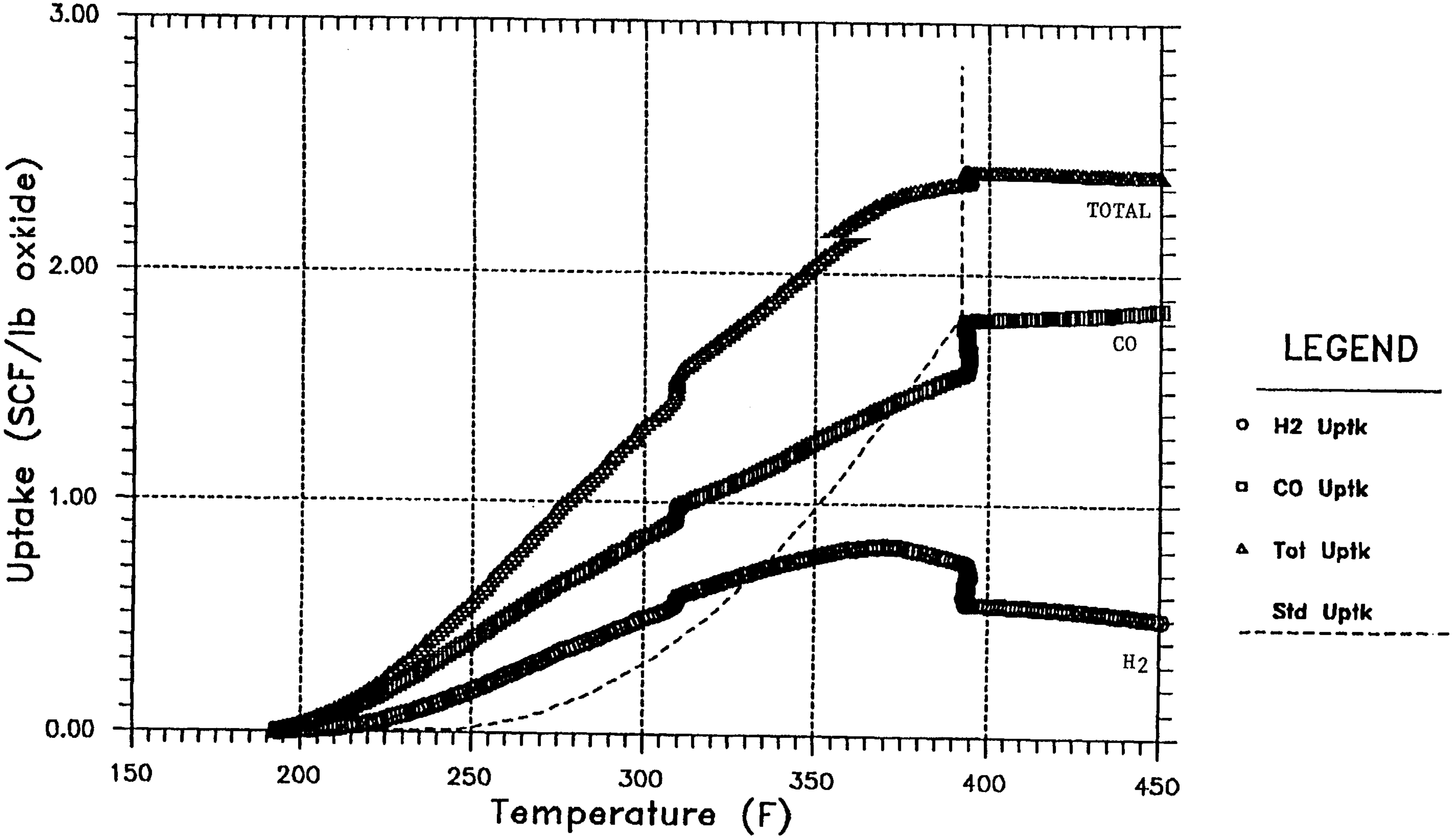
FIGURE 9

Reduction Gas Uptake vs. Temperature

LPMEOH



necessary, the fresh feed system will not be limited by the capacity of the 01.20 recycle compressor.

The AF-R9.1 data period concluded at 21:00 on March 22. Mass balances for each run condition appear in Appendix C. CO conversion averaged 14.5% per pass for the average conditions of 6832 sL/kg-hr space velocity, 750 psig, and 476°F. Notably, this result exactly matches the predicted conversion for one CSTR at these conditions. The methanol concentration in the reactor effluent averaged 9.1 mole%, and liquid production, measured from levels in the 22.16 day tank, averaged 11.1 tons/day (TPD) of contained methanol. Average oil concentration for the three liquid product samples taken during the data period was 0.243 wt%. NDG measurements showed an average gas holdup of 47.2% and a catalyst concentration of 45.4 wt%. Since predicted values were 42.9% holdup and 42.4 wt% catalyst loading, these results further substantiate the tendency of the NDG to overpredict the extrapolation of previous results to high superficial velocities, as seen in the two-phase holdup studies.

Reactor feed flow and composition swung over to data period AF-R9.2 (Kingsport gas) after 21:00. The transition proceeded very smoothly, and compositions lined out at the H_2-rich reactor feed (nominally 61% H_2, 25% CO, 4% N_2, 10% CO_2) by early morning on March 23. This condition was included in the run plan to obtain data on the proposed operating conditions and feed composition of the Kingsport, Tennessee commercial-scale reactor. The scheme included the collection of bulk liquid product for analysis and testing by Eastman Chemical, and installation of a new line to collect 150 cc high-pressure sample bombs of the methanol product for detailed analysis in Air Products' laboratories. That analysis was intended to quantify the impurity levels generated under these conditions, specifically lighter components such as methyl formate and methyl acetate and higher alcohol by-products such as ethanol. To ensure minimum oil levels in the product, the reactor effluent stream passed through both the 21.11 and the 27.14 separator for the duration of this test.

The AF-R9.2 data period ended at 8:30 on March 24. Overall, operations were smooth except for one significant disturbance in the high-pressure H_2 source pressure. The new tie-in location enabled the plant to stabilize quickly and continue operations at target conditions despite the disturbance.

Reconciling the mass balance required a 20% adjustment to the methanol reading in the reactor effluent stream to match the production recorded in the day tank. Once this adjustment was incorporated (to 17.1 mole%), the balance closed tightly. The standard used for reactor effluent calibration of the GCs contained 6% methanol, which is the maximum level for a gas standard. Measurements of methanol concentrations significantly higher or lower than the calibration value are subject to large errors because of the non-linearity of the calibration. Our on-site analytical expert confirmed that errors of 10-20% could be expected at these high concentrations.

CO conversion averaged 46.5% per pass for the average conditions of 4020 sL/kg-hr space velocity, 739 psig, and 483°F, while the predicted conversion at these conditions is 46.9% for three CSTRs. Liquid production, measured from levels in the product collection area, averaged 11.0 TPD of contained methanol. Average oil concentration for the four liquid product samples collected during the data period was 0.123 wt%. NDG measurements showed an average gas holdup of 33.5% and a catalyst concentration of 39.4 wt%, which compared well with the predicted value of 34.5% at 40.0 wt% catalyst loading.

