DOE/PC/80011-T9 10-T

DEVELOPMENT AND PROCESS EVALUATION OF
IMPROVED FISCHER-TROPSCH SLURRY CATALYSTS

DOE/PC/80011--T9 2.

DE92 016988

9th

QUARTERLY TECHNICAL PROGRESS REPORT
FOR THE PERIOD [1 OCTOBER TO 31 DECEMBER 1988]

1.88

4Q/88

by

Howard P. Withers

Air Products and Chemicals, Inc.

Allentown, PA 18195

and

Dragomir B. Bukur and Michael P. Rosynek

Departments of Chemical Engineering and Chemistry

Texas A&M University

College Station, TX 77843

WORK PERFORMED UNDER DOE CONTRACT NO. DE-AC22-85PC80011

FOR THE UNITED STATES DEPARTMENT OF ENERGY

THE PITTSBURGH ENERGY TECHNOLOGY CENTER

PITTSBURGH, PENNSYLVANIA

MASTER

OK

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, mark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Project Manager - George Cinquegrane
Liquid Fuels Division
Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania

Program Manager - John Shen
Office of Coal Preparation & Liquefaction
Department of Energy
Washington, DC

I. ABSTRACT

Seven fixed bed catalyst tests were completed. These tests were conducted to study promoter effects using stable H_2 reduced catalysts. Copper promoter alone improved catalyst activity and selectivity (less methane, more $C_{12}+$). Potassium had the same effect and catalyst activity increased as the level of potassium increased. Copper had a stronger effect on activity than potassium, which is believed to be due to the reduction enhancement provided by copper. Potassium had the strongest effect on catalyst selectivity. A doubly promoted catalyst showed that activity benefited from both copper and potassium, while selectivity seemed to be governed primarily by potassium.

The Fischer-Tropsch (FT) and water-gas shift (WGS) kinetics for four previous slurry runs have been determined. We found that the best rate expression depends on each particular catalyst. At low conversions, first order in H_2 kinetics are adequate for Fischer-Tropsch. At higher conversions, water and/or CO_2 inhibition may become important and a Langmuir-Hinshelwood rate expression is best. Water inhibits the reaction more strongly than does CO_2 , but good WGS activity will consume most of the water to produce CO_2 . For the WGS reaction, first order in CO or mass action kinetics were found to adequately correlate the data.

A single slurry reactor run was completed, using H_2 reduced 100 Fe/3.0 Cu/0.2 K catalyst. Only three mass balances were completed, and the run was terminated after 2.15 h due to severe catalyst deactivation. The initial activity of the catalyst was good, but wax withdrawals caused catalyst catalyst deactivation. After the run, we found that the withdrawals caused catalyst to cling to the reactor wall and settle on an internal wax filter.

Wax and catalyst recoveries for eight slurry runs (seven previous runs and one conducted in the past quarter), and related experimental procedures have been discussed. Wax recoveries for all runs appeared acceptable, however, it was not always possible to accurately estimate the catalyst recovery since catalyst composition changes during synthesis. Particle size distributions for used catalyst from some of the runs have been determined. The results show that used catalyst particles are significantly smaller than the original calcined catalyst.

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

Seven catalyst tests in fixed bed reactors have been completed during the past quarter. These tests were made to study the effect of promoters (copper and potassium) on catalyst performance. Hydrogen reduced catalyst was used in all tests. Previously, we studied the effect of promoters using CO reduced catalyst (Technical Progress Report for the period 1 July-30 September 1987), but the CO reduced catalysts often deactivated, masking the true effect of the promoters. The intent of our recent tests was to reinvestigate promoters with the more stable H₂ reduced catalysts.

The catalysts tested were: unpromoted precipitated iron, 100 Fe/3.0 Cu, 100 Fe/0.2, 0.5, and 1.0 K, and 100 Fe/3.0 Cu/0.2 K. Copper promoter alone improved catalyst activity for Fischer-Tropsch (FT) and the water-gas shift (WGS) reactions, as the (H₂+CO) conversions and the $P_{CO_2}P_{H_2}/P_{CO}P_{H_2O}$ ratios were higher than with the unpromoted catalyst. Copper also improved catalyst selectivity, with less methane and more C₁₂+ products than with the unpromoted catalyst. Potassium also improved catalyst activity, and the activity of the catalyst increased with higher potassium loadings. Methane was strongly suppressed by potassium, and selectivity shifted towards higher molecular weight products with increasing potassium levels. The activity of the doubly promoted catalyst (100 Fe/3.0 Cu/0.5 K) benefited from both promoters, and was higher than either of the singly promoted catalysts (100 Fe/3.0 Cu or 100 Fe/0.5 K). The selectivity of the 100 Fe/3.0 Cu/0.5 K catalyst appeared to be determined mostly by potassium.

The behavior of these H₂ reduced catalysts is believed to be related to the promoter's effect on catalyst reduction. Copper facilitates the reduction, and the catalyst is fully activated throughout the synthesis test. Potassium has an inhibiting effect on catalyst reduction (using H₂), preventing the K-containing catalysts from complete activation prior to the synthesis tests. All of the singly potassium promoted catalysts showed significant increases in activity with time on stream, while the copper-containing catalysts' activity remained more stable with time.

- Slurry Reactor Kinetics

We have used a number of kinetic equations for the FT and WGS reactions to analyze data from four previous slurry runs: SA-05-2957 (100 Fe/0.3 Cu/0.2 K), SB-07-0458 (H_2 reduced 100 Fe/0.3 Cu/0.5 K), SA-99-0888 (Ruhrchemie LP 33/81), and SB-66-2468 (100 Fe/5.0 Cu/4.2 K/24 SiO_2). Simple, first order rate expressions were used for both reactions, as well as more complex non-linear Langmuir-Hinshelwood type equations.

The best rate form for FT kinetics varied with the different catalysts. The 100 Fe/0.3 Cu/0.2 K catalyst showed rate inhibition by both water and CO_2 . A rate model which included inhibition by both species accurately described the experimental results, and was the best rate expression for this catalyst. Water or CO_2 inhibition were not important for the Ruhrchemie catalyst, which was probably due to the low H_2+CO conversions obtained from this catalyst. A first order in H_2 FT rate expression adequately correlated the data. The apparent activation energy of the FT reaction for both catalysts was 86 kJ/mol , which is in good agreement with values reported previously in the literature. The 100 Fe/5.0 Cu/4.2 K/24 SiO_2 catalyst was tested at a single temperature (250°C) and had an FT activity between the 100 Fe/0.3 Cu/0.2 K and Ruhrchemie catalysts. Using the 100 Fe/0.3 Cu/0.5 K catalyst, CO_2 inhibition was not important, and the best FT rate expression included only water in its denominator. The FT activation energy for this catalyst was 102 kJ/mol , which is within the range expected.

The kinetics of the WGS reaction were also studied, and it was found that a rate expression based on mass action kinetics gave the best fit to our data for the 100 Fe/0.3 Cu/0.2 K and Ruhrchemie catalysts. A simple first order in CO rate form gave the best description for the 100 Fe/5.0 Cu/4.2 K/24 SiO_2 and 100 Fe/0.3 Cu/0.5 K catalysts. The 100 Fe/0.3 Cu/0.2 K catalyst was the most active for the WGS reaction of the four catalysts tested, and the WGS was closer to equilibrium at similar process conditions than with the other two catalysts. The WGS activation energy was 132 kJ/mol for the 100 Fe/0.3 Cu/0.2 K and 100 Fe/0.3 Cu/0.5 K catalysts, and 137 kJ/mol for the Ruhrchemie catalyst.

- Slurry Reactor Catalyst Test

A single slurry reactor run was completed, using H₂ reduced 100 Fe/3.0 Cu/0.2 K catalyst. This run was initiated as a long term stability test, but rapid irreversible catalyst deactivation occurred during the run. Three mass balances were completed, and the run was terminated after approximately 245 h. The catalyst initially showed good activity, with an (H₂+CO) conversion of 77.2 % during the first mass balance (260 °C, 1.48 MPa, 2.0 Nl/g-cat·h, H₂/CO= 0.67). However, following wax withdrawals after the first balance, catalyst activity declined steadily. During the second and third balances at the same nominal process conditions, the (H₂+CO) conversion dropped to 37.6 and 15.2 %, respectively. The catalyst deactivation is thought to be due to the wax withdrawals. We found that during withdrawals, significant amounts of catalyst (~ 14 % of the charge) were deposited on the reactor wall and an internal filter used to remove wax.

- Wax and Catalyst Recoveries

The various procedures used to withdraw accumulated product wax from the slurry reactors are presented. Wax and catalyst recoveries for eight slurry bed tests (seven previous runs and one conducted in the past quarter) have been discussed. Wax recoveries were fairly good for all runs, with the weight of wax recovered from the reactor at the end of the run being between 90-106 % of the weight charged. It was not possible to estimate catalyst recoveries accurately for all runs, since the iron in the catalyst undergoes changes during the reduction and synthesis processes, effectively changing the weight of the catalyst. However, when used catalyst from one run was thermally treated (kept in an oven at 600 °C for 12 hours) and subsequently oxidized over a flame, the weight of catalyst recovered corresponded to about 81% of the amount of catalyst charged. The losses are mainly due to incomplete removal of solids at the end of the run (sticking to the walls and other internals), and losses during the wax/catalyst separation procedures. Particle size distributions for thermally treated used catalyst were determined using image analysis. These results indicate a significant reduction in the catalyst particle size during the run, and partly during the thermal treatment of the used catalyst.

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

The goal of this task was to study the effect of promoters, namely copper and potassium, on the activity and selectivity of iron Fischer-Tropsch catalysts. We studied the effect of promoters on catalyst performance previously with CO reduced catalysts, (Technical Progress Report for the period 1 July–30 September 1987). Deactivation was often observed during these runs, masking the effect of process variables on catalyst activity and selectivity. Our studies of pretreatment conditions on catalyst behavior (Technical Progress Report for the period 1 October–31 December 1987) showed that activations in pure CO or syngas resulted in catalysts with high activity and good selectivity towards high molecular weight products. However, these catalysts always deactivated during synthesis testing. On the contrary, H₂ reduced catalysts exhibited good stability, but favored production of methane and other lighter hydrocarbons. Therefore, we have decided to employ an H₂ activation procedure for a new series of promoter effect tests in fixed bed reactors.

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 H₂ 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-cat·h) at 1.48 MPa using H₂/CO = 1.0 (nominal) feed gas, on conversion and product distribution were studied during seven runs. Catalyst performance with no promoters was studied in a run using pure precipitated Fe (FB-00-3068), and the effect of copper alone was studied in a run using 100 Fe/3.0 Cu (FA-34-3068). The effect of potassium promoter was studied in four runs: 100 Fe/0.2 K (FB-45-2638, FB-45-3208), 100 Fe/0.5 K (FA-46-3368).

100 Fe/1.0 K (FA-47-2638). Also, a doubly promoted catalyst, 100 Fe/3.0 Cu/0.5 K (FB-27-3368), was tested to evaluate the synergistic effect of copper and potassium. 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 460 h), and included conditions using $H_2/CO = 0.72$ feed gas.

2.1.1. Run FB-00-3068 (Unpromoted Fe)

Table 1 lists the results of the mass balances carried out during run FB-00-3068 using the unpromoted precipitated iron catalyst. There was no apparent deactivation observed during the run. The (H_2+CO) conversion during the first balance (71.5 h, 249 °C, 2.00 Nl/g-cat·h) was 21.7 %, and during the fourth balance (144 h) at the same nominal conditions was 22.0 %. Catalyst selectivity between the two balances was essentially the same. For example, methane decreased slightly between the two balances, from 26.7 to 24.2 %, while the $C_{12}+$ product fraction increased from 6.4 to 7.2 %. The high selectivity towards methane was expected for the H_2 reduced catalyst. The olefin/paraffin ratios did not change with time. The largest difference was the C_8 ratio, which only increased slightly, from 1.07 to 1.27.

The effect of reaction temperature at 2.0 Nl/g-cat·h was studied in balances 3 (235 °C), 1 or 4 (250 °C), and 2 (265 °C). Catalyst activity increased with temperature, as expected, with the (H_2+CO) conversion increasing from 13.7 (235 °C) to 35.1 % (265 °C). However, catalyst selectivity remained relatively constant at the three temperatures. While there was an increase in the C_2-C_4 products from 35.2 to 41.1 % between 235 and 265 °C, the CH_4 fraction actually decreased from 25.9 to 23.0 %. However, these differences are not that significant, and the trends were not regular. Similarly, the olefin/paraffin ratios were stable with temperature as well. While the C_2 ratio decreased from 0.70 at 235 °C to 0.45 (250 °C) and 0.37 (265 °C), the ratios at other carbon numbers did not show any significant change with temperature.

Catalyst selectivity did not change appreciably with space velocity either, which was varied

in balances 5 (1.0 Nℓ/g-cat·h) and 1 or 4 (2.0 Nℓ/g-cat·h). The weight % of the C₁₂+ products increased with space velocity, from 4.0 % in balance 5 to 7.2 % in balance 4, which was a large relative change, but the other product fractions were less sensitive: 22.9 (CH₄), 43.0 (C₂-C₄), and 30.1 % (C₅-C₁₁) at 1.0 Nℓ/g-cat·h, compared to 24.2, 37.4, and 31.2 %, respectively, at 2.0 Nℓ/g-cat·h. The olefin/paraffin ratios were stable, although there was a small, regular increase in the ratios with space velocity. This observation is consistent with secondary hydrogenation of olefins.

2.1.2. Run FA-34-3068 (100 Fe/3.0 Cu)

The summary of results for the five mass balances carried out during the test of the singly copper promoted catalyst, 100 Fe/3.0 Cu (run FA-34-3068), is listed in Table 2. Catalyst activity increased slightly with time, and between balance 1 (72.5 h) and balance 5 (167 h), both at 250 °C, 2.0 Nℓ/g-cat·h, the (H₂+CO) conversion increased from 57.3 to 60.5 %. The CH₄ and C₂-C₄ product fractions were about the same as well, 16.6 and 38.1 % during balance 1 and 15.8 and 36.0 % during balance 5. Some shifting occurred between the C₅-C₁₁ and C₁₂+ products between the two balances: during balance 1 the C₅-C₁₁ and C₁₂+ distribution were 32.8 and 12.5 %, respectively, while in balance 5 the C₅-C₁₁ products increased to 39.8 % and the C₁₂+ products decreased to 8.4 %. The olefin/paraffin ratios were essentially the same between the two balances.

The effect of temperature was studied in balances 4 (235 °C), 1 or 5 (250 °C), and 3 (265 °C). Temperature had an unexpected effect on CH₄ selectivity, which decreased with temperature: 19.4 % at 235 °C to 16.6 (balance 1, 250 °C) and 15.8 % (265 °C). The C₂-C₄ products increased with temperature, as expected: 36.2 (235 °C), 38.1 (250 °C), and 41.9 % (265 °C), which was not a dramatic change, and the C₅-C₁₁ products remained constant, varying between 32.8-34.0 at the three temperatures. The C₁₂+ products initially increased from 10.5 to 12.5 % as the temperature increased from 235 to 250 °C, then decreased to 9.5 % at 265 °C. The C₃ and C₄ olefin/paraffin ratios were stable with temperature at 2.36-2.73, while the C₂, C₈, and C₁₀ ratios behaved erratically. For example, the C₂ ratios decreased with temperature, 0.48, 0.26, and 0.22

at 235, 250, and 265 °C, while the C₁₀ ratios were 1.12, 0.85, and 2.04 at the same temperatures. These variations in the olefin/paraffin ratios may be caused by errors in sample analysis.

Space velocity (2.0 Nℓ/g-cat·h in balance 1 and 4.0 Nℓ/g-cat·h in balance 2 at 250 °C) caused some changes in the CH₄ and C₁₂+ product selectivity. As the space velocity increased from 2.0 to 4.0, CH₄ increased from 16.6 to 20.2 % and C₁₂+ decreased from 12.5 to 6.2 %. The C₂-C₄ and C₅-C₁₁ selectivities were about the same at each space velocity, changing from 38.1 (C₂-C₄) and 32.8 % (C₅-C₁₁) to 39.5 and 34.1 %, respectively. The olefin/paraffin ratios were approximately equal or slightly higher at the higher space velocity.

2.1.3. Run FB-45-2638 (100 Fe/0.2 K)

The results of the five mass balances carried out during run FB-45-2638 using the 100 Fe/0.2 K catalyst are summarized in Table 3. Catalyst activity increased during the run, and the (H₂+CO) conversion at 235 °C increased from 13.9 % during balance 1 (48 h) to 24.5 % during the repeat in balance 5 (168 h). The hydrocarbon distribution between the two balances was roughly the same: 17.5 (CH₄), 29.2 (C₂-C₄), 32.3 (C₅-C₁₁), and 20.9 % (C₁₂+) during balance 1 and 16.0, 31.7, 33.0, and 19.3 %, respectively, during balance 5. The C₂ olefin/paraffin ratio decreased slightly from 1.16 to 0.99 between the two balances, while the olefin/paraffin ratios at other carbon numbers generally increased.

Temperature had only a weak effect on the hydrocarbon distribution between 235 and 250 °C, but the increase to 265 °C decreased CH₄ from 17.6 (balance 2, 250 °C) to 14.6 % and the C₁₂+ products from 17.8 to 13.9 %, with an increase in the C₂-C₄ (30.8 to 34.5 %) and C₅-C₁₁ (33.8 to 37.0 %) products. The trend in CH₄ selectivity was unexpected as the methane yield usually increases with temperature, however, the remaining product groups follow the expected trends with temperature. The olefin/paraffin ratios at 235 and 250 °C were also similar, and the largest change with temperature occurred between 250 and 265 °C, with an overall increase in the olefin/paraffin ratio at the higher temperature. At 250 °C the C₃, C₄, C₈, and C₁₀ ratios were 3.68, 3.07, 1.68,

and 1.27, while at 265 °C they were higher at 4.69, 4.06, 2.26, and 2.05, respectively. The C₂ olefin/paraffin ratio was approximately the same, 1.07 (250 °C) and 0.92 (265 °C).

An increase in space velocity from 2.0 to 4.0 Nℓ/g-cat·h at 250 °C (balances 2 and 3) increased the C₂-C₄ products from 30.8 to 34.1 % and decreased the C₁₂+ products from 17.8 to 15.4 %, which are relatively minor changes. The CH₄ and C₅-C₁₁ fractions were similar at both space velocities. The higher space velocity increased the olefin/paraffin ratios moderately. For example, the C₃ ratio increased from 3.15 (2.0 Nℓ/g-cat·h) to 3.68 (4.0 Nℓ/g-cat·h), and the C₈ ratio increased from 1.51 to 1.68. There was a slight decrease in the C₁₀ ratio, from 1.55 to 1.27 as the space velocity increased, but this can be attributed to analytical errors in the C₁₀ products.

2.1.4. Run FB-45-3208 (100 Fe/0.2 K)

This run was made as a repeat of FB-45-2638. In run FB-45-2638, the first balance was made at 235 °C and 2.0 Nℓ/g-cat·h, and catalyst activity increased with time (the conversion increased from 13.9 to 24.5 % between balances 1 and 5 over 120 h). Run FB-45-3208 employed a higher temperature (250 °C) during the first set of conditions in order to determine if the sequence of experimental conditions used during a test had any effect on catalyst activity and selectivity behavior. Table 4 summarizes the results of the five mass balances carried out during this run.

Catalyst activity increased during run FB-45-3208 as well, with the conversion increasing from 31.1 % during balance 1 (71.5 h) to 38.0 % during balance 5 (168 h). However, this increase in activity is less than that obtained in the previous run, where the (H₂+CO) conversion nearly doubled over about the same time interval. It appears that in the earlier run FB-45-2638, the catalyst did not achieve its ultimate activity until balance 3. During balance 2 of FB-45-2638 the (H₂+CO) conversion was measured at 30.9 %, which is in agreement with the conversion obtained during balance 1 of run FB-45-3208 at the same nominal conditions. However, we know from the results of balance 5 of FB-45-3208 that catalyst activity was still increasing during balance 1. In balance 3 of run FB-45-2638 (119 h, 250 °C, 4.0 Nℓ/g-cat·h) the (H₂+CO) conversion was 18.7

%, compared to the 18.6 % conversion obtained in FB-45-3208 during balance 2 (94.5 h) at the same conditions, thus by this time (balance 3 of FB-45-2638 and balance 2 of FB-45-3208) the catalyst in both runs appears to have reached the same activity level.

The hydrocarbon distribution did not show any effect of time (activity) for the two tests of this catalyst. The distribution in run FB-45-3208 was the same during the first and fifth balances: 16.7 (CH₄), 31.2 (C₂-C₄), 32.9 (C₅-C₁₁), and 19.2 % (C₁₂+) in balance 1 and 14.8, 31.4, 35.9, and 17.9 %, respectively, in balance 5. Furthermore, these distributions are very similar to the results obtained during balance 2 of run FB-45-2638 at the same conditions: 17.6, 30.8, 33.8, and 17.8 %. The hydrocarbon distributions at other process conditions were also similar for the two runs. The olefin/paraffin ratios increased slightly with time, which was also seen in run FA-45-2638. Between the first and fifth balances, for example, the C₂ and C₃ ratios increased from 1.75 and 3.68 to 1.84 and 3.86. Between the two runs, the C₂ ratios were consistently higher in run FB-45-3208 than in run FB-45-2638. The C₂ ratio varied between 0.89-1.16 in all balances of FB-45-2638, while in FB-45-3208 the range was 1.72-1.84. However, the ratios at other carbon numbers were similar or did not show any trends between runs.

