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Development of Improved Iron Fischer-Tropsch Catalysts

Quarterly Technical Progress Report
for the Period 1 January 1990 - 31 March 1990

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I. Executive Summary

Three tests have been completed during the past quarter using the Ruhrchemie catalyst LP 33/81 (100 Fe/4.3 Cu/4.1 K/25 SiO_2 in parts per weight). The objectives of these tests were to study the effect of pretreatment (activation) procedures on the catalyst performance during Fischer-Tropsch synthesis, and to familiarize new personnel with the reactor operating procedures, product analysis by gas chromatography, and the data reduction using the existing software.

In a fixed bed reactor test designated FA-99-3509, the catalyst was activated using manufacturer's procedure (H_2 reduction at 220°C for 1 h). The test was terminated voluntarily after 1170 h on stream. The catalyst was very stable during the first 1020 h on stream, but its activity at the end of the run (1020-1070 h) was lower than that during the first 450 h on stream. The (H_2+CO) conversion at 258°C, 200 psig, 2.5 N*l*/g Fe/h, $H_2/CO = 0.67$ was high (85-89%). Hydrocarbon selectivity shifted gradually towards lower molecular weight products with time-on-stream and with increase in reaction temperature. For example, methane selectivity varied between 4.3 and 7.1 wt% (at 250°C, during the first 500 h on stream), and between 8 and 11% (at 258°C, 520-1020 h on stream).

The same activation procedure was employed in run SB-99-0440. The catalyst was reduced in a fixed bed reactor and then transferred to a slurry reactor, where it was exposed to the synthesis gas with H_2:CO molar ratio of 2:3 at 200 psig (reaction temperature was either 250 or 258°C, and the space velocity 2 or 1.3 N*l*/g-cat/h). The catalyst stability was good during the first 420 h on stream, but the (H_2+CO) conversion was low (~30% at 250°C, SV = 2 N*l*/g-cat/h; 41% at 258°C, 1.3 N*l*/g-cat/h). Hydrocarbon selectivities were erratic due to problems in the product collection, handling and problems with one of the gas chromatograph (Carle 400 used for the tail gas analysis).

The effect of reduction temperature (H_2 at 280°C for 1 h) was studied in the test FB-99-0750 at 250°C, 200 psig, 2 N*l*/g-cat/h, and $H_2/CO = 1$ or 0.67 over 330 h on stream. The catalyst lost activity during the first 200 h of testing, and methane selectivity was unusually high (26-44%). We plan to repeat this test at some later time. The work on Task 3 Improved Iron/Silica Catalysts has been initiated in March. The catalyst synthesis apparatus has been assembled.

II. Objective and Scope of Work

The objective of proposed research is development of catalysts with enhanced slurry phase activity and better selectivity to fuel range products, through a more detailed understanding and systematic studies of the effects of pretreatment procedures and promoters/binders (silica) on catalyst performance. In order to accomplish this objective, the work shall be divided into several tasks which are described in the following subsections.

Task 1 – Project Management

Within 60 days of project initiation, the contractor shall prepare and submit to the DOE Project Manager a detailed project work plan covering the entire period of performance of the project. The plan shall present, in detail, all activities that will be performed to successfully complete proposed research and its shall consist of the following: (1) detailed description of the methods and technical approach that shall be used to achieve the objectives of this project; (2) a detailed project schedule for each task or other logical segment of work to be performed; (3) graphs reflecting cumulative estimated costs and person-hours expended by month for each task or other logical segment of work, and for the total project effort; (4) a project work chart showing the key personnel/groups planned to work on each task and percentage of their time devoted to the tasks; and (5) a Work Breakdown Structure (WBS) dictionary to establish the framework for contract execution and to report cost schedule and technical performance.

All project status, milestone schedule, and cost management reports, as well as topical reports, if any, shall be submitted in accordance with the DOE reporting requirements.

Task 2 – Catalyst Pretreatment Research

This task is aimed at developing optimal pretreatment conditions for precipitated unsupported (1 catalyst) and supported (or silica containing; 1-2) iron catalyst, and at providing a better understanding of the role of pretreatment on subsequent catalyst activity, selectivity and longevity during Fischer-Tropsch (F-T) synthesis. This shall be accomplished by examining the effect of various activation conditions on physical and chemical properties of the catalyst as well as on catalytic behavior in fixed and slurry bed reactors. Parameters such as type of reductant (H_2 vs. CO vs. syngas), reductant flow rate, temperature and duration shall be studied. Selected catalysts shall be extensively characterized using a variety of physical, chemical and instrumental techniques with the objective to establish correlations between the physical/chemical properties of the catalysts and their observed catalytic behavior during F-T synthesis.

