V. CATALYST DEVELOPMENT

A. Introduction

The ultimate catalysts developed under this contract evolved along a complex path. Catalytic phenomena are, in most cases, only partially understood, and therefore, the translation of this knowledge to the preparation of a catalyst that will function at real process conditions is a very difficult task. This is due to the fact that many critical steps are involved between the formulation of the catalyst and its testing at realistic process conditions. For example, catalyst component selection (base supports, binders, active metals, active metal salts, additives, component purity), formulation procedure (pretreatment, sequence, solvent content, extrusion aids), activation technique (time, temperature, rate and degree of oxidation and reduction), and even minor experimental variations and changes in the scale of the equipment all impact the ultimate results and can cloud the results of the experiment. Thus, the selection of the next step for future progress is often difficult and the need to test multiple possibilities, and to occasionally repeat an experiment, is necessary.

B. Development of the UCC F-T Catalyst

The starting point was the catalyst formulation that was developed under the initial exploratory contract in this area, (DE-AC22-81PC40077), Co/Th/X4/UCC-103+UCC-101. The ultimate goal was to develop a catalyst whose performance would be economically superior to F-T catalysts now in commercial service. The avenues of exploration included:

a) improvement of activity (increase CO + H2 conversion per pass),

b) improvement of selectivity (increase C5+ yield, decrease methane, increase olefin content of product, increase isomer content of the C4 fraction, provide a carbon number cut-off in the C5+ product),

c) extension of catalyst life, i.e., eliminate or minimize deactivation in service,

d) add watergas shift activity to the catalyst to increase overall performance,

e) attempt the rejuvenation of spent catalyst,

f) preparation of techno-economic studies to guide product and process development.

A review of the complete program follows with reference to key catalysts, important breakthroughs, and basic discoveries. This will be done in two steps. First, a brief review of all of the runs made will be presented. This will not provide a logical or systematic description of the development of the ultimate catalyst since this description follows the output of three catalyst test units, whose scheduling varied daily. Following this will be a review of the key developments which led to the evolution of the ultimate catalyst. The data sources will be referred to in the appropriate Quarterly Report with page references. A complete list of all runs made during the contract and the reference to the source of the original data in the Quarterly Reports will be found at the end of this section (Table A). Finally, the best performance achieved during the course of this contract will be presented.

C. A Review of the Catalysts Prepared and Results

As noted above, the starting point for this contract was the conclusion of the previous contract, the Co/Th/X4/UCC-103 + UCC-101 catalyst. The purpose of this contract was to optimize the Co/UCC-103 catalyst to its ultimate limit and to provide a techno-economic evaluation as to the commercial performance that this catalyst would offer as a means to produce liquid hydrocarbon fuels based upon coal. The study focused upon the following topics:

I. Components
   a) F-T active metal (seventeen runs)
   b) zeolite components (sixteen runs)
   c) promoters (eighteen runs)
II. Preparation Procedures
   a) formulation techniques (thirteen runs)
   b) calcination procedures (eleven runs)
   c) activation procedures (four runs)
III. Process Variables (twelve runs)
   a) Temperature
   b) Pressure
   c) Space velocity
   d) H2/CO ratio

    e) Catalyst particle size

IV. Catalyst Life

    a) ultimate life of new catalyst (five runs)

    b) feasibility of rejuvenation (seven runs)

It should be noted that of the 103 runs made, only eleven (11) repeats were due to equipment failure, process control excursions, or doubts about catalyst preparation.

The runs in this study are reviewed below and reference is made to the source of the original data in the Quarterly Reports. However, a guide is necessary to clarify the relationship of the various runs to the objectives and to the interrelationship of the runs themselves.

The first run tested the effect of adding UCC-107 to the Co/UCC-103 as a shape selective additive. The goal was to limit the carbon number based upon catalyst pore size. The catalyst was totally inactive and the run was aborted.

The second run tested Ruthenium as the active F-T component. The formulation employed the substitution of the Ru for the Co in the best catalyst tested up until that time, Co/Th/X4/UCC-103 + UCC-101. The stability was poor and the CH4 make was high. The run was terminated after 165 hours.