The remainder of March 24 was dedicated to testing of some of the new equipment. One of the test conditions required a feed rate of 200,000 SCFH, a point that broke new ground for the LP technology program. The reactor inlet superficial velocity for this case was 1.17 ft/sec. NDG analysis showed a slurry concentration of 44.2 wt% and 48.8% gas holdup. (In order to run this test condition without removing slurry from the reactor, it was necessary to thicken the slurry from the AF-R9.2 run.) The new reactor seemed to operate stably during this brief, two-hour test period.

Shutdown and Turnaround
The plant was shut down at 22:40 on March 24, 1994. The reactor was depressurized, cooled, drained, and flushed on March 25. The LPIBOH catalyst slurry was prepared in the 28.30 prep tank, as described below, and kept agitated, warm, and under N_2 purge. Meanwhile, flush oil was added to the reactor and heated to 300°F overnight to remove the residual methanol slurry in the system. On March 26 the flush oil was drained, and the LPIBOH catalyst slurry was transferred to the reactor.

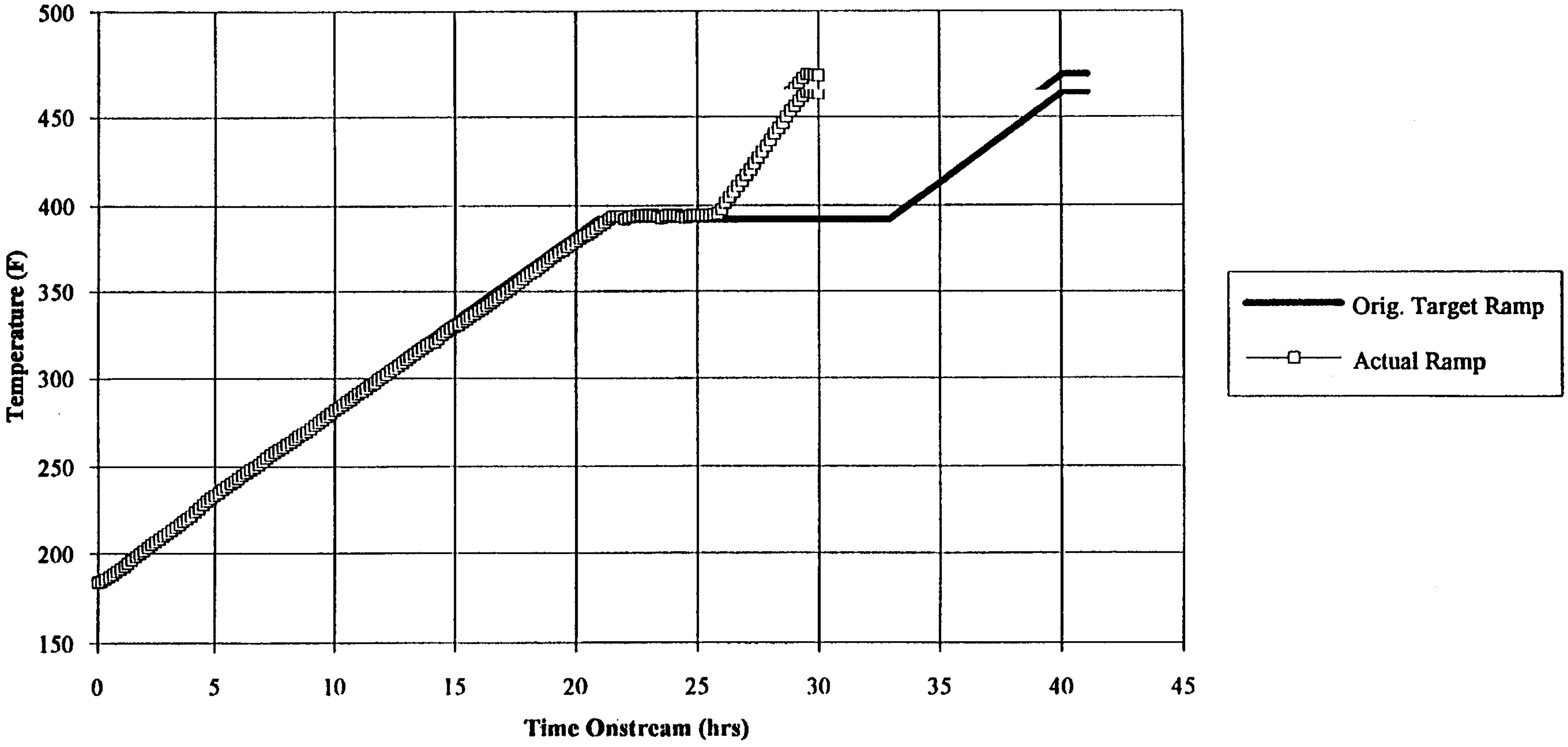
LPIBOH Demonstration

LPIBOH Catalyst Reduction
A 40 wt% oxide catalyst slurry was prepared in the 28.30 catalyst prep tank by mixing 1659 lbs of Drakeol-10 oil with 1106 lbs of LPIBOH catalyst (Cs-promoted BASF S3-86). The slurry was transferred to the reactor, and an additional 283 lbs of flush oil were added to the prep tank to remove any additional catalyst left from the transfer.

Reduction of the Cs-doped catalyst for isobutanol synthesis commenced on March 26 at 14:00, following the temperature ramp shown in Figure 10. Reduction proceeded under dilute synthesis gas (nominally 1.4% H_2, 2.1% CO, 96% N_2, 0.5% CO_2) at 14,000 SCFH and 60 psig. As in the case of LPMEOH, these conditions were decreased from the Test Authorization values to maintain stable flare ignition at the appropriate superficial velocity. The ramp proceeded at 10°F/hr to a hold temperature of 392°F. Notably, no "light-off" period occurred, which is typical of previous in-situ reductions in which the reaction exotherm caused the temperature to exceed the intended ramp rate. This phenomenon also failed to occur during the initial LPMEOH reduction and the subsequent transition to operations on synthesis gas. The apparent improvement in temperature control is attributed to the greater than threefold increase in heat transfer area for the new reactor, compared to the old reactor system in which the previous "light-off" experience occurred.

The traditional twelve-hour hold period at 392°F was shortened to four hours to duplicate the laboratory procedure, and the final ramp to 464°F proceeded at 18°F/hr. Both changes were also predicated on the comparison of synthesis gas uptake to the autoclave results, as shown in Figure 11. The final (H_2 + CO) uptake was 2.96 SCF/(lb of catalyst, as oxide). Theoretical maximum