Between 235 and 250 °C, the hydrocarbon product distributions were similar in run FB-45-3208 except for CH₄, which decreased from 18.3 % at 235 °C to 14.8 % at 250 °C. At 265 °C, CH₄ decreased further to 12.6 %. This decrease in CH₄ selectivity with temperature does not follow the expected trend with temperature. The selectivity of C₂-C₄ products, 31.3 % at 265 °C, was about the same as at the lower temperatures, and that of the C₅-C₁₁ products increased from 35.9 % at 250 °C (balance 5) to 41.5 % at 265 °C. Between the same balances, the C₁₂+ products showed a slight decrease from 17.9 to 14.6 %. The olefin/paraffin ratios increased as the temperature increased. For example, the C₃ ratios increased from 3.54 (235 °C) to 3.86 (250 °C, balance 5) and 4.53 (265 °C). The ratios at other carbon numbers behaved similarly.

The 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 decreased the amount of C₁₂+ products formed significantly, dropping from 19.2 % (balance 1, 2.0 Nℓ/g-cat·h) to 9.7 % (4.0 Nℓ/g-cat·h). The remaining fractions were all higher at the higher space velocity: 21.5 (CH₄), 33.3 (C₂-C₄), and 35.5 % (C₅-C₁₁) at 4.0 Nℓ/g-cat·h from 16.7, 31.2, and 32.9 %, respectively, at 2.0 Nℓ/g-cat·h. The olefin/paraffin ratios were about the same or slightly higher at the higher space velocity.

2.1.5. Run FA-46-3368 (100 Fe/0.5 K)

Table 5 summarizes the results of five mass balances carried out during run FA-46-3368 using the 100 Fe/0.5 K catalyst. Catalyst activity increased with time, and the (H₂+CO) conversion increased from 40.4 % in balance 1 (71.5 h, 250 °C, 2.0 Nℓ/g-cat·h) to 49.4 % in balance 5 (168 h) at the same nominal conditions. Catalyst selectivity was also different between the two balances. In balance 1, the distribution was 12.7 (CH₄), 24.8 (C₂-C₄), 29.5 (C₅-C₁₁), and 33.0 % (C₁₂+), while during balance 5, CH₄ remained about the same, 12.2 %, the C₂-C₄ and C₅-C₁₁ products increased to 29.6 and 36.2 %, and the C₁₂+ products decreased to 21.9 %. The olefin/paraffin ratios were about the same between the two balances. The C₂ ratio decreased, from 1.99 to 1.21, as did the C₁₀ ratio, while the C₃, C₄, and C₈ ratios all showed a slight increase.

Temperature had only a moderate effect on the hydrocarbon distribution, and the percentages varied between 12.2-12.8 (CH₄), 26.1-32.1 (C₂-C₄), 35.2-38.0 (C₅-C₁₁), and 19.9-21.9 % (C₁₂+) during balances 4 (235 °C), 5 (250 °C), and 3 (265 °C). The C₂ and C₈ olefin/paraffin ratios decreased with temperature, for example, C₂ was 2.07 at 235 °C and decreased to 1.21 and 1.09 at 250 and 265 °C. The C₃ and C₄ ratios increased with temperature, and the C₁₀ ratio was somewhat erratic, probably due to analytical errors.

Space velocity (balances 1 and 2 at 250 °C) had a strong effect on the product distribution, which is not the expected behavior. Methane increased with space velocity, from 12.7 % (2.0 Nℓ/g-cat·h) to 17.2 % (4.0 Nℓ/g-cat·h), and the C₂-C₄ and C₅-C₁₁ products also increased from 24.8 and 29.5 % to 28.9 and 33.0 %, respectively. These increases with space velocity caused the C₁₂+

products to decrease correspondingly, from 33.0 % (2.0 Nℓ/g-cat·h) to 20.9 % (4.0 Nℓ/g-cat·h). Taking into account the effect of time (*i.e.*, comparing balances 5 and 2) methane still shows an increase at higher space velocity and the C₅-C₁₁ products decrease. The C₂-C₄ and C₁₂+ products were the same at the two space velocities. The olefin/paraffin ratios between balances 1 and 2 were very similar, and no significant change with space velocity was observed.

2.1.6. Run FA-47-2638 (100 Fe/1.0 K)

The summary of results for the five mass balances carried out during run FA-47-2638 using 100 Fe/1 K are shown in Table 6. The (H₂+CO) conversion increased from 22.7 (48 h, balance 1) to 36.9% (169 h, balance 5) as catalyst activity increased during the run. The hydrocarbon distribution between the two balances was very similar: 9.2 (CH₄), 24.1 (C₂-C₄), 34.3 (C₅-C₁₁), and 32.4 % (C₁₂+) during balance 1 compared to 9.3, 27.1, 31.1, and 32.5 % during balance 5. The C₂ olefin/paraffin ratio decreased with time, from 2.46 to 2.07 between the two balances. The ratios at other carbon numbers increased, for example, C₃ increased from 3.31 to 3.55.

Temperature had a minor effect on the hydrocarbon distribution between 235 (balance 5) and 250 °C (balance 2). Methane increased from 9.3 to 11.0 % over this temperature rise, and the C₂-C₄ products increased an insignificant amount, from 27.1 to 28.7 %. The C₅-C₁₁ products were unchanged, and the C₁₂+ products decreased slightly from 32.5 to 29.2 %. Increasing the temperature further to 265 °C increased the CH₄, C₂-C₄, and C₅-C₁₁ products to 11.7, 30.1, and 34.6 %, with a decrease in the C₁₂+ products to 23.6 %. This trend to lower molecular weight products at higher temperatures is normally expected, however, in most of the other tests in this series of H₂ reduced catalysts, this has not occurred. The C₂ olefin/paraffin ratio was relatively stable with temperature, 2.07, 2.21, and 2.06 at 235, 250, and 265 °C, respectively, while the other ratios tended to increase at higher temperatures. C₃ increased from 3.55 to 4.15 and 6.32 as the temperature increased, for instance.

The effect of space velocity, studied in balances 2 (2.0 Nℓ/g-cat·h) and 3 (4.0 Nℓ/g cat·h)

was found to be a mild shift towards higher molecular weight products. The CH_4 , $\text{C}_2\text{-C}_4$, and $\text{C}_5\text{-C}_{11}$ products decreased from 11.0, 28.7, and 31.1 % at 2.0 $\text{Nl/g-cat}\cdot\text{h}$ to 9.9, 26.4, and 29.8 % at 4.0 $\text{Nl/g-cat}\cdot\text{h}$. The $\text{C}_{12}+$ products increased correspondingly, from 29.2 to 33.8 %. The olefin/paraffin ratios between the two balances were comparable, with some shifts in the C_8 and C_{10} products. For example, C_{10} increased from 2.04 to 2.58 with higher space velocity, while C_8 decreased from 1.74 to 1.42.

2.1.7. Run FB-27-3368 (100 Fe/3.0 Cu/0.5 K)

The summary of results of nine mass balances carried out during run FB-27-3368 with the doubly promoted 100 Fe/3.0 Cu/0.5 K is given in Table 7. The first four balances of this run were made using a $\text{H}_2/\text{CO} = 0.98$ to obtain the same nominal process conditions as the other promoter effect catalyst tests. A repeat of the initial conditions using the 0.98 feed gas was made during balances 4 and 9. Balances 5-8 used a $\text{H}_2/\text{CO} = 0.72$ feed gas in order to study the effect of feed ratio on catalyst performance. Also, the temperature (260°C) used during balances 7 and 8 allows us to compare results to those of Mobil.

The catalyst initially became slightly more active with time, and the $(\text{H}_2 + \text{CO})$ conversion at 250°C , 2.0 $\text{Nl/g-cat}\cdot\text{h}$, $\text{H}_2/\text{CO} = 0.98$ during balance 1 (71.5 h) was 75.8 %, while during balance 4 (143 h) at the same conditions it was slightly higher, 78.2 %. By the end of the run (balance 9, 457 h, same conditions as balances 1 and 4) catalyst activity declined, and the conversion was 69.5 %. Time did not have a significant effect on the hydrocarbon distribution between balances 1 and 4, and the largest change occurred for the $\text{C}_{12}+$ products, 18.2 % in balance 1 dropping to 15.6 % in balance 4. However, a shift towards lower molecular weight products was seen during balance 9, with an increase in the $\text{C}_2\text{-C}_4$ and a decrease in the $\text{C}_{12}+$ products. During balance 1, the distribution was 10.5 (CH_4), 30.8 ($\text{C}_2\text{-C}_4$), 40.4 ($\text{C}_5\text{-C}_{11}$), and 18.2 % ($\text{C}_{12}+$), while during balance 9 methane and $\text{C}_5\text{-C}_{11}$ products were about the same, 11.0 and 42.0 %, respectively, but the $\text{C}_2\text{-C}_4$ products increased to 36.7 % and the $\text{C}_{12}+$ products decreased to 10.4 %. The C_2

olefin/paraffin ratio decreased with time: 2.00 in balance 1 to 1.71 and 1.38 in balances 4 and 9. The ratios at other carbon numbers did not show any significant changes, and varied 4.16–4.60 (C_3), 3.18–3.43 (C_4), 2.17–2.53 (C_8), and 1.91–2.29 (C_{10}) between the three balances.

Temperature had a moderate effect on the hydrocarbon distribution. At 235 °C, $H_2/CO = 0.98$ (balance 3) the distribution was 11.1 (CH_4), 28.8 (C_2-C_4), 37.5 (C_5-C_{11}), and 22.7 % ($C_{12}+$). At 250 °C (balance 4), CH_4 decreased a very small amount to 10.5 %, and $C_{12}+$ decreased as well to 15.6 %. Both C_2-C_4 and C_5-C_{11} increased, to 32.7 and 41.2 %. Using the $H_2/CO = 0.72$ feed gas, raising the temperature from 250 (balance 6) to 260 °C (balance 7) gave similar trends, although the changes in selectivity were not too significant: CH_4 decreased from 8.6 to 7.9 %, C_2-C_4 was unchanged at 29.8 %, C_5-C_{11} increased from 41.8 to 44.1 %, and $C_{12}+$ decreased from 19.8 to 18.3 %.

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 (H_2+CO) conversion slightly, from 78.2 ($H_2/CO = 0.98$) to 79.9 % ($H_2/CO = 0.72$). The most significant change came in the hydrocarbon distribution, as the lower feed ratio favored production of higher molecular weight compounds. Methane and the C_2-C_4 products decreased to 7.4 and 25.6 %, respectively, when the lower feed ratio was used, compared to the 10.5 and 32.7 % obtained using the $H_2/CO = 0.98$ feed. The $C_{12}+$ products increased to 25.3 % from 15.6 %. The olefin/paraffin ratios using the different feed ratios were similar, although the ratios obtained using the lower feed ratio were consistently higher than with $H_2/CO = 0.98$. For example, the C_2 ratio was 1.71 in balance 4 ($H_2/CO = 0.98$) and increased to 2.00 in balance 5 ($H_2/CO = 0.72$). The other ratios 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 no strong effect on the hydrocarbon distribution. Methane increased slightly from 10.5 to 12.0 at the higher space velocity, while the C_5-C_{11} and $C_{12}+$ products decreased correspondingly. The C_2-C_4 products were unchanged. The space velocity at these conditions had little effect on the olefin/paraffin ratios as well.

We can compare the results obtained during balances 7 and 8 (260 °C, 2.0 Nℓ/g-cat·h, $H_2/CO = 0.72$) to the results of Mobil (Kuo *et al*, 1983). The average of our balances 7 (312 h) and 8 (409 h, made at the same conditions) are compared with Mobil's run CT-256-3, balance 13 in Table 8. Balance 13 was selected as it was made at approximately the same time on stream (360 h) as our tests. An Fe/Cu/K catalyst, activated with synthesis gas, was used in their run in a bubble column slurry reactor. Our catalyst had somewhat higher activity than theirs, giving an ($H_2 + CO$) conversion of 86.9 %. They achieved about the same conversion, 86.1 %, at lower space velocity (1.65 Nℓ/g-cat·h). Their catalyst produced more higher molecular weight products, 70.8 % C_5+ , than ours, 60.7 % C_5+ , with correspondingly lower amounts of CH_4 and C_2-C_4 products. The olefin/paraffin ratios obtained during our run were higher than Mobil's, for example, we measured a C_3 ratio of 6.04 compared to their ratio of 4.34. Our test of this catalyst has been one of the most successful to date, since the catalyst displayed high activity, good stability, and good selectivity.

2.1.8. Discussion of promoter effects— H_2 reduced catalyst

The effect of promoter (Cu and K) on catalyst FT activity (measured as ($H_2 + CO$) conversion) and water-gas shift (WGS) activity (measured as the $P_{CO_2}P_{H_2}/P_{CO}P_{H_2O}$ ratio) is shown in Table 9 at the common operating conditions used in the tests described above. The addition of 3 parts Cu alone had a dramatic impact on the ($H_2 + CO$) conversion. At the base case conditions (250 °C, 2.0 Nℓ/g-cat·h) the conversion increased from 21.7 % for pure Fe to 57.3 % for the 100 Fe/3.0 Cu catalyst. Similar increases were seen for other operating conditions as well. Addition of a small amount of potassium also increased the ($H_2 + CO$) conversion, to 31.1 % using 0.2 parts K, 40.4 % using 0.5 parts K, and 43.0 % using 1.0 parts K. This activity improvement was seen at all operating conditions used in our tests. The combined effect of both copper and potassium promoter (100 Fe/3.0 Cu/0.5 K) gave catalyst activity higher than that from either copper and potassium promoter alone. At the base case conditions, the ($H_2 + CO$) conversion was 75.8 %, compared to 57.3 % using 3 parts Cu alone, and 40.4 % using 0.5 parts K alone.

It is interesting to see that copper by itself leads to higher catalyst activity than does potassium. The $(\text{H}_2 + \text{CO})$ conversion obtained using the 100 Fe/3.0 Cu catalyst was comparable to or greater than any of the singly K promoted catalysts at all operating conditions. This behavior is probably due to incomplete reduction of the catalyst. In an earlier report, we summarized the results of the reduction behaviors of precipitated catalyst with H_2 reductant. Copper was found to facilitate the reduction of iron oxide, while potassium actually had a weak inhibiting effect on the reduction. Thus each catalyst may have been reduced to a different degree at the start of the run, making the observed activity a function of not only the promoter/promoter concentration but the oxidation state of the iron as well.

There is evidence that these catalysts were reduced to different degrees from our experiments. At 250 °C, 2.0 Nℓ/g-cat·h, the unpromoted iron catalyst gave an $(\text{H}_2 + \text{CO})$ conversion of 21.7 % in the first balance, which increased to 22.0 % in the fourth balance, a change of only 1.4 % (relative) over 72 h. Similarly, the relative $(\text{H}_2 + \text{CO})$ conversion increase for the 100 Fe/3.0 Cu catalyst was only 5.4 % over 95 h, and for the 100 Fe/3.0 Cu/0.5 K catalyst, 3.1 % over 72 h. However, the relative increase in $(\text{H}_2 + \text{CO})$ conversion for the 100 Fe/0.2 and 0.5 K catalysts were each 20 % over 96 h, and for 100 Fe/1.0 K catalyst (235 °C, 2.0 Nℓ/g-cat·h), the relative increase was 44.8 % over 120.5 h. It is clear that the catalysts containing potassium had lower activity, which continued to increase with time. This indirectly suggests that these catalysts were not fully activated during the reduction procedure. The catalysts which contained copper had more stable activity, which suggests that these catalysts were fully activated throughout the synthesis tests. Hence the activity increase due to copper may be caused by the reduced state of iron. Potassium electronically promotes the metal, but since the catalyst is not fully reduced, catalyst activity is lower than with copper alone. The synergistic effect of the doubly promoted catalyst is due to reduction enhancement by copper, which ensures a fully activated catalyst, plus the chemical promotion of potassium to give very high activity.

The measured $P_{CO_2}P_{H_2}/P_{CO}P_{H_2O}$ ratio increased when copper promoter was used, which indicates that the WGS reaction was promoted by copper. At the base conditions (250 °C, 2.0 Nℓ/g-cat·h) the unpromoted catalyst gave a ratio of 0.7, and adding 3 parts Cu increased the ratio to 7.4. The K-promoted catalysts gave ratios of 11.8, 41.0, and 38.1 at 0.2, 0.5, and 1.0 parts K, and the doubly promoted catalyst was 49.9. The equilibrium value for the $P_{CO_2}P_{H_2}/P_{CO}P_{H_2O}$ ratio at 250 °C is 83.2. The behavior at other process conditions was similar to the base case.

The effect of copper and potassium promoters on selectivity (hydrocarbon distribution and olefin/paraffin ratios) is shown in Table 10 at the process conditions used in our experiments. Copper suppressed formation of methane, for example, at the base conditions CH₄ was 25.5 % with the unpromoted catalyst, dropping to 16.2 % when 3 parts Cu were used. The C₁₂+ products increased when copper was added, increasing to 10.5 % from the 6.8 % with no promoters. This behavior was seen at all process conditions. The C₂-C₄ and C₅-C₁₁ product distributions were somewhat erratic, which is probably due to shifting between the intermediate product groups, however, the C₂-C₄ products remained the same or decreased when copper was added, and the C₅-C₁₁ products remained the same or increased. The copper promoter generally decreased the olefin/paraffin ratios obtained from the catalyst, although the decrease was typically small. At the base case with unpromoted catalyst, the ratios were 0.47 (C₂), 3.06 (C₃), 2.70 (C₄), 1.17 (C₈), and 1.04 (C₁₀), while with the 3 parts Cu catalyst, they decreased to 0.24, 2.41, 2.49, 1.07, and 0.87, respectively. Similar results were obtained at the other process conditions as well.

Potassium had a strong effect on CH₄ yields. Adding 0.2 parts K dropped CH₄ from 25.5 % (unpromoted at the base conditions) to 15.8 %. Additional potassium decreased CH₄ further, to 12.5 (0.5 parts K) and 11.1 % (1.0 parts K). At 265 °C, CH₄ remained constant with potassium, although there was a strong improvement over the unpromoted catalyst (23.0 % with unpromoted and 12.6 % with 0.2 parts K). The C₁₂+ products increased when potassium was used in all cases. These products increased from 6.8 % with unpromoted catalyst at the base conditions, to 18.5

(0.2 parts K), 27.5 (0.5 parts K), and 29.1 % (1.0 parts K). Potassium had a stronger effect on the hydrocarbon distribution than did copper. The C₂-C₄ and C₅-C₁₁ products tended to stay constant or decrease with increasing potassium, but as with copper promoter, the trends were erratic. Olefin/paraffin generally increased when potassium promoter was used, which is opposite of the trend seen with copper. The olefin/paraffin ratios obtained using 0.2 or 0.5 parts K were similar in most cases, while the ratios using 1 part K were typically higher. For example, considering the C₃ ratio at the base conditions, the ratio was 3.06 with unpromoted catalyst, increasing to 3.77 (0.2 parts K), 3.54 (0.5 parts K), and 4.23 (1.0 parts K).

The combined effect of copper and potassium on CH₄ was similar to the effect of potassium alone, and at the base case, CH₄ was 10.5 % compared to 16.2 % for 3 parts Cu alone and 12.5 % for 0.5 parts K alone. The C₂-C₄ products decreased regularly from the unpromoted catalyst, and the C₅-C₁₁ products increased. The C₁₂+ products (16.9 % at the base case) improved from the unpromoted catalyst, (6.8 % at the base case) but they did not show a strong improvement over the singly promoted catalyst (18.5 %). The effect of potassium on the olefin/paraffin ratios was stronger than copper, and the ratios were higher than those from the unpromoted catalyst. The C₂ ratio increased to 1.85 from 0.47, for example.

2.2. Slurry Reactor Kinetics Studies

In a previous report (Technical Progress Report for the period 1 January-31 March 1988) we investigated FT and WGS kinetics. Data for a single slurry run (SA-05-2957, 100 Fe/0.3 Cu/0.2 K, Technical Progress Report for the period 1 October-31 December 1987) were used, and we reported the results for a limited number of rate expressions. In this report, we consider a wider range of rate forms, and use data from four slurry runs: reanalysis of SA-05-2957, SB-07-0458 (H₂ reduced 100 Fe/0.3 Cu/0.5 K, Technical Progress Report for the period 1 January-31 March 1988), SA-99-0888 (Ruhrchemie LP 33/81, Technical Progress Report for the period 1 April-30 June 1988), and SB-66-2468 (100 Fe/5.0 Cu/4.2 K/24 SiO₂, Technical Progress Report for the

period 1 July–30 September 1988).

The data used to estimate the kinetic parameters are summarized in Tables 11–14, respectively, for each of the four runs. Only selected balances were used to estimate kinetic parameters. During run SA-05-2957, catalyst activity was increasing during the initial portion of the run due to incomplete activation, and balances 1–7 were not included in the data set. Also, balance 12 of this run had poor closures, and was excluded as well. The initial periods of the other three runs were also excluded as catalyst activity was not stable during these periods: balances 1–4 of SB-07-0458, balances 1–6 of SA-99-0888, and balances 1–4 of SB-66-2468.

2.2.1. Kinetics Background

Stoichiometry and Reaction Rates

The FT synthesis can be approximated as a pair of two simultaneous series-parallel reactions for the FT reaction and the WGS:

where n is the average carbon chain length of the hydrocarbon product and m is the average number of hydrogen atoms per hydrocarbon molecule. Both n and m vary with the catalyst and process conditions. In these four tests, n varied between 3.45–6.14 for the 100 Fe/0.3 Cu/0.2 K catalyst, 3.68–4.23 for the 100 Fe/5.0 Cu/4.2 K/24 SiO₂ catalyst, 4.36–6.00 for the 100 Fe/0.3 Cu/0.5 K catalyst, and 3.18–3.64 for the Ruhrchemie catalyst. The ratio of m/n was less sensitive, and varied between 2.16–2.42, 2.28–2.36, 2.16–2.22, and 2.27–2.36, respectively, in these tests.

