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IMPROVED FISCHER-TROPSCH SLURRY CATALYSTS

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I. ABSTRACT

Three fixed bed tests were completed during the reporting period. With these experiments promoter effect studies using H_2 reduced catalysts have been completed. Catalyst activity for singly promoted catalysts increased with an increase in copper content, and at the same time selectivity towards methane decreased significantly. A doubly promoted catalyst with lower potassium content than a previously tested catalyst showed that the catalyst with the lower potassium content was more active and stable than that with the higher potassium content, although the former had a higher selectivity towards CH_4 and other lighter products.

Wax from previous fixed and slurry bed runs was analyzed. Several models were used to interpret results obtained from analysis of wax produced during promoter effect tests (H_2 reduction) in the fixed bed reactor. Anderson-Schulz-Flory plots for the carbon number product distributions indicate the presence of two chain growth probabilities for all cases. Results show that α_I increases with an increase in potassium content, correctly indicating the increase in selectivity towards heavier compounds; however, no clear trends can be seen from α_{II} values. Several samples, withdrawn at different times on stream during a slurry bed run with the Ruhrchemie LP-33/S1 catalyst, were selected for analysis. Results from this analysis indicate that slurry wax composition does not undergo significant changes with time on stream.

II. OBJECTIVE AND SCOPE OF WORK

The objective of this contract is to develop a consistent technical data base on the use of iron-based catalysts in Fischer-Tropsch (FT) synthesis reactions. This data base will be developed to allow the unambiguous comparison of the performance of these catalysts with each other and with state-of-the-art iron catalyst compositions. Particular attention will be devoted to generating reproducible kinetic and selectivity data and to developing reproducible improved catalyst compositions. To accomplish these objectives, the following specific tasks will be undertaken.

TASK 1 - Project Work Plan

The objective of this task is to establish a detailed project work plan covering the entire period of performance of the contract. This includes estimated costs and manhours expended by month for each task.

TASK 2 - Slurry Catalyst Improvement

The primary purpose of this task is to develop improved iron-based catalysts, both precipitated and supported, that show enhanced activity and selectivity in slurry phase testing. This will be accomplished by gaining systematic understanding of the role of promoters, binders, supports and activation procedures in determining the activity and selectivity of iron-based catalysts. The catalyst development program will incorporate extensive physical and chemical characterization of these materials with the objective to establish correlations between the physical/chemical properties of these catalysts and the corresponding catalytic behavior for synthesis gas conversion.

TASK 3 - Process Evaluation Research

The purpose of this task is to subject the most improved catalysts (based on activity and selectivity) to a thorough process evaluation. This involves long term stability studies, investigation of a wide range of process variables, and determination of kinetic parameters.

TASK 4 - Economic Evaluation

The aim of this task is to develop the relative economic impact for each improved catalyst composition and compare these economics with the economics of using the base case catalyst.

III. SUMMARY OF PROGRESS

- Fixed bed catalyst tests

Three catalyst tests in fixed bed reactors were completed during the past quarter. These tests marked the completion of promoter effect studies using H_2 reduced catalysts. The catalysts tested were: 100 Fe/0.3 Cu, 100 Fe/3 Cu, and 100 Fe/3 Cu/0.2 K. The first two tests were conducted to determine the effect of copper content on catalyst performance. Catalyst activity increased with copper content at temperatures of 250 and 265°C, whereas activity for the two catalysts was similar at 235°C. Surprisingly, the selectivity of the 0.3Cu containing catalyst towards CH_4 was higher than both the unpromoted iron and the catalyst containing 3 parts of Cu. Both copper promoted catalysts were stable during the tests. The $(H_2 + CO)$ conversion increased slightly as the run progressed, with little change in catalyst selectivity. The doubly promoted 100 Fe/3 Cu/0.2 K catalyst was more stable than the previously tested 100 Fe/3 Cu/0.5 K catalyst, but it produced more methane and other light products.

The effect of copper and potassium promoters on the behavior of H_2 reduced catalysts is summarized. In general catalyst activity increases with the addition of Cu or K promoters, but Cu has a more pronounced effect on catalyst activity than does potassium. Both Cu and K promote the water-gas-shift (WGS) activity of the catalyst, with K being the more effective promoter. Also, potassium is much more effective than copper in reducing methane and C_2-C_4 yields, and in enhancing the olefin selectivity for the catalyst. A synergistic effect is observed with the activity of doubly promoted catalysts, which are more active than singly promoted catalysts. However, a similar effect on product selectivity was not observed, and these catalysts gave products that were lighter than those from catalysts promoted with potassium alone, but heavier than those from catalysts promoted with copper alone.

- Wax Analysis

Selected wax samples obtained during promoter effect studies (H_2 reduction) in the fixed bed reactor were analyzed. Several different approaches were used to estimate the chain growth

probability factors. The merits of the various approaches are discussed. Results indicate that α_I and α_{II} alone are not sufficient to describe the product distribution, and additional parameter such as β (fraction of type I sites on the catalyst) is necessary to completely describe the distribution. Furthermore, alpha values obtained from the slopes of the straight line segments on an Anderson-Schulz-Flory plot are noticeably different from those obtained using a non-linear 2-alpha model. This is because the former ignore the existence of two chain growth mechanisms over the entire carbon number range, while the latter procedure takes this into account. Values of α_I obtained using the slope of C₃-C₇ mole fractions on a log-linear ASF plot were similar to those obtained from the 2-alpha model. Trends in α_I support our earlier findings of increased catalyst selectivity for heavier compounds with an increase in potassium content. Whereas, no clear trends can be seen in α_{II} values.

Slurry wax samples withdrawn during a run with the Ruhrchemie LP-33/81 catalyst were analyzed. The samples selected for analysis represented the composition of the reactor wax at different time on stream values. The samples were filtered to remove entrained solids prior to analysis. ASF plots for the product (including wax) clearly indicate the presence of two chain growth probabilities. Furthermore, the analysis showed no significant changes in wax composition with time on stream. This means that it is not necessary to analyze wax after each balance period during slurry runs, instead, only selected samples can be analyzed to obtain the entire product distribution.

IV. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

TASK 1—PROJECT WORK PLAN

The project work plan was completed during the first quarter of this project and the detailed work plan was submitted to APCI.

TASK 2—SLURRY CATALYST IMPROVEMENT

2.1. Promoter Effect Research

During this quarter we completed tests for studying the effect of promoters (copper and potassium) on the activity and selectivity of iron Fischer-Tropsch catalysts reduced in H_2 . Three additional tests were made. For each test, the reactor was loaded with approximately 3.5 g of 30/60 mesh catalyst, diluted with about 24 g of glass beads of the same mesh size range. All catalysts were activated with H_2 at 220°C over a period of 8 h. The effect of process conditions, temperature (235, 250 and 265°C) and space velocity (2 and 4 $Nl/g\text{-cat}\cdot h$) at 1.48 MPa using $H_2/CO = 1.0$ (nominal) feed gas, on conversion and product distribution were studied during each run. With the 100 Fe/3 Cu/0.2 K catalyst, the effect of temperature was also studied using $H_2/CO = 0.72$ feed gas. The effect of copper alone was studied in two runs: FB-32-0409 (100 Fe/0.3 Cu), and FA-34-0409 (100 Fe/3 Cu). The latter run was a repeat of an earlier test FA-34-3068 (Technical Progress Report for the period 1 October 1988–31 December 1988). The repeat run was undertaken to verify high activity and selectivity towards high molecular weight products, obtained in the previous run, relative to unpromoted iron catalyst. A doubly promoted catalyst, 100 Fe/3.0 Cu/0.2 K, was evaluated in a test designated FB-25-0029. Five balances were made in each run over approximately 170 h, which included a replication of conditions to check for catalyst deactivation. The doubly promoted catalyst was subjected to a longer test (9 balances up to 435 h), and included conditions using $H_2/CO = 0.72$ feed gas.

2.1.1. Run FB-32-0409 (100 Fe/0.3 Cu)

The summary of results for the five mass balances carried out during the test of the singly

promoted catalyst, 100 Fe/0.3 Cu (run FB-32-0409), is listed in Table 1. Catalyst activity increased with time on stream, as indicated by results from repeat balances 1 (72 h) and 5 (168 h), both at 250°C, 2.0 Nℓ/g-cat·h. The (H₂+CO) conversion increased from 34.4 % during balance 1 to 40.7 % during balance 5. Hydrocarbon selectivity for the two balances was similar: 26.8 (CH₄), 38.6 (C₂-C₄), 29.6 (C₅-C₁₁), and 5.1 % (C₁₂+) during balance 1 vs. 25.7, 38.4, 28.8, and 7.1 %, respectively, during balance 5. Olefin/paraffin ratios for carbon numbers up to C₁₀ decreased slightly between the two balances.

Temperature had the expected effect on both, catalyst activity and hydrocarbon selectivity. When temperature was decreased from 265°C to 235°C (balances 3 and 4), other conditions remaining the same, (H₂+CO) conversion decreased from 47.8 % during balance 3 to 35.1 % during balance 4. During the same period, hydrocarbon selectivity shifted towards heavier products: 28.2 (CH₄), 37.9 (C₂-C₄), 29.4 (C₅-C₁₁), and 4.5 % (C₁₂+) during balance 3 vs. 24.5, 37.6, 32.6, and 5.3 %, respectively, during balance 4. A similar change in activity and selectivity was observed when temperature was increased from 235°C to 250°C (balances 4 and 5). (H₂+CO) conversion increased from 35.1 % during balance 4 to 40.7 % during balance 5. Hydrocarbon selectivity shifted towards lighter products, except for C₁₂+, which increased from 5.3 % at 235°C to 7.1 % at 250°C. The effect of temperature on the olefin/paraffin ratios was somewhat erratic, probably due to analytical errors.

