APPENDIX C

Chronolgy of Runs in Slurry Bubble Column Reactors

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CHRONOLOGY OF RUNS MADE IN THE SLURRY BUBBLE COLUMN REACTORS DURING THE FOURTH QUARTER OF 1994

Task 2.0 -- Catalyst Testing

Subtask 2.2 -- "Slurry Bubble Column Testing"

Run No. 22 in the M4-SBCR was started on October 3rd with a blend of two catalysts: 15.5 gm of Catalyst No. WGS.09 and 15.0 gm of Catalyst No. Co.005. The first catalyst is a water-gas shift catalyst and the second is a methane reduction catalyst. The CO conversion with this blend at startup conditions was considerably higher than observed with Catalyst No. Co.005 in Run 15 in M3-SBCR, 35.6% vs. 27.1%. Also, the CO_2 selectivity was much higher, 6.3% vs. 0.8%. Some water-gas shift activity has occurred with this catalyst blend as demonstrated by the higher CO_2 yield and increase in CO conversion. Several run periods were made in which the H_2/CO ratio was lowered to 1/1 and 0.7/1 at 240°, 260°, and 280°C reaction temperatures. The CO conversion decreased as the H_2/CO ratio was decreased and the CO conversion increased when the reaction temperature was raised. Water-gas shift activity was observed at all run conditions.

Run No. 30 in the M3-SBCR was started on October 10th with a charge of 29.6 gm of Catalyst No. Co.053-2. The purpose of this run was to run at conditions that would yield the highest CO conversion attainable in the SBCR. The CO conversion at startup conditions was 41.8%, the same as observed previously in Run 29 with the same catalyst charge. The CO conversion increased to 46.9% at 260°C reaction temperature. The CO conversion, however, dropped to 41.4% when the reaction temperature was increased to 280°C. The reaction temperature was increased to 300°C, 310°C, and finally to 320°C, but the CO conversion did not exceed 40% at any of these temperatures. The run was shut down after 279 hours after the gas preheater plugged when the heater temperature reached 550°C. It is speculated that the catalyst activity began to decrease above 260°C because the reaction temperature may have been increased too rapidly. This run will be repeated using the M4-SBCR.

Run No. 23 in the M4-SBCR was started on October 17th with a charge of 29.1 gm of Catalyst No. CAL.09. This was a catalyst that was supplied by Calsicat that was hydrogen reduced and coated with Soya. The catalyst was mixed with synfluid, heated, and charged to the SBCR under a nitrogen blanket. The CO conversion at the initial startup conditions was only 17.4%. The run was terminated after two run periods because the catalyst activity was only 60% of the expected activity.

Run No. 24 in the M4-SBCR was started on October 24th with a charge of 28.5 gm of Catalyst No. Co.053-3. The purpose of this run was to attain the highest CO conversion possible. The CO conversion at startup conditions was 50.4%, which is the highest conversion observed to date. The M4-SBCR appears to yield a little higher catalyst activity than M3-SBCR for some unknown reason. The CO conversion rose to 53.5% at 250°C reaction temperature (Period 2) and

to 55.3% at 260°C (Period 3). In Period No. 4, the N_2 feed rate was decreased from 60% of the total to 40% with a corresponding increase in the H_2 and CO feed rates. The CO conversion dropped to 52.8%, but the production rate increased from 1.36 to 2.13 gm C_1^+/gm catalyst/hr. The total gas feed rate was then lowered from 900 standard liter per hour (SLH) to 700 SLH for Period 5. The CO conversion rose to 58.9%. Increasing the total feed gas rate to 1080 SLH (50% N_2) lowered the CO conversion to 42.6% for Period 6. At this time the gas feed rates were returned to startup rates for an activity check. The CO conversion averaged 51.5% compared to 55.3% obtained in Period 3 made at the same run conditions. This was considered to be a normal loss of catalyst activity.

For Period 8, the total feed gas rate was reduced from 900 SLH to 632 SLH with about 32% N_2 in the feed. The CO conversion rose to 58.1%. Lowering the total feed gas rate to 540 SLH (20% N_2) for Period 9 yielded a CO conversion of 60.0%. It was decided to raise the reactor temperature to 270°C to further increase the CO conversion. The reaction temperature; however, increased rapidly and could not be controlled because the SBCR has no provision for heat removal. The reactor stabilized at 275°C for about 5 hours with a CO conversion of 72%. The reactor temperature then rose to 292°C before dropping to 255°C by the next morning. The reactor was stabilized at 260°C for an activity check. The CO conversion was only 49%, so it was decided to terminate the run. A chilled water cooling coil will be installed in the feed gas line before attempting high CO conversion runs. This run demonstrated that higher CO conversion levels can be obtained by reducing the N_2 feed composition and total gas feed rate. Also, a method to remove the heat of reaction must be found for the SBCR before attempting to reach higher CO conversion levels.