FIGURE 10



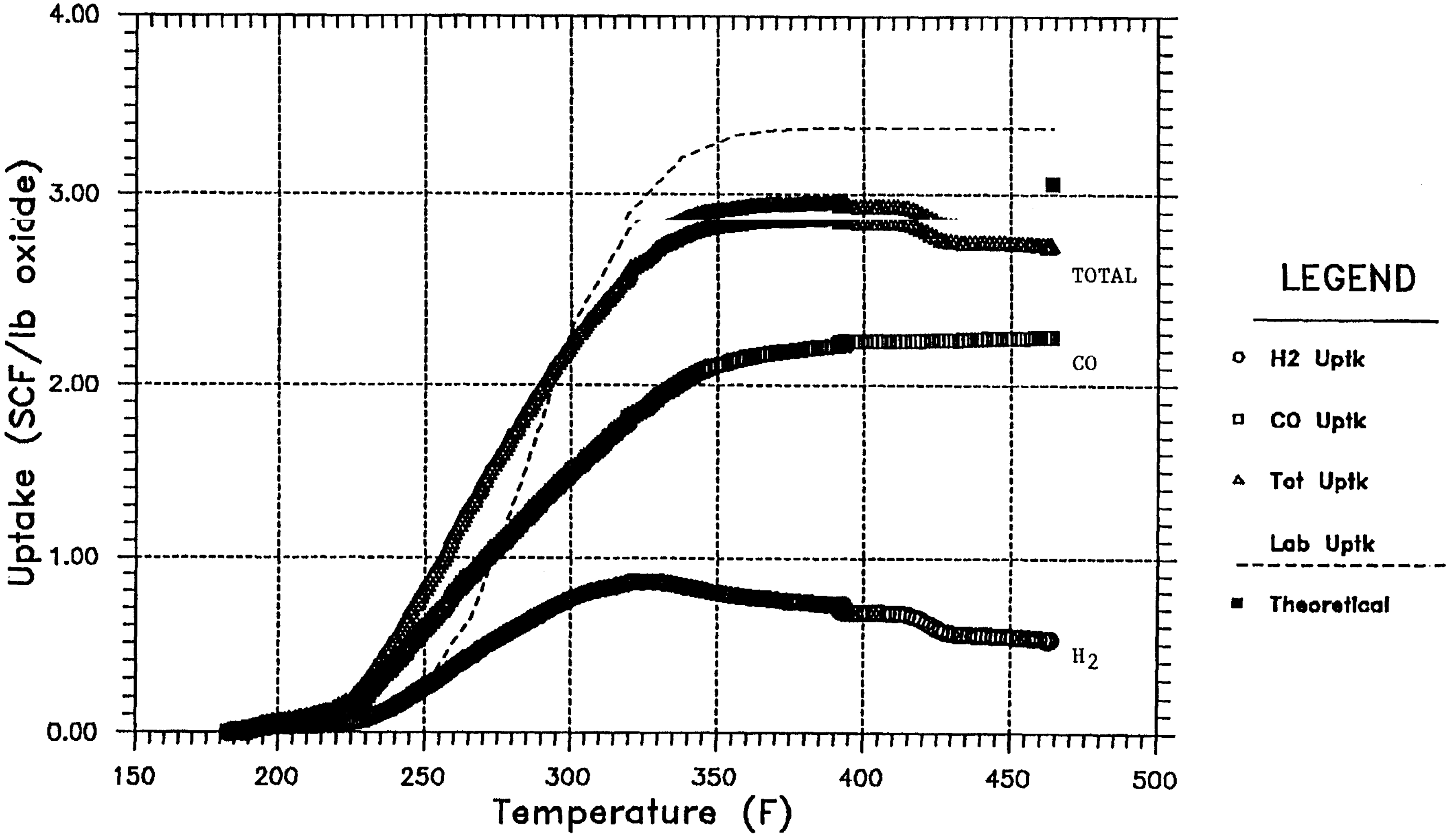
Reduction Temperature Ramp (IBOH Reduction)

3/28/94

FIGURE 11

Reduction Gas Uptake vs. Temperature

IBOH



uptake for the catalyst is 3.07 SCCF/lb oxide, and autoclave results exceeded this value, ranging from 3.38 - 3.59 SCF/lb oxide (on a LaPorte standard basis). This slight shortfall in uptake is typical for other LaPorte vs. autoclave experiments. Reduction concluded at 19:30 on March 27, and a Shell-gas blend (nominally 30% H_2, 66% CO, 1% N_2, 3% CO_2) was introduced a few hours later to begin isobutanol synthesis.

LPIBOH Operations
The run plan for the LPIBOH campaign is summarized in Table 1. Once finalized, this plan was duplicated in the laboratory prior to the run to provide performance and catalyst deactivation expectations. During the actual LaPorte trial, each condition was tested exactly according to plan, except for the durations. Note that 10.1 through 10.3 delineate a space velocity scan at the typical LPMEOH pressure; 10.3 through 10.5 define a pressure scan at the high space velocity condition; and 10.6 and 10.7 fill in some of the intermediate points. Conditions 10.8 and 10.9 complement 10.7 by using alcohol injection to simulate lower alcohol (methanol, ethanol, propanol) recycle to the reactor. Finally, point 10.10 returns to baseline (10.1) to quantify catalyst deactivation. Apart from operation at pressures up to 1750 psig, the campaign also broke new ground with successful demonstration of extended operation at an inlet superficial velocity of 1.0 ft/sec during run 10.3.

After catalyst reduction concluded at 19:30 on March 27, 1994, the "back-end" CO_2-removal system was cooled down, the GCs were recalibrated for isobutanol analysis, and a Shell-gas blend was introduced in once-through mode at 22:05. Plant pressure slowly increased to 750 psig at about 450°F. Once at pressure, recycle flow commenced, and the reactor temperature was increased slowly to the target of 572°F. Methanol first appeared in the reactor effluent at 22:53, and recycle synthesis gas was introduced to the CO_2-removal system at 23:00.

Typical startup problems persisted for the balance of the first two days of operation. Initially, efforts were directed toward troubleshooting instrumentation in the new CO_2-removal section and performing final calibration of the GCs. However, by the time the plant lined out the next morning, a pin-hole leak was discovered in a reactor thermocouple weld, necessitating a complete shutdown for repair. Shortly after the restart, communication problems developed between the GC computer and the DEC data collection system. Then the seals failed on the 10.80 methanol circulation pump, requiring isolation of the "back-end" CO_2-removal area. Finally, the 10.80 pump was returned to service and heatup commenced at 16:30 on March 29. The plant lined out by 21:00 and ran very smoothly at target conditions throughout the AF-R10.1 data period, which closed at 13:00 on March 30.

Initial operation at the baseline conditions showed performance slightly superior to the autoclave, as measured by the production of isobutanol and other higher alcohols (in g/kg oxide-hr) shown in Table 2. Again, mass balances for each run condition appear in Appendix C; the equivalent laboratory data sheets appear in Appendix D. CO conversion averaged 12.7% per pass for the average space velocity of 5044 sL/kg-hr at 750 psig and 573°F, compared to 11.3% in the laboratory. The isobutanol concentration averaged 0.17 mole% in the reactor effluent and 9.0 wt% in the liquid product. NDGG measurements showed an average gas holdup of 42.4% and a

TABLE 1
LAPORTE AFDU LPMEOH/LPIBOH RUN PLAN - MARCH 1994

Point	No. Days	Gas Type	Pressure psia	Space Velocity sL/kg-hr	Reactor Feed lbmol/hr	Inlet Sup. Velocity ft/sec	Slurry Wt% oxide
LPMEOH RUN							
AF-R9.1	2	Texaco	765	6700	373	0.84	42.5
AF-R9.2	3	Kingsport	750	4000	223	0.51	40.0
IBOH RUN							
AF-R10.1	2	Shell- Base Case	765	5000	247	0.61	40.3
AF-R10.1	2	Shell- Base Case	765	5000	247	0.61	40.3
AF-R10.2	1	Shell	765	3000	148	0.37	39.1
AF-R10.3	2	Shell	765	8200	405	1.00	41.5
AF-R10.4	2	Shell	1315	8200	405	0.58	42.0
AF-R10.5	2	Shell	1750	8200	405	0.44	42.3
AF-R10.6	1	Shell	1750	3000	148	0.16	39.8
AF-R10.7	1	Shell	1315	5000	247	0.36	40.7
AF-R10.8	1	Shell w/ full ROH recycle	1315	5000	247	0.36	40.7
AF-R10.9	1	Shell w/ partial ROH recycle	1315	5000	247	0.36	40.7
AF-R10.10	Optional	Shell- Base Case	765	5000	247	0.61	40.3
	18						

Point 8 is a case with total lower alcohol recycle
Point 9 is a co-product methanol/iboh point where not all of the methanol is recycled.