The third run tested X7 as an additive to reduce methane formation. The catalyst used for comparison was a Co/Th/UCC-103 + UCC-101. Methane make was reduced but at the expense of a drastically reduced activity. The run lasted 90 hours.

Run 4 tested higher levels of cobalt in the catalyst. The initial activity was higher, however, the stability was unacceptable. This run pointed to the need for methods to improve stability.

The catalyst prepared for Run No. 5 was the same as for that prepared for Run No. 4, but activated under higher pressure. This catalyst was inactive and the run was aborted.

The catalyst for Run No. 6 was a repeat of that prepared for Run No. 5 and was also inactive and aborted.

The catalyst prepared for Run No. 7 was for initial studies made in the area of rejuvenation and the results are reported in the following section of this report.

The catalyst for Run No. 8 added the Silicalite molecular sieve to the formulation to determine the effect of this shape selective catalyst on performance. The stability was inferior although the methane make was reduced. The run lasted 306 hours.

The catalyst for the Run No 9 run duplicated that of the second run in case an anomaly had occurred. This catalyst exhibited low stability and activity and the run was halted.

The catalyst for Run No. 10 was prepared in an attempt to improve on the performance obtained in the catalyst tested in Run No.6, by increasing the cobalt level. Although the initial activity was high, the utilization of the cobalt was poor. The methane make was low and after an initial rapid deactivation, the stability was good. The run lasted 188 hrs.

The preparation of the catalyst used for Run No. 11 employed a new method of preparation, which resulted in the highest initial activity achieved up to this point, over twelve times that of the reference catalyst developed under the previous contract. In addition, the catalyst demonstrated a high watergas shift activity. The stability was unsatisfactory, but this catalyst represented an important step forward. The run lasted 166 hours.

The catalyst used in Run No. 12 was a repeat of one employed in the previous contract, a thorium promoted cobalt oxide formed with UCC-103 and further promoted with X4. However, different ratios of the active metals were employed. The stability was lower as was the watergas shift activity. The run lasted 500 hours.

The catalyst for Run No. 13 was the same as that used for the previous run except that the UCC-101 was eliminated. The stability was poorer and only little effect was seen on product distribution. The run lasted 236 hours.

Run No. 14 was based upon the attempt to reactivate the spent catalyst from the previous run, and is discussed in the following section on rejuvenation.

Run No. 15 represents a major breakthrough. The thorium was replaced with X9 and X10 and further promoted with X4. This product provided the best stability up to this point and showed that thoria could be replaced. The run lasted 453 hrs.

Run No. 16 employed the X10, X9, X4 discovery of the previous run on the UCC-103 base prepared by the methods used in Run No. 11, which had yielded a high initial activity. The initial performance was so poor that the run was terminated after about 43 hours.

The preparation method used in Run No. 11 was used to prepare the catalyst used in Run No. 17, which used Fe as the F-T active metal. Although the activity was low, the catalyst demonstrated a lower methane yield and a desirable olefin content product. This run lasted 116 hours.

The catalyst for Run No. 18 was a duplicate of Run No. 17 but activated at a lower temperature. The activity and selectivity were inferior and the run was stopped at 43 hours.

Run No. 19 again attempted to repeat the preparation of the catalyst used in Run No. 16 (which was poor) with similar results. Subsequent tests showed that impurities in the X4 chemical source were poisoning the catalyst.

The formulation of the catalyst for Run No. 20 was similar to that of Run No. 11 but the preparation was the same as that employed for the catalyst used in Run No. 16. The results first indicated the presence of an impurity in the X4 source for the catalyst used in Run No. 16 and in addition exhibited a carbon number cutoff behavior. However, the stability was poor and the run terminated at 116 hours.

The catalysts prepared for Run Nos. 21 and 22 were to test variations of that employed in Run No. 15. Both employed the same cobalt content, but increased the X4 content in an attempt to raise the olefin content of the product. The catalyst in Run No. 21 tested the addition of UCC-112 to the formulation. Both catalyst exhibited poor activity but demonstrated that increasing X4 can increase the olefin content of the product. The UCC-112 was ineffective and the runs halted at 115 and 94 hours, respectively.