An increase in space velocity from 2.0 to 4.0 Nℓ/g-cat·h at 250°C (balances 1 and 2) increased the C₅-C₁₁ products from 29.6 to 34.7 % and decreased the C₁₂+ products from 5.1 to 1.9 %. The CH₄ and C₂-C₄ fractions were similar at both space velocities. The higher space velocity increased the C₂ and C₃ olefin/paraffin ratios moderately. The C₂ ratio increased from 0.4 (2.0 Nℓ/g-cat·h) to 0.7 (4.0 Nℓ/g-cat·h), and the C₃ ratio increased from 3.2 to 4.2. The C₄ ratio decreased from 3.4 to 2.5 as space velocity was increased. The C₁₀ ratio did not change with space velocity, while the C₁₂+ ratios showed a slight decrease. These variations in the olefin/paraffin ratios may be caused

by errors in sample analysis.

The activity of the 100 Fe/0.3 Cu catalyst is lower than that of the 100 Fe/3 Cu (run FA-34-0409, discussed next) at 250 and 265°C, whereas activities of the two catalysts were similar at 235°C. The selectivity towards CH_4 was significantly higher for the 100 Fe/0.3 Cu catalyst than was for the catalyst with 3 parts Cu (24.5-28.2 % vs. 12.3-15.5 %). The CH_4 selectivity of the 100 Fe/3 Cu catalyst, was also greater than that for the unpromoted iron catalyst. The observed trend that methane selectivity first increases with the addition of copper promoter (0.3Cu), and then decreases as Cu content is increased to 3 parts per 100 parts Fe, is difficult to explain.

2.1.2. Run FA-34-0409 (100 Fe/3 Cu)

This run was made as a repeat of run FA-34-3068 (Technical Progress Report for the period 1 October 1988-31 December 1988) to verify the high activity and selectivity towards high molecular weight products, observed in run FA-34-3068. Table 2 summarizes the results from five mass balances carried out during the new run. Catalyst activity increased slightly with time on stream, and between balance 1 (72 h) and balance 5 (168 h), both at 250°C, 2.0 Nℓ/g-cat·h, the ($\text{H}_2 + \text{CO}$) conversion increased from 60.6 to 62.1 %. This increase in activity is similar to that observed in the earlier run with the same catalyst, where the ($\text{H}_2 + \text{CO}$) conversion increased from 57.3 to 60.5 % over about the same time interval. Catalyst activity at other conditions was similar for the two repeat runs, with values from the new run being slightly higher than those from the previous run with this catalyst.

Some shifting occurred between the $\text{C}_5 - \text{C}_{11}$ and $\text{C}_{12} +$ products with time on stream during the present run: during balance 1 the $\text{C}_5 - \text{C}_{11}$ and $\text{C}_{12} +$ distribution were 42.1 and 13.3 %, respectively, while in balance 5 the $\text{C}_5 - \text{C}_{11}$ products decreased to 34.1 % and the $\text{C}_{12} +$ products increased to 20.5 %. Although both runs with the 100 Fe/3 Cu catalyst exhibited similar activities, there were considerable differences in hydrocarbon selectivities, with the present run producing more high molecular weight products. For example, at 250°C, 2.0 Nℓ/g-cat·h(balance 1), the product

distribution for the present run was 13.1 (CH₄), 31.5 (C₂-C₄), 42.1 (C₅-C₁₁), and 13.3 % (C₁₂+) vs. 16.5, 38.1, 32.8 and 12.5 %, respectively, for balance 1 in run FA-34-3068. Methane and C₁₂+ selectivities in the previous run were in the ranges 15.8-20.2 % and 8.4-12.5 %, respectively, compared to 12.3-15.5 % and 8.4-20.5 %, respectively, for the present run. The olefin/paraffin ratios did not change with time on stream for the present run. The ratios were essentially the same for balances 1 and 5, which also was the case in run FA-34-3068. The ratios were consistently higher for the present run, at all conditions, compared to the previous run. For example, the C₂ ratio varied in the range 0.5-0.9 in the present run compared to a range of 0.2-0.5 in the previous run. A similar trend was observed at other carbon numbers.

The effect of temperature on hydrocarbon selectivity can be seen from balances 3, 4 and 5. When temperature was decreased from 265°C to 235°C (balances 3 and 4), the effect on selectivity was as expected: i.e., more heavier products were produced at 235°C than at 265°C. The hydrocarbon distribution at 265°C was 14.8 (CH₄), 36.6 (C₂-C₄), 33.6 (C₅-C₁₁), and 14.9 % (C₁₂+) vs. 12.3, 30.2, 40.1 and 17.4 %, respectively, at 235°C. When temperature was increased from 235°C to 250°C (balances 4 and 5), the distribution shifted towards lighter products, except for C₁₂+ , which increased from 17.4 % at 235°C to 20.5 % at 250°C. Olefin/paraffin ratios generally increased with temperature. At 250°C (balance 5), the C₃, C₄, C₈, and C₁₀ ratios were 2.50, 2.66, 1.70, and 1.42, while at 256°C they were higher at 2.63, 3.23, 2.00, and 1.57, respectively. The C₂ ratios were 0.52 and 0.46, respectively, at the two temperatures. The trend was erratic between 235°C (balance 4) and 250 or 265°C, but this can be attributed to analytical errors.

The effect of space velocity was studied in balances 1 or 5 using 2.0 Nl/g-cat·h and balance 2 using 4.0 Nl/g-cat·h, at 250°C. The higher space velocity caused a moderate shift in hydrocarbon selectivity towards lighter components: 15.5 (CH₄), 36.8 (C₂-C₄), 39.3 (C₅-C₁₁), 8.4 % (C₁₂+) at 4.0 Nl/g-cat·h vs. 13.1, 31.5, 42.1, and 13.3 %, respectively at 2.0 Nl/g-cat·h. The olefin/paraffin ratios were consistently higher at the higher space velocity. For example, at 2 Nl/g-cat·h the

C₄ and C₁₀ ratios were 2.6 and 1.4, respectively, while at 4 Nℓ/g-cat·h they were 2.8 and 1.6, respectively.

2.1.3. Run FB-25-0029 (100 Fe/3.0 Cu/0.2 K)

The summary of results for nine mass balances carried out during run FB-25-0029 with the doubly promoted 100 Fe/3.0 Cu/0.2 K catalyst is given in Table 3. The first four balances of this run were made using a H₂/CO = 0.98 feed gas. A repeat of the initial conditions using the 0.98 feed gas was made during balances 4 and 9. Balances 5-8 used a H₂/CO = 0.72 feed gas in order to study the effect of feed ratio on catalyst performance.

The catalyst exhibited remarkable stability during the test. Over a 350 h period catalyst activity showed a slight increase: (H₂+CO) conversion at 250°C, 2.0 Nℓ/g-cat·h, H₂/CO = 0.98 was 75.7 % during balance 1 (71.5 h), while at the end of the run (balance 9, 429 h) it was 76.5 %. Also, the hydrocarbon distribution during the two balances was fairly similar. During balance 1, the distribution was 14.3 (CH₄), 33.6 (C₂-C₄), 38.0 (C₅-C₁₁), and 14.1 % (C₁₂+), while during balance 9 methane and C₅-C₁₁ products were about the same, 14.3 and 37.7 %, respectively, but the C₂-C₄ products decreased to 29.0 % and the C₁₂+ products increased to 19.0 %. The olefin/paraffin ratios also remained fairly stable during the course of the run. For example, the C₃ and C₁₀ ratios were 2.9 and 1.0, respectively, during balance 1, and were 3.1 and 1.1, respectively, during balance 9.

Temperature had a moderate effect on the hydrocarbon distribution. At 235°C, H₂/CO = 0.98 (balance 3) the distribution was 18.5 (CH₄), 35.5 (C₂-C₄), 33.1 (C₅-C₁₁), and 12.9 % (C₁₂+). At 250°C (balance 4), CH₄ decreased slightly to 17.7 %, and C₁₂+ decreased to 7.1 %. Both C₂-C₄ and C₅-C₁₁ increased, to 38.7 and 36.5 %, respectively. Using the H₂/CO = 0.72 feed gas, raising the temperature from 250 (balance 6) to 260°C (balance 7) did not affect CH₄ or C₅-C₁₁ significantly (12.4 and 42.5 % at 260°C vs. 11.1 and 43.8 % at 250°C), while selectivity for the remaining two groups changed by a larger amount: 35.6 (C₂-C₄) and 9.6 % (C₁₂+) at 260°C compared to 28.5

and 16.5 %, respectively, at 250°C.

The effect of feed ratio was studied in balances 4 and 5 (250°C, 2.0 Nℓ/g-cat·h). The lower feed ratio increased the (H₂+CO) conversion slightly, from 77.9 (H₂/CO = 0.98) to 79.9 % (H₂/CO = 0.72). The most significant change came in the hydrocarbon distribution, as the lower feed ratio favored production of higher molecular weight compounds. Methane and the C₂-C₄ products decreased to 12.7 and 30.4 %, respectively, when the lower feed ratio was used, compared to 17.7 and 38.7 % obtained using the H₂/CO = 0.98 feed. The C₅-C₁₁ and C₁₂+ products increased to 40.9 and 16.0 %, respectively, from 36.5 and 7.1 %. The olefin/paraffin ratios for all carbon numbers increased when the lower feed ratio was used. For example, the C₃ ratio was 2.63 in balance 4 (H₂/CO = 0.98) and increased to 3.51 in balance 5 (H₂/CO = 0.72). The ratios at other carbon numbers behaved similarly. Space velocity (250°C, balance 1 at 2.0 Nℓ/g-cat·h, balance 2 at 4.0 Nℓ/g-cat·h) had an effect on the hydrocarbon distribution. CH₄ and C₂-C₄ increased from 14.3 and 33.6 %, respectively, to 19.8 and 37.1 % at the higher space velocity, while the C₅-C₁₁ and C₁₂+ products decreased correspondingly. The higher space velocity at these conditions had a marginal effect on the olefin/paraffin ratios, with the ratios at 4 Nℓ/g-cat·h being consistently lower than those at 2 Nℓ/g-cat·h.