Table 2

Summary of AFDU vs. Autoclave Results

Run	P (psia)	Space Vel. (sL/kg-hr)	IBOH Productivity		C2-C6 OH Productivity	
			Lab (g/kg-hr)	AFDU (g/kg-hr)	Lab (g/kg-hr)	AFDU (g/kg-hr)
10.1	765	5000	22.8	25.8	65.1	70.0
10.2	765	3000	19.3	18.7	49.1	45.5
10.3	765	8200	20.6	16.6	69.0	50.5
10.4	1315	8200	24.8	20.8	92.8	86.9
10.5	1750	8200	26.2	23.2	103.0	95.9
10.6	1750	3000	27.7	23.8	71.4	60.6
10.7	1315	5000	23.1	19.2	75.3	64.2

catalyst concentration of 41.1 wt%, compared to predicted values of 40.2% and 40.2 wt%, respectively.

Notably, liquid product analysis was somewhat problematic because of measurable concentrations of numerous higher alcohol isomers. The chromatogram areas totalized well, but identified components typically composed only 90-97 wt% of each liquid product sample. By recommendation of the research staff, the balance was assumed to average C_6-alcohols. Furthermore, the traditional oil analysis by evaporation produced results of roughly 0.5-1.5 wt%, compared to 0.10-0.25 wt% for the LPMEOH cases, despite the observation that the samples were visually free of any oil. Again, the balance of the measured values is presumably other, less-volatile higher alcohols. This hypothesis is supported by the observation that, throughout the run, the samples with greater concentrations of higher alcohols (and lesser methanol concentrations) also exhibited greater concentrations of "oil" by evaporative analysis.

Data period AF-R10.2 ran from midnight to 17:00 on March 31. CO conversion averaged 13.7% per pass for the average space velocity of 3030 sL/kg-hr at 753 psig and 572°F, compared to 13.4% in the laboratory. However, the production of isobutanol and other higher alcohols fell slightly short of autoclave performance, as shown in Table 2. The isobutanol concentration averaged 0.21 mole% in the reactor effluent and 12.8 wt% in the liquid product, but these values declined slightly over the course of the data period. NDG measurements indicated 36.3% average gas holdup and 38.4 wt% slurry concentration, compared to predicted values of 36.4% and 39.1 wt%, respectively.

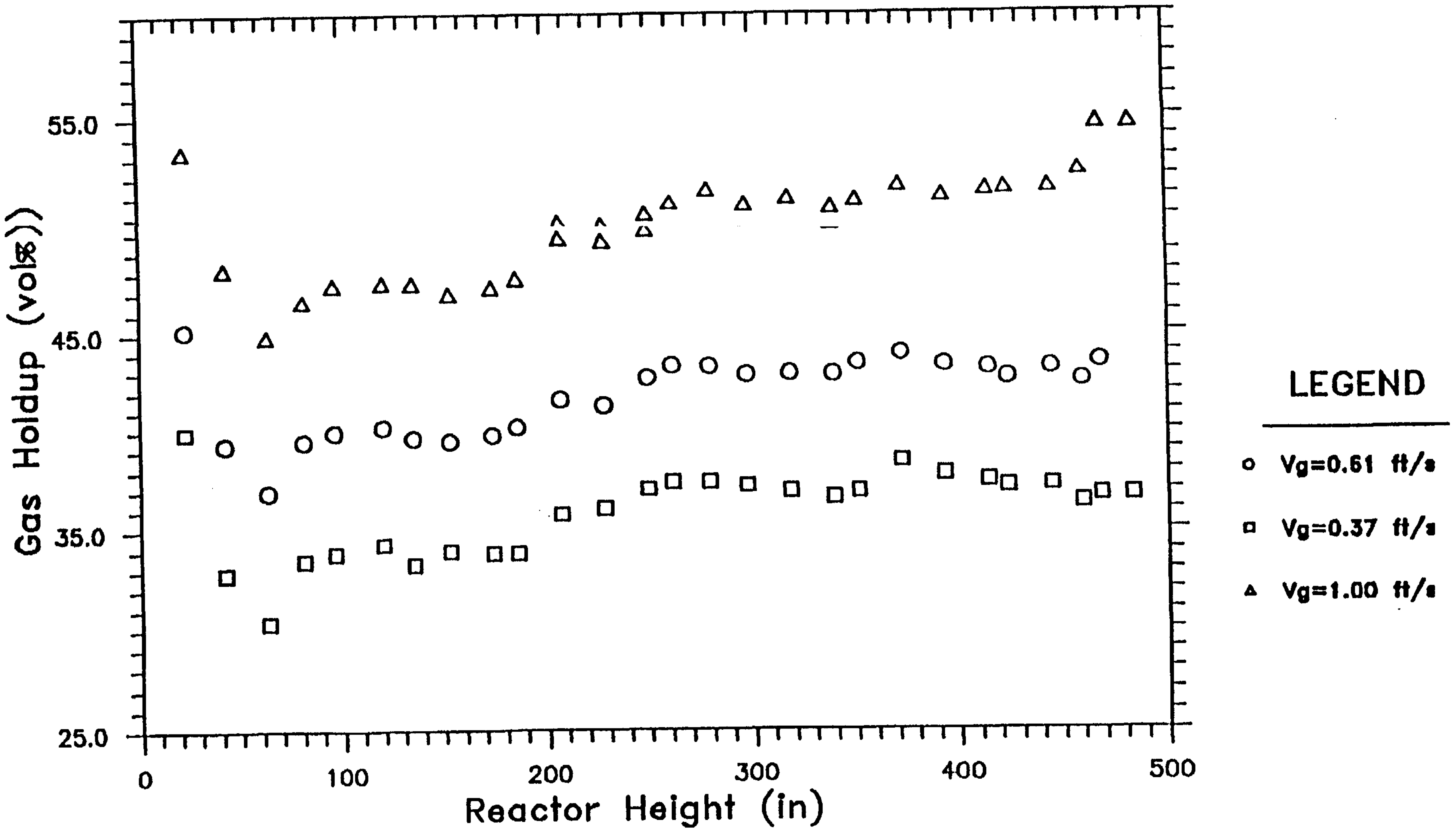
Condition AF-R10.3, which ran between 04:00 and 16:00 on April 1, provided the first clear evidence that catalyst productivity was decreasing faster in the AFDU than it did when the run plan was duplicated in the laboratory. CO conversion averaged 7.6% per pass for the average space velocity of 8242 sL/kg-hr at 751 psig and 572°F. The laboratory result was 8.5% with a space velocity of 8500 sL/kg-hr. Table 2 also shows that the production of isobutanol and other higher alcohols fell more significantly short of autoclave performance, despite the 3% difference in space velocity. Furthermore, this case upheld another disturbing trend: throughout the course of each data period, liquid samples taken from the product collection area of the plant showed increasing levels of methanol and decreasing levels of isobutanol. The isobutanol concentration averaged 0.07 mole% in the reactor effluent and 5.3 wt% in the liquid product, but this value declined 10% (relative) over a six and a half hour span in the middle of the data period. Thus, not only was the catalyst showing signs of deactivation, but it was also occurring at a faster rate than in the autoclave.