Water is generally believed to be the primary byproduct of the FT synthesis, and CO₂ is produced by the WGS (Dry *et al*, 1972). Oxygenated products, primarily alcohols, and the CO₂ formed by the Boudouard reaction, (2CO → C (s) + CO₂), are neglected in the scheme given by Eqs. 1 and 2. The WGS is a particularly important over potassium promoted iron catalysts, which

can have significant shift activity. In some cases, the WGS may approach equilibrium during the reaction (Huff and Satterfield, 1984 a,b; Nettelhoff *et al*, 1985; Bukur and Brown, 1987).

The uniform temperature, pressure, and concentrations achieved in a slurry stirred tank reactor simplifies calculation of reaction rates. Assuming that the reactor is at steady state, the rates of the FT and WGS reactions are given by:

$$r_{FT} = \left(\frac{P_S}{RT_S} \right)^s \frac{f_{H_2+CO}}{2 + m/2n} \quad (3)$$

$$r_{WGS} = \left(\frac{P_S}{RT_S} \right)^s \frac{1 + m/2n - U}{(1 + U)(2 + m/2n)} f_{H_2+CO} \quad (4)$$

Note that the rate of syngas consumption (H_2+CO) differs from the FT reaction rate only by stoichiometry, $(-r_{H_2+CO}) = (2 + m/2n)r_{FT}$, and that the FT and WGS reaction rates are related by the H_2/CO usage ratio and stoichiometry.

Reaction rates are functions of temperature and liquid phase concentrations in a slurry reactor. Assuming that the gas and liquid phase concentrations are in equilibrium, the gas phase is ideal, and that the gaseous species obey Henry's Law in the liquid phase, partial pressures may be used in the rate equations in place of liquid concentrations or activities. Henry's Law behavior in typical slurry liquids for the principal products and reactants of the FT synthesis (CO , CO_2 , H_2 , H_2O) has been reported in the literature (*e.g.*, Peter and Weinert, 1955; Albal *et al*, 1984; Matsumoto and Satterfield, 1985; Huang *et al*, 1988). Preliminary calculations showed that the gas phase behaved ideally. We assumed that the average hydrocarbon product (C_nH_m) had the physical properties of propylene, and were able to estimate the gas phase fugacity coefficients using the Redlich-Kwong equation of state. The values estimated for the fugacity coefficients were better than 1.00 ± 0.05 for all species at all conditions employed in this report. Under these conditions, the partial pressures and liquid concentrations can be related directly: $C_{l,j} = H_j P_j$. The use of liquid concentrations, activities, or partial pressures will effect the dimensions of any constants in the rate expression. Furthermore, since Henry's constants are functions of temperature, activation

energies will also change when different concentration terms are used. If the Henry's constants are assumed to follow an Arrhenius temperature dependence, their activation energies are in the range -10.8 to 4.6 kJ/mol (Nettelhoff *et al*, 1985). In this report, we base our estimates using partial pressures in the rate equations. Also, literature values of rate constants were converted to our units for consistency, however, reported activation energies were not adjusted to account for the temperature dependence of the Henry's Law constants.

Kinetic Models

The first order dependence of the FT reaction rate on H_2 partial pressure is well known:

$$r_{FT} = k_1 P_{H_2} \quad (5)$$

Anderson (1956, pp 283-297) found that the first order rate fit the data well up to H_2+CO conversions of 60 %. The activation energies from the precipitated catalysts tested by Pichler (reported by Anderson) were 87 kJ/mol , and for the fused or precipitated catalysts tested at the U. S. Bureau of Mines, 84 and 87 kJ/mol . Nitrided fused iron catalysts had activation energies in the range $80-88$ kJ/mol . Dry *et al* (1972) studied a fused, promoted iron catalyst in a differential fixed bed reactor, and found that the reaction rate was first order in H_2 partial pressure. The activation energy was 70 kJ/mol . Under the conditions of their study (i.e., low conversions) no rate dependence on CO partial pressure was observed.

Rate inhibition by water can occur at higher conversions (>60 %). Anderson (1956) proposed a rate equation which included water inhibition, which had the form:

$$r_{FT} = \frac{k_0 P_{CO} P_{H_2}}{P_{CO} + a P_{H_2O}} \quad (6)$$

Dry (1976) was able to derive this equation from the enol mechanism (Storch *et al*, 1951, pp 581-593) by assuming that the hydrogenation of chemisorbed CO was the rate determining step:

where we have used $|$ to denote a bond of indefinite order.

Dry assumed Langmuir adsorption, and considered competitive adsorption of CO, CO₂, H₂, and H₂O. Assuming that the fraction of sites covered by the active intermediate COH₂ is small, then the surface fraction of CO is given by:

$$\theta_{\text{CO}} = \frac{K_{\text{CO}} P_{\text{CO}}}{1 + K_{\text{CO}} P_{\text{CO}} + K_{\text{CO}_2} P_{\text{CO}_2} + K_{\text{H}_2} P_{\text{H}_2} + K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}} \quad (9)$$

and the rate from Eq. 8 is:

$$r_{\text{FT}} = k_0 \theta_{\text{CO}} P_{\text{H}_2} = \frac{k_0 K_{\text{CO}} P_{\text{CO}}}{1 + K_{\text{CO}} P_{\text{CO}} + K_{\text{CO}_2} P_{\text{CO}_2} + K_{\text{H}_2} P_{\text{H}_2} + K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}} \quad (10)$$

He further suggested that $K_{\text{CO}} P_{\text{CO}} + K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}} \gg 1 + K_{\text{CO}_2} P_{\text{CO}_2} + K_{\text{H}_2} P_{\text{H}_2}$ to arrive at the expression given by Eq. (6), with $a = K_{\text{H}_2\text{O}}/K_{\text{CO}}$.

Atwood and Bennett (1979) used Eq. 6 for data taken over a fused, nitrided ammonia synthesis catalyst (CCI). Water inhibition was important only at the highest temperatures and conversions. They determined the activation energy of k_0 to be 85 kJ/mol, and for the adsorption term, a , -9 kJ/mol. (In our work, we assume that all constants appearing in the rate expressions follow an Arrhenius temperature dependence). Huff and Satterfield (1984a) found that the adsorption term a decreased linearly with H₂ partial pressure. A commercial fused iron ammonia synthesis catalyst was used in their work as well (United Catalysts, Inc., C-73). Anderson (1956) also mentioned that the rate constants appearing in Eq. 6 showed trends with feed composition.

To account for this dependence, Huff and Satterfield were able to derive an alternate rate form, using two different mechanisms: the carbide mechanism, assuming that the hydrogenation of surface carbon was the rate determining step, and an enol/carbide mechanism, with the hydrogenation of surface enol as the rate determining step. The carbide mechanism proposes that CO

adsorbs dissociatively to form an active surface carbon species. Methylene groups formed by the hydrogenation of the surface carbon polymerize to produce hydrocarbons, and water is produced via the reaction of hydrogen with surface oxygen:

Assuming that the fraction of sites covered by the methylene groups is small, the surface coverage of active carbon is given by:

$$\theta_{\text{C}} = \frac{K_{\text{CO}}^d K_1 P_{\text{CO}} P_{\text{H}_2}}{K_{\text{CO}}^d K_1 P_{\text{CO}} P_{\text{H}_2} + (1 + \frac{P_{\text{H}_2\text{O}}}{K_1 P_{\text{H}_2}}) P_{\text{H}_2\text{O}}} \quad (14)$$

Assuming that $1 + P_{\text{H}_2\text{O}}/K_1 P_{\text{H}_2} \approx 1$, then the rate can be written from Eq. 13 as:

$$r_{\text{FT}} = \frac{k_0 P_{\text{CO}} P_{\text{H}_2}}{P_{\text{CO}} P_{\text{H}_2} + b P_{\text{H}_2\text{O}}} \quad (15)$$

where $b = 1/K_{\text{CO}}^d K_1$. The assumption that $1 + P_{\text{H}_2\text{O}}/K_1 P_{\text{H}_2} \approx 1$ is the same as assuming the surface fraction of O to be very small.

The combined enol/carbide mechanism proposes that the methylene groups are formed by eliminating water from the enol in the rate limiting step:

Considering the adsorption of species per Eq. 7, the surface concentration of the enol intermediate is given by:

$$\theta_{\text{COH}_2} = \frac{K_2 K_{\text{CO}} P_{\text{CO}} P_{\text{H}_2}}{1 + K_{\text{CO}} P_{\text{CO}} + K_{\text{CO}_2} P_{\text{CO}_2} + K_{\text{H}_2} P_{\text{H}_2} + K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}} \quad (18)$$

If H_2O adsorbs strongly compared to the other species, such that $K_2 K_{\text{CO}} P_{\text{CO}} P_{\text{H}_2} + K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}} \gg 1 + K_{\text{CO}} P_{\text{CO}} + K_{\text{CO}_2} P_{\text{CO}_2} + K_{\text{H}_2} P_{\text{H}_2}$, then the rate from Eq. 17 is given by:

$$r_{\text{FT}} = \frac{k_0 P_{\text{CO}} P_{\text{H}_2}^2}{P_{\text{CO}} P_{\text{H}_2} + b P_{\text{H}_2\text{O}}} \quad (19)$$

This has the same form as Eq. 15, where b is now given by $K_{\text{H}_2\text{O}}/K_2 K_{\text{CO}}$. Furthermore, Eqs. 6 and 15 have the same form if the constant a (Eq. 6) is a function of H_2 partial pressure, i.e., $a = b/P_{\text{H}_2}$.

For the data of Huff and Satterfield (1984a), Eq. 15 gave a better fit. In order to obtain as good a correlation using Eq. 6, a constant term had to be included in the denominator. The activation energy for the FT rate constant, k_0 , was 83 kJ/mol . Nettelhoff *et al* (1985) considered both Eqs. 6 and 15 for their data taken over a precipitated, unpromoted iron catalyst. At 270°C , both rate forms agreed reasonably well with their data, although Eq. 6 gave a slightly higher statistical correlation (the R^2 correlation coefficient was 0.99 for Eq. 6 and 0.95 for Eq. 15). At conversions below 60 %, the rate was first order, with an activation energy of 89 kJ/mol .

Inhibition by CO_2 is generally not as strong as inhibition by water due to the large adsorption coefficient of water relative to CO and CO_2 . In slurry reactors, inhibition by water is further enhanced by its high solubility in typical slurry reactor waxes. However, CO_2 inhibition may become important when a large fraction of the water produced from the FT reaction reacts with CO to produce CO_2 via the WGS (Eq. 2). This situation may occur when the catalyst has high WGS activity and/or low H_2/CO feed ratios are employed. Ledakowicz *et al.* (1985) derived a rate expression which incorporated inhibition by CO_2 from the enol mechanism (Eqs. 7-10),

but assumed that CO_2 was the dominant term in the denominator of Eq. 10 (thus $K_{\text{CO}}P_{\text{CO}} + K_{\text{CO}_2}P_{\text{CO}_2} \gg 1 + K_{\text{H}_2}P_{\text{H}_2} + K_{\text{H}_2\text{O}}P_{\text{H}_2\text{O}}$). Their rate expression was then given by:

$$r_{\text{FT}} = \frac{k_0 P_{\text{CO}} P_{\text{H}_2}}{P_{\text{CO}} + c P_{\text{CO}_2}} \quad (20)$$

where $c = K_{\text{CO}_2}/K_{\text{CO}}$.

For their precipitated catalyst (100 Fe/1.3 K), which showed high WGS activity, most of the water produced from the FT synthesis subsequently reacted to form CO_2 . Catalyst activity, particularly at higher temperatures, did not follow first order kinetics. The constant c in Eq. 20 was estimated at 0.115, and was relatively insensitive to temperature. The FT activation energy was 103 kJ/mol. Nettelhoff *et al* (1985) considered Eq. 20 for a commercial fused iron ammonia synthesis catalyst (BASF S6-10). This catalyst also had high WGS activity, and did not show inhibition by product water.

A summary of the rate forms and parameter estimates for the FT reaction appearing in the recent literature is given in Table 15. Some conclusions can be drawn from the previous studies: (1) The activation energy for the FT reaction was about 80–103 kJ/mol, regardless of catalyst type, in these recent studies. This is within the range 63–105 kJ/mol of Huff and Satterfield (1984a) who reviewed a broader range of reaction studies; (2) Water inhibited the rate more strongly than CO_2 . CO_2 inhibition was overshadowed by water inhibition, except when the WGS reaction consumed most of the product water; (3) All of the proposed FT rate expressions reduced to first order in H_2 partial pressure at low conversions. This simple relationship can be used below conversions in the range 40–70 % in a stirred tank reactor (Huff and Satterfield, 1984b).

To account for inhibition by both water and CO_2 , Ledakowicz *et al* (1985) proposed a general kinetic model which has the same form as either Eqs. 6 or 20, and is obtained directly from Eq. 10 assuming that both water and CO_2 are significant terms in the denominator. (thus $K_{\text{CO}}P_{\text{CO}} +$

$$K_{CO_2}P_{CO_2} + K_{H_2O}P_{H_2O} \gg 1 + K_{H_2}P_{H_2}):$$

$$r_{FT} = \frac{k_0 P_{CO} P_{H_2}}{P_{CO} + a P_{H_2O} + c P_{CO_2}} \quad (21)$$

This generalized rate expression may be used for catalysts with low WGS activity, where water concentrations are high, as well as for catalysts with high shift activity which shows inhibition by CO_2 .

The WGS is important for slurry processing since it enables CO rich feeds to be utilized efficiently without the need for an external shift. Both Eqs. 1 and 2 for the FT and WGS reactions must be considered to accurately predict both $H_2 + CO$ conversions and H_2/CO usage ratios, which requires knowledge of WGS kinetics. The shift reaction occurs readily over potassium promoted iron catalysts, such as those considered here, and may approach equilibrium in some situations. There have only been a few studies of WGS kinetics in conjunction with the FT synthesis reported in the literature. Feimer *et al* (1981) used a first order in CO rate equation for the WGS:

$$r_{WGS} = k_w P_{CO} \quad (22)$$

They studied a potassium and copper promoted, precipitated iron catalyst (100 Fe/20 Cu/0.8 K), and determined an apparent activation energy of 124 kJ/mol for the WGS.

Kuo *et al* (1983) and Leib and Kuo (1984) considered mass action kinetics for the WGS, with a denominator shared with their FT rate expression, which had the form of Eq. 6:

$$r_{WGS} = \frac{k_{w,0}(P_{CO}P_{H_2O} - P_{CO_2}P_{H_2}/K_P)}{P_{CO} + aP_{H_2O}} \quad (23)$$

Bohlbro (1969, pp 27-34) derived a rate expression for the WGS from the reactions of CO and H_2 with oxidized surface sites (Kulkova and Temkin mechanism):

He assumed that the surface concentration of oxygen was described by a Langmuir isotherm. The numerator of the rate equation followed mass action kinetics, while the denominator contained terms for CO, CO₂, H₂, and H₂O:

$$r_{\text{WGS}} = \frac{k_r(P_{\text{CO}}P_{\text{H}_2\text{O}} - P_{\text{CO}_2}P_{\text{H}_2}/K_P)}{P_{\text{CO}} + \frac{k_{-f}}{k_f}P_{\text{CO}_2} + \frac{k_r}{k_f}P_{\text{H}_2\text{O}} + \frac{k_{-r}}{k_f}P_{\text{H}_2}} \quad (26)$$

This expression has the same form as Eq. 23 if it is assumed that $P_{\text{CO}} + \frac{k_r}{k_f}P_{\text{H}_2\text{O}} \gg \frac{k_{-f}}{k_f}P_{\text{CO}_2} + \frac{k_{-r}}{k_f}P_{\text{H}_2}$, where $k_{w,0} = k_r$ and $a = k_r/k_f$. The constants appearing in the denominator of Eq. 26 are rate constants, not adsorption coefficients, and the definition of a from Eq. 26 differs from the definition using the FT rate expression, Eq. 6. Also, there are differences in the surface species and sites between a WGS catalyst and an FT catalyst, however, it seems reasonable that for kinetics, the FT and WGS rate equations can share the same form of denominator, as was used by Kuo *et al.*

2.2.2. Results and Discussion

First Order Kinetics

The first order rate constants for the four catalysts were estimated by plotting the FT reaction rate against the H₂ partial pressure. These plots are shown in Fig. 1 for the unsupported catalysts (100 Fe/0.3 Cu/0.2 K, 100 Fe/0.3 Cu/0.5 K) and Fig. 2 for the silica-containing catalysts (100 Fe/5.0 Cu/4.2 K/24 SiO₂, Ruhrchemie). The rate constant, k_1 , on this type of plot was calculated as the slope of the best line through the origin. The estimated rate constants for the four catalysts are shown on an Arrhenius diagram in Fig. 3, and are compared numerically in Table 16.

Catalyst activity was highest for the 100 Fe/0.3 Cu/0.2 K catalyst, followed by the 100 Fe/5.0 Cu/4.2 K/24 SiO₂ catalyst, the Ruhrchemie catalyst, and the 100 Fe/0.3 Cu/0.5 K catalyst. The activation energies for the 100 Fe/0.3 Cu/0.2 K and Ruhrchemie catalysts were both 86 kJ/mol.

which is within the range expected from the literature. The activation energy for the 100 Fe/0.3 Cu/0.5 K catalyst was higher, 102 kJ/mol , which is still within the expected range. The activation energy for the 100 Fe/5.0 Cu/4.2 K/24 SiO₂ catalyst was not calculated since data were available at only a single temperature (250 °C). This simple rate expression fit the data accurately for all four catalysts at the conditions employed during our tests, and the R² correlation coefficient ranged between 0.940 and 0.998.

Inhibition by Water

The effect of water inhibition for the catalysts was evaluated considering Eqs. 6 and 15. The range of H₂O partial pressures measured in run A-2957 (100 Fe/0.3 Cu/0.2 K) was 0.006–0.117 MPa and in run B-0458 (100 Fe/0.3 Cu/0.5 K) was 0.011–0.059 MPa , which at similar process conditions were generally lower than those encountered during run A-0888 (Ruhrchemie), 0.055–0.268 MPa and B-2468 (100 Fe/5.0 Cu/4.2 K/24 SiO₂), 0.055–0.101 MPa . Huff and Satterfield (1984a) indicated that inhibition was not important below water partial pressures of 0.1–0.15 MPa for their fused catalyst.

Equations 6 and 15 can be linearized as:

$$P_{H_2}/r_{FT} = \frac{1}{k_0} + \frac{a}{k_0} \frac{P_{H_2O}}{P_{CO}} \quad (27)$$

$$P_{H_2}/r_{FT} = \frac{1}{k_0} + \frac{b}{k_0} \frac{P_{H_2O}}{P_{CO}P_{H_2}} \quad (28)$$

Plotting the data in this form, P_{H_2}/r_{FT} versus P_{H_2O}/P_{CO} (Eq. 27) or $P_{H_2O}/P_{CO}P_{H_2}$ (Eq. 28), should give a straight line which has an intercept $1/k_0$ and a slope a/k_0 (Eq. 27) or b/k_0 (Eq. 28). The constants were calculated from the least squares slope and intercept of the linearized equation for all of Eqs. 6, 15, and 20. The constants estimated in this manner for all three catalysts are summarized in Table 17.

The linear plot of Eq. 6 for the four catalysts is shown in Fig. 4. The Ruhrchemie and 100 Fe/0.3 Cu/0.5 K catalysts show only mild inhibition by water, with $a = 0.73$ and 0.99, respectively.

The weak effect of water on the reaction rate may be due to the low conversions and/or the low H_2O partial pressures obtained under the reaction conditions employed in this study. The H_2+CO conversions varied between 35.9–56.1 % for the points shown for Ruhrchemie catalyst. The 100 Fe/0.3 Cu/0.2 K catalyst was more active than the Ruhrchemie catalyst, and the conversions and H_2O partial pressures were higher. A stronger inhibition effect was seen for this catalyst ($a = 4.2$), as well as for the 100 Fe/5.0 Cu/4.2 K/24 SiO_2 catalyst ($a = 3.9$). Catalyst activity followed the same trend seen with the first order rate constants: 100 Fe/0.3 Cu/0.2 K > 100 Fe/5.0 Cu/4.2 K/24 SiO_2 > Ruhrchemie > 100 Fe/0.3 Cu/0.5 K. The results shown for the 100 Fe/0.3 Cu/0.5 K catalyst are at 265 °C, but it has comparable activity to the Ruhrchemie catalyst at 250 °C. For each catalyst, k_0 was greater than the first order rate constant k_1 (0.035, 0.027, 0.020, and 0.026 *mols/g-cat·h*, respectively). This was expected since the k_1 is an apparent rate constant, which incorporates inhibition by water and/or CO_2 (i.e., the denominators of Eqs. 6, 15, 20, or 21).

The linear plot of Eq. 15 is shown in Fig. 5. Equation 15 gave a poorer fit to the data for the 100 Fe/0.3 Cu/0.2 K catalyst, and the R^2 correlation coefficient was 0.38 using Eq. 15 and 0.66 for Eq. 6 (Fig. 4). The fit for the 100 Fe/5.0 Cu/4.2 K/24 SiO_2 catalyst was approximately the same, with R^2 correlation coefficients of 0.893 (Eq. 6) and 0.919 (Eq. 15), and the 100 Fe/0.3 Cu/0.5 K catalyst showed a strong improvement, $R^2 = 0.323$ (Eq. 6) and 0.933 (Eq. 15). The 100 Fe/0.3 Cu/0.2 K catalyst showed the strongest water inhibition effect and gave $b = 5.5 MPa$, compared to $b = 1.3 MPa$ for the 100 Fe/5.0 Cu/4.2 K/24 SiO_2 catalyst and $b = 1.6 MPa$ for the 100 Fe/0.3 Cu/0.5 K catalyst. Water inhibition was virtually non-existent for the Ruhrchemie catalyst when Eq. 15 was used, and the rate constant, $k_1 = 0.021 mols/g-cat·h$, was nearly the same as the apparent first order rate constant.