The catalyst used in Run No. 23 employed a different source of the X4 promoter. The catalyst formulation employed in Run No. 11 was duplicated except that the UCC-103 and the new sourced X4 were contacted before mixing with the X9 and X10. A low initial activity led to an early halt in testing, specifically after 44 hours on-stream.

Run No. 24 was intended to test another support as a shape selective component. UCC-113 was substituted for UCC 103 (Run No. 20). The catalyst showed a high initial activity followed by a rapid deactivation. An early temperature excursion may have contributed to this behavior. The run was halted after 163 hours.

The catalyst tested in Run No. 25 employed another source of X4 (vs. that used for Run Nos. 16, 19, and 23). High initial activity and poor stability were observed. The run was stopped after 140 hours.

The next run (catalyst number 26) was aimed at measuring the effect of operating conditions upon stability with the catalyst employed in Run No. 20. The stability proved to be excellent at temperatures of 250 C or less. The run lasted for 523 hours.

Run No. 27 also tested the effect of operating temperature upon stability. The catalyst was prepared similarly to that used for Run No. 24. The results were similar to those of Run No. 26. The run lasted 378 hours.

Run No. 28 was aimed at achieving the stabilizing benefits observed from the addition of X4 to an X9, X10 promoted catalyst. However, a low concentration of cobalt in the final catalyst obscured the result and the run was halted after 68 hours.

The purpose of Run No. 29 was to determine the efficacy of the cobalt level in the catalyst formulation used for Run No. 11. The results (along with those of Run No. 26) proved that the catalyst performance was uniform across the cobalt concentration range of 7.8 to 11.9 percent. The run lasted 146 hours.

Run No. 30 tested the impact of X3 upon the performance of the X9, X10 promoted catalyst. The activity was increased slightly but the stability was decreased. The run lasted just 282 hours.

The effect of calcination was determined in Run No. 31. Specifically, the catalyst tested in Run No. 30 was rerun without calcination. The activity was very poor and the run terminated after less than 100 hours.

Run No. 32 proved to be a key run in this study. It was aimed at testing a new additive, X11. The catalyst was prepared similarly to that of Run No. 26 except X11 replaced X10. This additive provided a much greater stability as well as a better selectivity. The performance of this catalyst pointed to the need for much longer runs. Lower methane generation and a higher olefin content in the product were achieved. The run lasted 476 hours.

Run No. 33 employed the catalyst tested in Run No. 28 plus the addition of X3, which appeared to enhance performance in some previous tests. However, stability was poor, and the run was stopped after 117 hours.

Run No. 34 used the same formulation as the very successful catalyst tested in Run No. 32 except that UCC-114 was substituted for UCC-103. The catalyst exhibited low initial activity and the run was stopped after 20 hours.

UCC-115 was used in the formulation of the catalyst for Run No. 35 (same as that for Run No. 32). The activity was low and the methane make was high. The run lasted 43 hours.

The catalyst for Run No. 36 was prepared in the same manner as that for the successful Run No. 32 except that the cobalt level was increased. The catalyst exhibited the highest activity seen up to this point in the project. However, the run was stopped due to a power failure after 50 hours.

A pretreatment procedure that had demonstrated some promise in terms of carbon number cutoff (Runs 20 and 31) was applied to the catalyst prepared for Run No. 37. The formulation was that used for the promising catalyst tested in Run No. 32. This catalyst showed improved activity and stability but selectivity was inferior. More importantly, no cutoff was observed in the carbon number. The run lasted over 401 hours.

Run No. 38 was a repeat of Run No. 36 which was cut short by a power failure. The results demonstrated that increasing the cobalt had a mixed effect: increasing conversion but decreasing stability. The run lasted over 400 hours.

Run No. 39 tested the addition of X12. Higher activity, lower methane, higher C5+ and better stability were achieved in a run which lasted over 553 hours. This was a key run.