This catalyst was found to be somewhat more active and stable than the previously tested catalyst, 100 Fe/3 Cu/0.5 K (run FB-27-3368, Technical Progress Report for the period 1 October 1988-31 December 1988), however, it produced more methane and other lighter products than the 100 Fe/3 Cu/0.5 K catalyst.

2.1.4. Discussion of promoter effects—H₂ reduced catalyst

The effect of promoter (Cu and K) on catalyst FT activity are discussed here. The recent series of runs for studying promoter effects with H₂ reduced catalysts showed a relatively high amount of CH₄ (10 ~ 20 wt.% selectivity) relative to our previous tests with CO activated catalysts (< 10 wt.%) Also, in some instances the change of CH₄ selectivity with temperature exhibited

unexpected trends. For example, in run FB-45-2638 (100 Fe/0.2 K catalyst - Technical Progress Report for the period 1 October 1988-31 December 1988) CH₄ decreased from 17.6 to 14.6 % when temperature was increased from 250 to 260°C, while the remaining product groups followed the expected trends with temperature. Usually methane yield increases with temperature. We decided to investigate this unusual behavior of CH₄ selectivity by looking closely at the original results. We discovered that relatively high CH₄ concentration coupled with the proximity of CH₄ and CO peaks, on the GC trace from tail gas analysis (from the Carle AGC-400 Gas Chromatograph), had affected the integrator's ability to resolve the two peaks and properly allocate areas of these two components. To circumvent this problem we reanalyzed our data using CH₄ peak area obtained from the tail gas analysis on the Sigma 1B GC. The Sigma 1B trace is normally used to detect the concentration of C₅-C₁₀ components, even though it does detect the CH₄ concentration in the tail gas. The reanalyzed data showed the expected trends in methane selectivity with temperature. The discussion presented here is based on results obtained when CH₄ peak area from the Sigma 1B GC was used.

Selected results from catalytic tests at different process conditions are summarized in Tables 4-7. All runs were conducted at a pressure of 1.48 MPa with synthesis gas feed of H₂:CO = 1:1 molar ratio. The effect of temperature (235, 250 and 265°C) was studied at gas hourly space velocity of 2 Nl/g-cat·h (Tables 4-6) and the effect of gas flow rate (SV = 2 and 4 Nl/g-cat·h) was studied at reaction temperature of 250°C (Table 7).

Activity and Stability of Catalysts

Effects of reaction temperature and time on stream at 250°C on FTS activity, measured by (H₂+CO) conversion are shown in Figures 1a and 1b, respectively. (H₂+CO) conversion increases with the addition of either copper or potassium, but Cu has a more pronounced effect on catalyst activity than does K at all three reaction temperatures. The activity increases significantly with increasing K content up to 0.5 g of K per 100 g of iron, but beyond this promoter concentration

the effect is small (0.5 vs. 1K per 100Fe). A synergistic effect is observed with doubly promoted catalysts, which have higher activity than singly promoted catalysts. Also, activities of the two doubly promoted catalysts were similar at both, 235 and 250°C, i.e., the activity was independent of K content in the catalyst (0.2 vs. 0.5K per 100Fe). The latter trend was not observed in runs with catalysts promoted with K alone. These results show that K promotion effect in doubly promoted catalysts may be both qualitatively and quantitatively different than that observed with singly K promoted catalysts. (H_2+CO) conversion increases with increasing reaction temperature, as expected.

FTS activity measured by (H_2+CO) conversion, at 250°C and 2 Nl/g-cat·h is illustrated in Figure 1b at different times on stream. The activity of all catalysts during the first mass balance at 250°C (72 hours on stream) was lower than the activity at 142-168 hours when the base conditions were repeated. The increase in activity was rather small, less than 5 % for the two doubly promoted catalysts, the unsupported iron catalyst and the 100 Fe/3 Cu catalyst. This means that these catalysts have achieved their steady state activity after about 40 hours at 250°C. However, catalysts promoted with K alone showed a marked increase in activity over the same period of time as shown in Figure 1b for 100 Fe/0.5 K, Table 4 (100 Fe/0.2 K), and Table 5 (100 Fe/1 K at 235°C).

The two doubly promoted catalysts were tested over a longer period of time. These two catalysts were exposed to the synthesis gas with $H_2:CO = 2:3$ molar feed ratio at 250 and 260°C between about 150 and 400 hours on stream, and then the base conditions (250°C, $H_2:CO=1:1$) were repeated. Results at the base conditions at 428-456 h on stream are shown in Figure 1b and in Table 4. The catalyst with lower K content (100 Fe/3 Cu/0.2 K) had exhibited remarkable stability and its activity at 430 h on stream was nearly the same as its maximum activity at about 143 h on stream (76.8 vs. 78.1 % (H_2+CO) conversion). The catalyst with higher K content (100 Fe/3 Cu/0.5 K) had lost nearly 9 % in activity between 143 and 457 h on stream. This loss in activity is

rather small, particularly in view of the fact that the catalyst was exposed to a variety of process conditions during this period of time.

The FTS reaction on iron catalyst is accompanied by a reversible water-gas-shift (WGS) reaction. One measure of the WGS activity is the CO_2 selectivity defined as the rate of CO_2 production divided by the total rate of CO consumption. This assumes that all of CO_2 is produced by the WGS reaction. The WGS activity of selected catalysts as a function of reaction temperature is shown in Figure 2. The WGS reaction proceeds nearly to completion (i.e., CO_2 selectivity is approximately 0.5) at all reaction temperatures (235–265°C) with catalysts which contain K as promoter. The WGS activity of the unpromoted iron catalyst increases markedly with the reaction temperature, but even at 265°C the CO_2 selectivity is only 0.41. The WGS activity of the 100 Fe/3 Cu catalyst is significantly greater than that of the unpromoted iron, and approaches the limiting value at 265°C. These results show that both Cu and K promote the WGS activity of the catalyst, with K being the more effective promoter. All catalysts, except the unpromoted iron catalyst attain their steady state activity after about 40 h at 250°C (i.e., 72 hours on stream) as can be seen from Table 4 by comparing CO_2 selectivities at 72 and 142–168 hours on stream.

Reproducibility of Results

Before describing results on catalyst selectivity in detail we shall briefly address the important issue of reproducibility of experimental data. In our study the reproducibility was checked by performing at least two mass balances under the same set of process conditions. The base conditions were: 1.48 MPa, 2 Nℓ/g-cat·h, $\text{H}_2/\text{CO} = 1$ and either 235°C (for the 100 Fe/0.5 K catalyst) or 250°C (for the other six catalysts). As described in the previous section, the activity of the catalyst promoted with Cu (either singly or doubly) and the unpromoted iron catalyst did not change significantly with time on stream (72 and 143–168 hours), i.e., the results were reproducible. As can be seen from Table 4 the product selectivities (hydrocarbon distribution, olefin and oxygenates selectivities) did not vary much between the two mass balances. With the two doubly promoted

catalysts the base conditions were repeated one more time after 430-456 hours on stream and activities and selectivities were similar to those obtained in the previous two mass balances.

As stated earlier, the activity of the three catalysts promoted with K alone increased markedly with time on stream (Figure 1b, Tables 4 and 5). This indicates that these catalysts were undergoing changes in composition with time on stream, leading to an increase in the number of active sites. In general, the product selectivities were reproducible for all three catalysts, which means that the nature of catalyst sites (or ensembles of sites) did not change significantly with time on stream.

From these results it may be concluded that the operating procedures employed in our study ensure achievement of steady state conditions during the mass balance periods at all process conditions, resulting in good reproducibility of data.

Selectivity

In this section we shall describe effects of promoters and process conditions on product distribution.

Hydrocarbon product distribution:

The effects of promoters (Cu and K) on hydrocarbon distribution are presented in Tables 4-7 and Figures 3 and 4.

Figure 3 illustrates promotional effects of Cu or K on hydrocarbon distribution at 250°C and 72-94 hours on stream. The addition of Cu to the unpromoted catalyst leads to a marked decrease in methane selectivity, and to an increase in higher molecular weight hydrocarbons ($C_{12}+$ fraction). Potassium promotion produces qualitatively similar trends, and potassium is much more effective than copper in reducing methane and C_2-C_4 hydrocarbon yields. The product distribution shifts towards higher molecular weight hydrocarbons with increase in K content of the catalyst. Similar trends were observed at the other process conditions as illustrated in Tables 5 and 7.

Hydrocarbon distributions obtained with the two doubly promoted catalysts, and comparison with singly promoted catalysts with equivalent amounts of promoters are shown in Figure 4. Al-

though, both Cu and K favor formation of higher molecular weight hydrocarbons, relative to the unpromoted catalysts, we do not observe the anticipated synergistic effect with the two catalysts containing both promoters. The average molecular weight of hydrocarbon products obtained with the doubly promoted catalysts is higher than that of the 100 Fe/3 Cu catalyst, but is lower than that of the corresponding catalysts promoted with equivalent amounts of potassium (0.2 or 0.5K per 100Fe). Similar trends were observed at the other process conditions (Tables 5-7). In general, it seems that the hydrocarbon product distribution is primarily determined by the potassium loading of the catalyst. The hydrocarbon distributions of the two catalysts containing 0.5 parts of K per 100Fe (100 Fe/0.5 K and 100 Fe/3 Cu/0.5 K) were similar at different process conditions.

With the lower potassium loading (0.2K per 100Fe) the presence of Cu in the doubly promoted catalyst (100 Fe/3 Cu/0.2 K) yields higher methane selectivity relative to the 100 Fe/0.2 K catalyst, but other than that the hydrocarbon distributions of these two catalysts were similar.

The effects of reaction temperature (235-265°C) and gas space velocity (2 and 4 Nl/g-cat·h at 250°C) on hydrocarbon product distribution were similar for all catalysts. It was found that as the reaction temperature increases the product distribution shifts towards lower molecular weight products. This is illustrated in Figure 5 for selected catalysts. The increase in space velocity did not have marked effect on hydrocarbon distribution of the catalysts (see Tables 4 and 7). With the unpromoted iron catalysts the increase in space velocity favored the production of higher molecular weight products, whereas the opposite trend was observed with the 100 Fe/0.2 K, 100 Fe/0.5 K, and 100 Fe/3 Cu catalysts.