We can compare our results obtained using Eq. 6 to those of Atwood and Bennett (1979), Leib and Kuo (1984), and Nettelhoff *et al* (1985), who all used the same form of rate equation. The catalysts we tested were significantly more active than the fused iron catalyst used by Atwood and

Bennett. Their catalyst was also less active than the other catalysts shown in Table 15, which is seen by comparing k_0 values. Leib and Kuo (1984) estimated their rate constants from experiments conducted in a bubble column reactor using an Fe/Cu/K catalyst (67 weight % Fe). Their activity at higher temperature was similar to our 100 Fe/0.3 Cu/0.2 K catalyst, $k_0 = 0.062$ (265 °C) versus 0.057 (250 °C) $\text{mols/g-cat}\cdot\text{h}\cdot\text{MPa}$, and had a lower adsorption coefficient. The catalyst tested by Nettelhoff *et al* (unpromoted Fe) was also less active than the catalysts tested in our work. At 270 °C, their rate constant k_0 was less than the values obtained for our catalyst tests at 250 °C. Our higher activity may be due to the potassium promotion in the catalysts we tested. Their adsorption coefficient (4.51) was similar to that for the 100 Fe/0.3 Cu/0.2 K (4.2) and 100 Fe/5.0 Cu/4.2 K/24 SiO₂ catalysts (3.9). The parameters estimated from Eq. 15 can be compared to the results of Huff and Satterfield (1984a). The Ruhrchemie catalyst had comparable activity to the fused iron catalyst used in their study, with similar first order rate constants, although we did not find any effect of water using Eq. 15. The 100 Fe/0.3 Cu/0.2 K catalyst was more active, and at 250 °C, its k_0 was about 2.9 times greater than that for the fused catalyst, although water inhibited the FT reaction rate more strongly for our catalyst. The 100 Fe/5.0 Cu/4.2 K/24 SiO₂ catalyst showed somewhat higher activity than the fused iron (about 1.4 times greater) with approximately the same water inhibition effect. At 265 °C, the 100 Fe/0.3 Cu/0.5 K catalyst was less active than their fused iron, with a similar H₂O adsorption coefficient.

Inhibition by CO₂

The rate expression derived by Ledakowicz *et al* (1985) to account for inhibition by CO₂ (Eq. 20) was studied in a similar manner. The linear form of Eq. 20 is given by:

$$P_{\text{H}_2}/r_{\text{FT}} = \frac{1}{k_0} + \frac{c}{k_0} \frac{P_{\text{CO}_2}}{P_{\text{CO}}} \quad (29)$$

A linear plot of Eq. 20 is shown in Fig. 6. The CO₂ partial pressures during run A-0888 (Ruhrchemie) were too low, 0.052-0.350 MPa, to be used with this rate equation. The data for

the other three catalysts show inhibition by CO_2 , and the constant c in Eq. 20 was estimated at 0.21, 0.69, 0.09 for the 100 Fe/0.3 Cu/0.2 K, 100 Fe/5.0 Cu/4.2 K/24 SiO_2 , and 100 Fe/0.3 Cu/0.5 K catalysts, respectively. Inhibition by water was much stronger than for CO_2 , and the adsorption coefficient, a , in the analogous Eq. 6 was about 20 times greater than that for CO_2 with the 100 Fe/0.3 Cu/0.2 K catalyst, about 6 times greater for the 100 Fe/5.0 Cu/4.2 K/24 SiO_2 catalyst, and about 11 times greater using the 100 Fe/0.3 Cu/0.5 K catalyst.

The 100 Fe/0.3 Cu/0.2 K and 100 Fe/5.0 Cu/4.2 K/24 SiO_2 catalysts were significantly more active than the S6-10 fused catalyst studied by Nettelhoff *et al* (1985). The 100 Fe/0.3 Cu/0.2 K catalyst had comparable activity to the 100 Fe/1.2 K catalyst used by Ledakowicz *et al* (1985). Our rate constant k_0 at 250 °C was approximately the same as for their catalyst, as was our estimate of the CO_2 adsorption coefficient, c . Their catalyst was more active than the 100 Fe/5.0 Cu/4.2 K/24 SiO_2 catalyst, and showed a weaker CO_2 inhibition effect. The S6-10 fused iron was significantly more active than the 100 Fe/0.3 Cu/0.5 K catalyst.

The analysis of our data for the 100 Fe/0.3 Cu/0.2 K catalyst using Eqs. 6, 15, and 20 showed that both CO_2 and water potentially inhibited the reaction rate, thus we also considered Eq. 9, which includes inhibition by both product species. Eq. 9 was linearized, and the constants estimated via multiple linear regression of the 250 °C data. A parity plot of experimental and expected rates is shown in Fig. 7 for the 100 Fe/0.3 Cu/0.2 K and Ruhrchemie catalysts. The 100 Fe/5.0 Cu/4.2 K/24 SiO_2 and 100 Fe/0.3 Cu/0.5 K catalysts gave negative adsorption coefficients when fit to this equation, thus were not used. The model fits our data, although some scatter in the data is apparent. The trends seen previously with CO_2 and water inhibition were also observed for this model. Water was adsorbed much more strongly than CO_2 , and the ratio of the adsorption coefficients (a/c) was about 35 for the 100 Fe/0.3 Cu/0.2 K catalyst. However, since this catalyst has good WGS activity, the CO_2 partial pressures were high enough to cause rate inhibition. The constant c for the Ruhrchemie catalyst was nearly zero, contributing little to the denominator of

Eq. 21.

Water-Gas Shift Kinetics

A comparison of the measured $P_{\text{CO}_2}P_{\text{H}_2}/P_{\text{CO}}P_{\text{H}_2\text{O}}$ ratios from our data to the equilibrium constant (Newsome, 1980) is shown in Fig. 8. The measured $P_{\text{CO}_2}P_{\text{H}_2}/P_{\text{CO}}P_{\text{H}_2\text{O}}$ ratios generally approach equilibrium at higher temperatures as the WGS reaction rate increases. The 100 Fe/0.3 Cu/0.2 K catalyst is also seen to have higher WGS activity than either the Ruhrchemie or 100 Fe/5.0 Cu/4.2 K/24 SiO₂ catalysts, and its ratios were closer to equilibrium at all temperatures. Since most of the measured points fall far away from equilibrium, it is important to consider the kinetics of the WGS.

The first order plots for the WGS reaction are shown for the 100 Fe/0.3 Cu/0.2 K and 100 Fe/0.3 Cu/0.5 K catalysts in Fig. 9, and for the Ruhrchemie and 100 Fe/5.0 Cu/4.2 K/24 SiO₂ catalysts in Fig. 10. The slope of the best line through the origin on these plots is the estimate of the rate constant. The first order in CO rate constants (Eq. 22) from our tests are plotted on an Arrhenius diagram in Fig. 11, and are compared numerically in Table 18. The rate constants from the 100 Fe/0.3 Cu/0.2 K catalyst were higher than those from the other three catalysts by a factor of about 4–5, regardless of temperature. The activation energies measured for the WGS reaction were 132 kJ/mol for the 100 Fe/0.3 Cu/0.2 K and 100 Fe/0.3 Cu/0.5 K catalysts, and 137 kJ/mol for the Ruhrchemie catalyst. These values are in good agreement with the 124 kJ/mol reported by Feimer *et al*, who also considered first order in CO WGS kinetics.

The mass action kinetic equation (Eq. 23) was also used for the WGS. The rate constant $k_{w,0}$ was estimated in the following manner: using the same value of a (Eq. 6) obtained for the FT kinetics, Eq. 23 was multiplied through by the denominator of the right-hand side. The resulting equation is linear with respect to $k_{w,0}$, and the rate constant was then calculated as the slope of the best line through the origin. We also considered mass action kinetics with the denominators of the FT rate expressions given by Eqs. 15, 20, and 21 as well. The rate constants $k_{w,0}$ for

these rate forms were estimated in the same manner as described above. The results for the rate constants $k_{w,0}$ are given in Table 19 for all catalysts. Equation 23 gives a good fit to the data for 100 Fe/0.3 Cu/0.2 K, 100 Fe/0.3 Cu/0.5 K, and Ruhrchemie catalysts, and is superior to the first order in CO rate expression. The fit for the 100 Fe/5.0 Cu/4.2 K/24 SiO₂ catalyst did not show an improvement, and the first order in CO kinetics was superior ($R^2 = 0.987$ at 250 °C). Leib and Kuo (1984) estimated $k_{w,0}$ at 0.66 *mols/g-cat·h · MPa* for $a = 0.58$ for their iron based catalyst (265 °C). Their rate constant is comparable to our estimate for the 100 Fe/0.3 Cu/0.2 K catalyst, and is higher than the constants obtained for either the Ruhrchemie, 100 Fe/0.3 Cu/0.5 K, or 100 Fe/5.0 Cu/4.2 K/24 SiO₂ catalysts.

TASK 3—PROCESS EVALUATION RESEARCH

3.1. Slurry Reactor Catalyst Study

3.1.1. Run SB-25-2878 (100 Fe/3.0 Cu/0.2 K)

Slurry run SB-25-2878 was made using H₂ reduced 100 Fe/3.0 Cu/0.2 K catalyst. As stated earlier, our prior studies on the effect of pretreatment conditions on subsequent catalytic performance showed that pretreatment in pure CO or syngas resulted in active catalysts which favored production of liquid products and wax (Technical Progress Report for the period 1 October–31 December 1987). However, these catalysts deactivated fairly rapidly during synthesis testing. On the other hand, H₂ reduced catalysts exhibited good stability, but favored production of methane and other gaseous hydrocarbons. To minimize catalyst deactivation and achieve better stability, an H₂ reduction was employed in this run.

The reactor was initially charged with 35 g of catalyst and 283 g of purified *n*-octacosane. The catalyst was activated in the slurry reactor using H₂ at 230 °C for 8 h. Following the activation, 40 g of wax was withdrawn from the reactor to an external settling tank, and the feed was switched to a H₂/CO = 0.67 syngas at 2.0 Nℓ/g-cat·h. The reactor pressure was raised to 1.48 MPa, and the temperature was gradually increased to 260 °C. These conditions were maintained throughout the run. The major events occurring during run SB-66-2878 are listed in Table 20, and the wax and solids inventory is shown in Table 21. Three mass balances were completed before the run was terminated at about 245 h, and the results from these balances are summarized in Table 22.

During the first balance at 70 h, the (H₂+CO) conversion was 77.2 %. An activity plot, which shows gas contraction versus time on stream, is given in Fig. 12. This figure also shows the times at which wax withdrawals were made and the amount of wax removed during each withdrawal. A stability plot for this run, (H₂+CO) conversion versus time on stream, is shown in Fig. 13. Catalyst activity was high and stable up through the first mass balance. Catalyst selectivity favored methane and C₂–C₄ products. The distribution during the balance was 10.4 (CH₄), 24.1 (C₂–C₄),

39.2 (C₅-C₁₁), and 26.3 % (C₁₂+). The relatively high methane selectivity was expected for an H₂ reduced catalyst. Following balance 1, a withdrawal was made to the external settling tank (40 g removed) and a second withdrawal (127 g removed) was made through an internal filter (20 μ, 3/8" OD by 1.5"). This caused the (H₂+CO) conversion to drop to 67.3 %, and catalyst activity continued to decline steadily with time from that point on. Catalyst activity improved after about 150 h, but during the second balance (166 h), the (H₂+CO) conversion was only 37.6 %. A withdrawal of 65 g wax after the second mass balance decreased catalyst activity again, and the (H₂+CO) conversion was only 13.7 %. We attempted to regain activity by adding 59 g wax in order to suspend any catalyst on the reactor wall and/or the withdrawal filter, but this effort was unsuccessful. During the third balance (240 h), the (H₂+CO) conversion was only 15.2 %. The run was terminated after this balance was completed due to the strong catalyst deactivation.

Inspection of the reactor after the run showed that as the wax level dropped during withdrawal, about 5 g of the catalyst settled on the filter and adhered to the sides of the reactor. This loss in suspended catalyst can account for some of the decline in activity observed following wax withdrawals. While we knew from the previous slurry run (SB-66-2468, Technical Progress Report for the period 1 July-30 September 1988) that adding wax after withdrawals restored catalyst activity, we decided not to add wax during this run, but to make more frequent withdrawals to prevent an excessive rise in the slurry level. It was felt that the slow rise in the wax level during the course of reaction could wash the filter element and reactor walls, restoring catalyst activity. In Fig. 12 we see a large increase in contraction from 11 to 27 % at about 170 h, and an appreciable increase in contraction after 200 h on stream, which is due to slow buildup of wax in the reactor. It is clear from this run that following wax withdrawals, wax needs to be reintroduced immediately to clean the filter element and reactor walls. Also use of a vertical filter element, instead of the horizontal orientation employed in this run, would provide less area for catalyst deposition.

At the end the run, the slurry was removed from the reactor, and the solids recovered by

filtration and washed with toluene. While the initial catalyst charge was 35 g, we recovered only 27 g from the slurry, a weight loss of 23 %. In addition to losses of catalyst, the weight loss is also due to changes in catalyst composition. If we assume that the catalyst is completely reduced to metal (i.e., Fe_2O_3 , CuO , $\text{K}_2\text{O} \rightarrow \text{Fe}$, Cu , K) then the expected weight loss is 30 %. Similarly, if we assume that all iron in the catalyst is converted to Hägg carbide ($\text{Fe}_{2.2}\text{C}$), the weight loss would be about 23 %. Burning the catalyst in a furnace should reoxidize the metal, restoring the weight loss. However, when we burned the catalyst recovered from this run, the catalyst lost additional weight (5 g) for a total weight loss of about 40 %. This additional loss must have been due to carbon and/or wax on the catalyst prior to burning which had not been removed by washing. A detailed discussion of wax withdrawal techniques and catalyst recoveries is given in the following section.

3.1.2. Wax and Catalyst Recoveries for Slurry Runs

The reactor volume for slurry bed reactors is determined by the amount of slurry present in the reactor. During the course of an experiment, in these reactors, the slurry volume changes due to the production of wax. Allowing the wax to accumulate over multiple balances caused difficulties, such as poor mass closures and inaccurate selectivities resulting from the unaccounted accumulation of wax. We therefore used various methods to withdraw accumulated product wax from the slurry reactors during catalyst tests. During these withdrawals some of the catalyst is also removed from the reactor, effectively decreasing the catalyst loading for the test. In order to monitor wax production and the amount of catalyst remaining in the reactor, an inventory of wax and catalyst was maintained for each test in the slurry reactor, and their recoveries estimated at the end of the run. In this section, wax and catalyst recoveries for eight slurry bed tests, and related experimental procedures are discussed.

The slurry reactor is loaded with FT-300 wax or *n*-octacosane, and calcined catalyst prior to the initialization of a run. The amount of wax charged is slightly greater (50-70 ml) than the steady state operating volume, as determined by the slurry withdrawal dipleg location. Following catalyst

reduction, any excess slurry is removed from the reactor. The amount of wax remaining in the reactor following reduction is reconciled with the quantity recovered from the reactor following the end of the run. The two quantities are expected to be the same for the case where there is no loss or gain in the wax present in the reactor. Any wax produced during the run is withdrawn using one of several procedures discussed below so as to maintain a constant reactor volume. Similarly, the weight of catalyst charged to the reactor is reconciled with the total weight of catalyst recovered from the reactor. The total catalyst recovered is the sum of amounts removed due to periodic slurry withdrawals during the run and the amount recovered from the reactor at the end of the run.

Slurry Withdrawal Procedures

We have used several procedures to withdraw slurry from the reactor in a continuous effort to improve the technique and minimize the effect of slurry withdrawal on catalyst activity. The various procedures used or experimented with are discussed here in chronological order. The earliest procedure involved the stopping of the reactor stirrer and bypassing the reactor feed in order to allow the catalyst to settle from the slurry. After a settling period of about thirty minutes wax was withdrawn through a dipleg located at a preset height in the reactor. While this procedure was simple to implement and was generally reliable, our experience showed that this major disturbance in the reactor operation appeared to cause or accelerate catalyst deactivation.

Three methods were then tested which permitted the withdrawal of accumulated wax at the end of each mass balance period with a minimum of interference to reactor operation: (1) wax withdrawal through 10 and 20 μm , 0.5" diameter, 1/16" thick sintered metal filters located internal to the reactor, (2) wax withdrawal through the same filters external to the reactor, and (3) withdrawal of excess slurry to an external settling tank, with a return of catalyst to the reactor. The first two procedures were abandoned due to problems with plugging of filters. The filters were readily cleaned by backflushing with helium, but continued to plug with repeated attempts to withdraw wax. The third procedure was successful and is briefly described here.

Following the end of a balance period, feed gas flow to the reactor was shut off and the stirrer speed reduced from 1250 RPM to 600 RPM to allow the catalyst to settle. After a two minute settling period, excess slurry was withdrawn through a dipleg to a 500 cc external settling tank. Feed to the reactor was then resumed and stirrer speed restored. The catalyst was allowed to settle in the settling tank for about 45 minutes, and clear wax in the top of the settling tank was siphoned to a collection vessel. The concentrated slurry remaining in the settling tank (about 80 ml) was then returned to the reactor using an overpressure of about 50 *psi*. After draining the concentrated slurry, the tank was rinsed with 50-75 ml of *n*-hexane to remove any catalyst sticking to the walls of the settler, and this dilute slurry was also drained to the reactor. The procedure worked well, but small amounts of catalyst were found in the clear wax removed from the settling tank.

The latest procedure to withdraw excess wax from the reactor involved the use of a 20 μm cylindrical filter element (3/4" OD, 1.5" long with a 1/16" wall thickness), attached to the end of the dipleg inside the reactor. Tests showed that it was possible to remove wax from the reactor without any apparent catalyst loss and without interfering with the run itself. Also, the procedure could be completed within a reasonable amount of time, although, some of the catalyst accumulated in the vicinity of the filter and on the reactor wall following the withdrawal. Some wax had to be returned to the reactor to flush the walls and the filter element and restore the drop in activity caused by the removal of some of the catalyst from the synthesis zone. For runs where this procedure was implemented, the settling tank withdrawal method (described above) was used as a standby.

For each of the withdrawal procedures discussed above, the reactor volume is determined by the amount of slurry remaining in the reactor following withdrawal. For the case where both stirrer and gas flow are stopped (the earliest procedure used), reactor volume can be estimated fairly accurately and is equal to the reactor vessel volume between the dipleg and the reactor bottom. Some uncertainty is involved while estimating reactor volume when the external settling tank is used for slurry withdrawal. This is because, the stirrer is on (at 600 RPM) during slurry withdrawal.

The resulting slurry motion and possible vortex formation at the slurry surface, makes it difficult to accurately estimate the volume of slurry left in the reactor following withdrawal even though the dipleg is located at a preset height. The uncertainty is even greater for the last procedure where both gas flow and stirrer are on (at 1250 RPM) during the withdrawal procedure. This is because of gas hold-up in the slurry and turbulent slurry motion due to the higher stirrer speed. To offset some of the uncertainty involved in determining reactor volume, we conducted tests prior to implementing the procedures and determined the amount of slurry remaining in the reactor following withdrawal. For the same preset dipleg height (or internal filter location) it is obvious that the largest volume of slurry remaining in the reactor would be for the first procedure and the lowest for the last procedure described above.

Wax Recovery

Table 23 summarizes the wax recovery results for the eight slurry runs. The amount of wax charged is an estimated quantity. It is the difference between the quantity of wax loaded in the reactor and the amount withdrawn from the reactor following reduction. Also shown in Table 23 is the amount of wax produced during the run (or withdrawn during the run), and type of withdrawal procedure implemented for the particular run. Percent wax recovery is defined as the amount of wax recovered at the end of the run as a percent of the quantity charged. The recoveries are fairly good for the various slurry runs, with values ranging between 89.4 and 105.9%. The recoveries are consistently higher when *n*-octacosane is used as the starting liquid (102.4 to 105.9%) than when FT-300 wax is used as the starting medium (89.4 to 98.8%). A probable explanation for this difference is as follows. FT-300 is a wax with an average molecular weight of about 700, whereas *n*-octacosane has a molecular weight of 394. During synthesis, it is expected that the majority of the products formed are lighter than FT-300, and the average molecular weight of the wax at the end of the run is lower than that of FT-300. If this were true, the weight of wax removed from the reactor at the end of the run (when FT-300 is used as the starting medium) would be less than the

weight charged (pure FT-300) giving recoveries lower than 100% (assuming that the starting and ending liquid volumes are the same). Whereas, for runs where *n*-octacosane is used as the starting medium, the average molecular weight of the wax recovered at the end of the run would be greater than that for *n*-octacosane. Therefore, the recoveries for these runs would be greater than 100%.

For slurry run SB-25-2878, percent wax recovery could not be estimated because of the different procedures used to withdraw slurry during the run. Following reduction, the external settling tank was used to remove excess wax, whereas the internal filter arrangement was used in subsequent withdrawals. Therefore, the amount of wax remaining in the reactor following reduction (243 g) was significantly higher than that remaining at the end of the run (172 g), as would be expected based on our earlier discussion on withdrawal procedures.