Run Nos. 40 and 41 further tested the use of the X11 promoter in F-T performance. The runs were 187 and 90 hours, respectively, too short to allow for meaningful life estimates, but both showed desirable product yields, low methane and high C5+ yield.

Run No. 42 was aimed at evaluating the effect of the level of the X11 additive. The results showed equivalent performance to that observed in Run No. 38 with no apparent benefit upon an increase of the X11 component. The run lasted over 330 hours.

Run No. 43 was aimed at duplicating the performance of that obtained in Run No. 32. The results of the two tests were equivalent with a slightly higher deactivation rate of the catalyst prepared for Run No. 43.

The catalyst prepared for Run No. 44 was intended to duplicate the carbon number cut-off behavior observed in Run No. 20. The catalyst exhibited a low initial activity and no carbon number cut-off. The run was stopped after 230 hours.

The catalyst prepared for Run No. 45 proved to be another major step forward in the development of high performance F-T catalysts. This catalyst substituted UCC-123 for UCC-103 in the formulation used for Run No. 32. The catalyst provided a stability unmatched to that point as well as a high conversion and low methane make. The run lasted 1568 hours (twice any previous run) and demonstrated that this catalyst could run in a hydrogen rich syngas.

Run No. 46 tested UCC-133 in the formulation employed for Run Nos. 32 and 45. In brief, the catalyst was superior to that of Run No. 32 but inferior to that of Run No. 45. The run lasted about 647 hours.

Run No. 47 was a further attempt to achieve a carbon number cutoff via molecular size effects. This was attempted by varying the formulation and activation procedure employed for Catalyst No 20 and 31. Specifically, an exposure to air was employed between hydrogen activation steps. The initial activity was negligible and the run terminated at 73 hours. No determination could be made as to carbon number cut-off.

The catalyst prepared for Run No. 48 substituted UCC-123 for UCC-103 used in Run No. 39. The activity was higher but all other properties were inferior. The test was terminated after 500 hours.

The purpose of Run No. 49 was to test the behavior of gamma-alumina versus the molecular sieve based catalyst. Gamma-alumina was used in place of the molecular sieve in the catalyst preparation used for Run No. 45. The initial activity was equivalent. However, the methane make was higher, the C5+ yield lower, and the stability was poor, especially at 260 C.

The molecular sieve UCC-121 was tested as a replacement for UCC-123 in Run No. 50. The formulation was similar to that employed for Run No. 45. The activity and selectivity were lower, the methane make higher, and the isomerization was higher on this catalyst. The run only lasted 166 hours, so the ultimate stability is questionable.

A major improvement was achieved with the formulation tested in Run No. 51. The additive X9 was tested and proved to be a winner. In addition, it proved to have advantages at extremes of operating conditions. The run lasted over 478 hours.

Run No. 52 tested the "residual F-T activity" of the reactor system by running syngas over quartz chips. No activity was observed.

Run 53 addressed the desire to promote the watergas shift reaction in the reactor during F-T synthesis. To this end, a K/Ni/Mo/gamma-alumina catalyst was added to the reactor (30% by volume) filled with the catalyst tested in Run No. 45 and the combination tested under syngas conditions. In summary, the initial shift activity is quickly lost and the net result is a dilution of the F-T activity. However, the presence of the shift catalyst does not impair the performance of the F-T catalyst performance.

The catalyst prepared for Run No. 54 employed X13 as a promoter. This additive proved to improve activity but reduced selectivity. The run lasted about 507 hours.

Run No. 55 duplicated the preparation of the catalyst for Run No. 51 but added an additional calcination step to enhance stability. Two key results were obtained; first, the performance of the catalyst tested in Run No. 51 was duplicated and second, high stability was achieved. The run lasted over 1145 hours.

Run No. 56 explored reducing the level of the X11 additive in the formulation of the catalyst employed in Run No. 55. The results showed that selectivity and stability were inferior but that activity was higher. The run lasted over 360 hours.

Run No. 57 tried to define the contribution of the X9 additive. The Run No. 55 formulation was used except that the X9 was eliminated. The conversion performance was equal but the stability was drastically reduced. The run lasted 600 hours.