Operationally, the plant achieved long-term, stable hydrodynamic performance with a record inlet gas superficial velocity of 1.0 ft/sec. NDG measurements remained steady throughout the run and indicated 50.1% average gas holdup and 44.8 wt% slurry concentration. Predicted values of 44.3% and 41.5 wt%, respectively, further illustrate the impact of high gas velocity on the accuracy of the NDG. In addition, a reactor slump test at the end of the period indicated 47.5% gas holdup. Three-phase gas holdup data are plotted vs. reactor height for the first three run conditions in Figure 12. As expected, the holdup increases with increasing linear velocity, and the plots show the same characteristic shape as the two-phase data reported earlier.

FIGURE 12

Gas Holdup vs. Reactor Height

Run #'s AF-R10.1 - 10.3



The deactivation trend continued during conditions AF-R10.4 and 10.5, as seen in graphical form in Figure 13. To minimize deactivation, the run plan was accelerated as much as possible, especially during these harsh high pressure, high flow conditions. As a result, by the end of data period 10.5, the actual AFDU run plan was about sixty hours ahead of the autoclave schedule. Thus, in Figure 13, the time plotted along the x-axis corresponds to the AFDU on-stream time, not the laboratory hours on-stream.

The mass balance period for AF-R10.4 ran from 21:00 on April 1 to 07:00 on April 2. The run ended prematurely when the refrigerant CO_2 supply ran out, forcing a shutdown of the "back-end" scrubbing unit. However, the plant ran very smoothly during the ten-hour data collection period. CO conversion averaged 12.7% per pass for the average space velocity of 8227 sL/kg-hr at 1300 psig and 572°F, compared to 13.3% in the laboratory. Again, productivities of isobutanol and other higher alcohols were significantly lower than those observed in the autoclave, as shown in Table 2. For example, the isobutanol production rate was 20.8 g/kg-hr, compared to 24.8-27.3 g/kg-hr observed in the laboratory at similar conditions. The autoclave results reflect about a 10% decrease in productivity after 24 hours operation at this condition. The AFDU's shorter time at this harsh condition, coupled with the overall shorter on-stream time, contributes to the observation that the AFDU vs. autoclave productivity gap seemed to close somewhat during this data period and the next.

The isobutanol concentration averaged 0.09 mole% in the reactor effluent and 2.6 wt% in the liquid product, but again this value declined slightly over the course of the data period. NDG measurements showed an average gas holdup of 44.0% and a catalyst concentration of 41.9 wt%, compared to predicted values of 46.0% and 42.0 wt%, respectively.

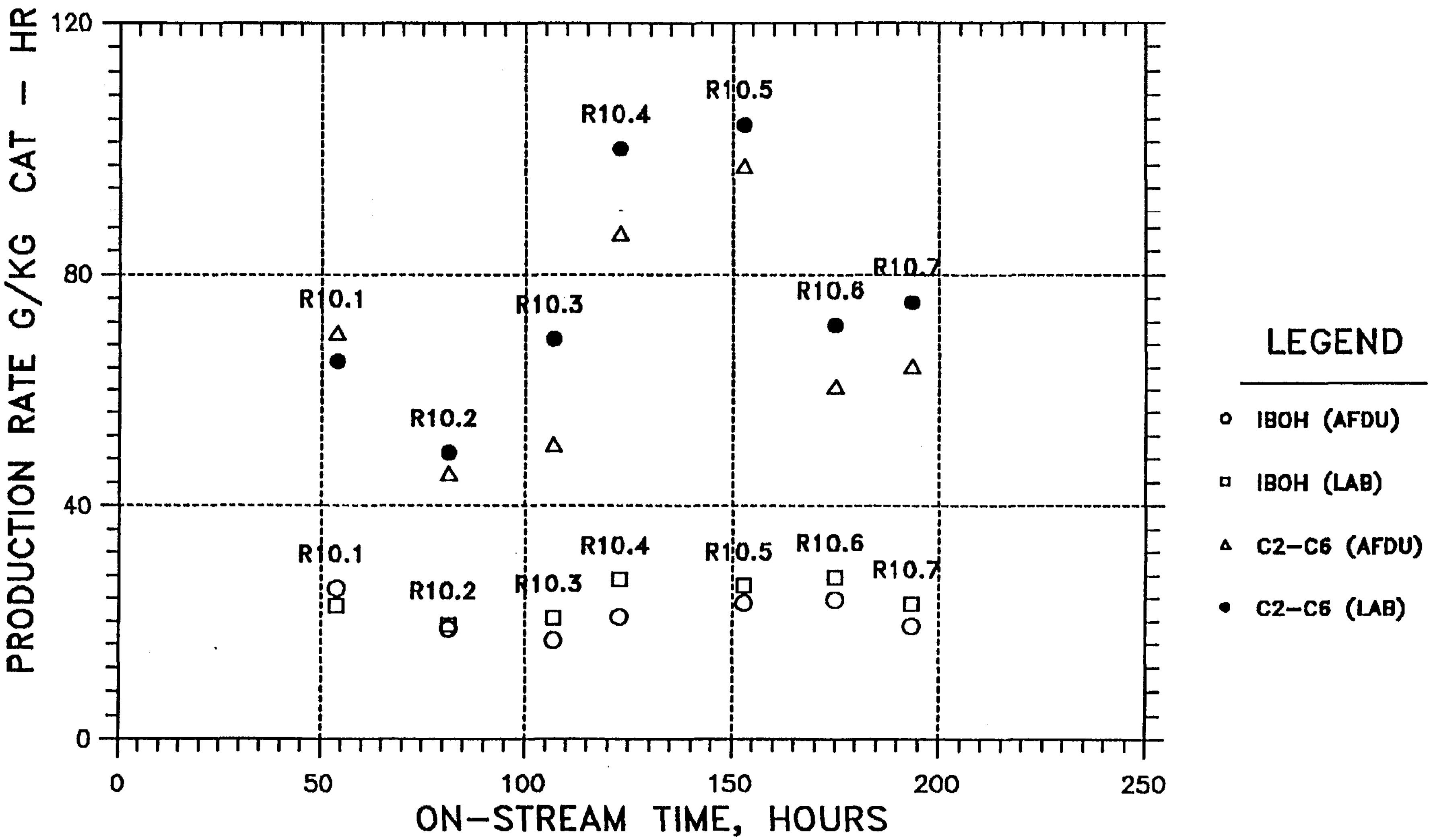
An alcohol spill and fire occurred at 15:20 on Saturday, April 2, when a product trailer was overfilled during a day tank transfer. About 25 gallons of alcohol spilled through the supplemental flare, caught fire, and were extinguished with a nearby fire monitor without damage or injury. Recent installation of this particular fire monitor was an action item from a Hazard Review that identified an alcohol spill in the trailer area as a fire hazard. Another 300 gallons of alcohol spilled near the trailer. The area was covered with an alcohol foam and subsequently cleaned up by EmTech Environmental Services.

