APPENDIX B

CHRONOLOGY OF RUNS IN SLURRY BUBBLE COLUMN REACTORS

CHRONOLOGY OF RUNS MADE IN THE SLURRY BUBBLE COLUMN REACTORS DURING THE THIRD QUARTER OF 1995

Task 2.0 -- Catalyst Testing

Subtask 2.2 - Slurry Bubble Column Testing

Run No. 48 in the M3-SBCR was started on July 5th with a charge of 15.5 gm of Catalyst No. CoW.13. This catalyst contained 10% Co, 10% Fe, and 0.5% Ru on alumina support. The CO conversion at startup conditions (240°C) was low, 8.5%, with a CH_4 selectivity at 10.8%. CO conversion increased to 20.0% at 260°C, 25.2% at 280°C, 28.0% at 300°C, and dropped to 2.6% at 240°C. This catalyst showed low initial reactivity and lost some reactivity as the reaction temperature was increased. The CO conversion dropped to 2.6% when the temperature was lowered to 240°C. This was only 30% of the initial conversion. This catalyst showed low resistance to deactivation at higher temperatures.

Run No. 49 in the M3-SBCR was started on July 13th with a charge of 15.5 gm of Catalyst No. Co.068. This catalyst contained 20% Co and 1% Pd on alumina support. The CO conversion at startup conditions averaged 26.7%. The reaction temperature was increased to 260°C and the CO conversion rose immediately to 41%, but dropped to 34% in a 24-hour period. At 280°C, the conversion peaked at 50%, but decayed to 33%. At 300°C the CO conversion rose to 45%, but again drifted down to about 28% after 24 hours. The conversion at 240°C was only 3.8%, or about 15% of the initial conversion. This catalyst showed low resistance to deactivation at higher temperatures.

Run No. 50 was started in the M3-SBCR on July 24th with a charge of 15.5 gm of Catalyst No. Co.066. This catalyst contained 15% Co, 5% Fe, and 0.5% Ru on alumina. The CO conversion at startup conditions was 21.1% with a CH_4 selectivity of 11.3%. The catalyst activity was in the range expected for a 15% Co catalyst. At 260°C the CO conversion peaked at 45.5% and dropped down to 36.1%. At 280°C the CO conversion peaked at 47.6% and then dropped down to 36.9%. Finally, at 300°C the conversion reached 48% and settled down to 31.1% a few hours later. The conversion at 240°C was down to 3.7% or about 17.5% of the initial CO conversion. This catalyst is typical of other cobalt catalysts which have good initial catalytic activity, but deactivate fairly rapidly at reaction temperatures of 240°C and higher due to carbon or coke formation. Addition of Fe does not appear to reduce the activity loss.

Run No. 51 was started in the M3-SBCR on August 2nd with a charge of 58 gm of Catalyst No. C.3950. This catalyst is a sample of the iron catalyst used in the F-T Run II at Laporte, Texas. The catalyst was reduced in-situ as prescribed and the run conditions were changed to baseline conditions: 175 psi pressure, 270°C reaction temperature, 0.7 H_2/CO feed ratio, and a total gas feed space velocity of 3,335 SL/hr/Kg-Fe. The CO conversion was 17.4%, the CH_4 selectivity was 9.3%, and the CO_2 selectivity was 51.1%. The reactor temperature was raised to 300°C, the pressure to 600 psi, and the gas space velocity to 15,517 SL/hr/Kg-Fe. After 5 hours at these run conditions, the

bottom reactor thermocouple rose to 437°C. Within 2 hours the reactor plugged near the bottom just above the inlet filter. The run was terminated at this time and it will be repeated as soon as the reactor is cleaned out.

Run No. 52 was started in the M3-SBCR on August 10th with a charge of 58 gm of Catalyst No. C.3950. After reducing the catalyst in-situ as before, the conditions were changed to 270°C, 450 psi, 2/1 H_2/CO ratio, and a total gas flow of 900 SLH (approximately 15,517 SL/hr/Kg-Fe space velocity). The CO conversion was 19.0%, CH_4 selectivity was 33.4%, and the CO_2 selectivity was 34.8%. The CO conversion increased to 29.2% at 276°C, 29.4% at 279°C, 35.8% at 288°C and 92.3% at 299°C. The CO conversion increased to 97.8% when the pressure was raised to 600 psi. At this time the H_2/CO ratio was changed from 2/1 to 1/1. Within 2 hours, the temperature in the top section began to increase rapidly. The reactor heaters were turned off and the syngas flow was stopped, but the temperature increased above 350°C and the reactor plugged. The unit was shut down and clean out again.

Run No. 53 was started in the M3-SBCR on August 23rd with a charge of 58 gm od Catalyst No. C.3950. After reducing the catalyst in-situ as before, the reaction conditions were changed to 270°C, 450 psi, a 1/1 H_2/CO feed ratio, and a total gas flow of 900 SLH. The CO conversion was 21.9%, CH_4 selectivity was 12.9%, and the CO_2 selectivity was 45.6%. The higher CO content in the feed gas resulted in lower CH_4 selectivity, but much higher CO_2 selectivity. The CO conversion increased to 25.7% at 280°C, 25% at 290°C, and 28.5% at 300°C. The H_2/CO ratio was then lowered to 0.7/1. The CO conversion stayed at 27.2% and the CO_2 selectivity was essentially the same at 47.2%. The reactor pressure was then increased to 600 psi. The CO conversion increased slightly to 29.4%, but the CH_4 and CO_2 selectivities were unchanged. Over a period of 4 hours, the reaction temperature gradually increased until it reach 360°C at which time the reactor plugged again in the top section near the internal filter.