UCC-124 was tested in Run No. 58 as a replacement for UCC-123. It proved to be inferior.

Run No. 59 tested the impact of higher levels of cobalt. There were no apparent benefits.

The effect of increasing the X9 level was tested in Run No. 60. It proved detrimental to stability and had no impact upon activity or selectivity.

Run No. 61 followed upon Run No. 58 to test an additional calcination step upon the performance of UCC-124. The activity was reduced and the run halted.

Run No. 62 tested the use of another molecular sieve support component, UCC-201. The isomerization was improved, but otherwise this catalyst was inferior.

The catalyst prepared for Run No. 63 was a duplicate of that used for Run No. 55. The purpose was to provide a material for testing at other process conditions. This proved to be an excellent catalyst, was run for 679 hours, and generated a great deal of data.

Run No. 64 tested UCC-211 as a catalyst support. The catalyst was inactive.

Cobalt and UCC-123 were tested without X9 and X11 in Run No. 65. This run proved that X11 greatly improved activity, selectivity, and stability. In addition, the improvement in stability provided by X9 was demonstrated.

Run No. 66 tested the use of UCC-12365 as a catalyst support. Performance was similar to UCC-123 but the activity was inferior (conversion of only 20%) and the run was terminated after 330 hours.

The calcination procedure employed to produce the catalyst tested in Run No. 55 was varied to produce the catalyst prepared for Run No. 67. In this case, the revised calcination procedure produced an equivalent catalyst when tested at 240 C but an inferior catalyst when tested at 260 C due to a higher deactivation rate. The run was terminated after 314 hours.

The performance of the catalyst in Run No. 55 warranted an evaluation of the impact of the level of cobalt metal on the catalyst effectiveness. Run Nos. 68, 70, and 73 were made to evaluate this fact and evaluated 8, 10, and 12% cobalt levels in the catalyst. Run No. 68 (8%) corresponded to the cobalt level employed in Run No. 55. Increasing the level of cobalt above the level employed in the catalyst tested in Run No. 55 (8%) yielded inferior performance. Run No. 68, at the same cobalt level, provided equivalent or better conversion, greater C5+ product yield, less methane, and a better olefin to paraffin ratio. Initially, the catalyst in Run No. 68 appeared to deactivate more rapidly than that of Run No. 55. However, by the end of the run, the stability of the catalyst used in Run No. 68 had plateaued and was exhibiting a stability superior to that of the catalyst employed in Run No. 55. Further testing was recommended. The run was terminated at 835 hours. Run No. 70 was stopped at 431 hours and Run No. 73 at 550 hours.

Run No. 69 completed a series of runs made to evaluate the calcination procedure upon catalyst performance. The two previous runs were nos. 55 and 67. The severity of calcination from least to most severe was Run No. 55 - Run No. 69 - Run No. 67. As in the case of Run No. 67, which performed equivalently to the catalyst in Run No. 55 at the low temperature conditions, the catalyst in Run No. 69 also performed well. However, at the more severe operating conditions (260 C), the more severe calcination conditions resulted in an increased conversion accompanied with an increased methane production. The increased severity of calcination did increase the olefin to paraffin ratio of the product. It should be noted that an upset during Run No. 69 resulted in conditions which may have damaged the catalyst. The catalyst preparation and test was repeated in Run No. 72.

Run No. 71 tested a catalyst which contained X14 as a promoter. When compared to the X11 additive, this catalyst was significantly less active.

As noted previously, the catalyst for Run No. 72 was a repeat of that used in Run No. 69, which was feared to have been damaged by an upset in process operating conditions. The purpose of the test was to evaluate the impact of calcination conditions upon the performance of the catalyst. The results were equivalent to those obtained from Run No. 69 which provided two conclusions. First, that the results from Run No. 69 were valid, and that the more severe calcination conditions resulted in an inferior performance, and, second, that this family of catalysts could tolerate a low pressure excursion without an intolerable impact upon the catalysts long term performance!