Data period AF-R10.5 ran from 02:00 to 14:00 on April 3. CO conversion averaged 15.7% per pass for the average space velocity of 8281 sL/kg-hr at 1735 psig and 573°F, compared to 16.3% in the laboratory. The isobutanol production rate was 23.2 g/kg-hr, compared to 26.2 g/kg-hr in the autoclave, but the laboratory data were obtained at 212 hours on-stream, compared to 153 hours for the AFDU. The isobutanol concentration averaged 0.10 mole% in the reactor effluent and 2.2 wt% in the liquid product, but these values continued to drop through the course of the mass balance period, despite steady operating conditions. NDG measurements indicated 41.8% average gas holdup and 40.9 wt% slurry concentration, compared to predicted values of 46.9% and 42.2 wt%, respectively. These results were the first to show poor agreement between predictions and the NDG at relatively low superficial velocities.

FIGURE 13

LIQUID PHASE ISOBUTANOL RESULTS

BUBBLE COLUMN VS. AUTOCLAVE



Condition AF-R10.6, which ran between midnight and noon on April 4, represented the high-pressure, low space velocity case with the minimum superficial velocity (0.16 ft/sec). CO conversion peaked for the run at 20.9% per pass for the average space velocity of 3026 sL/kg-hr at 1735 psig and 572°F. The laboratory result was 21.8%. Again, Table 2 and Figure 13 indicate a widening productivity gap between AFDU and autoclave performance. For example, the isobutanol production rate was 23.8 g/kg-hr at 175 hours on-stream, compared to 27.7 g/kg-hr observed in the laboratory at similar conditions after 239 hours on-stream. The isobutanol concentration averaged 0.29 mole% in the reactor effluent and 7.2 wt% in the liquid product. NDG measurements remained steady throughout the run and showed an average gas holdup of 27.9% and a catalyst concentration of 35.5 wt%, compared to predicted values of 38.7% and 39.8 wt%, respectively. These data, coupled with the AF-R10.5 results and the expectation that the NDG is accurate at lower gas velocities, indicate that the correlation for predicting gas holdup is probably inadequate at high pressures.

Condition AF-R10.7, the precursor to the alcohol injection cases at intermediate pressure and space velocity, ran from 17:00 on April 4 to 08:00 on April 5. CO conversion averaged 14.2% per pass for the average space velocity of 5070 sL/kg-hr at 1300 psig and 572°F. The laboratory result was 14.6% with a space velocity of 5225 sL/kg-hr. As shown in Table 2, the isobutanol production rate was 19.2 g/kg-hr at 193 hours on-stream, compared to 23.1 g/kg-hr observed in the laboratory at 3% higher space velocity and after 261 hours on-stream. These results continue to show that the catalyst deactivated at a faster rate in the AFDU than in the parallel autoclave run. The isobutanol concentration averaged 0.13 mole% in the reactor effluent and 4.1 wt% in the liquid product. Again, however, the concentration of isobutanol in the liquid product declined 15% (relative) over a five-hour span in the middle of the data period, despite steady operating conditions. At the same time, the methanol concentration rose 3%. NDG measurements indicated 37.5% average gas holdup and 38.9 wt% slurry concentration, compared to predicted values of 41.7% and 40.7 wt%, respectively. Thus, the holdup prediction appears more accurate at the lower pressure, but again, less accurate than at 750 psig where the correlation was developed.

Table 3 summarizes the AFDU performance through all of the cases prior to alcohol injection. Remember that points AF-R10.3 through 10.5 show the pressure effect at the high space velocity condition. As the pressure increased, conversion and productivity increased, but selectivity decreased, as expected. Similarly, runs AFR-10.1 through 10.3 show the space velocity effect at 750 psig, although not in increasing order. As space velocity increased, conversion and selectivity decreased, presumably because of the reduction in residence time. However, productivity was greatest for the intermediate (baseline) condition. Each of these trends was also observed in the laboratory runs.

Run AF-R10.8 duplicates the conditions of AF-R10.7, while also using alcohol injection into the synthesis gas feed to demonstrate the effect of total lower alcohol recycle on higher alcohol synthesis. The injection composition was nominally 84% methanol, 5% ethanol, and 11% 1-propanol at a rate of about 1.8 gpm. During AF-R10.9, the composition was altered to 73% methanol, 9% ethanol, and 18% 1-propanol at a rate of about 0.4 gpm.

Table 3

Summary of AFDU Performance

Run	P (psia)	Space Vel. (sL/kg-hr)	CO Conversion (%)	IBOH Concentration (wt%)	IBOH Productivity (g/kg-hr)	C2-C6 OH Productivity (g/kg-hr)
10.1	765	5000	12.5	9.0	25.8	70.0
10.2	765	3000	13.7	12.8	18.7	45.5
10.3	765	8200	7.6	5.3	16.6	50.5
10.4	1315	8200	12.7	2.6	20.8	86.9
10.5	1750	8200	15.7	2.2	23.2	95.9
10.6	1750	3000	20.9	7.2	23.8	60.6
10.7	1315	5000	14.2	4.1	19.2	64.2

The mass balance period for AF-R10.8 ran from 03:00 to 20:00 on April 6. CO conversion averaged 6.8% per pass for the average space velocity of 5494 sL/kg-hr at 1300 psig and 572°F, compared to 8.3% in the laboratory. As seen in Table 4, the isobutanol and C_2-C_6 alcohol production rates increased nearly threefold over AF-R10.7, which was identical in all other respects. This result supports the chain growth mechanism for production of higher alcohols from lower alcohols. The isobutanol concentration averaged 0.31 mole% in the reactor effluent and 4.8 wt% in the liquid product. NDG measurements indicated 40.6% average gas holdup and 40.1 wt% slurry concentration, compared to predicted values of 43.2% and 41.1 wt%, respectively.

Condition AF-R10.9, using alcohol injection to simulate partial lower-alcohol recycle to the reactor, ran from 16:00 on April 7 to 04:00 on April 8. CO conversion averaged 11.2% per pass for the average space velocity of 5154 sL/kg-hr at 1300 psig and 572°F. The autoclave result was 12.5%. However, throughout the course of this case, catalyst activity began to decline dramatically. The isobutanol concentration in the liquid product dropped from 3.7 wt%, shortly after the start of the data period, to 2.0 wt% nine hours later. Another three hours after that, at the close of the period, the concentration had fallen to 1.6 wt%. NDG measurements remained steady throughout the run and showed an average gas holdup of 37.9% and a catalyst concentration of 39.1 wt%, compared to predicted values of 44.4% and 42.0 wt%, respectively.

Since the AF-R10.9 mass balance indicated that the alcohol injection rate was significantly below target (0.4 gpm vs. 0.7 gpm), the pumping rate was increased with the intent of establishing a new condition (AF-R10.9a) until the alcohol feedstock was exhausted. However, during this period it became increasingly apparent that the catalyst was deactivating very rapidly, and specifically because of this alcohol injection case. Isobutanol and methanol concentrations in the reactor effluent are plotted as a function of on-stream time in Figure 14. The isobutanol concentration shows a rapid decline after 260 hours on-stream, while the methanol concentration begins dropping at about 275 hours. Utility oil inlet and outlet temperatures, as well as the average reactor temperature, are plotted in Figure 15. Apparently, after 237 hours on-stream, the heat of reaction suddenly increased. This coincides with switching the alcohol feed to a different composition at the beginning of AF-R10.9, and is expected because the lower alcohol injection rate results in higher synthesis gas conversion. However, the heat of reaction began declining dramatically after 250 hours on-stream, confirming that the catastrophic deactivation began in the early stages of AF-R10.9. An additional sample of the alcohol feedstock was collected to help determine the reason for the deactivation.