Olefin Selectivity

It is well known that the principal type of hydrocarbon formed by the primary synthesis is the 1-alkene (or α -olefin). The two main secondary reactions are hydrogenation of 1-alkene to a normal paraffin and isomerization to the 2-alkene (β -olefin). The effects of promoters, reaction temperature and the gas space velocity on the extent of secondary reactions will be described in

this section.

Olefin content (i.e. hydrogenation activity)

a. Promoter effects:

Potassium promoted catalysts (Fe/K) have higher olefin content than the unpromoted catalyst as shown in Tables 4-7 for the C_2-C_4 fraction, and in more detail in Figure 6 as a function of carbon number (up to C_{10}). The olefin content reached the maximum at C_3-C_4 and then decreased with increased carbon number for both unpromoted and K promoted catalysts (Figure 6). The rate at which the olefin selectivity decreases with increasing carbon number is much lower for Fe/K catalysts. Also, hydrogenation of olefins decreases slightly with the increase in potassium loading.

The addition of Cu results in slightly higher hydrogenation activity relative to the unpromoted catalyst, and this trend is observed at all process conditions as shown in Tables 4-7 for C_2-C_4 hydrocarbons. The addition of small amounts of potassium (~ 0.2 wt.%) to the 100 Fe/3 Cu catalyst was not sufficient to suppress the hydrogenation activity of the catalyst, as can be seen by comparing results from tests with 100 Fe/3 Cu and 100 Fe/3 Cu/0.2 K catalysts. However, upon increasing potassium loading to about 0.5 wt.%, the promotional effect of K on suppressing the hydrogenation activity of the catalyst becomes evident. The olefin contents of C_2-C_4 hydrocarbons of the 100 Fe/0.5 K and 100 Fe/3 Cu/0.5 K catalysts are nearly the same, and are significantly higher than that of the 100 Fe/3 Cu catalyst.

b. Effect of temperature:

The effect of reaction temperature on total olefin content is not the same for all catalysts studied, and the observed trends vary somewhat with the carbon number. The catalysts promoted with K exhibit different type of behavior than those which do not contain potassium. Figure 7 shows results for the 100 Fe/1 K, 100 Fe/3 Cu, and the unpromoted catalyst, which are representative of all catalysts employed in our study. The olefin content of products in the C_2-C_{11} range for potassium promoted catalysts increases with the reaction temperature, whereas in the case of unpromoted iron

the olefin content of C_2 - C_4 hydrocarbons decreases with the reaction temperature in the range 235-265°C, and that of the C_5 - C_{11} hydrocarbons remains constant. The 100 Fe/3 Cu catalyst follows the same trend as the unpromoted catalyst in the C_2 - C_4 range, but the olefin content of C_5 - C_{11} hydrocarbons passes through a minimum at 250°C. The behavior of the two doubly promoted catalysts is determined by their potassium content, i.e., 100 Fe/3 Cu/0.2 K follows the trend observed with the 100 Fe/3 Cu catalyst, whereas the 100 Fe/3 Cu/0.5 K catalyst follows the same trend as the three Fe/K catalysts.

c. Effect of gas space velocity:

As shown in Tables 4 and 7, the olefin content of C_2 - C_4 and C_5 - C_{11} hydrocarbons either remained unchanged (catalysts with potassium content greater than ~0.5 wt.%) or increased with an increase in space velocity (catalysts with higher hydrogenation activity, i.e., 100 Fe/3 Cu, 100 Fe/3 Cu/0.2 K, and unpromoted iron). The latter is consistent with the fact that olefins are the primary reaction products.

Olefin isomerization

The ratio of 2-butene to 1-butene was chosen as a measure of isomerization activity, and its value is listed in Tables 4-7 for all catalysts at different process conditions. The catalyst composition, i.e., its potassium content, has the strongest effect on this ratio, whereas the effects of process conditions (temperature and gas space velocity) are minor in comparison to the former. Potassium promotion suppresses the olefin isomerization reaction and the 2-butene/1-butene ratio varied between .02 and .07 for the catalysts containing ~0.5-1. wt.% of potassium, whereas the highest values were obtained with the 100 Fe/3 Cu catalyst (0.27-0.70). It turns out that catalysts which favor olefin hydrogenation (Fe, 100 Fe/3 Cu, 100 Fe/3 Cu/0.2 K) also favor the olefin isomerization reaction.

The olefin isomerization activity (2-butene/1-butene) did not vary much with the gas space velocity (Tables 4 and 7) nor with the reaction temperature for most of the catalysts. The increase

in isomerization activity with the increase in temperature was observed with the two catalysts which also exhibited the highest hydrogenation activity, i.e. 100 Fe/3 Cu and the unpromoted catalyst. For these two catalysts the 2-butene/1-butene ratio increased from 0.27 to 0.70, and 0.24 to 0.36, respectively, as the reaction temperature was increased from 235 to 265°C. This behavior is consistent with that shown in Figure 7, where the olefin content of C₂-C₄ hydrocarbons for these two catalysts decreased as the temperature increased.

Oxygenates selectivity

The selectivity of oxygenates, expressed as percent CO converted to oxygenates, is shown in Tables 4-7 for all catalysts at different reaction conditions. Oxygenates comprise only a small fraction of products formed and consist primarily of normal alcohols, plus small amounts of aldehydes and ketones. No clearly discernable trends are observed in oxygenates selectivity as a function of promoter concentrations, temperature and space velocity. The highest oxygenates selectivity was obtained with the unpromoted catalyst and the 100 Fe/3 Cu/0.5 K catalyst. At some process conditions (235 and 250°C) the selectivity of oxygenates increased with potassium concentration in the 0.2 to 1 wt.% range. Also, the oxygenates selectivity of the doubly promoted catalysts was somewhat higher than that of the Fe/K catalysts containing the same amount of potassium.

2.2. Wax Analysis Results

We analyzed products collected in the hot trap of the fixed bed reactor systems during promoter effect study runs. The samples selected for analysis were those collected during balances at 250°C, H₂/CO = 1.0, 1.48 MPa, 2 Nl/g-cat·h. These results were then incorporated into the existing data to extend the range of carbon numbers included in the mass balances and selectivity calculations. The chain growth probabilities associated with FTS products can be estimated using several approaches, particularly when the Anderson-Schulz-Flory (ASF) plot suggests the existence of two chain growth probabilities (double- α), i.e., when a break in the slope of the ASF plot is observed. We have applied these approaches to our data and estimated the various parameters

associated with the models used to describe the product distributions. The various approaches are briefly described here.

Asymptotic alphas:

This model assumes that each portion of the ASF plot can be described by an independent single chain growth probability model

$$m_n = (1 - \alpha_i)\alpha_i^{n-1}; \quad i = I, II \quad (1)$$

α_I and α_{II} are then estimated using the slopes of the straight line segments on a log-linear plot of the product distribution. Although this is a straightforward procedure, it does not conform with the common belief that the two chain growth probability models, responsible for the double alpha product distribution, are simultaneously in effect over the entire range of carbon numbers. Furthermore, only at the asymptotes of the ASF plot is the distribution influenced by just one of the two chain growth probabilities. As a further refinement of this procedure, α_I is often estimated using only the C₃-C₇ products (i.e., products with low carbon numbers - close to the first asymptote of the distribution). It is expected that products in this range of carbon numbers are almost entirely influenced by the first chain growth mechanism.

Double-alpha model (Huff and Satterfield, 1984):

Huff and Satterfield (1984) proposed a double- α model that could be used to describe the FTS product distribution.

$$m_n = \beta(1 - \alpha_I)\alpha_I^{n-1} + (1 - \beta)(1 - \alpha_{II})\alpha_{II}^{n-1} \quad (2)$$

In this model, two single chain growth models are weighted and added together such that the sum of the weights equals unity. As a result, a third parameter is introduced, β , which is defined as the fraction of type *I* sites on the catalyst or mole fraction of organic product synthesized on Site I. α_I and α_{II} are the chain growth probabilities associated with the type *I* and type *II* sites,

respectively. The procedure used to estimate the three parameters in Eq. 2 is described later in this section.

Double-alpha model (Donnelly et al., 1988):

Donnelly *et al.* (1988) proposed a double- α model based on rigorous statistical techniques, which also assumes that two chain growth mechanisms determine the FTS product distribution.

$$m_n = \frac{\alpha_I^{n-1} + (\alpha_I/\alpha_{II})^{\xi-1} \alpha_{II}^{n-1}}{1/(1-\alpha_I) + (\alpha_I/\alpha_{II})^{\xi-1} [1/(1-\alpha_{II})]} \quad (3)$$

In Eq. 3, ξ is the carbon number corresponding to the point at which the two single chain growth models intersect on the ASF plot. This model places no artificial constraints on the system since Eq. 3 was derived on a purely mathematical basis. The procedure used to estimate the three parameters in Eq. 3 is described next.