Synfluid was not fed continuously during any of the above three runs. Some synfluid was added daily to try to maintain the liquid slurry height in the reactor. Since there is no way to remove the heat of reaction, there was little we could do to stop the reactor temperature from running away once it got started. The reactor plugs may have been due to foaming or carbon formation during the temperature runaway. It has been difficult to run the iron catalyst in the SBCR. One more run will be made as soon as the run conditions are determined.

Run No. 55 was started in the M3-SBCR on September 21st with a charge of 43 gm of Catalyst No. C.3950 (the fourth run with this catalyst). After reducing the catalyst in-situ as before, the reaction conditions were changed to 270°C, 175 psi, an 0.7 H_2/CO feed ratio, and a total gas flow of 355 SHL (6,670 SL/hr/Kg-Fe space velocity). The CO conversion was 18.7%, production rate - 0.27 gm C_1+/gm cat/hr, CH_4 selectivity - 9.5%, and the CO_2 selectivity was 49.1%. These were similar to those obtained in Run M3-51. The total gas rate was reduced in half to 180 SLH, and the CO conversion increased to 28.1%. The production rate dropped to 0.21 gm/gm/hr, the CH_4 selectivity dropped to 8.8%, and the CO_2 selectivity was similar at 48.6%.

The reaction temperature was increased to 300°C and the following yields were obtained: CO conversion - 35.5%, production rate - 0.26 g/g/hr, CH_4 selectivity - 12.5%, and CO_2 selectivity -

48.6%.

The reaction pressure was raised to 500 psi and the total gas rate was increased to 475 SLH. At this time the reaction temperature in the bottom of the reactor began to rise (up to 320°C) and the top temperature dropped to 290°C. The N_2 flow rate was increased to help remove the heat of reaction and to increase the gas superficial velocity to improve mixing. After 4 hours, the bottom temperature stabilized at 303°C, but the top temperature leveled out at 285°C, an 18°C differential temperature. Four hours later, while the unit was unattended, the reactor bottom temperature rose to 360°C and the reactor plugged solid. Up to this point, the CO conversion reached 65.1%, production rate - 1.31 g/g/hr, CH_4 selectivity - 18.7%, and the CO_2 selectivity peaked at 51.0%. It is obvious to us now that the heat removal capabilities of our unit had been exceeded, plus the operation requires a technician on duty whenever the more severe operating conditions are reached.

Task 4.0 - Catalyst Aging Studies

Run No. 37 was started in the M4-SBCR on August 14th with a charge of 25.0 gm of Catalyst No. Co.005. This was a base case catalyst containing 20% Co on an alumina support with no promoters. The synfluid feed was stopped on August 29th after 350 hours on stream. For the next 96 hours, the CO conversion stayed at 12.5%, the THC rate averaged 0.36 gm C_1+/gm cat/hr, while the CH_4 selectivity was 5.2%.

At 449 hours the N_2 feed rate was lowered from 62% to 40% of the total gas feed rate and the H_2 and CO feed rates were increased at a 2/1 ratio while maintaining the same total gas feed rate. The CO conversion dropped to 8.6%, but the THC production rate increased to 0.41 gm/gm/hr, and the CH_4 selectivity jumped to 10.4%. These conditions were held for 240 hours and the CO conversion dropped to 7.6%, the THC production rate to 0.36 gm/gm/hr while the CH_4 selectivity averaged 10.8%.

At 663 hours on stream, the H_2/CO ratio was changed to 1.5/1 while maintaining the same total gas feed rate. The CO conversion dropped to 5.6%, THC production rate to 0.32 gm/gm/hr, and the CH_4 selectivity dropped to 8.4%.

The N_2 feed rate was lowered from 40% to 33% while maintaining the same total feed gas rate at 687 hours on stream. The CO conversion dropped again to 4.8%, the THC rate went down to 0.29 gm/gm/hr while the CH_4 selectivity rose up to 10.3%. The synfluid feed was restarted at 735 hours on stream. The CO conversion rose to 5.6%, the THC went up to 0.35 gm/gm/hr, and the CH_4 selectivity dropped to 8.6%. There is some beneficial effect of adding synfluid continuously during the operation.

At 759 hours the reaction conditions were returned to the initial conditions for Period 3. The CO conversion averaged 10.4%, the THC was 0.31 gm/gm/hr, and the CH_4 selectivity averaged 4.7%. This was a loss of about 28% of the initial catalyst activity after 806 hours on stream.

The run was extended for one more day to check the catalyst activity at 33% N_2 feed rate at a 1.5/1 H_2/CO feed ratio. The CO conversion returned to about the same value, 4.5% vs. 4.8%, the

THC to 0.28 gm/gm/hr vs. 0.29, and the CH_4 selectivities were similar, 9.7% vs. 10.3%. This run was shut down on September 18th after 830 hours of successful operation.

Run No. 38 in M4-SBCR was started on September 28th with a charge of 31 gm of Catalyst No. CAL.14. This catalyst contained 20% Co, 0.5% Ru, and 0.3% K on alumina support that was reduced and coated with soya wax. The CO conversion at startup conditions was 25.5%, the THC production rate was 1.23 gm C_1+/gm cat/hr, and the CH_4 selectivity was 6.2%. Calsicat had prepared this new batch of catalyst using a modified H_2 reduction and wax coating procedure to improve catalyst activity. The CO conversion was about 10% lower than a comparable catalyst (CAL.13) that was H_2 reduced as a powder and charged into the reactor slurried with synfluid under nitrogen. The THC production rates and CH_4 selectivities were very similar. The new catalyst reduction and waxing procedure by Calsicat has been improved. It would greatly simplify the preparation and charging of large batches of catalyst into a commercial reactor if the catalyst can be prepared with wax.