The catalyst tested in Run No. 74 evaluated the use of X15 as a promoter vs. X11. The activity was half that of X11. The run was terminated after 263 hours.

The catalyst used in Run No. 68 showed an initial poor performance which improved with time on stream. The catalyst prepared for Run No. 75 was prepared to check this peculiar behavior. Unfortunately, mechanical problems occurred which resulted in an early termination of this run (235 hours). The run was repeated (Run No. 81).

Run No. 76 was a part of the catalyst rejuvenation study and is reported in the following section of this report.

The catalyst tested in Run No. 77 was formulated like that tested in Run No. 45 with the exception that TC-123 was replaced by TC-103. The purpose of the run was to evaluate the impact of the H2/CO ratio upon the performance of the catalyst. The TC-103 proved to be inferior to the TC-123.

The catalyst preparation and Run No. 78 were made to provide a catalyst sample for the regeneration/rejuvenation studies. Surprisingly, the attempt to rapidly deactivate the catalyst under low H2/CO feed ratios failed. Although the preparation of a deactivated catalyst failed, the resilience of this catalyst to successfully survive excursions in process conditions was demonstrated once again.

The catalyst prepared for Run No. 79 was the same as the most successful catalyst developed during the course of this program, namely, that tested during Run No. 55. The purpose of this run was to test that catalyst at higher pressures as a means to broaden the understanding of process operating conditions. Unfortunately, process flow control problems resulted in an early termination of this run at (333 hours). It was repeated.

Run No. 80 tested the X16 promoter vs. the X9 material. The activity was found to be half, the olefin/paraffin ratio down, the methane up, and the C5+ yield down. The run was stopped after 163 hours.

The catalyst preparation and testing for Run No. 81 were the same as those employed for Run No. 68, which had shown a marginal improvement upon those observed for Run No. 55. In addition, the preparation offered an incentive in catalyst manufacturing cost production. The catalyst performed similarly to that of Run No. 55 and further long term deactivation tests were recommended.

The catalyst preparation and Run No. 82 were made to repeat a previous preparation and to evaluate the performance of the best catalyst prepared to date under higher pressure conditions (Run No. 55). No significant impact was observed.

Run No. 83 was a test of the performance of the catalyst regenerated from Run No. 81 and is reported in the rejuvenation section of this report.

Run No. 84 was made to test the reproducibility of the catalyst prepared and tested in Run No. 55 (the best catalyst tested to date during the course of this development). The results showed this catalyst to be equal to or better than the catalyst tested in Run No. 55 in all respects.

Run No. 85 was part of the rejuvenation study and is reported in the next section of this report.

The catalyst tested in Run No. 86 was prepared in a manner similar to that used to prepare the catalyst for Run No. 55 except that the calcination conditions were altered to reduce the residual carbon. This was achieved via a higher temperature and resulted in an inferior catalyst performance, i.e., lower conversion and lower stability.

The catalyst employed for Run No. 55 was again tested in Run No. 87. Specifically, two hydrogen activations were employed. The performance was slightly inferior.

Run No. 88 was part of the rejuvenation study and is reported in the following section.

A catalyst similar to that used for the catalyst tested in Run No. 55 was prepared except that the final product was extruded into one-sixteenth inch pellets instead of the conventional one-eighth inch pellets. The purpose was to determine the effect of diffusion limitations upon the catalyst performance. This catalyst was tested in Run Nos. 89 and 90. The results of these tests were inconclusive. Both catalysts exhibited a higher initial activity but a much higher deactivation rate and were inferior.

The catalyst formulation employed for Run No. 55 was tested in Run Nos. 91, 93, and 96 to establish long term stability and performance data for use in techno-economic studies. Run No. 91 was terminated due to an unexplained inferior performance. Run Nos. 93 and 96 were plagued with mechanical problems and were halted at 300 and 1000 hours, respectively. These runs were the first to clearly demonstrate the problems of obtaining long term life data using the Berty reactors.