Parameter estimation procedure:

The parameters for Eqs. 2 and 3 were estimating using non-linear regression and obtaining the best fit of the data in the least squares sense. Since the mole fraction data span several orders of magnitude in any one sample, the regression involved the minimization of the sum of square errors (SSE) as defined by

$$SSE = \sum_{n=3}^{n=m} [\ln \hat{m}_n - \ln m_n]^2 \quad (4)$$

where $\hat{m}_n$ is the predicted mole fraction and m_n is the experimental value. The NLIN procedure in the SAS software was used to estimate the parameters. The Marquardt iterative method was used to regress the residuals onto the partial derivatives of the model with respect to the paramters until the iterations converged. For each case, a range of starting values were specified for each parameter, allowing NLIN to determine the best set of values to start the iterative algorithm, based on the residual sum of squares at each combination of values. Additionally, the search was restricted to the logical range for each parameter, i.e., within the range 0 to 1 for α_i and β , and the range 3 to m (where m=carbon number of the heaviest component for which data was available) for the

estimate of ξ . The limit on maximum number of iterations was placed at 50, and the convergence criterion used was

$$\frac{SSE_{i-1} - SSE_i}{SSE_i + 10^{-6}} < 10^{-8} \quad (5)$$

In majority of the cases, convergence was achieved within 10 iterations. It was found that in some cases the parameter estimates were unusually sensitive to the convergence criterion used. When a value of 0.01 instead of 10^{-8} was used in Eq. 5, the resulting estimates were significantly different from those obtained with the more stringent criterion. The mean square error ($MSE = SSE/(\# \text{ of points} - \# \text{ of parameters})$) in most cases was less than 0.05. Data for carbon number ≥ 3 was used since literature indicates that experimentally obtained C_1 and C_2 products frequently do not obey Schulz-Flory distribution. The same data set for a given sample was used with each of the models described here.

Results and discussion:

The results from selected promoter effect study fixed bed catalyst tests are summarized in Table 8. The samples analyzed were obtained from balances at 250°C , 1.48 MPa , $\text{H}_2/\text{CO} = 1.0$, and $2 \text{ Nl/g-cat}\cdot\text{h}$, except for the sample for unpromoted iron which was from the balance at $1 \text{ Nl/g-cat}\cdot\text{h}$, since insufficient amount of wax was collected at $2 \text{ Nl/g-cat}\cdot\text{h}$. Three estimates for α_I (C_3 - C_7 range, asymptotic, and the $2-\alpha$ models), and two estimates of α_{II} (asymptotic and the $2-\alpha$ models) are shown in Table 8. For each catalyst, mole fractions for carbon numbers in the range 3 to 32 were used. The asymptotic α_I was estimated in most cases using data for the carbon number range $3 \sim 15$. The estimates of α_I and α_{II} from Eq. 2 and from Eq. 3 were exactly the same. It can be shown that Eqs. 2 and 3 are in fact identical and describe the same model in two different ways. While Eq. 2 is based on the existence of two types of sites on the catalyst, Eq. 3 requires no such assumption. Furthermore, it can be shown that β and ξ are related by

$$\xi = 1 + \frac{\ln \left[\frac{(1-\beta)(1-\alpha_{II})}{\beta(1-\alpha_I)} \right]}{\ln(\alpha_I/\alpha_{II})} \quad (6)$$

The estimates of β and ξ obtained from non-linear regression (Table 8) do follow the relationship shown in Eq. 6. It was not possible to estimate α_{II} from the slope or to obtain parameters for the 2- α models from data obtained in a test with the unpromoted iron catalyst. The data at carbon numbers greater than 12 were not accurate due to the small amount of product collected.

Some interesting and useful conclusions can be drawn from results shown in Table 8. The value of α_I estimated from the slope (column 2) is always higher than the value estimated using the two- α model (column 3). The reverse is true for α_{II} estimates, i.e., value from the slope (column 4) is always lower than the value from the 2- α model (column 5). This is not unexpected since the estimates from slopes assume that the entire product, in the corresponding range of carbon numbers, is solely due to just one chain-growth probability, while the 2- α model allocates the product to two chain growth probabilities. Since α_I is always lower than α_{II} , not allocating products to the two chain growth probabilities (as is the case when slopes are used) would increase the value of α_I and decrease the value of α_{II} . When α_I was estimated using product in the range C₃-C₇ (column 1 in Table 8), these values were much closer to α_I values from the 2- α model (column 3) than were values obtained using the slope (column 2). This confirms the earlier assertion that products in this range more accurately reflect the α_I chain growth probability.

Our results also show that reporting α_I and α_{II} values alone may lead to inaccurate inferences about catalyst selectivity. The two alphas do not sufficiently describe the product distribution, and an additional parameter (i.e., β or ξ) is necessary to complete the description. For example, for the 100 Fe/3 Cu catalyst, α values from slopes are 0.65 and 0.86, respectively, while values for the 100 Fe/1.0 K catalyst are 0.74 and 0.88, respectively. The comparable α_{II} value for the two catalysts (0.86 vs. 0.88) would imply that the two catalysts had similar selectivities for higher molecular weight products, when in fact the K promoted catalyst had C₁₂+ selectivity of 36.7 % compared to 8.3 % for the Cu promoted catalyst. The value of β for the 100 Fe/3 Cu catalyst was 0.99 compared to a value of 0.88 for the 100 Fe/1.0 K catalyst, correctly indicating that the

α_I chain growth probability accounted for most of the product for the former catalyst (i.e., lighter products), whereas product for the latter catalyst was due to both chain growth probabilities (i.e., relatively heavier product).

The α_I values (from each of the three approaches) are in general agreement with the expected trends. α_I for the unpromoted iron catalyst is the lowest (0.56–0.60), and the value increases with an increase in the potassium content of the catalyst. For catalyst promoted with 0.2 parts of K, α_I from the three approaches is in the range 0.61–0.67, the range for catalyst with 0.5 parts K is 0.68–0.73, and for 1 part K it is 0.65–0.74. The difference in α_I is less pronounced when values for catalysts with 0.5 and 1 part K are compared. A similar trend can be seen for catalysts promoted with copper. For the singly promoted 100 Fe/3 Cu catalyst α_I is in the range 0.62–0.65, whereas for the 100 Fe/3 Cu/0.2 K catalyst the range is 0.62–0.72, and 0.69–0.72 for the 100 Fe/3 Cu/0.5 K catalyst, i.e., a progressive increase in α_I with increasing potassium content. The trends in α_I are in good agreement with results illustrated in Figure 3, i.e., product distribution shifts towards heavier products with an increase in potassium content of the catalyst. Trends in α_{II} are erratic and no conclusive inferences can be made from these values. There appears to be a strong correlation between α_{II} and β , the two parameters have very similar trends. Our analysis shows that the covariance coefficient for the estimates of α_{II} and β is >0.95 for most of the catalysts. Figure 8 shows Anderson-Schulz-Flory distributions for the 100 Fe/3 Cu with 0, 0.2 and 0.5 parts K catalyst. For each catalyst, the product distribution predicted by the corresponding two- α model (Eq. 2) is also shown. In all cases, the model appears to describe our data very well.

TASK 3—PROCESS EVALUATION RESEARCH

3.1. Slurry Wax Analysis

We analyzed slurry wax samples from the run SA-99-0888 (Ruhrchemie LP 33/81 catalyst). This was a long term stability run (Technical Progress Report for the period 1 April 1988–30 June 1988) and slurry was withdrawn following each balance period using an external settling tank. A

total of thirteen slurry samples were available from the run (collected over a 722 h period), of which five were selected for analysis. The selected samples represent the composition of the reactor wax at different times on stream distributed over the 722 h period. Four of the samples were those withdrawn following mass balance periods, while the fifth sample analyzed was that from the reactor after the run was completed. The slurry samples were filtered through a 2 μ m sintered metal plate filter prior to analysis, to remove entrained catalyst and/or carbon particles.

Results from the wax analysis were incorporated into the existing data to extend the range of carbon numbers included in the mass balances and selectivity calculations. In each instance, the product distribution indicated the existence of double alpha values. The chain growth probabilities associated with the FTS products were estimated using slopes of the two straight line segments on a log-linear Anderson-Schulz-Flory product distribution plot. Table 9 summarizes the alpha values for distributions from the four balance periods. Alpha values obtained from the slope of the first line (products in the range C_1 - C_{10}) are in the range 0.71-0.77, whereas those obtained from the slope of the second line (products in the range C_{20} - C_{45}) are in the range 0.89-0.92. When the product distribution for wax alone was plotted, alpha values for the five samples were in the range 0.87-0.92. Wax product distributions for samples withdrawn at 95, 482, and 722 hours on stream are compared in Figure 9. These results indicate that the slurry wax composition does not go through any significant changes during the run. This means that for slurry runs it is not necessary to analyze wax after each balance period, instead, only selected samples can be analyzed to obtain the entire product distribution.

Task 4 - Economic Evaluation

No work on this task was scheduled during this quarter

V. NOMENCLATURE

m_n	=	mole fraction of products containing n carbon atoms
$\hat{m}_n$	=	predicted mole fraction value for products containing n carbon atoms
n	=	number of carbon atoms
SSE	=	sum of squared errors as defined by Eq. 4

Greek Letters

α	=	chain growth probability
β	=	fraction of type I sites on the catalyst
ξ	=	carbon number at intersection of two chain growth probabilities

Subscripts

I	=	number associated with the chain growth probability
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VI. LITERATURE REFERENCES

Huff, G. A., Jr., and C. N. Satterfield "Evidence for Two Chain Growth Probabilities on Iron Catalysts in the Fischer-Tropsch Synthesis," *J. Catal.*, **85**, 370-379 (1984).

Donnelly, T. J., I. C. Yates, and C. N. Satterfield "Analysis and Prediction of Product Distributions of the Fischer-Tropsch Synthesis," *Energy & Fuels*, **2**, 734-739 (1988).

Table 1. Summary of results for fixed bed run FB-32-0409 .