Catalyst Recovery

The procedures used to quantify the catalyst present in the slurry, withdrawn from the reactor, are briefly discussed first. During early slurry withdrawals from the reactor, we separated the solids from the slurry by allowing them to settle. The slurry was diluted with Varsol (mineral spirits) using two volumes of the solvent per volume of the slurry and the solution was kept at about 100 °C in a conical flask. After the solids settled down (based on visual inspection of the solution), the clear liquid was decanted and more solvent was added to the remaining slurry to wash off residual wax. This procedure was repeated till the decanted liquid appeared to be free of wax. The residue was then dried and the solids were weighed. We attempted to improve upon this procedure by separating the solids from the slurry by filtration. A filter chamber was fabricated with a 2 μm sintered metal plate filter at the bottom of the chamber. The slurry was first diluted with Varsol (1:2 of slurry:solvent) and poured into the chamber. The contents were maintained at about 100 °C under a pressure of 10 to 15 *psig* to filter out the solids. The procedure was repeated with more solvent added each time until the filtrate was clear of any wax (usually three filtration cycles were sufficient). The solids were then dried and weighed. In the last two slurry runs, the solids

were heated in a furnace at 600 °C for 12 hours and weighed. Results from eight slurry runs are summarized in Table 24. Also shown in Table 24 is the initial catalyst concentration in the slurry for each of the runs. For majority of the runs, catalyst concentration was about 10 wt %.

The catalyst is calcined prior to being loaded in the reactor. During the reduction process and subsequently during the synthesis period, the iron in the catalyst undergoes changes, effectively changing the weight of the catalyst. In Table 24 the weight of catalyst charged is the weight of the calcined catalyst. Catalyst in this form contains iron as Fe_2O_3 , copper as CuO , and potassium is in the form of K_2O . Following reduction and synthesis periods, majority of the iron in the catalyst is expected to be in the carbide form. The various iron carbide phases are ϵ - carbide (Hexagonal carbide, $Fe_{2.2}C$), χ -carbide (Hägg carbide, Fe_5C_2), and θ -carbide (Cementite, Fe_3C). Of these, the most common is the Hägg carbide, Fe_5C_2 . The used catalyst also may contain some Fe_2O_3 , Fe_3O_4 , and Fe . The copper component of the catalyst (originally as CuO) also undergoes changes and reduces to Cu , whereas potassium remains as K_2O . The stoichiometric equations relating the various forms of iron carbides to hematite (Fe_2O_3) and the resulting percent weight changes (ΔW) are as follows:

Since the catalyst contains iron, copper and potassium compounds (and silica for supported catalysts), the change in weight of the entire catalyst, due to changes in the forms of iron and copper, depends on the actual catalyst composition.

The total amount of solids recovered during a given run is listed in column 6 of Table 24. In all cases the amount of solids recovered was lower than the amount of catalyst charged in the

form of Fe_2O_3 . The theoretical amount of catalyst expected if all Fe_2O_3 in the calcined catalyst were converted into Fe_5C_2 (Hägg carbide) is given in column 7 of Table 24. A comparison of the corresponding values in columns 6 and 7 reveals that the amount of solids recovered was either equal to or greater than (up to 25%) the theoretical amount based on the assumption that all iron in the used catalyst is in the form of Fe_5C_2 . This is not unexpected, since the used catalyst (solids recovered) may contain some iron in the form of Fe_3O_4 (magnetite) and Fe_2O_3 , as well as carbonaceous deposits in the form of CH_x , elemental carbon, as well as some residual wax. All of these factors would contribute to the increased mass of the used catalyst relative to the theoretical value on Fe_5C_2 basis.

In the last two slurry runs (SB-66-2468 and SB-25-2878) the solids recovered were heated in an oven at 600 °C for 12 hours, and the resulting weights are listed in column 9 of Table 24. It was expected that this treatment would lead to complete removal of residual wax and elemental carbon deposited on the catalyst, and to the oxidation of iron carbides. If all carbonaceous deposits were completely removed, and all iron oxidized into Fe_2O_3 , the total amount of solids would be expected to be the same as the amount of catalyst charged. However, we have experienced some loss in the mass of solids after this treatment has actually decreased. This is consistent with an assumption that most of the carbonaceous deposits were removed as a result of this treatment, but apparently the iron carbides were not completely oxidized to Fe_2O_3 . A small sample (~ 1 g) of the thermally treated material from Run SB-66-2468 was oxidized in air over a Bunsen burner flame for 4 hours and its weight increased by 33%. Based on the total amount of thermally treated material this corresponds to 28.3g, i.e. 80.6% recovery (columns 10 and 11 in Table 24) of the amount of catalyst charged. This means that about 20% (6.8 g) of the catalyst initially charged is unaccounted for. The two principal reasons for this loss are as follows: (1) Some of the solids were not completely collected at the end of the run (sticking to the walls and other internals), and (2) Loss during the filtration process and/or along with the "clear" liquid in the settling procedure

described previously. Particle size measurements of the thermally treated solids (600 °C for 12 h) reveal that a large fraction of the catalyst was less than 1 μm in size. This could explain the loss of solids during filtration and/or decantation processes.

In summary, the above results show that the solids recovered after filtration (or decantation) and drying still contain some residual wax deposits and/or other carbonaceous species. Both of these can be removed by thermal treatment or by oxidation in air. It appears that some of the catalyst is lost during the process of slurry (wax) removal from the reactor by use of either the settling method or the internal filter, due to the catalyst particle disintegration to a submicron size range. Also, a better procedure is needed for complete oxidation of solids recovered from the slurry reactor.

3.1.3. Particle Size Distribution for Used Catalysts

The calcined catalyst is sized before being loaded into the slurry reactors. The size range of the catalyst particles is shown in column 4 of Table 24. For the last three slurry runs, catalyst particles were initially in the range 45-53 μm . The used catalyst recovered from these runs was thermally treated (kept in an oven at 600 °C for 12 hours) and its particle size distribution was determined. Results from these measurements are discussed here.

The particle size distributions were measured using image analysis. A small amount of the catalyst (usually ; 0.5 g) was dispersed on a glass slide and particle size measurements were made for samples at two to three different locations on each slide. Each sample consisted of 150-300 particles. Catalyst recovered from run SB-27-2168 was sized using a Bausch & Lomb Omnicon Image Analysis System (located in the Department of Chemical Engineering at Kansas State University). A video camera and staging microscope attached to the image analysis system, was used to feed a magnified image of the dispersion to the analyzer. This analysis showed that over 95% of the particles were less than 5 μm in size. Thermally treated catalyst from runs SB-66-2468 and SB-25-2878 were measured using a Zeiss-Kontron Image Analysis System interfaced to a video camera attached to a

staging microscope (located in the Electron Microscopy Center at Texas A&M University). During this analysis it was found that 99 % of the particles were less than 1 μm .

The particle size distribution of thermally treated catalyst is significantly different from the original size of the calcined catalyst (45-53 μm). We believe that some of the disintegration took place during the actual run while the catalyst was in the reactor, whereas some may have resulted from the thermal treatment of the catalyst after it was removed from the reactor.

Task 4 - Economic Evaluation

No work on this task was scheduled during this quarter.

V. NOMENCLATURE

a	=	H ₂ O adsorption coefficient, Eqs. 6, 21
b	=	H ₂ O adsorption coefficient, Eq. 15 (MPa)
c	=	CO ₂ adsorption coefficient, Eqs. 20, 21
$C_{l,j}$	=	Liquid phase concentration of species j (mols/l)
E	=	Activation energy (kJ/mol)
$f_{\text{H}_2+\text{CO}}$	=	Fractional H ₂ +CO conversion
H_j	=	Henry's Law constant for species j (mols/l · MPa)
k_0	=	FT rate constant, Eqs. 6, 15, 20, 21 (mols/g-cat·h · MPa)
k_1	=	FT first order rate constant, Eq. 5 (mols/g-cat·h · MPa)
k_f	=	Rate constant of forward Eq. 24 (mols/g-cat·h · MPa)
k_{-f}	=	Rate constant of reverse Eq. 24 (mols/g-cat·h · MPa)
k_r	=	Rate constant of forward Eq. 25 (mols/g-cat·h · MPa)
k_{-r}	=	Rate constant of reverse Eq. 25 (mols/g-cat·h · MPa)
k_w	=	WGS first order rate constant, Eq. 22 (mols/g-cat·h · MPa)
$k_{w,0}$	=	WGS rate constant, Eq. 23 (mols/g-cat·h)
K_1	=	Equilibrium constant defined by Eq. 12
K_2	=	Equilibrium constant defined by Eq. 16 (MPa ⁻¹)
K_j	=	Adsorption equilibrium constant, Eq. 7 (MPa ⁻¹)
K_P	=	WGS equilibrium constant, Eq. 23
m	=	Average number of hydrogen atoms per product molecule, Eq. 1
n	=	Average carbon chain length of product molecule, Eq. 1
P_j	=	Partial pressure of species j (MPa)
P_S	=	Standard pressure (0.101 MPa)
R	=	Gas constant (8.314·10 ⁻³ l-MPa/mol · K)
R^2	=	Correlation coefficient
r_k	=	Rate of reaction k (mols/g-cat·h)
$(-r_{\text{H}_2+\text{CO}})$	=	Rate of syngas disappearance (mols/g-cat·h)
s	=	Space velocity (Nl/g-cat·h)
T_S	=	Standard temperature (273 K)
U	=	H ₂ /CO usage ratio
<i>Subscripts</i>		
FT	=	Fischer-Tropsch
j	=	Species index ($j = \text{C}_n\text{H}_m, \text{CO}, \text{CO}_2, \text{H}_2, \text{or } \text{H}_2\text{O}$)
k	=	Reaction index ($k = \text{FT or WGS}$)
WGS	=	Water-gas shift
<i>Superscripts</i>		
d	=	Dissociative adsorption

VI. LITERATURE REFERENCES

- Albal, R. S., Shah, Y. T., Carr, N. L. and A. T. Bell "Mass Transfer Coefficients and Solubilities for Hydrogen and Carbon Monoxide under Fischer-Tropsch Conditions", *Chem. Eng. Sci.* **39**, 905-907 (1984).
- Anderson, R. B. "Catalysts for the Fischer-Tropsch Synthesis", In *Catalysis*, Vol. IV, P. H. Emmett, Ed., Van Nostrand-Reinhold, New York (1956), 257-371.
- Atwood, H. E. and C. O. Bennett "Kinetics of the Fischer-Tropsch Reaction over Iron", *Ind. Eng. Chem. Process Des. Dev.* **18**, 163-170 (1979).
- Bohlbro, H. "An Investigation on the Kinetics of the Conversion of Carbon Monoxide with Water Vapour over Iron Oxide Based Catalysts", Haldor Topsøe, Vadbæk, Denmark (1969).
- Bukur, D. B. and R. F. Brown "Fischer-Tropsch Synthesis in a Stirred Tank Reactor — Reaction Rates", *Can. J. Chem. Eng.* **65**, 604-612 (1987).
- Bukur, D. B., Lang, X., Rossin, J. A., Zimmerman, W. H. and M. P. Rosynek, M. P. "Synthesis Gas Conversion to Liquid Fuels — Activation Studies", Paper presented at the Pac. Area Chem. Eng. Cong., Acapulco, Mex. (Oct 19-22, 1988).
- Deckwer, W.-D., Serpemen, Y., Ralek, M. and B. Schmidt "Fischer-Tropsch Synthesis in the Slurry Phase on Mn/Fe Catalysts", *Ind. Eng. Chem. Process Des. Dev.* **21**, 222-231 (1982).
- Dry, M. E., Shingles, T. and L. J. Boshoff "Rate of the Fischer-Tropsch Reaction Over Iron Catalysts", *J. Catal.* **25**, 99-104 (1972).
- Dry, M. E. "Advances in Fischer-Tropsch Chemistry", *Ind. Eng. Chem. Prod. Res. Dev.* **15**, 282-286 (1976).
- Feimer, J. L., Silveston, P. L. and R. R. Hudgins "Steady-State Study of the Fischer-Tropsch Reaction", *Ind. Eng. Chem. Prod. Res. Dev.* **20**, 609-615 (1981).
- Frohning, C. D., Kölbel, H., Ralek, M., Rottig, W., Schnur, F. and H. Schulz "Fischer-Tropsch Synthesis", In *Chemicals from Coal*, J. Falbe, Ed., Thieme, Stuttgart (1977), 219-417.
- Huang, S. T., Lin, H., Tsai, F. and K. Chao "Solubility of Synthesis Gases in Heavy *n*-Paraffins and Fischer-Tropsch Wax", *Ind. Eng. Chem. Res.* **27**, 162-169 (1988).
- Huff, G. A., Jr., and C. N. Satterfield "Intrinsic Kinetics of the Fischer-Tropsch Synthesis on a Reduced Fused-Magnetite Catalyst", *Ind. Eng. Chem. Process Des. Dev.* **23**, 696-705 (1984a).
- Huff, G. A., Jr., and C. N. Satterfield "Some Kinetic Design Considerations in the Fischer-Tropsch Synthesis on a Reduced Fused-Magnetite Catalyst", *Ind. Eng. Chem. Process Des. Dev.* **23**, 851-854 (1984b).
- Kuo, J. C. W., et al. "Slurry Fischer-Tropsch/Mobil Two Stage Process of Converting Syngas to High Octane Gasoline", Final Report DOE Contract No. DE-AC22-80PC30022, Mobil Research and Development Corp., Paulsboro, N. J. (1983).
- Ledakowicz, S., Nettelhoff, H., Kokuun, R. and W.-D. Deckwer "Kinetics of the Fischer-Tropsch Synthesis in the Slurry Phase on a Potassium-Promoted Iron Catalyst", *Ind. Eng. Chem. Process Des. Dev.*, **24**, 1043-1049 (1985).

- Matsumoto, D. K. and C. N. Satterfield "Solubility of Hydrogen and Carbon Monoxide in Selected Nonaqueous Liquids", *Ind. Eng. Chem. Process Des. Dev.* **24**, 1297-1300 (1985).
- Leib, T. B. and J. C. W. Kuo "Modeling the Fischer-Tropsch Synthesis in Slurry Bubble-Column Reactors", Paper presented at the AIChE Annual Meet., San Francisco, Calif. (Nov. 25-30, 1984).
- Nettelhoff, H., Kokuun, R., Ledakowicz, S. and W.-D. Deckwer "Studies on the Kinetics of Fischer-Tropsch Synthesis in Slurry Phase", *Ger. Chem. Eng.* **8**, 177-185 (1985).
- Newsome, D. S. "The Water-Gas Shift Reaction", *Catal. Rev.—Sci. Eng.* **21**, 275-318 (1980).
- Peter, S. and M. Weinert "Solubility of H_2 , CO, CO_2 , and Water Vapor in Liquid Hydrocarbons", *Z. Phys. Chem. N. F.* **5**, 114-121 (1955).
- Storch, H. H., Golumbic, H. and R. B. Anderson "The Fischer-Tropsch and Related Syntheses", Wiley, New York (1951).

Table 1. Summary of results for fixed bed run FB-00-3068.
Catalyst: 3.45 g^a, Pure Fe
Diluent: 38.6 g, Glass beads
Catalyst volume: 2.60 cc
Diluent Volume: 25.0 cc

Period	1	2	3	4	5
Date	10/07/88	10/08/88	10/09/88	10/10/88	10/11/88
Time on Stream (h)	71.5	95.5	119	143	167
Balance Duration (h)	8.00	7.00	8.00	7.20	7.50
Average Temperature (°C)	249	265	235	250	250
Maximum Δ Temperature (°C) ^b	2.00	3.00	2.00	3.00	3.00
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48
H ₂ /CO Feed Ratio	0.98	0.98	0.98	0.98	0.98
Space Velocity (NI/g-cat.h) ^a	2.00	2.00	2.00	2.00	1.00
Space Velocity (NI/g-Fe.h)	2.86	2.86	2.86	2.86	1.43
GHSV (h ⁻¹) ^c	246	246	246	246	123
CO Conversion (%)	21.5	36.1	13.7	22.6	37.3
H ₂ +CO Conversion (%)	21.7	35.1	13.7	22.0	34.8
H ₂ /CO Usage	0.99	0.93	0.98	0.93	0.85
STY (mols H ₂ +CO/g-cat.h) ^a	0.019	0.031	0.012	0.020	0.016
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	0.70	1.80	0.60	1.10	2.40
Weight % of Outlet					
H ₂	5.16	4.28	5.79	5.20	4.50
H ₂ O	5.06	4.87	2.94	4.07	4.06
CO	73.5	58.8	82.0	72.6	58.9
CO ₂	9.10	21.3	4.33	10.7	22.2
Hydrocarbons	6.18	9.42	4.43	6.53	9.29
Oxygenates	0.86	1.01	0.37	0.72	0.85
Wax ^d	0.16	0.31	0.14	0.18	0.20
Yield (g/Nm ³ H ₂ + CO Converted)					
CH ₄	52.5	43.7	57.3	49.6	41.9
C ₂ -C ₄ Hydrocarbons	75.5	78.2	78.0	76.5	78.7
C ₅ -C ₁₁ Hydrocarbons	56.2	56.9	72.6	63.8	55.0
C ₁₂ + Hydrocarbons	12.6	11.6	13.6	14.8	7.35
Wax ^d	5.01	6.02	6.62	5.44	3.89
Oxygenates	26.8	19.8	18.2	22.0	16.4
Total	224	210	240	227	199
1+2 Olefins/n-Paraffin Ratio					
C ₂	0.45	0.37	0.70	0.49	0.37
C ₃	2.99	3.13	3.16	3.13	3.00
C ₄	2.59	2.94	2.72	2.81	2.77
C ₈	1.07	1.34	1.15	1.27	1.05
C ₁₀	1.02	1.10	1.04	1.05	1.00

^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-00-3068.

Weight % of Hydrocarbons	Period				
	1	2	3	4	5
CH ₄	26.7	23.0	25.9	24.2	22.9
Ethane	7.77	8.81	6.86	7.63	9.06
Ethylene	3.26	3.05	4.50	3.47	3.12
Propane	3.73	3.93	3.03	3.43	4.20
Propylene	10.6	11.7	9.14	10.5	12.0
n-Butane	3.48	3.28	3.04	3.19	3.72
1+2 Butenes	8.70	9.32	7.99	8.63	9.96
C ₄ Isomers	0.80	0.95	0.64	0.76	0.95
n-Pentane	3.80	3.53	3.53	3.49	4.07
1+2 Pentenes	6.88	6.50	6.71	6.72	7.22
C ₅ Isomers	1.06	1.43	1.18	1.15	1.57
n-Hexane	2.27	2.33	3.41	2.81	2.53
1+2 Hexenes	3.56	3.67	5.03	4.26	3.56
C ₆ Isomers	0.75	0.81	0.96	0.97	0.79
n-Heptane	1.43	1.48	2.40	1.82	1.57
1+2 Heptenes	1.82	1.81	3.13	2.34	1.72
C ₇ Isomers	0.37	0.45	0.49	0.74	0.38
n-Octane	0.79	1.02	1.28	0.94	0.95
1+2 Octenes	0.83	1.34	1.44	1.17	0.98
C ₈ Isomers	0.04	0.26	0.16	0.18	0.13
n-Nonane	0.63	0.72	0.30	0.45	0.72
1+2 Nonenes	0.66	0.85	0.28	0.52	0.75
C ₉ Isomers	0.04	0.11	0.02	0.05	0.07
n-Decane	0.87	0.85	0.57	0.78	0.84
1+2 Decenes	0.88	0.92	0.58	0.81	0.83
C ₁₀ Isomers	0.09	0.15	0.04	0.10	0.10
n-Undecane	0.89	0.77	0.62	0.89	0.64
1+2 Undecenes	0.79	0.73	0.58	0.80	0.55
C ₁₁ Isomers	0.10	0.15	0.06	0.18	0.09
C ₂ -C ₄	38.4	41.1	35.2	37.4	43.0
C ₅ -C ₁₁	28.5	29.9	32.8	31.2	30.1
C ₁₂ +	6.40	6.07	6.16	7.24	4.02
Wax ^d	2.54	3.16	2.99	2.66	2.12

^d Unanalyzed products collected from hot trap

Table 2. Summary of results for fixed bed run FA-34-3068.
Catalyst: 3.50 g^a, 100 Fe/3.0 Cu
Catalyst volume: 3.40 cc
Diluent: 36.9 g, Glass beads
Diluent Volume: 24.0 cc

Period	1	2	3	4	5
Date	10/07/88	10/08/88	10/09/88	10/10/88	10/11/88
Time on Stream (h)	72.5	95.5	119	143	167
Balance Duration (h)	6.20	6.00	6.80	6.20	6.50
Average Temperature (°C)	250	250	265	235	250
Maximum Δ Temperature (°C) ^b	4.50	3.80	5.10	2.70	3.00
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48
H ₂ /CO Feed Ratio	1.04	1.04	1.04	1.04	1.04
Space Velocity (Nl/g-cat-h) ^a	1.97	3.98	1.97	1.97	1.97
Space Velocity (Nl/g-Fe-h)	2.89	5.84	2.89	2.89	2.89
GHSV (h ⁻¹) ^c	251	506	251	251	251
CO Conversion (%)	65.9	44.6	91.2	38.1	70.8
H ₂ +CO Conversion (%)	57.3	41.2	78.4	34.3	60.5
H ₂ /CO Usage	0.77	0.89	0.75	0.84	0.75
STY (mols H ₂ +CO/g-cat-h) ^a	0.050	0.073	0.069	0.030	0.053
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	7.40	3.60	32.8	3.00	12.0
Weight % of Outlet					
H ₂	3.61	4.32	2.33	4.84	3.40
H ₂ O	3.73	3.88	3.22	3.81	2.92
CO	32.2	51.4	8.02	57.7	26.9
CO ₂	43.2	28.9	63.9	23.6	48.8
Hydrocarbons	15.5	10.6	20.3	8.44	16.2
Oxygenates	0.53	0.67	1.72	1.02	1.04
Wax ^d	0.77	0.18	0.42	0.57	0.73
Yield (g/Nm ³ H ₂ + CO Converted)					
CH ₄	30.5	34.8	28.0	33.5	29.4
C ₂ -C ₄ Hydrocarbons	70.3	68.2	74.3	62.3	66.9
C ₅ -C ₁₁ Hydrocarbons	60.4	58.9	58.1	58.5	74.1
C ₁₂ + Hydrocarbons	23.1	10.7	16.8	18.0	15.6
Wax ^d	8.71	2.90	3.61	10.9	7.99
Oxygenates	11.1	10.8	14.7	19.5	11.5
Total	195	183	192	192	197
1+2 Olefins/n-Paraffin Ratio					
C ₂	0.26	0.33	0.22	0.48	0.23
C ₃	2.50	2.48	2.36	2.70	2.31
C ₄	2.53	2.62	2.73	2.57	2.45
C ₆	1.07	1.10	1.51	1.42	1.07
C ₁₀	0.85	0.98	2.04	1.12	0.89

^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-34-3068.