The plant operating conditions were quickly returned to the baseline case, as planned, to check on catalyst activity. However, by the time the reactor had lined out at 19:00 on March 8, the isobutanol had disappeared completely from the effluent, and methanol continued to decline below 1%. As a result, the opportunity to quantify the degree of catalyst deactivation for the duration of the campaign was lost, and was replaced by a search for catalyst poisons. The mass balance from then until 08:00 on March 9 is included with the others in Appendix C. Several liquid samples were collected, but the production rate was too low to flush out the product collection section from the previous run condition. Only after intentionally pushing most of the liquid out of the system was a potentially representative sample collected. NDG scans during the

Table 4

Summary of AFDU Performance

Run	P (psia)	Space Vel. (sL/kg-hr)	CO Conversion (%)	IBOH Concentration (wt%)	IBOH Productivity (g/kg-hr)	C2-C6 OH Productivity (g/kg-hr)
10.1	765	5000	12.5	9.0	25.8	70.0
10.2	765	3000	13.7	12.8	18.7	45.5
10.3	765	8200	7.6	5.3	16.6	50.5
10.4	1315	8200	12.7	2.6	20.8	86.9
10.5	1750	8200	15.7	2.2	23.2	95.9
10.6	1750	3000	20.9	7.2	23.8	60.6
10.7	1315	5000	14.2	4.1	19.2	64.2
10.8 (Al-1)	1315	5000	6.8	4.8	55.9	190.8
10.9 (Al-2)	1315	5000	11.2	3.7	18.4	79.4

FIGURE 14

REACTOR EFFLUENT CONCENTRATIONS DURING LPIBOH

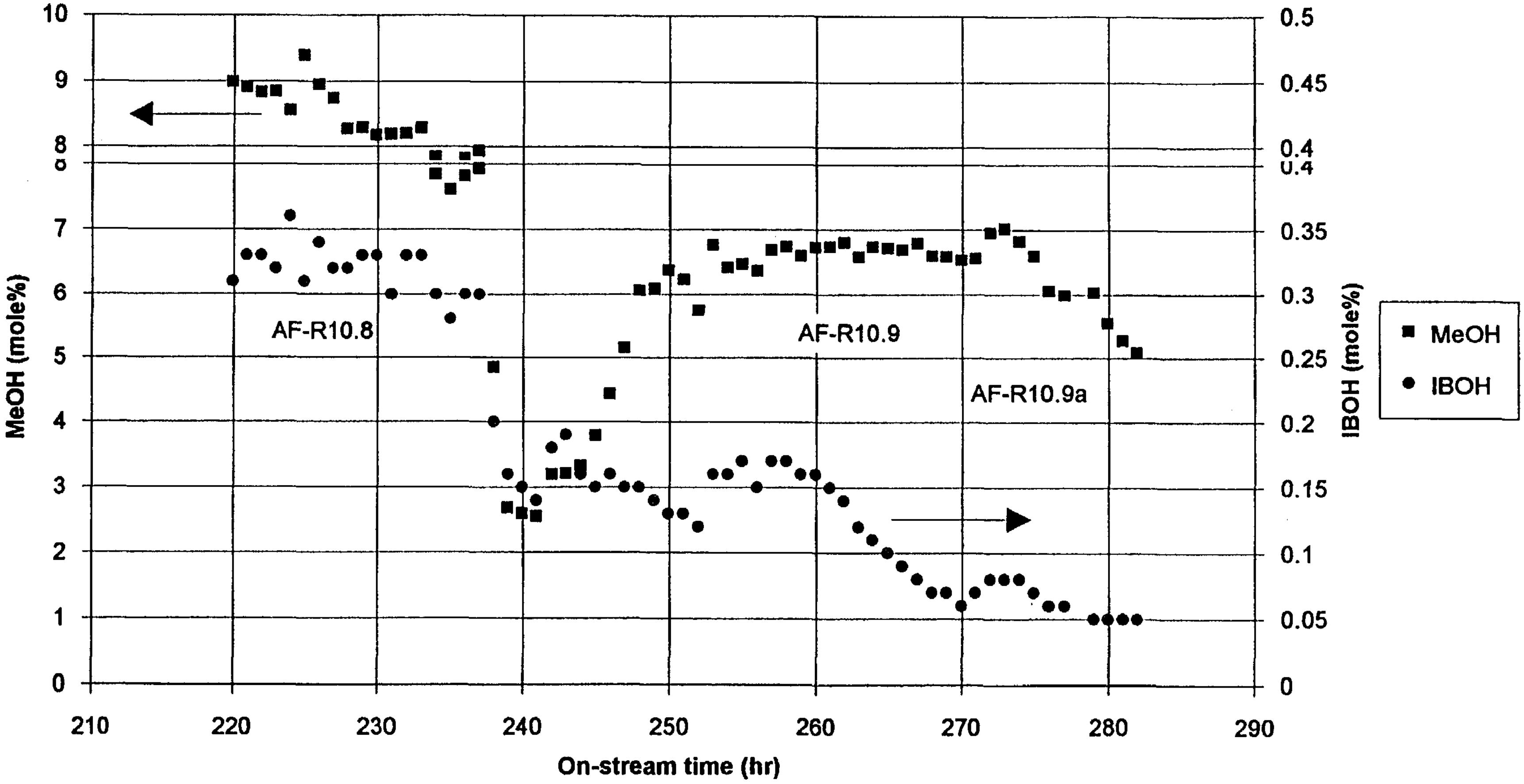
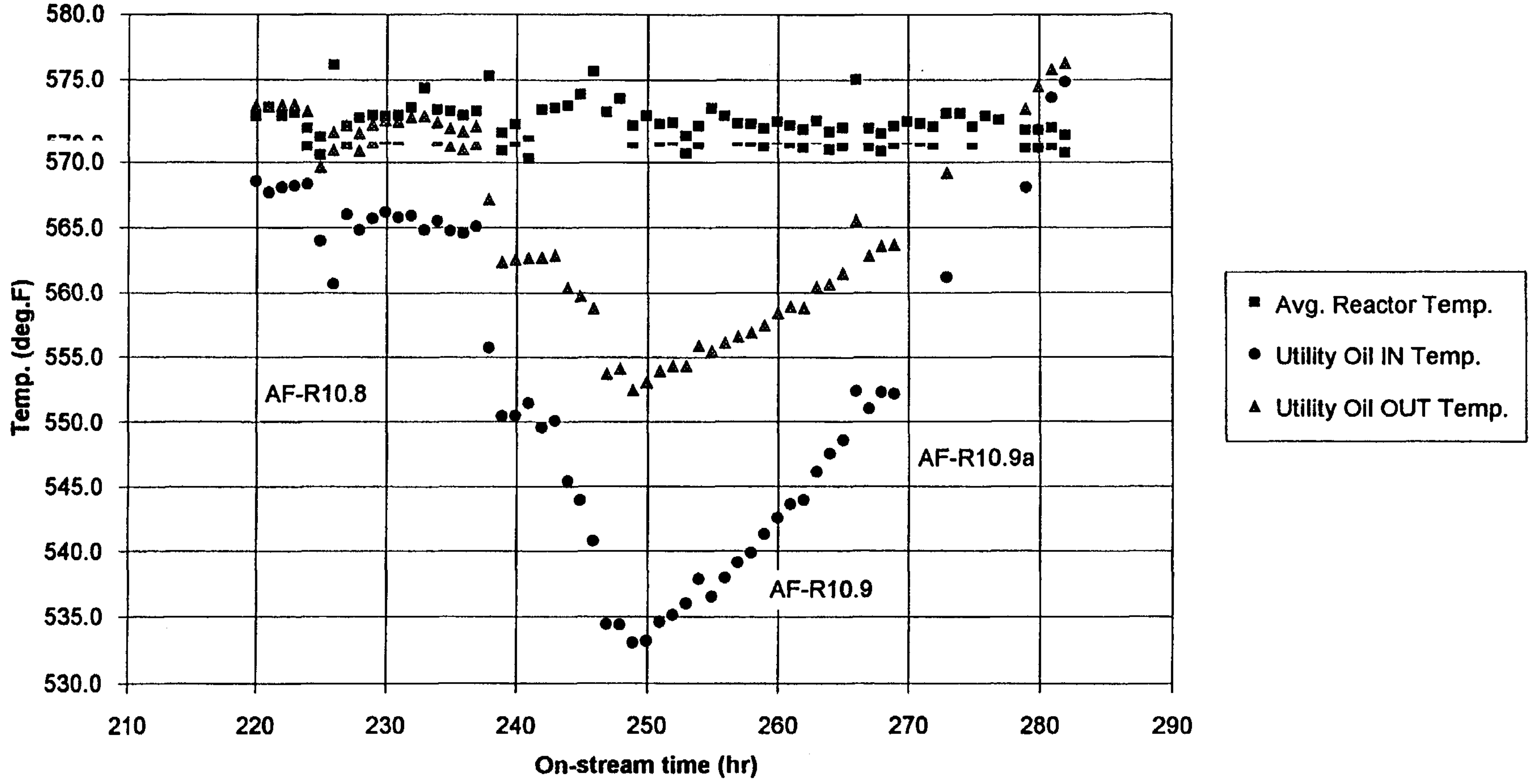