Run Nos. 92, 95, and 97 were made on the catalyst tested in Run No. 55 to provide operating performance data over a range of operating conditions to provide a data base for techno-economic studies. The process conditions ranged from

240 to 260 C, 300 to 500 psig, space velocities of 300 and 1000, and H2:CO ratios from 1.0 to 1.5.

Run No. 94 was made with a catalyst prepared in a manner similar to that used for Run No. 55 except that TC-111 was added. This material had demonstrated the ability to reduce the pour point of the F-T product when used with the Fe/K catalyst. The activity was less than that obtained from the reference (Run No. 55). However, it was not as low as expected based upon the active metal content. The product appeared to have a lower melting point, qualitatively.

The catalyst employed for Run Nos. 98, 99, 100, and 101 was the same as that used for Run No. 55 (Co/X11/X9/TC-123). Run Nos. 99 and 101 were aimed at extending the long term stability data of the catalyst and were repeats of Run Nos. 91, 93, and 96 which terminated early due to equipment problems. Good performance was obtained, however, long term runs were not achieved due to mechanical problems. Run Nos. 98 and 100 were made to extend the data base on the performance of the catalyst for the techno-economic studies.

Run No. 102 used the preferred formula (Co/X11/X9) but was supported on gamma-alumina vs. TC-123. The gamma-alumina supported catalyst exhibited a lower initial activity and, more importantly, showed a much higher deactivation rate.

Run No. 103 employed the UCC support (TC-123) as the base for an iron F-T catalyst. The activity of this catalyst was significantly lower than a cobalt counterpart. The stability was better than anticipated based upon other Fe containing catalysts tested and may have been due to the TC-123 support.

D. Evolution of Optimized Catalyst Concept

Although the preceding section provides a compact summary of the results of the runs, it is remiss in providing the thought that resulted in the sequence of the runs selected. This section will attempt to explain the logic used to select the development plan and by doing so will demonstrate how the program led to the catalyst/process combination that was the result of the overall program.

The starting point was the catalyst identified by the previous contract, a molecular sieve based, promoted cobalt metal F-T catalyst (Co/Th/X4/UCC-103 + UCC-101). The performance of that catalyst is presented in Table V-1 (material balances and product data obtained during the run) and Figures V-1 and V-2 (conversion of syngas, H2, and CO vs. time and product distribution vs. time). Further details, which include C4 olefin production, C5 isomerization, simulated distillation curves of the product, Schulz-Flory product distribution plots, and chromatograms of the product, will be found in the reports cited.

The purpose of this contract was to develop new and improved catalysts based upon the discoveries of the previous contract which would offer significant improvements over commercially available catalysts. Thus, improvements would be based upon exploration of alternative zeolites and promoters based upon the cobalt F-T component. In addition, variations in the preparation (formulation and methodology) would have to be examined. Finally, it would be necessary to; a) test the commercially accepted F-T components in the equivalent atmosphere (Fe on a molecular sieve support), b) test the reactor for inherent F-T activity, and c) test the other F-T active element (Ru) as a possible candidate.

It should be noted that, although the following discussion will focus on the few key discoveries that led to the ultimate catalyst, which provided the basis for the techno-economic evaluation that was the final result of this report, the intervening runs were the stepping stones that led to each of the specified landmarks. As such, they represent negative data points which provided the direction needed to identify the key runs reported below and, although not described in detail herein, they provide important information regarding the catalytic performance of this family of materials.

The first significant breakthrough was discovered in Run No 11. This catalyst was the first to employ a new method of combining the F-T metal with the zeolite molecular sieve via a solvent that allowed intimate dispersion of the metal throughout the zeolite structure. The resulting catalyst exhibited an activity of 12.5 times that of the initial (Co/Th/X4/UCC-101 + UCC-103) material, a conversion of 91.5%! After 166 hours the activity had declined to 4.0 times that of the reference and the conversion to 68%. This catalyst also exhibited watergas shift activity that enhanced the performance of the catalyst. The data, equivalent to that presented for the reference catalyst, are presented in Table V-2 and Figures V-3 and V-4. The additional data will be found in the Third Quarterly report.