Weight % of Hydrocarbons	Period				
	1	2	3	4	5
CH ₄	16.5	20.2	15.8	19.4	15.8
Ethane	8.52	8.56	9.47	7.18	8.11
Ethylene	2.05	2.65	1.94	3.24	1.70
Propane	4.35	4.46	5.11	3.77	4.30
Propylene	10.4	10.5	11.5	9.70	9.48
n-Butane	3.46	3.51	3.52	3.28	3.42
1+2 Butenes	8.44	8.86	9.25	8.15	8.08
C ₄ Isomers	0.96	0.95	1.12	0.84	0.86
n-Pentane	3.72	3.73	3.75	3.55	3.63
1+2 Pentenes	5.74	6.29	5.87	6.48	5.70
C ₅ Isomers	1.70	1.63	2.20	1.12	1.56
n-Hexane	2.52	2.40	2.24	2.46	2.65
1+2 Hexenes	2.78	3.24	3.05	3.89	3.10
C ₆ Isomers	0.69	0.72	0.72	0.81	0.63
n-Heptane	1.78	1.63	1.32	1.60	2.30
1+2 Heptenes	1.60	1.78	1.66	2.22	2.21
C ₇ Isomers	0.35	0.43	0.41	0.51	0.40
n-Octane	1.64	1.43	1.14	1.17	2.34
1+2 Octenes	1.72	1.55	1.69	1.64	2.46
C ₈ Isomers	0.30	0.17	0.21	0.35	0.24
n-Nonane	1.50	1.43	1.00	1.10	2.35
1+2 Nonenes	1.42	1.50	1.81	1.28	2.30
C ₉ Isomers	0.29	0.20	0.18	0.12	0.35
n-Decane	1.36	1.55	0.93	1.35	2.16
1+2 Decenes	1.14	1.49	1.88	1.49	1.90
C ₁₀ Isomers	0.33	0.24	0.24	0.19	0.44
n-Undecane	1.13	1.36	0.66	1.25	1.63
1+2 Undecenes	0.78	1.10	1.64	1.21	1.18
C ₁₁ Isomers	0.27	0.26	0.21	0.19	0.31
C ₂ -C ₄	38.1	39.5	41.9	36.1	36.0
C ₅ -C ₁₁	32.8	34.1	32.8	34.0	39.8
C ₁₂ +	12.5	6.19	9.49	10.5	8.41
Wax ^d	4.72	1.68	2.04	6.35	4.30

^d Unanalyzed products collected from hot trap

Table 3. Summary of results for fixed bed run FB-45-2638.
Catalyst: 3.80 g^a, 100 Fe/0.2 K
Diluent: 38.3 g, Glass beads
Catalyst volume: 2.60 cc
Diluent Volume: 25.0 cc

Period	1	2	3	4	5
Date	09/21/88	09/23/88	09/24/88	09/25/88	09/26/88
Time on Stream (h)	48.0	94.5	119	144	167
Balance Duration (h)	23.0	8.00	8.00	6.20	8.00
Average Temperature (°C)	235	250	250	266	234
Maximum Δ Temperature (°C) ^b	3.00	3.00	5.00	7.00	5.00
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48
H ₂ /CO Feed Ratio	0.98	0.98	0.98	0.98	0.98
Space Velocity (NI/g-cat·h) ^a	2.01	2.01	3.99	2.01	2.01
Space Velocity (NI/g-Fe·h)	2.87	2.87	5.72	2.87	2.87
GHV (h ⁻¹) ^c	272	272	542	272	272
CO Conversion (%)	17.2	37.6	22.6	69.6	29.4
H ₂ +CO Conversion (%)	13.9	30.9	18.7	57.5	24.5
H ₂ /CO Usage	.60	.63	.64	.64	.65
STY (mols H ₂ +CO/g-cat·h) ^a	.012	.028	.033	.051	.022
P _{CO₂} · P _{H₂} / P _{CO} · P _{H₂O}	5.10	9.00	5.80	21.7	9.40
Weight % of Outlet					
H ₂	5.95	5.00	5.67	3.61	5.32
H ₂ O	0.94	1.42	1.15	1.65	0.99
CO	78.0	58.4	72.9	28.4	66.1
CO ₂	11.0	26.2	15.0	49.5	20.4
Hydrocarbons	3.28	7.36	4.44	14.9	5.78
Oxygenates	0.24	0.54	0.39	0.86	0.49
Wax ^d	0.51	1.09	0.49	1.09	0.92
Yield (g/Nm ³ H ₂ + CO Converted)					
CH ₄	32.0	32.4	30.8	27.4	29.6
C ₂ -C ₄ Hydrocarbons	53.2	56.8	60.3	64.7	58.6
C ₅ -C ₁₁ Hydrocarbons	58.9	62.3	58.5	69.3	60.9
C ₁₂ + Hydrocarbons	38.1	32.9	27.1	26.1	35.6
Wax ^e	24.6	23.9	17.6	12.8	25.5
Oxygenates	11.7	11.9	13.9	10.1	13.4
Total	194	196	191	197	198
1+2 Olefins/n-Paraffin Ratio					
C ₂	1.16	0.89	1.07	0.92	0.99
C ₃	2.70	3.15	3.68	4.69	3.22
C ₄	2.15	2.78	3.07	4.06	2.73
C ₆	1.09	1.51	1.68	2.26	1.75
C ₁₀	0.81	1.55	1.27	2.05	1.46

^a Based on unreduced catalyst

^b Maximum axial temperature difference

^c Based on reactor volume

^d Unanalyzed products collected from hot trap

Table 3 (cont'd). Summary of results for fixed bed run FB-45-2638.

Weight. % of Hydrocarbons	Period				
	1	2	3	4	5
CH ₄	17.5	17.6	17.4	14.6	16.0
Ethane	5.54	5.63	5.51	5.07	5.10
Ethylene	5.99	4.67	5.52	4.37	4.71
Propane	2.60	2.67	2.59	2.37	2.74
Propylene	6.68	8.02	9.11	10.6	8.43
n-Butane	2.56	2.48	2.64	2.28	2.73
1+2 Butenes	5.31	6.68	7.83	8.92	7.20
C ₄ Isomers	0.52	0.65	0.91	0.87	0.81
n-Pentane	2.87	2.72	3.04	2.82	3.09
1+2 Pentenes	5.16	6.00	7.43	7.49	6.18
C ₅ Isomers	1.00	1.01	0.93	0.77	0.85
n-Hexane	2.58	1.62	2.10	1.01	1.81
1+2 Hexenes	4.11	3.75	5.18	3.08	4.33
C ₆ Isomers	1.21	0.92	1.30	0.53	0.97
n-Heptane	2.00	1.13	1.48	0.86	1.43
1+2 Heptenes	2.88	2.41	3.23	2.21	2.55
C ₇ Isomers	1.13	0.67	0.84	0.34	0.61
n-Octane	1.34	1.19	0.91	1.35	1.24
1+2 Octenes	1.44	1.76	1.50	3.01	2.13
C ₈ Isomers		0.03	0.02	0.23	0.10
n-Nonane	0.97	1.40	0.54	1.56	0.97
1+2 Nonenes	0.64	1.85	0.59	3.18	1.23
C ₉ Isomers	0.02	0.10	0.05	0.32	0.08
n-Decane	1.35	1.49	0.81	1.42	1.13
1+2 Decenes	1.08	2.28	1.02	2.86	1.62
C ₁₀ Isomers	0.05	0.17	0.12	0.39	0.14
n-Undecane	1.30	1.07	0.56	1.08	0.86
1+2 Undecenes	1.09	2.07	1.30	2.17	1.53
C ₁₁ Isomers	0.08	0.18	0.14	0.30	0.13
C ₂ -C ₄	29.2	30.8	34.1	34.5	31.7
C ₅ -C ₁₁	32.3	33.8	33.1	37.0	33.0
C ₁₂ +	20.9	17.8	15.3	13.9	19.3
Wax ^d	13.5	12.9	9.97	6.82	13.8

^d Unanalyzed products collected from hot trap

Table 4. Summary of results for fixed bed run FB-45-3208.

Catalyst: 3.50 g^a, 100 Fe/0.2 K
 Catalyst volume: 2.80 cc
 Diluent: 37.6 g, Glass beads
 Diluent Volume: 25.0 cc

Period	1	2	3	4	5
Date	11/18/88	11/19/88	11/20/88	11/21/88	11/22/88
Time on Stream (h)	71.5	94.5	119	144	167
Balance Duration (h)	7.00	7.00	6.00	7.00	6.20
Average Temperature (°C)	250	250	265	235	250
Maximum Δ Temperature (°C) ^b	9.00	9.00	10.00	5.00	7.00
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	2.01	5.96	2.01	2.01	2.01
Space Velocity (NI/g Fe-h)	2.88	5.69	2.88	2.88	2.88
GHSV (h ⁻¹) ^c	251	495	251	251	251
CO Conversion (%)	37.3	22.2	67.5	28.3	45.2
H ₂ +CO Conversion (%)	31.1	18.6	58.6	24.5	38.0
H ₂ /CO Usage	0.69	0.69	0.76	0.75	0.70
STY (moles H ₂ +CO/g-cat-h) ^a	0.028	0.033	0.052	0.022	0.034
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	11.8	13.6	22.6	6.10	19.1
Weight % of Outlet					
H ₂	5.12	5.85	3.47	5.44	4.75
H ₂ O	1.11	0.51	1.35	1.43	0.89
CO	58.4	73.0	30.7	67.0	51.3
CO ₂	26.3	15.3	47.3	19.0	32.1
Hydrocarbons	7.18	4.76	13.9	5.80	8.70
Oxygenates	0.63	0.29	1.52	0.54	0.82
Wax ^d	1.25	0.28	1.81	0.83	1.42
Yield (g/Nm ³ H ₂ + CO Converted)					
CH ₄	30.0	38.4	22.1	32.7	26.1
C ₂ -C ₄ Hydrocarbons	56.1	59.5	54.9	55.2	55.3
C ₅ -C ₁₁ Hydrocarbons	59.1	63.4	72.9	60.9	63.2
C ₁₂ + Hydrocarbons	34.6	17.4	25.6	30.2	31.4
Wax ^c	26.6	9.77	20.2	22.4	24.8
Oxygenates	13.3	10.4	16.9	14.6	14.2
Total	193	189	193	194	190
1+2 Olefins/n-Paraffin Ratio					
C ₂	1.75	1.72	1.76	1.66	1.84
C ₃	3.68	3.76	4.53	3.54	3.86
C ₄	2.96	3.01	3.56	2.91	3.06
C ₈	1.15	1.29	1.86	1.38	1.39
C ₁₀	1.26	1.92	1.64	1.28	1.53

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

Table 4 (cont'd). Summary of results for fixed bed run FB-45-3208.

Period	1	2	3	4	5
Weight % of Hydrocarbons					
CH ₄	16.7	21.5	12.6	18.3	14.8
Ethane	3.84	4.48	3.43	3.78	3.52
Ethylene	6.28	7.17	5.62	5.84	6.05
Propane	2.43	2.44	2.19	2.47	2.43
Propylene	8.51	8.75	9.44	8.33	8.96
n-Butane	2.40	2.45	2.17	2.51	2.39
1+2 Butenes	6.85	7.11	7.46	7.05	7.08
C ₄ Isomers	0.90	0.90	0.98	0.89	0.98
n-Pentane	2.94	3.07	2.86	3.11	2.96
1+2 Pentenes	5.79	7.32	6.19	5.89	5.92
C ₅ Isomers	0.89	1.32	0.83	1.13	0.82
n-Hexane	1.87	2.50	1.39	2.34	1.72
1+2 Hexenes	3.64	4.95	4.03	4.13	3.61
C ₆ Isomers	1.23	1.75	0.93	1.34	1.10
n-Heptane	1.46	1.86	1.33	1.58	1.17
1+2 Heptenes	2.16	3.11	3.33	2.80	2.12
C ₇ Isomers	0.78	1.18	0.62	0.92	0.68
n-Octane	1.33	1.20	1.89	1.37	1.16
1+2 Octenes	1.50	1.52	3.46	1.86	1.58
C ₈ Isomers	0.38	0.09	0.45	0.08	0.69
n-Nonane	1.19	0.75	1.95	0.93	1.42
1+2 Nonenes	1.38	0.65	3.18	1.06	2.02
C ₉ Isomers	0.19	0.10	0.53	0.15	0.21
n-Decane	1.36	0.67	1.75	1.14	1.80
1+2 Decenes	1.69	1.26	2.83	1.43	2.73
C ₁₀ Isomers	0.33	0.18	0.61	0.29	0.42
n-Undecane	0.99	0.64	1.06	0.86	1.38
1+2 Undecenes	1.46	1.22	1.90	1.34	2.12
C ₁₁ Isomers	0.28	0.17	0.41	0.26	0.25
C ₂ -C ₄	31.2	33.3	31.3	30.9	31.4
C ₅ -C ₁₁	32.8	35.5	41.5	34.0	35.9
C ₁₂ +	19.2	9.74	14.6	16.9	17.8
Wax ^d	14.8	5.47	11.5	12.5	14.1

^d Unanalyzed products collected from hot trap

Table 5. Summary of results for fixed bed run FA-46-3368.
Catalyst: 3.50 g^a, 100 Fe/0.5 K
Diluent: 36.4 g, Glass beads
Catalyst volume: 2.80 cc
Diluent Volume: 24.0 cc

Period	1	2	3	4	5
Date	11/18/88	11/19/88	11/20/88	11/21/88	11/22/88
Time on Stream (h)	71.5	94.5	120	144	168
Balance Duration (h)	6.00	7.00	6.00	7.00	6.00
Average Temperature (°C)	250	250	265	235	250
Maximum Δ Temperature (°C) ^b	5.00	4.00	6.00	2.00	3.00
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48
H ₂ /CO Feed Ratio	0.98	0.98	0.98	0.98	0.96
Space Velocity (NI/g-cat·h) ^a	1.99	3.99	2.00	2.00	2.00
Space Velocity (NI/g-Fe·h)	2.92	5.87	2.94	2.87	2.87
GHSV (h ⁻¹) ^c	260	522	261	251	261
CO Conversion (%)	50.6	28.1	84.9	33.4	58.8
H ₂ +CO Conversion (%)	40.4	22.1	70.2	28.3	49.4
H ₂ /CO Usage	0.58	0.56	0.64	0.68	0.65
STY (mols H ₂ +CO/g-cat·h) ^a	0.036	0.039	0.063	0.025	0.044
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	41.0	42.5	52.3	43.1	89.5
Weight % of Outlet					
H ₂	4.71	5.64	2.98	5.11	3.97
H ₂ O	0.49	0.21	1.40	0.26	0.28
CO	47.2	68.5	14.2	62.8	39.1
CO ₂	35.4	19.1	61.0	24.0	43.1
Hydrocarbons	8.18	5.23	16.3	6.43	10.9
Oxygenates	0.81	0.42	1.28	0.12	0.28
Wax ^d	3.26	0.89	2.84	1.28	2.35
Yield (g/Nm ³ H ₂ + CO Converted)					
CH ₄	23.9	31.6	23.4	22.8	22.0
C ₂ -C ₄ Hydrocarbons	46.5	53.1	58.7	47.5	53.1
C ₅ -C ₁₁ Hydrocarbons	55.3	60.5	64.5	69.2	65.1
C ₁₂ + Hydrocarbons	61.8	38.3	36.5	42.6	39.4
Wax ^c	53.4	26.8	27.2	30.3	31.9
Oxygenates	13.2	12.5	12.3	2.82	3.77
Total	201	196	195	185	183
1+2 Olefins/n-Paraffin Ratio					
C ₂	1.99	2.02	1.09	2.07	1.21
C ₃	3.50	3.53	4.77	3.09	3.59
C ₄	2.73	2.76	3.85	2.41	2.85
C ₈	1.51	1.59	2.18	2.71	1.89
C ₁₀	1.74	1.92	2.34	1.58	1.29

^a Based on unreduced catalyst

^c Based on reactor volume

^b Maximum axial temperature difference

^d Unanalyzed products collected from hot trap

Table 5 (cont'd). Summary of results for fixed bed run FA-46-3368.

Weight % of Hydrocarbons	Period				
	1	2	3	4	5
CH ₄	12.7	17.2	12.8	12.5	12.2
Ethane	2.88	3.63	4.82	2.99	4.47
Ethylene	5.36	6.84	4.91	5.78	5.05
Propane	2.02	2.22	2.19	2.32	2.43
Propylene	6.74	7.49	9.96	6.86	8.33
n-Butane	1.96	2.17	1.97	2.23	2.25
1+2 Butenes	5.14	5.80	7.33	5.20	6.19
C ₄ Isomers	0.69	0.78	0.88	0.72	0.86
n-Pentane	2.36	2.64	2.44	2.62	2.60
1+2 Pentenes	4.95	5.85	6.20	4.74	5.30
C ₅ Isomers	0.44	0.80	0.48	0.40	0.44
n-Hexane	1.12	1.96	1.08	1.84	1.30
1+2 Hexenes	2.86	4.17	3.60	3.68	3.34
C ₆ Isomers	0.99	1.59	0.81	1.36	1.00
n-Heptane	0.81	1.25	0.97	1.37	1.48
1+2 Heptenes	1.74	2.80	2.65	3.65	3.05
C ₇ Isomers	0.66	0.88	1.15	0.96	1.20
n-Octane	1.06	1.01	1.19	0.97	1.41
1+2 Octenes	1.57	1.57	2.54	2.58	2.63
C ₈ Isomers	1.52	0.14	0.57	0.99	1.26
n-Nonane	1.26	1.11	1.15	1.26	1.63
1+2 Nonenes	1.83	0.95	2.68	3.02	2.44
C ₉ Isomers	0.16	0.14	0.52	0.11	0.34
n-Decane	1.18	0.98	1.06	1.74	1.57
1+2 Decenes	2.02	1.85	2.45	2.70	1.99
C ₁₀ Isomers	0.24	0.27	0.62	0.25	0.39
n-Undecane	0.73	0.94	0.75	1.58	1.18
1+2 Undecenes	1.62	1.80	1.73	1.94	1.42
C ₁₁ Isomers	0.38	0.25	0.58	0.23	0.27
C ₂ -C ₄	24.8	28.9	32.0	26.1	29.6
C ₅ -C ₁₁	29.5	33.0	35.2	36.0	36.3
C ₁₂ +	33.0	20.9	19.9	23.4	21.9
Wax ^d	28.5	14.6	14.8	16.6	17.7

^d Unanalyzed products collected from hot trap

Table 6. Summary of results for fixed bed run FA-47-2638.

Catalyst: 3.50 g^a, 100 Fe/1.0 K
 Catalyst volume: 2.80 cc
 Diluent: 38.3 g, Glass beads
 Diluent Volume: 24.5 cc

Period	1	2	3	4	5
Date	09/21/88	09/23/88	09/24/88	09/25/88	09/26/88
Time on Stream (h)	48.0	94.5	119	144	168
Balance Duration (h)	22.1	7.00	7.00	6.00	6.00
Average Temperature (°C)	235	250	250	265	235
Maximum Δ Temperature (°C) ^b	4.50	3.50	4.10	4.10	3.90
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48
H ₂ /CO Feed Ratio	1.04	1.04	1.04	1.04	1.04
Space Velocity (NI/g-cat·h) ^a	2.01	2.01	3.99	2.01	2.01
Space Velocity (NI/g-Fe·h)	2.89	2.89	5.74	2.89	2.89
GHSV (h ⁻¹) ^c	256	256	508	256	256
CO Conversion (%)	30.2	53.8	32.2	88.3	44.5
H ₂ +CO Conversion (%)	23.4	43.0	26.3	73.0	36.9
H ₂ /CO Usage	0.58	0.63	0.67	0.69	0.69
STY (mols H ₂ +CO/g-cat·h) ^a	0.021	0.039	0.047	0.066	0.033
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	10.1	38.1	22.4	34.6	24.7
Weight % of Outlet					
H ₂	5.72	4.65	5.64	2.98	4.90
H ₂ O	1.12	0.65	0.49	2.73	0.70
CO	64.1	42.4	64.2	11.1	51.6
CO ₂	22.3	40.0	21.9	61.7	32.0
Hydrocarbons	4.71	9.10	5.77	16.8	7.56
Oxygenates	0.57	0.83	0.55	1.31	1.18
Wax ^d	1.41	2.33	1.42	3.45	2.08
Yield (g/Nm ³ H ₂ + CO Converted)					
CH ₄	15.8	19.6	17.6	20.9	16.0
C ₂ -C ₄ Hydrocarbons	41.6	51.3	46.8	53.7	46.6
C ₅ -C ₁₁ Hydrocarbons	56.0	54.7	52.8	61.9	53.5
C ₁₂ + Hydrocarbons	60.5	51.6	59.9	42.2	55.9
Wax ^e	40.0	36.1	35.0	30.4	37.1
Oxygenates	16.2	12.8	13.6	11.6	21.1
Total	190	190	191	190	193
1+2 Olefins/n-Paraffin Ratio					
C ₂	2.46	2.09	2.21	2.06	2.07
C ₃	3.31	4.23	4.15	6.32	3.55
C ₄	2.47	3.39	3.24	5.08	2.74
C ₈	1.15	1.74	1.42	3.28	1.68
C ₁₀	1.09	2.04	2.58	3.14	1.95

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

Table 6 (cont'd). Summary of results for fixed bed run FA-47-2638.