FIGURE 15

TEMPERATURES DURING LPIBOH



period were equivalent to those taken during AF-R10.1 (42.1% gas holdup and 40.8 wt% catalyst concentration).

Post-Run Inspection and Investigation

The post-run carbonyl survey at baseline and high-pressure conditions showed little difference from results prior to the start of the LPMEOH operations. Notably, the 02.63 steam preheater, used to superheat the alcohol feed to the reactor, did not seem to contribute inordinately to carbonyl generation. This unit, with its high skin temperatures, proved to be a significant source of carbonyls during the burnout period and was not in service between then and the alcohol injection cases.

Following the carbonyl tests, cool down commenced at 18:20 on March 9. At 23:00 the synthesis gas feed was withdrawn and replaced with N_2 to purge. Prior to inspection, the reactor was flushed with oil at 275-300°F for 18 hours. During the reactor inspection, less than 5 lbs of catalyst were found in the bottom head, a location where packed, dried catalyst usually collected in the old reactor. The shell and internal heat exchanger were free of catalyst in areas contacted by flush oil, while the freeboard space and top head were still covered with a thin layer of catalyst.

The sample taken from the alcohol injection trailer after AF-R10.9 appeared pale yellow, unlike the samples taken prior to the run, which were clear. Later analysis of the anomalous sample revealed a significant quantity of 1,1,1-trichloroethane, a formerly common cleaning solvent no longer present on the AFDU site. . The yellow color may be explained by the presence of trace dissolved iron which was also discovered.

A sample of the spent, end-of-run catalyst was washed to remove the mineral oil and then, along with a sample of the fresh catalyst, was analyzed for elemental composition and crystallite size by XRD. Elemental analysis revealed no iron uptake on the spent catalyst, a good sign that iron carbonyl production was low in the new plant equipment and that the iron present in the injected alcohol did not deposit in a measurable quantity on the catalyst. The only known catalyst poison found was chloride, present at 0.79 wt%, while the fresh catalyst contained no chloride. This level of chloride contamination would certainly cause measurable deactivation of the catalyst.

Interestingly, the Cu crystallite size (via XRD) was very large at 337 ± 13 A. By comparison, the Cu crystallite size determined after the laboratory simulation of the entire LPIBOH run plan was 250 ± 7 A. Though no direct evidence exists, we hypothesize that the formation of copper chloride (CuCl or $CuCl_2$) explains the large Cu crystallite size observed. Since both CuCl and $CuCl_2$ have a much lower melting point than Cu metal, their presence under synthesis conditions may cause increased mobility of copper, resulting in faster sintering.

The evidence indicates that the inadvertent presence of 1,1,1-trichloroethane in the injected alcohol reactant caused the rapid loss in catalytic activity observed during AF-R10.9. The 1,1,1-trichloroethane decomposed on the catalyst surface to produce chloride, which is a known poison for the $Cu/ZnO/Al_2O_3$ substrate. Apparently the alcohol feedstock trailer was cleaned with the solvent and improperly rinsed, leaving trace quantities of the 1,1,1-trichloroethane in the subsequent alcohol blend. GC analysis of a sample prior to injection focused only on bulk compositional analysis and failed to detect any trace contamination.

The inadvertent poisoning of the catalyst during AF-R10.9 significantly hindered the investigation of the faster rate of catalyst deactivation observed throughout the campaign at the AFDU. Typically, spent (end-of-run) catalyst analysis is used to provide information on catalyst deactivation mechanisms experienced during the run. For example, analysis of Cu crystallite size by XRD could provide clues about the rate of sintering, as it did in this case. Unfortunately, however, it is impossible to distinguish results of this type between pre-10.9 and post-10.9 trends. The cause for the faster deactivation of the catalyst in the early part of the campaign remains unknown.

Conclusions and Future Plans

Apart from the catalyst deactivation, the thirteen-day LPIBOH campaign successfully demonstrated mixed alcohol synthesis in a slurry bubble-column reactor, as well as all of the new equipment installed for the trial. Although the full capabilities of the new system will not be tested until future runs, all of the design objectives for the modifications were met with respect to the isobutanol run, and show every indication of being applicable to other chemistries. The catalyst and reactor systems were tested at a wide range of pressures (750-1735 psig) and space velocities (3000-8200 sL/kg-hr), representing numerous first-of-a-kind run conditions for the AFDU. Inlet gas superficial velocities spanned an impressive 0.16 to 1.0 ft/sec. Stable reactor performance for a full twelve-hour data period at 1.0 ft/sec represented a significant milestone event for the liquid phase technology program. Additionally, the reactor appeared to exhibit stable hydrodynamic performance during a brief test period at 1.17 ft/sec.

Although the catalyst demonstrated in this run was state-of-the-art for isobutanol synthesis, its performance was still short of economic targets for production of MTBE. Work involving collaboration between Air Products and academic researchers will continue on the development of new, improved catalysts.

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