The next significant breakthrough was in the catalyst used for Run No. 15. In this run, the mildly radioactive thorium was replaced with promoters X9 and X10 and further promoted with X4. This product exhibited an outstanding stability, a breakthrough in itself, and also, allowed the elimination of the thorium. The conversion was initially 63% and decreased to 56% after 191 hours. The product selectivity was excellent and as noted the stability was outstanding. The data are presented in Table V-3 and Figures V-5 and V-6. The detailed results will be found in the Third Quarterly report.

The discovery of the benefits of X11 occurred in Run No. 32. The product selectivity and enhanced stability marked X11 as a key promoter. The C5+ yield increased from 73% in Run No. 15 to 81% in this run. In addition, the methane was reduced and the olefin/paraffin ratio doubled! This run also demonstrated the need for longer runs for stability testing purposes. The data are presented in Table V-4 and Figures V-7 and V-8. The detailed results are reported in the Fourth Quarterly report.

Run 43 was important in that it was the first attempt to reproduce a technically significant catalyst, namely, the catalyst tested in Run No. 32. The results were equivalent, demonstrating the capability to reproduce the catalysts. The data are presented in Table V-5 and Figures V-9 and V-10. Details will be found in the Fifth Quarterly report.

Run No. 45 introduced the benefits of UCC-123 over UCC-103. The preparation was the same as that used for Run No. 32. The run extended to an impressive 1568 hours. This catalyst yielded high conversion, low methane, and high olefin content product along with a low deactivation rate. In addition, the low methane generation allows operation in a more hydrogen rich atmosphere. The data are reported in Table V-6 and Figures V-11 and V-12. The detailed results are found in the Sixth Quarterly Report.

Run No. 51 was responsible for the discovery of the benefits of X9. The performance was superior to any catalyst tested and it performed well when the operating conditions were pushed to severe levels. Data are presented in Table V-7 and Figures V-13 and V-14. The run was limited by mechanical problems. Detailed results were presented in the Seventh Quarterly report.

Run No. 55 was a duplication of Run No. 51 , which had exhibited some excellent properties. However, an additional calcination step was added to enhance stability. This catalyst represents the next major breakthrough in the program. The deactivation rate at elevated reaction temperatures was about one percent (1%) reduction in conversion per 170 hours on stream. The results are presented in Table V-8 and Figures V-15 and V-16. Detailed results were reported in the Eighth Quarterly report. The performance of the catalyst tested in Run No. 55 was not exceeded during the remainder of this study. There were numerous duplications, minor variations in formulation, etc., but the performance of the catalyst used in Run No. 55 was not surpassed. Tests made to attempt equivalent preparations at lower cost were unsuccessful. For example, lower levels of the promoters yielded inferior catalysts and lower cost supports also provided inferior catalysts. A number of runs were made to establish ultimate catalyst life and to determine process performance data at alternative process conditions. These are listed in Table B. Based upon the life and process variable studies, the techno-economic evaluation was completed.

It should be noted that when compared to the starting point (the end point of the previous contract) the improved products developed in this contract exhibit a specific activity increase of a factor of nine to twelve and a deactivation rate that was initially fair to one that was nearly insignificant. A comparison of the performance of the key catalysts is presented in Table V-9 to provide a concise comparison of the performance improvement achieved in the catalyst over the course of this contract. The results presented in this table are based upon data at 260 C, although similar results will be obtained at other conditions. Every performance factor exhibits improvement. Additional data are provided for Run No. 55.

In addition, the improvements achieved in supports and promoters were applied to iron F-T catalysts to determine if the benefits achieved would translate to the iron system (they did not).

Further, it should be noted that the addition of watergas shift activity to the catalyst was successful, but temporary. Finally, the rejuvenation study failed to yield any significant leads towards the possibility of extending the ultimate life of a spent catalyst. The results indicated that the deactivation was due to agglomeration of the F-T metal species into larger (and fewer) particles, which reduced the activity, rather than a deactivation of the active sites due to poisoning or coking, which might be reversible.

During the course of this work, codes were assigned to promoter elements and zeolite supports. A listing of these codes is presented in Table V-10.