Period	1	2	3	4	5
Weight % of Hydrocarbons					
CH ₄	9.11	11.0	9.94	11.7	9.28
Ethane	2.46	3.22	2.95	3.01	2.88
Ethylene	5.65	6.30	6.06	5.79	5.56
Propane	1.96	2.02	1.86	1.62	2.25
Propylene	6.17	8.17	7.36	9.76	7.63
n-Butane	2.08	1.96	1.80	1.51	2.18
1+2 Butenes	4.95	6.40	5.61	7.42	5.76
C ₄ Isomers	0.67	0.89	0.80	0.95	0.85
n-Pentane	2.45	2.43	2.21	2.10	2.53
1+2 Pentenes	5.22	6.23	5.34	6.33	5.05
C ₅ Isomers	0.57	0.65	0.61	0.41	0.49
n-Hexane	1.40	1.17	1.34	0.92	1.27
1+2 Hexenes	3.08	2.84	3.02	3.78	2.82
C ₆ Isomers	1.31	0.82	1.02	0.82	0.84
n-Heptane	0.98	0.94	0.98	0.83	0.89
1+2 Heptenes	2.12	2.12	1.94	3.02	1.77
C ₇ Isomers	1.02	0.44	0.65	0.53	0.45
n-Octane	1.39	1.16	0.93	0.99	1.17
1+2 Octenes	1.57	1.98	1.30	3.19	1.93
C ₈ Isomers	0.04	0.07	0.06	0.50	0.09
n-Nonane	1.64	1.18	1.26	0.98	1.35
1+2 Nonenes	1.55	2.12	1.71	2.95	2.36
C ₉ Isomers	0.13	0.21	0.11	0.48	0.20
n-Decane	1.85	1.09	1.04	0.83	1.36
1+2 Decenes	1.99	2.20	2.64	2.56	2.62
C ₁₀ Isomers	0.20	0.28	0.22	0.46	0.27
n-Undecane	1.56	0.77	0.91	0.60	1.10
1+2 Undecenes	1.90	1.93	2.31	1.94	2.36
C ₁₁ Isomers	0.20	0.24	0.20	0.41	0.21
C ₂ -C ₄	23.9	29.0	26.4	30.0	27.1
C ₅ -C ₁₁	32.2	30.9	29.8	34.6	31.1
C ₁₂ +	34.8	29.1	33.8	23.6	32.5
Wax ^d	23.0	20.4	19.8	17.0	21.6

^d Unanalyzed products collected from hot trap

Table 7. Summary of results for fixed bed run FB-27-3368.
 Catalyst: 3.50 g^a, 100 Fe/3.0 Cu/0.5 K
 Catalyst volume: 3.80 cc
 Diluent: 36.0 g, Glass beads
 Diluent Volume: 23.5 cc

Period	1	2	3	4	5
Date	10/24/88	10/25/88	10/26/88	10/27/88	10/29/88
Time on Stream (h)	71.5	95.5	119	142	189
Balance Duration (h)	7.70	6.20	6.80	6.50	6.50
Average Temperature (°C)	249	250	235	250	250
Maximum Δ Temperature (°C) ^b	5.60	5.60	2.60	3.90	3.90
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48
H ₂ /CO Feed Ratio	0.93	0.98	0.98	0.98	0.72
Space Velocity (NI/g-cat·h) ^a	1.99	4.01	1.99	1.99	1.99
Space Velocity (NI/g-Fe·h)	2.93	5.91	2.93	2.93	2.93
GHSV (h ⁻¹) ^c	254	511	254	254	253
CO Conversion (%)	91.0	64.6	69.0	93.8	85.8
H ₂ +CO Conversion (%)	75.8	52.7	55.5	78.2	79.9
H ₂ /CO Usage	0.65	0.62	0.59	0.65	0.60
STY (mols H ₂ +CO/g-cat·h) ^a	0.067	0.094	0.049	0.069	0.071
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	49.9	44.0	62.9	64.1	291
Weight % of Outlet					
H ₂	2.61	3.93	3.83	2.49	1.34
H ₂ O	2.29	0.72	0.61	2.50	0.13
CO	8.39	33.2	28.9	5.85	13.0
CO ₂	64.5	47.3	50.6	66.1	63.6
Hydrocarbons	18.1	11.8	11.6	18.4	16.9
Oxygenates	2.37	1.32	1.93	2.88	1.86
Wax ^d	1.71	1.74	2.57	1.74	3.06
Yield (g/Nm ³ H ₂ + CO Converted)					
CH ₄	18.7	20.8	19.2	18.3	14.7
C ₂ -C ₄ Hydrocarbons	54.7	53.5	49.9	56.8	50.7
C ₅ -C ₁₁ Hydrocarbons	71.6	69.1	64.9	71.7	82.7
C ₁₂ + Hydrocarbons	32.3	30.3	39.3	27.1	50.1
Wax ^e	15.3	22.3	31.4	15.0	30.3
Oxygenates	21.2	16.9	23.5	24.9	18.4
Total	198	191	197	199	217
1+2 Olefins/n-Paraffin Ratio					
C ₂	2.00	2.24	2.14	1.71	2.00
C ₃	4.24	3.96	3.19	4.34	4.60
C ₄	3.19	3.04	2.39	3.30	3.43
C ₈	2.29	1.90	1.79	2.32	2.53
C ₁₀	2.17	2.03	1.77	2.08	2.29

^a Based on unreduced catalyst

^c Based on reactor volume

^b Maximum axial temperature difference

^d Unanalyzed products collected from hot trap

Table 7 (cont'd). Summary of results for fixed bed run FB-27-3368.

Period	6	7	8	9
Date	11/01/88	11/03/88	11/07/88	11/09/88
Time on Stream (h)	263	311	408	456
Balance Duration (h)	6.50	6.50	6.00	6.00
Average Temperature (°C)	250	260	260	250
Maximum Δ Temperature (°C) ^b	3.70	4.20	4.70	2.10
Pressure (MPa)	1.48	1.48	1.48	1.48
H ₂ /CO Feed Ratio	0.72	0.72	0.72	0.98
Space Velocity (NI/g-cat.h) ^a	1.99	1.99	1.99	1.99
Space Velocity (NI/g-Fe.h)	2.93	2.93	2.93	2.93
GHSV (h ⁻¹) ^c	253	253	253	253
CO Conversion (%)	85.2	92.5	91.9	83.8
H ₂ +CO Conversion (%)	79.2	87.1	86.6	69.5
H ₂ /CO Usage	0.60	0.62	0.62	0.64
STY (mols H ₂ +CO/g-cat.h) ^a	0.070	0.077	0.077	0.062
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	273	64.8	86.5	81.1
Weight % of Outlet				
H ₂	1.46	0.98	1.01	2.93
H ₂ O	0.14	0.83	0.59	0.84
CO	14.4	6.98	7.60	14.9
CO ₂	64.3	67.5	67.8	60.7
Hydrocarbons	15.2	19.0	18.9	17.5
Oxygenates	1.72	2.10	2.16	2.23
Wax ^d	2.72	2.52	1.98	0.89
Yield (g/Nm ³ H ₂ + CO Converted)				
CH ₄	14.5	15.1	15.6	20.0
C ₂ -C ₄ Hydrocarbons	50.3	57.2	60.9	66.6
C ₅ -C ₁₁ Hydrocarbons	70.5	84.9	68.7	76.2
C ₁₂ + Hydrocarbons	33.4	35.2	41.5	18.9
Wax ^d	25.7	22.5	17.7	8.76
Oxygenates	16.2	18.8	19.3	22.0
Total	185	211	206	204
1+2 Olefins/n-Paraffin Ratio				
C ₂	1.70	1.91	1.80	1.38
C ₃	4.65	5.96	6.12	4.16
C ₄	3.48	4.46	4.54	3.18
C ₅	2.48	2.94	1.30	2.17
C ₁₀	2.27	2.56	1.02	1.91

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

Table 7 (cont'd). Summary of results for fixed bed run FB-27-3368.

Period	1	2	3	4	5
Weight % of Hydrocarbons					
CH ₄	10.5	12.0	11.1	10.5	7.44
Ethane	3.24	3.18	2.93	3.66	2.52
Ethylene	6.04	6.63	5.86	5.85	4.70
Propane	2.26	2.28	2.57	2.39	1.78
Propylene	9.15	8.64	7.82	9.93	7.83
n-Butane	2.28	2.34	2.65	2.37	1.87
1+2 Butenes	7.02	6.86	6.11	7.54	6.17
C ₄ Isomers	0.84	0.87	0.86	0.90	0.69
n-Pentane	2.86	2.99	3.19	2.96	2.45
1+2 Pentenes	6.38	6.92	5.63	6.58	5.59
C ₅ Isomers	0.49	0.72	0.48	0.46	0.36
n-Hexane	1.53	1.69	1.74	1.67	1.54
1+2 Hexenes	3.99	4.36	3.67	4.11	4.24
C ₆ Isomers	0.69	3.73	0.86	0.75	0.68
n-Heptane	1.18	1.25	1.41	1.40	1.37
1+2 Heptenes	2.78	3.01	2.93	3.28	3.42
C ₇ Isomers	0.38	0.60	0.72	0.43	0.49
n-Octane	1.53	1.45	1.68	1.66	1.58
1+2 Octenes	3.44	2.70	2.96	3.79	3.91
C ₈ Isomers	0.28	0.36	0.22	0.49	0.40
n-Nonane	1.73	1.27	1.64	1.69	1.75
1+2 Nonenes	3.68	2.35	2.77	3.51	3.95
C ₉ Isomers	0.33	0.25	0.24	0.44	0.38
n-Decane	1.51	1.08	1.43	1.40	1.54
1+2 Decenes	3.23	2.16	2.50	2.86	3.47
C ₁₀ Isomers	0.36	0.28	0.25	0.41	0.42
n-Undecane	1.20	0.77	1.03	1.00	1.19
1+2 Undecenes	2.57	1.69	1.89	2.06	2.65
C ₁₁ Isomers	0.22	0.16	0.19	0.27	0.33
C ₂ -C ₄	30.8	30.8	28.8	32.6	25.6
C ₅ -C ₁₁	40.4	39.8	37.4	41.2	41.7
C ₁₂ +	18.2	17.4	22.7	15.6	25.3
Wax ^d	8.64	12.8	18.1	8.61	15.3

^d Unanalyzed products collected from hot trap

Table 7 (cont'd). Summary of results for fixed bed run FB-27-3368.

Period		6	7	8	9
Weight % of Hydrocarbons					
CH ₄		8.59	7.86	8.38	11.0
Ethane		3.28	2.86	3.31	4.90
Ethylene		5.20	5.10	5.56	6.31
Propane		2.06	1.73	1.85	2.76
Propylene		9.15	9.84	10.8	10.9
n-Butane		2.14	1.77	1.88	2.60
1+2 Butenes		7.17	7.62	8.26	7.97
C ₄ Isomers		0.83	0.83	0.92	1.18
n-Pentane		2.83	2.49	2.65	3.21
1+2 Pentenes		6.46	6.64	6.98	7.15
C ₅ Isomers		0.44	0.40	0.47	0.75
n-Hexane		1.66	1.50	0.99	1.62
1+2 Hexenes		4.66	4.87	2.95	4.06
C ₆ Isomers		0.85	0.84	0.86	0.89
n-Heptane		1.29	1.52	0.80	1.50
1+2 Heptenes		3.35	4.14	1.55	3.32
C ₇ Isomers		0.58	0.66	0.37	0.55
n-Octane		1.55	1.63	1.12	1.69
1+2 Octenes		3.78	4.72	1.43	3.60
C ₈ Isomers		0.59	0.48	0.20	0.41
n-Nonane		1.66	1.51	2.08	1.68
1+2 Nonenes		3.73	3.90	2.20	3.23
C ₉ Isomers		0.34	0.65	0.14	0.34
n-Decane		1.36	1.20	2.89	1.47
1+2 Decenes		3.04	3.02	2.90	2.78
C ₁₀ Isomers		0.34	0.57	0.30	0.37
n-Undecane		0.95	0.85	2.94	1.12
1+2 Undecenes		2.07	2.12	2.61	2.03
C ₁₁ Isomers		0.27	0.39	0.34	0.21
C ₂ -C ₄		29.8	29.7	32.6	36.6
C ₅ -C ₁₁		41.8	44.1	36.8	42.0
C ₁₂ +		19.8	18.3	22.2	10.4
Wax ^d		15.2	11.7	9.48	4.82

^d Unanalyzed products collected from hot trap

Table 8. Comparison of doubly promoted catalyst results (FB-27-3368) to Mobil.

Run	Mobil	TAMU
	CT-256-3-13	FB-27-3368 ^(a)
TOS (h)	370	360
T (°C)	260	260
P (MPa)	1.48	1.48
SV (Nℓ/g-cat·h)	1.65 ⁽²⁾	2.00
H ₂ /CO	0.683	0.72
Conversion (%)		
H ₂ +CO	86.1	86.9
CO	90.0	92.2
Weight % of Hydrocarbons		
CH ₄	7.14	8.2
C ₂ -C ₄	22.1	31.2
C ₅ +	70.8	60.7
(1+2)-Olefins/n-Paraffin		
C ₂	0.48	1.86
C ₃	4.34	6.04
C ₄	3.43	4.50

^(a) Average of balances 7 (312 h) and 8 (409 h).

^(b) Calculated from their 2.62 Nℓ/g-Fe·h, using 0.67 g-Fe/g-cat, 6.3 % N₂ in feed.

Table 9. Effect of copper and potassium promoters on catalyst activity.

T	(H ₂ +CO) Conversion (%)				
	Pure Fe	3.0 Cu	0.2 K (a)	0.5 K	1.0 K
235 °C ^(b)	13.7	34.3	24.5	28.3	36.9 ^(c)
250 °C ^(b)	21.7 ^(c)	57.3 ^(c)	31.1 ^(c)	40.4 ^(c)	43.0 ^(f)
250 °C ^(d)	—	41.2	18.6	22.1	26.3
265 °C ^(b)	35.1	78.4	58.6	70.2	73.0
					—

T	P _{CO} , P _{H₂} /P _{Co} P _{H₂O}				
	Pure Fe	3.0 Cu	0.2 K (a)	0.5 K	1.0 K
235 °C ^(b)	0.6	3.0	16.1	43.1	24.7 ^(c)
250 °C ^(b)	0.7 ^(c)	7.4 ^(f)	11.8 ^(c)	41.0 ^(c)	38.1
250 °C ^(d)	—	3.6	13.6	42.5	22.4
265 °C ^(b)	1.8	32.8	22.6	52.3	34.6
					—

(a) Run FB-45-3208

(c) Balance 5 results

(e) Balance 1 results

(b) 1.48 MPa, 2.0 Nℓ/g-cat·h, H₂/CO = 1.0

(d) 1.48 MPa, 4.0 Nℓ/g-cat·h, H₂/CO = 1.0

(f) Balance 2

Table 10. Effect of copper and potassium promoters on catalyst selectivity^(a).

Conditions		235 °C, 1.48 MPa, 2.0 Nl/g-cat·h, H ₂ /CO = 1.0									
Parts		Weight % of Hydrocarbons					(1+2)-Olefins/n-Paraffin				
Cu	K	CH ₄	C ₂ -C ₄	C ₅ -C ₁₁	C ₁₂ +	C ₂	C ₃	C ₄	C ₈	C ₁₀	C ₁₀
-	-	25.9	35.2	32.8	6.2	0.70	3.16	2.72	1.15	1.04	1.04
3.0	-	19.4	36.1	34.0	10.5	0.48	2.70	2.57	1.42	1.12	1.12
-	0.2 ^(b)	18.3	30.9	34.0	16.9	1.66	3.54	2.91	1.38	1.28	1.28
-	0.5	12.5	26.1	38.0	23.4	2.07	3.09	2.41	2.71	1.58	1.58
-	1.0	9.2	25.5	31.7	33.6	2.26	3.43	2.61	1.42	1.52	1.52
3.0	0.5	11.1	28.8	37.5	22.7	2.14	3.19	2.39	1.79	1.77	1.77

Conditions		250 °C, 1.48 MPa, 2.0 Nl/g-cat·h, H ₂ /CO = 1.0									
Parts		Weight % of Hydrocarbons					(1+2)-Olefins/n-Paraffin				
Cu	K	CH ₄	C ₂ -C ₄	C ₅ -C ₁₁	C ₁₂ +	C ₂	C ₃	C ₄	C ₈	C ₁₀	C ₁₀
-	-	25.4	37.9	29.9	6.8	0.47	3.06	2.70	1.17	1.04	1.04
3.0	-	16.2	37.0	36.3	10.5	0.24	2.41	2.49	1.07	0.87	0.87
-	0.2 ^(b)	15.8	31.3	34.4	18.5	1.79	3.77	3.01	1.27	1.40	1.40
-	0.5	12.5	27.2	32.9	27.5	1.60	3.54	2.79	1.70	1.52	1.52
-	1.0	11.1	29.0	30.9	29.1	2.09	4.23	3.39	1.74	2.04	2.04
3.0	0.5	10.5	31.7	40.8	16.9	1.25	4.29	3.25	2.30	2.13	2.13

Conditions		250 °C, 1.48 MPa, 4.0 Nl/g-cat·h, H ₂ /CO = 1.0									
Parts		Weight % of Hydrocarbons					(1+2)-Olefins/n-Paraffin				
Cu	K	CH ₄	C ₂ -C ₄	C ₅ -C ₁₁	C ₁₂ +	C ₂	C ₃	C ₄	C ₈	C ₁₀	C ₁₀
3.0	-	20.2	39.5	34.1	6.2	0.33	2.48	2.62	1.10	0.98	0.98
-	0.2 ^(b)	21.5	33.3	35.5	9.7	1.72	3.76	3.01	1.29	1.92	1.92
-	0.5	17.2	28.9	33.0	20.9	2.02	3.53	2.76	1.59	1.92	1.92
-	1.0	9.9	26.4	29.8	33.8	2.21	4.15	3.24	1.42	2.58	2.58
3.0	0.5	12.0	30.8	39.8	17.4	2.24	3.96	3.04	1.90	2.03	2.03

Conditions		265 °C, 1.48 MPa, 2.0 Nl/g-cat·h, H ₂ /CO = 1.0									
Parts		Weight % of Hydrocarbons					(1+2)-Olefins/n-Paraffin				
Cu	K	CH ₄	C ₂ -C ₄	C ₅ -C ₁₁	C ₁₂ +	C ₂	C ₃	C ₄	C ₈	C ₁₀	C ₁₀
-	-	23.0	41.1	29.9	6.1	0.37	3.13	2.94	1.34	1.10	1.10
3.0	-	15.8	41.9	32.8	9.5	0.22	2.36	2.73	1.51	2.04	2.04
-	0.2 ^(b)	12.6	31.3	41.5	14.6	1.76	4.53	3.56	1.86	1.64	1.64
-	0.5	12.8	32.0	35.2	19.9	1.09	4.77	3.85	2.18	2.34	2.34
-	1.0	11.7	30.1	34.6	23.6	2.06	6.32	5.08	3.28	3.14	3.14

^(a) Average of results from repeated conditions

^(b) Run FB-45-3208 results

Table 11. Summary of kinetic data for run SA-05 2057 (10.0 Fe/0.3 Cu/0.2 K catalyst).

Balance	8	9	10	11	13	14	15	16	17	18
T (°C)	220	235	250	250	265	250	250	250	250	250
P (MPa)	1.48	1.48	1.48	1.48	1.48	0.79	1.48	1.48	2.24	2.96
SV (Nl/g cat-h)	2.00	2.11	2.03	4.07	2.24	1.12	1.00	2.00	3.00	4.00
Feed H ₂ /CO	0.67	0.69	0.71	0.72	0.71	0.67	0.68	1.06	1.03	1.03
CO Conversion (%)	21.3	42.8	76.2	50.2	83.6	57.9	84.7	82.0	80.8	78.8
(H ₂ +CO) Conversion (%)	20.5	40.6	70.2	49.4	76.8	58.9	84.7	67.1	68.8	66.1
(H ₂ /CO) Usage	0.60	0.61	0.58	0.69	0.57	0.70	0.68	0.69	0.72	0.70
P _{CO₂} P _{H₂} /P _{CO} P _{H₂O}	3.5	5.6	18.8	9.7	23.5	25.2	94.6	63.1	27.2	17.2
P _{CO} (MPa)	0.813	0.677	0.376	0.638	0.262	0.323	0.321	0.220	0.380	0.539
P _{CO₂} (MPa)	0.086	0.239	0.580	0.319	0.668	0.223	0.815	0.492	0.739	0.900
P _{H₂} (MPa)	0.556	0.514	0.427	0.476	0.371	0.202	0.218	0.608	0.875	1.206
P _{H₂O} (MPa)	0.017	0.033	0.035	0.024	0.040	0.006	0.006	0.022	0.062	0.117
n	5.72	5.10	6.14	5.10	3.57	3.52	4.72	3.45	3.66	4.01
m/n	2.18	2.20	2.16	2.19	2.37	2.33	2.25	2.42	2.38	2.33
Wt % of Hydrocarbons										
CH ₄	1.4	1.6	2.4	1.6	10.9	5.5	3.8	12.4	9.3	7.9
C ₂ -C ₄	7.2	7.2	9.0	6.4	29.1	16.1	11.0	30.4	25.3	23.2
C ₅ -C ₁₁	13.4	12.0	20.6	11.9	40.4	20.9	24.7	38.6	33.3	38.2
C ₁₂ +	78.0	79.2	68.0	80.1	19.6	57.5	60.5	18.6	32.1	30.7
(1+2)-Olefins/n-Paraffin										
C ₂	1.46	2.66	1.64	3.36	0.35	0.97	0.57	0.23	0.30	0.51
C ₄	4.16	4.89	5.59	5.95	3.38	5.53	4.34	2.26	2.52	2.81
C ₈	2.08	2.29	2.78	2.39	1.34	1.72	1.74	0.70	0.70	1.23
C ₁₀	1.29	2.70	2.43	2.43	1.00	1.25	1.25	0.55	0.67	0.88

Table 12. Summary of kinetic data for run SB-07-0458 (100 Fe/0.3 Cu/0.5 K catalyst).