Catalyst: 3.51 g ^a , 100Fe/0.3Cu/9K Catalyst volume: 3.20 cc		Diluent: 36.90 g, Glass beads Diluent Volume: 24.00 cc			
Period	1	2	3	4	5
Date	2/12/89	2/13/89	2/14/89	2/15/89	2/16/89
Time on Stream (h)	71.5	95.5	120	144	168
Balance Duration (h)	6.00	6.00	6.00	7.00	6.50
Average Temperature (°C)	250	250	265	235	250
Maximum Δ Temperature (°C) ^b	3.00	3.00	4.00	4.00	4.00
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48
H ₂ /CO Feed Ratio	1.02	1.02	1.02	1.02	1.02
Space Velocity (NI/g-cat·h) ^a	1.98	3.96	1.98	1.98	1.98
Space Velocity (NI/g-Fe·h)	2.84	5.68	2.84	2.84	2.84
GHSV (h ⁻¹) ^c	255	511	255	255	255
CO Conversion (%)	35.7	21.5	51.7	35.8	42.1
H ₂ +CO Conversion (%)	34.4	21.0	47.8	35.1	40.7
H ₂ /CO Usage	0.94	0.97	0.87	0.98	0.95
STY (mols H ₂ +CO/g-cat·h) ^a	0.030	0.037	0.042	0.031	0.036
P _{CO₂} · P _{H₂} / P _{CO} · P _{H₂O}	4.10	1.90	7.40	3.10	4.40
Weight % of Outlet					
H ₂	4.57	5.50	3.85	4.54	4.18
H ₂ O	2.38	2.38	2.25	2.90	2.66
CO	59.8	74.0	45.4	60.5	54.2
CO ₂	22.2	10.8	34.5	21.3	27.0
Hydrocarbons	10.2	6.84	13.3	10.1	11.3
Oxygenates	0.50	0.42	0.59	0.52	0.52
Wax ^d	0.36	0.09	0.18	0.13	0.17
Yield (g/Nm ³ H ₂ + CO Converted)					
CH ₄	54.8	56.7	52.4	46.9	48.1
C ₂ -C ₄ Hydrocarbons	78.7	80.9	70.4	72.0	71.8
C ₅ -C ₁₁ Hydrocarbons	60.3	75.2	54.7	62.5	53.9
C ₁₂ + Hydrocarbons	10.4	4.03	8.35	10.2	13.2
Wax ^d	6.98	2.86	2.51	2.34	2.72
Oxygenates	9.76	13.1	8.16	9.71	8.43
Total	214	230	194	201	195
1+2 Olefins/n-Paraffin Ratio					
C ₂	0.43	0.71	0.34	0.44	0.41
C ₃	3.20	4.19	2.93	3.12	3.13
C ₄	3.36	2.46	3.04	3.17	3.18
C ₈	1.06	1.21	1.29	1.17	1.02
C ₁₀	1.02	1.00	1.10	0.82	0.93

^a Based on unreduced catalyst^c Based on reactor volume^b Maximum axial temperature difference^d Unanalyzed products collected from hot trap

Table 1 (cont'd). Summary of results for fixed bed run FB-32-0409 .

Period	1	2	3	4	5
Weight % of Hydrocarbons					
CH ₄	26.8	26.1	28.2	24.5	25.7
Ethane	9.85	8.59	9.55	9.35	9.66
Ethylene	3.92	5.70	3.06	3.85	3.69
Propane	3.35	2.53	3.61	3.32	3.42
Propylene	10.3	10.1	10.1	9.88	10.2
n-Butane	2.41	2.10	2.69	2.51	2.54
i+2 Butenes	7.83	4.99	7.89	7.67	7.80
C ₄ Isomers	0.95	3.31	1.00	1.02	1.05
n-Pentane	2.68	2.53	2.99	2.93	2.92
i+2 Pentenes	6.80	10.1	6.96	7.55	7.24
C ₅ Isomers	1.49	3.19	2.54	2.98	2.80
n-Hexane	3.92	3.25	3.00	2.85	2.23
i+2 Hexenes	3.64	3.58	2.46	3.40	2.89
C ₆ Isomers	1.04	1.23	0.82	1.02	0.95
n-Heptane	2.18	2.05	1.58	1.95	1.26
i+2 Heptenes	2.02	2.26 ^s	1.65	2.05	1.43
C ₇ Isomers	0.80	1.00	0.59	2.40	0.72
n-Octane	1.19	1.74	0.49	0.84	0.59
i+2 Octenes	1.25	2.07	0.62	0.96	0.59
C ₈ Isomers	0.42	0.40	0.06	0.65	0.17
n-Nonane	0.27	0.21	0.78	0.17	0.50
i+2 Nonenes	0.28	0.21	0.92	0.10	0.42
C ₉ Isomers	0.02	0.02	0.11	0.02	0.06
n-Decane	0.37	0.24	0.92	0.52	0.91
i+2 Decenes	0.37	0.24	0.99	0.42	0.83
C ₁₀ Isomers	0.04	0.03	0.16	0.09	0.20
n-Undecane	0.38	0.18	0.83	0.78	0.95
i+2 Undecenes	0.34	0.16	0.78	0.68	0.87
C ₁₁ Isomers	0.04	0.03	0.16	0.24	0.32
C ₂ -C ₄	38.6	37.3	37.9	37.6	38.4
C ₅ -C ₁₁	29.6	34.7	29.4	32.6	28.8
C ₁₂ +	5.07	1.86	4.49	5.31	7.06
Wax ^d	3.42	1.32	1.35	1.22	1.46

^d Unanalyzed wax collected from hot trap

Table 2. Summary of results for fixed bed run FA-34-0409 .

Catalyst: 3.50 g^a, 100Fe/3Cu/0K
Catalyst volume: 3.40 cc

Diluent: 36.00 g, Glass beads
Diluent Volume: 24.00 cc

Period	1	2	3	4	5
Date	2/12/89	2/13/89	2/14/89	2/15/89	2/16/89
Time on Stream (h)	71.5	95.5	121	144	168
Balance Duration (h)	6.00	6.00	6.00	7.00	6.50
Average Temperature (°C)	250	250	265	235	250
Maximum Δ Temperature (°C) ^b	2.50	4.00	3.00	4.00	3.00
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48
H ₂ /CO Feed Ratio	1.02	1.02	1.02	1.02	1.02
Space Velocity (NI/g-cat·h) ^a	1.99	4.10	1.99	1.99	1.99
Space Velocity (NI/g-Fe·h)	2.92	6.02	2.92	2.92	2.92
Space Velocity (NI/g-Fe·h)	254	524	254	254	254
GHSV (h ⁻¹) ^c	72.8	50.0	95.5	40.8	75.3
CO Conversion (%)	60.6	41.5	81.1	34.4	62.1
H ₂ +CO Conversion (%)	0.68	0.68	0.72	0.70	0.67
H ₂ /CO Usage	.054	.076	.072	.031	.055
STY (mols H ₂ +CO/g-cat·h) ^a	32.6	24.1	66.4	9.20	32.5
P _{CO₂} · P _{H₂} /P _{CO} · P _{H₂O}					
Weight % of Outlet					
H ₂	3.47	4.59	2.29	5.00	3.54
H ₂ O	1.28	0.83	3.00	1.50	1.39
CO	25.0	46.9	4.30	56.1	23.4
CO ₂	52.9	35.7	65.7	27.1	52.7
Hydrocarbons	15.5	11.1	21.6	8.93	16.3
Oxygenates	0.94	0.66	0.91	0.61	0.89
Wax ^d	0.89	0.18	2.24	0.79	1.76
Yield (g/Nm ³ H ₂ + CO Converted)					
CH ₄	23.8	27.7	28.4	22.6	26.6
C ₂ -C ₄ Hydrocarbons	57.3	65.8	70.1	55.7	59.5
C ₅ -C ₁₁ Hydrocarbons	76.4	70.3	64.4	73.9	64.5
C ₁₂ + Hydrocarbons	24.0	15.0	28.6	32.1	38.8
Wax ^d	9.88	2.80	18.0	14.9	18.5
Oxygenates	10.5	10.4	7.31	11.6	9.33
Total	192	189	199	196	199
1+2 Olefins/n-Paraffin Ratio					
C ₂	0.46	0.66	0.46	0.91	0.52
C ₃	2.62	2.78	2.63	2.75	2.50
C ₄	2.80	3.03	3.23	2.68	2.66
C ₈	1.48	1.65	2.00	1.52	1.70
C ₁₀	1.36	1.58	1.57	1.35	1.42

^a Based on unreduced catalyst

^c Based on reactor volume

^b Maximum axial temperature difference

^d Unanalyzed products collected from hot trap

Table 2 (cont'd). Summary of results for fixed bed run FA-34-0409 .

Period	1	2	3	4	5
Weight % of Hydrocarbons					
CH ₄	13.1	15.5	14.8	12.3	14.0
Ethane	6.71	7.40	7.52	5.84	6.93
Ethylene	2.88	4.57	3.23	4.95	3.36
Propane	3.33	3.60	4.05	2.86	3.42
Propylene	8.32	9.55	10.2	7.50	8.15
n-Butane	2.58	2.75	2.58	2.30	2.45
1+2 Butenes	6.97	8.04	8.05	5.97	6.30
C ₄ Isomers	0.74	0.90	1.00	0.80	0.83
n-Pentane	2.72	3.03	2.78	2.56	2.77
1+2 Pentenes	6.36	9.01	6.44	8.04	6.44
C ₅ Isomers	1.79	2.90	1.75	1.95	1.63
n-Hexane	2.41	2.08	2.32	2.52	1.57
1+2 Hexenes	3.27	2.99	3.16	3.58	2.47
C ₆ Isomers	0.75	0.83	0.96	0.90	0.62
n-Heptane	1.24	1.37	1.44	1.72	1.12
1+2 Heptenes	1.53	1.92	2.35	2.29	1.70
C ₇ Isomers	0.53	0.57	0.66	0.84	0.97
n-Octane	1.82	1.09	1.01	1.45	1.17
1+2 Octenes	2.64	1.75	1.98	2.17	1.95
C ₈ Isomers	2.60	0.64	0.58	0.52	0.76
n-Nonane	2.01	1.28	0.92	1.47	1.32
1+2 Nonenes	2.83	2.07	1.61	2.07	2.01
C ₉ Isomers	0.76	0.42	0.72	0.30	0.90
n-Decane	1.95	1.42	0.85	1.66	1.31
1+2 Decenes	2.62	2.20	1.31	2.20	1.84
C ₁₀ Isomers	0.78	0.37	0.68	0.42	0.47
n-Undecane	1.35	1.25	0.71	1.35	1.17
1+2 Undecenes	1.72	1.82	0.95	1.63	1.46
C ₁₁ Isomers	0.43	0.32	0.48	0.45	0.42
C ₁₂ -C ₄	31.5	36.8	36.6	30.2	31.4
C ₅ -C ₁₁	42.1	39.3	33.6	40.1	34.1
C ₁₂ +	13.3	8.37	14.9	17.4	20.5
Wax ^d	5.44	1.56	9.40	8.09	9.77

^d Unanalyzed wax collected from hot trap

Table 3. Summary of results for fixed bed run FB-25-0029 .