Run No. 31 in the M3-SBCR was started on October 31st with a charge of 15.0 gm of Catalyst No. Co.055. This catalyst contained 20 wt% Co plus 1.0 wt% Re and 1.0 wt% La_2O_3 promoters on an alumina catalyst support. The CO conversion at startup conditions was good, 30.0%, with a high production rate, 1.46 gm C_1^+/gm catalyst/hr, but the CH_4 selectivity, however, was quite high, 23.7%. The catalyst is similar to Co.001, the original startup benchmark catalyst used in Run 2 in the M3-SBCR, but without K added.

Run No. 25 in the M4-SBCR was started on November 8th with a charge of 15.0 gm of Catalyst No. Co.056. This catalyst contained 20 wt% Co plus 8.5% La_2O_3 on silica catalyst support. The CO conversion at startup conditions was only 11.4% and 4.5% at 220°C reaction temperature. The run was terminated after 63 hours on stream due to the low catalyst activity.

Run No. 32 in the M3-SBCR was started on November 14th with a charge of 16.4 gm of Catalyst No. Co.044. This catalyst contained 20 wt% Co plus 15% Zr promoter on silica support. The purpose of this run was to determine the effect of adding a larger amount of Zr on catalyst activity. The greater amount of Zr yielded a 21% CO conversion compared to 25% CO conversion with an 8.5% Zr on a cobalt-silica catalyst and 23.2% CO conversion with a 0.7% Zr promoter on a cobalt-silica catalyst.

Run No. 26 in the M4-SBCR was started on November 17th with a charge of 15.6 gm of Catalyst No. CAL.10. This catalyst which was received from Calsicat contained 20 wt% Co with 0.3% K and 0.5% Ru on Condea alumina. The Condea alumina is similar to Vista B alumina which has demonstrated good attrition resistance. The CO conversion at startup conditions was only 21.9%

versus 26.5% obtained with Catalysts CAL.04 and CAL.05 which were made with Vista B alumina support. It was decided not to follow the usual schedule of run conditions, but to investigate the effect of lowering the total syngas and nitrogen flows into the reactor on catalyst activity. The reaction was held at 240°C, 450 psi pressure, and 2/1 H_2/CO feed ratio with lower total gas flow rates. Lowering the total gas rate from 900 SLH (60% N_2) to 540 SLH (20% N_2) did not affect the CO conversion, but increased the hydrocarbon production rate about 30%. Lowering the N_2 feed concentration to 12%, and then to 6% decreased rather than increased the CO conversion. This run was terminated because the catalyst activity was too low. It was decided to install a smaller N_2 mass flow meter to improve the accuracy at lower N_2 feed rates. Since the CO and H_2 conversions are calculated from both the mass flow meter rates and from G.C. analyses of the feed and product gases using N_2 as an internal standard, it is necessary to get accurate low N_2 flow rates.

Run No. 33 in the M3-SBCR was started on November 28th with a charge of 31.4 gm of Catalyst No. Co.053-4. This was another attempt to obtain the highest CO conversion possible. A chilled water precooler coil was installed on the feed gas line to help heat removal during high conversion levels. The CO conversion at startup conditions was only 41.4%, but was the same as Runs 29 and 30 in M3-SBCR. The M4-SBCR gave higher CO conversion, 50.4%, for some unknown reason. In Period No. 2, the three gas feed rates were decreased proportionally to 60% of startup (540 SLH) and the reaction pressure was lowered to 300 psi. The CO conversion dropped to 35.2% and the C_1^+ production rate decreased 50%. Lowering the total gas rate to 400 SLH raised the CO conversion to 38.7%. The CO conversion rose to 39.6% at 250°C reaction temperature, and dropped to 37.7% at 260°C temperature. Raising the pressure back to 450 psi only increased the CO conversion to 45.0%. For Period 7, the N_2 composition was lowered from 60 to 40%. The CO conversion stayed the same, 45.7%. Lowering the N_2 composition to 25% increased the CO conversion to 49.2%. The run conditions were changed to startup conditions. The CO conversion dropped to 16.1% vs. 41.4% in Period 1. There was considerable loss of catalyst activity over the duration of this run, probably when the reaction temperature was raised to 260°C.

Run No. 27 in the M4-SBCR was started on December 5th with a charge of 14.6 gm of Catalyst No. Co.050. This catalyst contained 20% Co plus 0.5% Ru, 8.5% Zr, and 0.1% K promoters on silica support. The CO conversion at startup conditions was 20.4%, which is the same as obtained with Catalyst No. Co.048 that contained 0.3% K. The methane selectivities were also similar, approximately 10%. The optimum amount of K to add for methane reduction without significantly lowering catalyst activity is somewhere between 0.1 and 0.3 wt%.

Run No. 34 in the M3-SBCR was started on December 12th with a charge of 15.6 gm of Catalyst No. Co.060. This catalyst contained 30 wt% Co on alumina support with no promoters. The CO conversion was 31.4%, which is in the range that was expected without any metals or promoters added. The methane selectivity was approximately 14%, which was also in the expected range.

During the shutdown period over the Christmas holiday, a number of routine maintenance checks were made. A smaller N_2 mass flow meter was installed and calibrated on M4-SBCR. All other gas flow meters had calibration rechecks made and were found to be in good order. All necessary repairs were made on both SBCR reactor systems.