Balance TOS (h)	5	6	7	8	9	10
T (°C)	236	284	332	380	428	452
P (MPa)	250	265	265	235	250	265
SV (Nl/g-cat·h)	1.48	1.48	1.48	1.48	1.48	2.96
Feed H ₂ /CO	1.00	2.03	1.02	1.02	2.05	2.05
	0.74	0.70	0.72	0.71	1.06	0.73
CO Conversion (%)	42.2	53.0	74.4	27.1	40.7	79.2
(H ₂ +CO) Conversion (%)	39.1	48.4	69.0	25.2	31.2	73.0
(H ₂ /CO) Usage	0.61	0.55	0.60	0.59	0.58	0.59
P _{CO} , P _{H₂} /P _{CO} P _{H₂O}	10.9	25.8	39.7	10.8	13.5	25.3
P _{CO} (MPa)	0.645	0.586	0.379	0.737	0.523	0.681
P _{CO₂} (MPa)	0.246	0.330	0.598	0.156	0.180	1.205
P _{H₂} (MPa)	0.535	0.511	0.410	0.556	0.731	0.844
P _{H₂O} (MPa)	6.019	0.011	0.016	0.011	0.019	0.059
n	5.24	4.68	4.76	6.00	4.95	4.36
m/n	2.19	2.21	2.20	2.16	2.20	2.22

Table 13. Summary of kinetic data for run SA-99-0888 (Ruhrcemie LP 33/81 catalyst).

Balance	7	8	9	10	11	12	13
T (°C)	250	235	235	265	250	250	250
P (MPa)	1.48	1.48	1.48	1.48	1.48	1.48	2.96
SV (Nℓ/g-cat·h)	1.00	2.01	1.00	2.00	2.02	2.02	4.03
Feed H ₂ /CO	0.65	0.65	0.67	0.67	0.67	1.00	1.02
CO Conversion (%)	56.0	18.8	30.6	57.3	32.8	48.5	36.6
(H ₂ +CO) Conversion (%)	56.1	23.0	35.8	56.9	35.9	45.4	39.8
(H ₂ /CO) Usage	0.66	1.01	0.95	0.65	0.83	0.87	1.20
P _{CO₂} P _{H₂} /P _{CO} P _{H₂O}	2.5	0.4	0.7	4.4	1.1	2.0	0.6
P _{CO} (MPa)	0.605	0.847	0.788	0.584	0.768	0.530	1.258
P _{CO₂} (MPa)	0.316	0.052	0.124	0.350	0.138	0.182	0.172
P _{H₂} (MPa)	0.319	0.481	0.428	0.400	0.455	0.595	1.156
P _{H₂O} (MPa)	0.080	0.071	0.096	0.055	0.072	0.105	0.268
n	3.55	3.51	3.64	3.37	3.34	3.18	3.61
m/n	2.30	2.27	2.27	2.34	2.31	2.36	2.30
Wt % of Hydrocarbons							
CH ₄	5.8	5.8	5.6	8.2	7.0	9.4	6.7
C ₂ -C ₄	26.6	30.0	27.0	29.4	28.8	34.5	29.3
C ₅ -C ₁₁	32.5	37.0	35.9	35.4	32.7	33.2	34.9
C ₁₂ +	35.1	27.2	31.5	27.1	31.5	23.0	29.1
(1+2)-Olefins/n-Paraffin							
C ₂	0.84	2.19	1.70	0.70	1.47	0.86	1.44
C ₄	5.73	6.61	6.58	5.12	6.59	4.85	4.62
C ₈	2.28	2.98	2.85	2.23	2.53	2.13	2.50
C ₁₀	1.85	2.39	2.34	1.71	2.05	1.63	1.92

Table 14. Summary of kinetic data for run SB-66-2468 (100 Fe/5.0 Cu/4.2 K/24 SiO₂ catalyst).

Balance	5	6	7
TOS (h)	453	500	549
T (°C)	250	250	250
P (MPa)	1.48	1.48	1.48
SV (Nℓ/g-cat·h)	2.00	4.00	1.00
Feed H ₂ /CO	0.69	0.69	0.69
CO Conversion (%)	42.3	22.3	61.0
(H ₂ +CO) Conversion (%)	44.3	26.2	61.1
(H ₂ /CO) Usage	0.78	0.99	0.76
$P_{\text{CO}_2} P_{\text{H}_2} / P_{\text{CO}} P_{\text{H}_2\text{O}}$	1.51	0.89	2.73
P_{CO} (MPa)	0.695	0.817	0.522
P_{CO_2} (MPa)	0.202	0.080	0.367
P_{H_2} (MPa)	0.441	0.499	0.391
$P_{\text{H}_2\text{O}}$ (MPa)	0.085	0.055	0.101
n	4.23	3.90	3.68
m/n	2.28	2.28	2.36

Table 15. Summary of FT kinetic expressions and parameter values from the literature.

Atwood and Bennett (1979)	CCI fused iron	$r_{FT} = \frac{k_0 P_{CO} P_{H_2}}{P_{CO} + a P_{H_2O}}$	T (°C)	$k_0^{(a)}$	a
			250	0.0017	0.028
			282	0.0049	0.028
			315	0.013	0.028
			E (kJ/mol)	85	-8.8
Leib and Kuo (1984)	Fe/Cu/K	$r_{FT} = \frac{k_0 P_{CO} P_{H_2}}{P_{CO} + a P_{H_2O}}$	T (°C)	$k_0^{(a)}$	a
			265	0.062	0.58
Nettelhoff et al. (1985)	Precipitated Fe	$r_{FT} = \frac{k_0 P_{CO} P_{H_2}}{P_{CO} + a P_{H_2O}}$	T (°C)	$k_0^{(a)}$	a
			270	0.018	4.51
			E (kJ/mol)	89	
Huff and Satterfield (1984a)	C-73 fused iron (United Catalysts, Inc.)	$r_{FT} = \frac{k_0 P_{CO} P_{H_2}^2}{P_{CO} P_{H_2} + b P_{H_2O}}$	T (°C)	$k_0^{(a)}$	b (MPa)
			232	0.013	2.56
			248	0.025	1.15
			263	0.042	0.67
			E (kJ/mol)	83	-100
Nettelhoff et al. (1985)	S6-10 fused iron (BASF)	$r_{FT} = \frac{k_0 P_{CO} P_{H_2}}{P_{CO} + c P_{CO_2}}$	T (°C)	$k_0^{(a)}$	c
			240	0.010	0.19
			E (kJ/mol)	81	
Ledakowicz et al. (1985)	Precipitated 100 Fe/1.2 K	$r_{FT} = \frac{k_0 P_{CO} P_{H_2}}{P_{CO} + c P_{CO_2}}$	T (°C)	$k_0^{(a)}$	c
			220	0.0088	0.255
			240	0.025	0.210
			250	0.049	0.229
			260	0.058	0.237
			E (kJ/mol)	103	0

^(a) Units of k_0 are mols/g-cat-h-MPa

Table 16. Summary of FT first order rate constants.

Run	SA-05-2957		SB-07-0458		SA-99-0888		SB-66-2468	
T (°C)	$k_0^{(1)}$	R ²	$k_0^{(1)}$	R ²	$k_0^{(1)}$	R ²	$k_0^{(1)}$	R ²
220	0.011	(2)	—	—	—	—	—	—
235	0.024	(2)	0.0067	(2)	0.013	0.995	—	—
250	0.035	0.940	0.012	0.993	0.020	0.997	0.027	0.986
265	0.065	(2)	0.026	0.998	0.040	(2)	—	—
E (kJ/mol)	85.6	0.985	102	0.989	85.7	0.983	(2)	—

(1) Units of k_0 are mols/g-cat·h·MPa

(2) Only 1 data point available

Table 17. Summary of FT kinetic parameter estimates.

Run T (°C)	SA-05-2957 250	SB-07-0458 265	SA-99-0888 250	SB-66-2468 250
Eq. (5)				
$k_0^{(1)}$	0.057	0.027	0.023	0.039
a	4.2	0.99	0.73	3.9
R^2	0.662	0.323	0.353	0.893
Eq. (6)				
$k_0^{(1)}$	0.073	0.029	(2)	0.036
b	5.5	1.6		1.3
R^2	0.380	0.933		0.919
Eq. (7)				
$k_0^{(1)}$	0.054	0.029	(2)	0.033
c	0.21	0.09		0.69
R^2	0.176	0.838		0.960
Eq. (8)				
$k_0^{(1)}$	0.066	(2)	0.024	(2)
a	4.6		0.80	
c	0.13		0.08	
R^2	0.702		0.396	

(1) Units of k_0 are mols/g-cat.h.MPa.

(2) Zero or negative parameter estimates.

Table 18. Summary of WGS first order rate constants.

Run	SA-05-2957		SB-07-0458		SA-99-0888		SB-66-2468	
T (°C)	$k_{w,0}^{(1)}$	R ²	$k_{w,0}^{(1)}$	R ²	$k_{w,0}^{(1)}$	R ²	$k_{w,0}^{(1)}$	R ²
220	0.0068	(2)	—	—	—	—	—	—
235	0.017	(2)	0.0047	(2)	0.0042	0.998	—	—
250	0.048	0.920	0.012	0.879	0.0096	0.921	0.013	0.987
265	0.095	(2)	0.027	0.989	0.025	(2)	—	—
E (kJ/mol)	132	0.996	132	1.000	136	0.997	(2)	—

(1) Units of $k_{w,0}$ are mols/g-cat.h.MPa

(2) Only 1 data point available

Table 19. Summary of WGS kinetic parameter estimates.

Run T (°C)	SA-05-2957 250	SB-07-0458 265	SA-99-0888 250	SB-66-2468 250
Eq. (5) $k_{w,0}^{(1)}$ R^2	0.74 0.926	0.43 0.922	0.047 0.899	0.17 0.751
Eq. (6) $k_{w,0}^{(2)}$ R^2	0.84 0.988	0.29 0.837	(3)	0.069 0.596
Eq. (7) $k_{w,0}^{(1)}$ R^2	0.56 0.830	0.43 0.925	(3)	0.14 0.659
Eq. (8) $k_{w,0}^{(1)}$ R^2	0.85 0.929	(3)	0.048 0.896	(3)

(1) Units of $k_{w,0}$ are mols/g-cat.h.MPa.

(2) Units of $k_{w,0}$ are mols/g-cat.h.

(3) FT parameters not estimated.

Table 20. Major events occurring in run SB-25-2878.

TOS (h)	Event
-3	Catalyst Pretreatment: H_2 , 230 °C, 8 h
-1	Pressurized to 1.48 M Pa using H_2
0	Run initiated
5	Achieved desired operating conditions: 260°C, 1.48 M Pa, $\text{H}_2/\text{CO}=0.69$, 2 Nl/g-cat.h
71	Conditions stable, H_2+CO conversion = 77.2%
98	Drop in catalyst activity following wax withdrawals
121	Further drop in catalyst activity following wax withdrawal
167	H_2+CO conversion = 41.0%
194	Further drop in catalyst activity following wax withdrawal
198	Wax added but no improvement in activity observed
241	Conditions unstable, H_2+CO conversion = 17.5%
245	Voluntary termination of run SB-25-2878

Table 21. Wax and solids inventory for run SB-25-2878.

TOS(h)	Event
- 24	Slurry loading: 283 g-wax, 35 g catalyst
- 0	Wax withdrawal using dipleg: 40 g
76	Wax withdrawal using dipleg: 40 g
79	Wax withdrawal through filter: 127 g
100	Wax withdrawal through filter: 26 g
172	Wax withdrawal through filter: 65 g
198	Wax returned to reactor: 59 g
245	Slurry removed at end of run:
	Wax=166g, solids=27g, after burning=21g
	112 % wax recovery, 78 %solids recovery

Table 22. Summary of results for slurry run SB-25-2878.

Catalyst: 35.0 g^a, 100 Fe/3.0 Cu/0.2 K

Slurry liquid: 243 g, n-octacosane

Reactor volume: 375 cc^b

Period	1	2	3
Date	10/17/88	10/21/88	10/24/88
Time on Stream (h)	70.0	165	239
Balance Duration (h)	6.00	6.00	6.00
Average Temperature (°C)	260	260	260
Pressure (MPa)	1.48	1.48	1.48
H ₂ /CO Feed Ratio	0.79	0.72	0.72
Space Velocity (NI/g-cat·h) ^a	2.01	2.01	2.11
Space Velocity (NI/g-Fe·h)	2.95	2.95	3.10
GHSV (h ⁻¹) ^b	187	187	187
CO Conversion (%)	85.3	38.8	15.7
H ₂ +CO Conversion (%)	77.2	37.6	15.2
H ₂ /CO Usage	0.62	0.67	0.66
STY (mols H ₂ +CO/g-cat·h) ^a	0.069	0.034	0.014
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	39.0	11.4	6.50
Weight % of Outlet			
H ₂	1.78	3.12	4.30
H ₂ O	1.15	0.78	0.46
CO	14.1	57.0	81.2
CO ₂	62.4	28.6	9.96
Hydrocarbons	18.6	9.41	4.00
Oxygenates	0.69	0.19	0.10
Wax ^c	1.32	0.92	0.00
Yield (g/Nm ³ H ₂ + CO Converted)			
CH ₄	19.6	21.0	32.0
C ₂ -C ₄ Hydrocarbons	45.7	48.4	54.2
C ₅ -C ₁₁ Hydrocarbons	74.4	66.2	55.7
C ₁₂ + Hydrocarbons	49.9	78.2	55.9
Wax ^c	12.5	19.0	0.00
Oxygenates	6.56	4.00	5.00
Total	196	218	203
1+2 Olefins/n-Paraffin Ratio			
C ₂	0.30	1.40	1.40
C ₃	2.88	4.20	3.90
C ₄	2.42	3.30	2.98
C ₅	1.21	2.53	2.45
C ₁₀	0.87	1.65	1.88

^a Based on unreduced catalyst^b Based on static slurry volume^c Unanalyzed wax withdrawn from reactor

Table 22 (cont'd). Summary of results for slurry run SB-25-2878.

Period	1	2	3
Weight % of Hydrocarbons			
CH ₄	10.4	9.83	16.2
Ethane	5.05	3.17	4.43
Ethylene	1.41	4.15	5.77
Propane	2.46	1.59	1.95
Propylene	6.77	6.37	7.24
<i>n</i> -Butane	2.36	1.61	1.89
1+2 Butenes	5.51	5.12	5.43
C ₄ Isomers	0.52	0.63	0.71
<i>n</i> -Pentane	2.64	2.04	2.13
1+2 Pentenes	4.38	6.00	6.34
C ₅ Isomers	0.64	0.86	1.04
<i>n</i> -Hexane	1.59	1.24	2.21
1+2 Hexenes	2.11	3.30	4.27
C ₆ Isomers	1.72	0.72	1.29
<i>n</i> -Heptane	2.42	0.81	1.18
1+2 Heptenes	3.01	2.44	2.64
C ₇ Isomers	0.26	0.47	0.96
<i>n</i> -Octane	2.36	0.79	0.58
1+2 Octenes	2.80	1.96	1.39
C ₈ Isomers	0.34	0.17	0.13
<i>n</i> -Nonane	2.43	0.93	0.33
1+2 Nonenes	2.38	1.72	0.62
C ₉ Isomers	0.20	0.17	0.03
<i>n</i> -Decane	2.58	1.27	0.47
1+2 Decenes	2.22	2.07	0.87
C ₁₀ Isomers	0.32	0.22	0.05
<i>n</i> -Undecane	2.59	1.52	0.57
1+2 Undecenes	1.90	2.12	1.00
C ₁₁ Isomers	0.35	0.15	0.07
C ₂ -C ₄	24.1	22.6	27.4
C ₅ -C ₁₁	39.2	31.0	28.2
C ₁₂ +	26.3	36.6	28.2
Wax ^c	6.60	8.89	0.00

Table 23. Wax recovery for runs conducted in the slurry bed reactors.

Run no.	Liquid Medium	Withdrawal Details		Liquid Charged (g)	Produced or Withdrawn During the run (g)	Recovered at the end of Run (g)	% Recovery ^a
		Procedure	Gas Flow				
SA-05-2957	FT-300	Settling in Reactor	off	344	706	308	89.5
SA-25-3057	n-Octacosane	Settling in Reactor	off	304	621	322	105.9
SB-07-0458	FT-300	External Settler	off	274	649	245	89.4
SA-07-0468	FT-300	External Settler	off	244	1187	241	98.8
SA-99-0888	n-Octacosane	External Settler	off	300	1258	315	105.0
SB-27-2168	n-Octacosane	External Settler	off	252	655	258	102.4
SB-66-2468	n-Octacosane	Internal Filter	on	149	964	153	102.7
SB-25-2878	n-Octacosane	Ext. Settler + Int. Filter	off/on ^b	243	244	172	^d

^a recovery = 100 x recovered at end of run/liquid charged

^b off when external settler was used, on when internal filter was used

^c 600 when external settler was used, 1250 when internal filter was used

^d recovery could not be estimated since weight charged is based on external settler withdrawal, while weight recovered at end of run is based on internal filter withdrawal

Table 24. Catalyst recovery for runs conducted in the slurry bed reactors.

1	2	3	4	5	6	7	8	9	10	11
Run no.	Catalyst Composition ^a	Weight Charged ^b (g)	Initial Particle Size (μm)	wt.% Catalyst in Slurry	Solids Recovered During the Run (g)	Catalyst Mass on χ -Carbide Basis ^c (g)	% Recovery ^d	Solids Recovered After Thermal Treatment (g)	Catalyst Mass After Burning (g)	% Recovery ^e
SA-05-2957	100/0.3/0.2	30.4	<53	8.1	28.2	23.1	122	N/A	-	-
SA-25-3657	100/3/0.2	38.6	<53	11.3	34.8	29.4	118	N/A	-	-
SB-07-0458	100/0.3/0.5	30.0	<53	9.9	22.6	22.8	99	N/A	-	-
SA-07-0468	100/0.3/0.5	30.3	<53	11.1	28.7	23.0	125	N/A	-	-
SA-99-0888	100/5/4.2-25SiO ₂	34.6	<53	10.3	28.8	27.7	104	N/A	-	-
SB-27-2168	100/3/0.5	45.2	45-53	15.2	38.5	34.6	112	N/A	-	-
SB-66-2468	100/5/4.2-24SiO ₂	35.1	45-53	19.1	29.3	28.1	104	N/A	28.3	81
SB-25-2878	100/3/0.2	35.0	45-53	12.6	27.1	26.6	102	21.3	-	-

^a catalyst composition is given as parts by weight of Fe/Cu/K

^b weight charged is based on calcined catalyst (Fe₂O₃/CuO/K₂O)

^c based on conversion of Fe₂O₃ and CuO to Fe₅C₂ and Cu, respectively

^d recovery = 100 x (Column 6/Column 7)

^e recovery = 100 x (Column 10/Column 3)

Figure 1. FT first order plot for the 100 Fe/0.3 Cu/0.2 K (SA-05-2957) and 100 Fe/0.3 Cu/0.5 K (SB-07-0458) catalysts.

Figure 2. FT first order plot for the Ruhrchemie LP 33/81 (SA-99-0888) and 100 Fe/5.0 Cu/4 $\pm$ K/24 SiO₂ (SB-66-2468) catalysts.

Figure 3. Arrhenius plot of the FT first order rate constants.

Figure 4. Linear plot of the FT rate expression given by Equation 5 (H₂O inhibition).

Figure 5. Linear plot of the FT rate expression given by Equation 14 (H₂O inhibition).

Figure 6. Linear plot of the FT rate expression given by Equation 19 (CO₂ inhibition).

Figure 7. Parity plot of the FT rate expression given by Equation 20 (CO_2 and H_2 inhibition).

Figure 8. Comparison of measured $P_{CO_2} P_{H_2} / P_{CO} P_{H_2O}$ ratios to WGS equilibrium.

Figure 9. WGS first order plot for the 100 Fe/0.3 Cu/0.2 K (SA-05-2957) and 100 Fe/0.3 Cu/0.5 K (SB-07-0458) catalysts.

Figure 10. WGS first order plot for the Ruhrchemie LP 33/81 (SA-99-0888) and 100 Fe/5.0 Cu/4.2 K/24 SiO₂ (SB-66-2468) catalysts.

Figure 11. Arrhenius plot of the WGS first order rate constants.

Figure 13. Stability plot, (H₂+CO) conversion versus time on stream, for run SB-25-2878.

END

**DATE
FILMED**

8/21/92