Catalyst: 3.50 g^a, 100/3/0.2
 Catalyst volume: 3.60 cc
 Diluent: 37.40 g, Glass beads
 Diluent Volume: 24.40 cc

Period	1	2	3	4	5	6	7	8	9
Date	1/5/89	1/6/89	1/7/89	1/8/89	1/10/89	1/13/89	1/15/89	1/18/89	1/20/89
Time on Stream (h)	71.5	95.5	112	143	190	264	310	380	429
Balance Duration (h)	6.50	5.80	6.20	6.50	6.50	6.50	6.00	6.00	6.00
Average Temperature (°C)	250	250	235	250	250	250	260	260	250
Maximum Δ Temperature (°C) ^b	5.00	4.00	3.00	3.00	7.00	8.00	8.00	7.00	5.00
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48	1.48	1.48	1.48	1.48
H ₂ /CO Feed Ratio	0.98	0.98	0.98	0.98	0.72	0.72	0.72	0.77	0.98
Space Velocity (NI/g-cat-h) ^a	2.01	3.96	2.01	2.00	2.00	2.00	2.00	1.99	2.00
Space Velocity (NI/g-Fe-h)	2.95	5.82	2.95	2.94	2.94	2.94	2.94	2.92	2.94
GHSV (h ⁻¹) ^c	251	495	251	250	250	250	250	249	250
CO Conversion (%)	89.3	60.1	63.9	91.3	84.5	89.5	97.6	96.2	90.2
H ₂ +CO Conversion (%)	75.7	50.9	53.9	77.9	79.9	84.1	93.0	89.6	76.5
H ₂ /CO Usage	0.69	0.68	0.67	0.69	0.62	0.61	0.63	0.65	0.69
STY (mols H ₂ +CO/g-cat-h) ^a	0.68	0.90	0.48	0.70	0.71	0.75	0.83	0.80	0.68
P _{CO₂} · P _{H₂} /P _{CO} · P _{H₂O}	34.2	20.9	18.0	54.9	71.3	79.5	385	153	39.5
Weight % of Outlet									
H ₂	2.50	3.92	3.79	2.37	1.27	1.15	0.67	0.99	2.46
H ₂ O	2.56	1.22	1.61	1.95	0.44	0.54	0.31	0.71	2.34
CO	10.1	38.1	34.4	8.25	14.5	9.99	2.30	3.68	9.25
CO ₂	62.5	43.4	46.2	65.7	62.8	65.8	72.6	70.8	61.3
Hydrocarbons	20.1	11.7	11.5	19.7	18.3	20.3	22.1	21.4	21.4
Oxygenates	1.38	0.95	1.20	1.23	0.85	0.55	0.28	0.63	0.98
Wax ^d	0.82	0.71	1.38	0.87	1.77	1.78	1.74	1.70	2.28
Yield (g/Nm ³ H ₂ + CO Converted)									
CH ₄	26.7	32.0	29.2	31.5	24.8	22.4	24.1	24.6	30.0
C ₂ -C ₄ Hydrocarbons	62.6	59.9	56.0	68.7	59.9	57.3	69.2	64.1	60.7
C ₅ -C ₁₁ Hydrocarbons	70.9	55.1	52.3	64.9	80.5	88.2	82.7	80.0	78.9
C ₁₂ + Hydrocarbons	26.3	14.5	20.3	12.5	31.5	33.2	18.6	22.5	39.6
Wax ^d	7.32	9.29	16.9	7.52	17.4	16.2	14.2	14.1	20.1
Oxygenates	12.3	12.3	14.8	10.6	8.36	4.98	2.32	5.21	8.64
Total	199	174	173	188	205	206	197	196	218
1+2 Olefins/n-Paraffin Ratio									
C ₂	0.29	0.57	0.55	0.20	0.33	0.28	0.32	0.32	0.29
C ₃	2.90	3.11	2.99	2.63	3.51	3.51	4.15	4.12	3.08
C ₄	2.39	2.54	2.38	2.29	2.91	2.86	3.04	3.61	2.93
C ₈	1.28	1.73	1.49	1.18	1.55	1.47	1.73	1.81	1.46
C ₁₀	0.95	1.40	1.25	0.85	1.20	0.98	1.16	1.31	1.10

^a Based on unreduced catalyst^c Based on reactor volume^b Maximum axial temperature difference^d Unanalyzed products collected from hot trap

Table 3 (cont'd). Summary of results for fixed bed run FB-25-0029 .

Period	1	2	3	4	5	6	7	8	9
Weight % of Hydrocarbons									
CH ₄	14.3	19.8	18.5	17.7	12.7	11.1	12.4	12.9	14.3
Ethane	7.89	7.60	6.93	9.22	5.91	5.46	6.38	6.08	6.32
Ethylene	2.16	4.01	3.53	1.73	1.83	1.42	1.90	1.84	1.72
Propane	3.34	3.39	3.41	4.30	2.78	2.60	2.89	2.73	2.79
Propylene	9.25	10.1	9.71	10.8	9.31	8.72	11.5	10.7	8.20
n-Butane	3.08	3.25	3.38	3.70	2.62	2.58	2.68	2.53	2.41
1+2 Butenes	7.11	7.97	7.77	8.18	7.36	7.13	9.42	8.81	6.81
C ₄ Isomers	0.74	0.78	0.75	0.80	0.63	0.59	0.86	0.82	0.75
n-Pentane	3.25	3.51	3.65	3.77	2.88	2.86	3.28	3.05	2.80
1+2 Pentenes	5.67	7.89	6.66	5.87	5.71	5.62	7.07	6.43	4.84
C ₅ Isomers	0.72	1.13	0.67	1.09	0.73	0.77	1.46	1.55	1.56
n-Hexane	1.94	2.28	1.98	2.22	1.88	2.19	2.41	2.49	2.42
1+2 Hexenes	3.16	4.09	3.75	3.12	4.14	4.25	3.98	3.95	3.43
C ₆ Isomers	0.52	0.83	0.75	0.54	0.59	0.50	0.74	0.69	0.73
n-Heptane	1.91	1.54	1.35	2.02	1.94	2.50	2.15	1.92	2.07
1+2 Heptenes	2.53	2.64	2.38	2.34	3.10	3.94	3.76	3.31	3.03
C ₇ Isomers	0.35	0.66	0.40	0.31	0.36	0.33	0.38	0.44	0.45
n-Octane	2.21	1.11	1.37	2.17	2.18	2.68	2.18	1.91	1.97
1+2 Octenes	2.71	1.93	2.00	2.53	3.32	3.86	3.70	3.39	2.82
C ₈ Isomers	0.45	0.22	0.14	0.26	0.25	0.31	0.45	0.48	0.52
n-Nonane	2.31	0.87	1.29	2.19	2.41	2.60	2.00	1.90	1.79
1+2 Nonenes	2.46	1.25	1.67	2.06	3.18	3.00	2.78	2.68	2.07
C ₉ Isomers	0.20	0.10	0.09	0.20	0.23	0.18	0.35	0.63	0.62
n-Decane	2.10	0.88	1.26	1.81	2.10	2.32	1.58	1.55	1.55
1+2 Decenes	1.96	1.22	1.55	1.52	2.47	2.24	1.81	2.00	1.68
C ₁₀ Isomers	0.22	0.17	0.10	0.19	0.22	0.16	0.29	0.61	0.45
n-Undecane	1.77	0.77	0.94	1.30	1.59	1.98	1.07	1.17	1.31
1+2 Undecenenes	1.33	0.97	1.04	0.87	1.49	1.41	0.88	1.30	1.24
C ₁₁ Isomers	0.17	0.11	0.08	0.18	0.18	0.11	0.17	0.41	0.36
C ₂ -C ₄	33.6	37.1	35.5	38.7	30.4	28.5	35.6	33.5	29.0
C ₅ -C ₁₁	38.0	34.1	33.1	36.5	40.9	43.8	42.5	41.9	37.7
C ₁₂ +	14.1	8.98	12.9	7.06	16.0	16.5	9.56	11.8	19.0
Wax ^d	3.92	5.75	10.7	4.23	8.82	8.06	7.30	7.35	9.62

^d Unanalyzed wax collected from hot trap

Table 4. Effect of Promoters on Catalyst Activity and Selectivity at 250°C, 1.48 MPa, H₂/CO=1, SV=2 Nl/g - cat.h^a.

Run Number	B-3068		B-3208		A-3368		A-2638		A-3058		B-0029		B-3368	
Catalyst ^b	100/0/0		100/0/0.2		100/0/0.5		100/0/1.0		100/3/0		100/3/0.2		100/3/0.5	
Time on Stream (h)	71.5	143.5	71.5	167.5	71.5	168.0	94.5	72.5	167.0	71.5	142.5	428.5	71.5	142.5
H ₂ +CO Conversion (%)	21.4	21.8	30.9	37.8	40.2	53.8	44.4	57.3	60.6	76.0	78.1	76.8	75.9	78.3
CO Conversion (%)	21.3	22.4	37.1	45.0	50.5	61.9	55.0	65.9	70.8	89.3	91.3	90.2	91.0	93.8
HIC Selectivities (wt.%)														
CH ₄	22.6	20.7	14.2	12.3	11.5	9.2	10.3	17.1	16.6	16.7	16.2	15.7	11.6	11.9
C ₂ -C ₄	40.5	39.1	32.2	32.4	25.2	20.8	24.9	37.9	35.6	32.5	29.9	27.4	30.4	32.1
C ₅ -C ₁₁	30.1	32.6	33.9	37.0	29.9	48.3	28.1	32.6	39.5	37.0	37.2	37.4	39.9	40.7
C ₁₂ +	6.8	7.6	19.7	18.3	33.4	21.7	36.7	12.4	8.3	13.8	16.7	19.5	18.1	15.3
CO Conversion to Products (%)														
Hydrocarbons	58.0	59.0	46.1	45.6	45.8	47.5	50.9	50.7	50.4	49.5	47.2	48.5	46.1	45.4
Oxygenates	5.5	4.5	2.7	3.0	2.7	2.3	3.4	2.1	2.3	2.5	2.1	1.8	4.4	5.1
CO ₂	29.2	32.6	48.5	48.7	46.9	48.0	49.1	44.2	47.6	47.2	48.2	48.0	48.2	47.6
Unaccounted	7.3	3.9	2.7	2.7	4.6	2.2	-3.4	3.0	-0.3	0.8	2.5	1.7	1.3	1.9
Olefin Selectivity														
C ₂ -C ₄ (wt.%)	56.7	57.4	71.0	72.2	71.7	72.5	74.0	51.6	50.3	52.0	49.8	54.5	73.8	72.7
C ₅ -C ₁₁ (wt.%)	61.0	61.6	63.0	64.8	67.2	68.2	69.9	54.7	54.5	58.4	56.3	59.4	70.0	69.7
2-Butene/1-Butene	.23	.27	.15	.11	.03	.05	.06	.52	.49	.19	.32	.54	.03	.05

^a Space velocity based on unreduced catalyst

^b Catalyst composition given as parts by weight of Fe/Cu/K

Table 5. Effect of Promoters on Catalyst Activity and Selectivity at 235°C, 1.48 MPa, $H_2/CO=1$, $SV=2 \text{ Nl/g} - \text{cat.h}^a$.

Run Number	B-3068	B-3208	A-3368	A-2638	A-3068	B-0029	B-3368
Catalyst ^b	100/0/0	100/0/0.2	100/0/0.5	100/0/1.0	100/3/0	100/3/0.2	100/3/0.5
Time on Stream (h)	119.0	144.0	144.0	48.0	143.5	119.5	119.5
H_2+CO Conversion (%)	13.4	24.2	29.0	23.5	34.1	53.9	55.4
CO Conversion (%)	13.4	28.1	34.0	30.2	37.9	63.9	68.9
HC Selectivities (wt.%)							
CH_4	20.1	13.8	10.7	9.9	16.8	16.4	10.3
C_2-C_4	38.0	32.6	26.6	23.7	37.4	32.0	29.1
C_5-C_{11}	35.3	35.9	38.7	31.9	35.1	36.3	37.8
$C_{12}+$	6.6	17.7	24.0	34.5	10.7	15.3	22.8
CO Conversion to Products (%)							
Hydrocarbons	64.1	46.8	45.7	44.7	47.8	45.3	43.9
Oxygenates	3.8	3.1	3.5	3.5	4.0	4.4	4.8
CO_2	21.7	46.2	47.2	49.1	42.6	48.3	49.2
Unaccounted	10.4	3.9	3.6	1.7	5.6	2.0	2.1
Olefin Selectivity							
C_2-C_4 (wt.%)	59.8	70.3	70.8	72.9	56.3	57.5	71.4
C_5-C_{11} (wt.%)	61.1	63.4	67.0	63.2	61.2	62.3	65.4
2-Butene/1-Butene	.24	.21	.05	.05	.27	.11	.02

^a Space velocity based on unreduced catalyst

^b Catalyst composition given as parts by weight of Fe/Cu/K

Table 6. Effect of Promoters on Catalyst Activity and Selectivity at 265°C, 1.48 MPa, H₂/CO=1, SV=2 Nl/g - cat.h^a

Run Number	B-3068	B-3208	A-3368	A-2638	A-3068
Catalyst ^b	100/0/0	100/0/0.2	100/0/0.5	100/0/1.0	100/3/0
Time on Stream (h)	95.5	119.5	120.0	144.0	119.0
H ₂ +CO Conversion (%)	35.0	58.6	70.4	72.9	78.6
CO Conversion (%)	36.0	67.4	85.0	88.3	91.3
H/C Selectivities (wt.%)					
CH ₄	22.1	12.1	14.6	11.3	18.0
C ₂ -C ₄	41.5	31.5	31.3	30.2	40.7
C ₅ -C ₁₁	30.2	41.8	34.5	34.8	32.0
C ₁₂ +	6.2	14.6	19.6	23.7	9.3
CO Conversion to Products (%)					
Hydrocarbons	55.8	47.9	47.4	47.0	48.8
Oxygenates	3.9	3.0	2.5	3.0	3.1
CO ₂	41.0	47.3	48.2	48.8	48.2
Unaccounted	-0.7	1.8	1.9	1.2	-0.1
Olefin Selectivity					
C ₂ -C ₄ (wt.%)	55.8	73.5	74.0	77.8	50.8
C ₅ -C ₁₁ (wt.%)	61.4	68.4	72.5	77.1	61.4
2-Butene/1-Butene	.36	.12	.07	.05	.71

^a Space velocity based on unreduced catalyst

^b Catalyst composition given as parts by weight of Fe/Cu/K

Table 7. Effect of Promoters on Catalyst Activity and Selectivity at 250°C, 1.48 MPa, $H_2/CO=1$, $SV=4 \text{ Nl/g-cat.h}^a$.

Run Number	B-3208	A-3368	A-2638	A-3068	B-0029	B-3368
Catalyst ^b	100/0/0.2	100/0/0.5	100/0/1.0	100/3/0	100/3/0.2	100/3/0.5
Time on Stream (h)	94.5	94.5	119.0	95.5	95.5	95.5
H_2+CO Conversion (%)	18.3	21.9	26.3	41.1	50.9	52.6
CO Conversion (%)	21.9	27.9	32.2	44.5	60.1	64.5
HC Selectivities (wt.%)						
CH_4	16.8	13.9	10.8	19.2	18.6	11.6
C_2-C_4	35.3	30.1	26.2	40.0	34.7	30.9
C_5-C_{11}	37.6	34.3	29.5	34.6	36.6	40.0
$C_{12}+$	10.3	21.7	33.5	6.2	10.1	17.5
CO Conversion to Products (%)						
Hydrocarbons	44.7	43.2	45.1	49.7	44.7	43.8
Oxygenates	2.2	2.5	3.0	2.1	2.8	3.5
CO_2	47.4	45.9	47.6	44.5	48.3	49.8
Unaccounted	5.7	8.4	4.3	3.7	4.2	2.9
Olefin Selectivity						
C_2-C_4 (wt.%)	70.6	71.6	74.2	53.0	57.6	74.1
C_5-C_{11} (wt.%)	66.7	67.1	68.7	57.7	65.4	69.7
2-Butene/1-Butene	.13	.06	.04	.45	.14	.03

^a Space velocity based on unreduced catalyst

^b Catalyst composition given as parts by weight of Fe/Cu/K

Table 8. Chain growth probability factors
(Fixed bed data at 250°C, 1.48 MPa, $H_2/CO=1$, $SV=2 \text{ NI/g} - \text{cat.h}^a$)

	1	2	3	4	5	6	7
Catalyst	α_I			α_{II}			ξ
	C_3-C_7	Asymptotic	2- α Model	Asymptotic	2- α Model	β	
100Fe ^b	0.56	0.60	-	-	-	-	-
100Fe/0.2K	0.65	0.67	0.61	0.77	0.84	0.88	9.9
100Fe/0.5K	0.68	0.73	0.68	0.93	0.94	0.96	16.3
100Fe/1.0K	0.65	0.74	0.66	0.88	0.88	0.88	11.6
100Fe/3Cu	0.62	0.65	0.63	0.86	0.91	0.99	17.6
100Fe/3Cu/0.2K	0.63	0.72	0.62	0.77	0.79	0.76	8.2
100Fe/3Cu/0.5K	0.72	0.70	0.69	0.82	0.93	0.98	20.2

^a Based on unreduced catalyst

^b Data at 1 NI/g - cat.h

Table 9. Chain growth probability factors for Run SA-99-0888^a
(Ruhchemie LP-33/81 catalyst, 100Fe/5Cu/4.2K/25SiO₂)

TOS (h)	T (°C)	SV (Nl/g - cat.h) ^b	α_i	α_{ii}
95	250	2	0.75	0.91
385	250	4	0.77	0.92
482	235	2	0.71	0.89
619	250	2	0.73	0.90

^a All data are at 1.48 MPa, (H₂/CO)=0.67
^b Based on unreduced catalyst

Figure 1. Promoter effects on catalyst activity and stability; (a) Effect of temperature on (H₂ + CO) conversion; (b) Stability plot, (H₂ + CO) conversion vs. time on stream.

Figure 2. Effect of promoter type and temperature on CO₂ selectivity (i.e., water-gas-shift activity).

Figure 3. Promoter effects on hydrocarbon distribution (250°C, 1.48 MPa, H₂/CO = 1, SV = 2 Nl/g-cat.h; catalyst composition given as parts by weight of Fe/Cu/K).

Figure 4. Promoter effects on hydrocarbon distribution (250°C, 1.48 MPa, H₂/CO = 1, SV = 2 NL/g-cat.h; catalyst composition given as parts by weight of Fe/Cu/K).

Figure 5. Effect of temperature on hydrocarbon distribution
(1.48 MPa, H₂/CO = 1, SV = 2 NL/g-cat.h)

Figure 6. Promoter effect on olefin content at different carbon numbers.

Figure 7. Effect of promoter type and temperature on olefin content.

Figure 8. Anderson-Schulz-Flory plots for catalysts promoted with Cu and 0, 0.2 or 0.5 parts K (250°C, 1.48 MPa, $H_2/CO = 1$, $SV = 2 \text{ Nl/g-cat.h}$).

Figure 9. Time on stream effects on slurry wax composition.

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