Task 3 – Improved Iron/Silica Catalysts

The objective of this task is to determine optimal concentrations of silica and K_2O in a catalyst with composition 100 Fe/5 Cu/xK_2O/ySiO_2 (in parts per weight). The effect of SiO_2 and K_2O on catalytic activity, selectivity and stability shall be determined to arrive at promoter/binder concentrations for an improved catalyst performance. The screening tests shall be conducted in fixed bed reactors to obtain preliminary indication of F-T activity and selectivity at different process conditions. Catalysts which show enhanced activity and/or selectivity towards transportation fuels shall be tested in slurry reactors up to 30 days on stream. Selected catalysts shall be extensively characterized, to determine relations between the physico-chemical properties of catalyst and their catalytic behavior during F-T synthesis.

III. Detailed Description of Technical Progress

III-1. Task 2. Catalyst Pretreatment Research

III-1.1 Run FA-99-3509 with the Ruhrchemie LP 33/81 Catalyst

A long term stability test of commercial Ruhrchemie catalyst LP 33/81 (100 Fe/4.3 Cu/ 4.1 K/25 SiO_2 in parts per weight) was conducted in a fixed bed reactor over a period of 1170 h on stream. The purpose of this run was to determine the effect of pretreatment conditions on catalyst activity, selectivity and longevity, and to familiarize new personnel with operating procedures, analytical techniques for product analysis and computer software for data reduction. The catalyst (30/60/mesh) was reduced in situ following manufacturer's procedure (H_2 at 220°C, at superficial gas velocity of 1.5 m/s for 1 h). The synthesis gas with H_2:CO ratio of 2:3 was used as feed and the reaction pressure was 200 psig (~1.5 MPa) during the entire duration of the test. The catalyst was tested at 250°C and gas space velocity of 2 N*l*/g-cat/h (230 h^{-1}) during the first 450 h on stream (Mass balances 1-5), followed by 70 h of testing at 1.3 N*l*/g-cat/h (Balance 6). At 520 h on stream the reaction temperature was raised to 258°C and the test was conducted at these conditions over next 500 h (Balances 7-16). During the last portion of the test (1050-1170 h) the catalyst was tested again at the baseline conditions (250°C, 2 N*l*/g-cat/h). Results from eighteen balances of run FA-99-3509 are listed in Table 1.

Catalyst Activity and Stability

Catalyst activity, measured by volumetric gas contraction and (H_2+CO) conversion, is shown in Figures 1 and 2, respectively. Both contraction and conversion increased somewhat with time-on-stream (TOS) during the first 400 h, which is not unusual for catalysts reduced in hydrogen (Bukur et al., 1989a, b). As space velocity decreased to 1.3 N*l*/g-cat/h (450-520 h) the catalyst activity increased. The catalyst stability was excellent at 258°C and 1.3 N*l*/g-cat/h, and the (H_2+CO) conversion was high (85-89%). However, upon returning to the baseline conditions (250°C, 2 N*l*/g-cat/h) the conversion dropped to 46-52%. These values are significantly lower than those obtained during the first 450 h on stream (62-69%), indicating that the catalyst had deactivated. This is unexpected since the catalyst had inhibited excellent stability throughout the run. Nevertheless, the entire test may be characterized as very successful in terms of catalyst activity and stability over a long period of time of operation with the synthesis gas feed with low H_2:CO molar ratio.

The water-gas-shift (WGS) activity may be expressed in several ways, e.g. (1) (H_2/CO) usage ratio; (2) ratio of partial pressures ($P_{CO_2}P_{H_2}/P_{CO}P_{H_2O}$); (3) extent of WGS reaction, $P_{CO_2}/(P_{CO_2} + P_{H_2})$, and (4) CO_2 selectivity, i.e. (r_{CO_2}/r_{CO}). The first two of these measures are listed in Table 1, and both of them show that the WGS activity of the catalyst increases with temperature (usage decreases, whereas the ratio of partial pressures increase with increasing temperature). Also, the WGS activity of the catalyst at the reactor exit was high and approached equilibrium at all reaction conditions. The values of equilibrium constant at 250°C and 258°C are 83.1 and 72.9, respectively.

Catalyst Selectivity

We have experienced problems with analysis of the tail gas samples on Carle refinery gas chromatographs throughout this run. Our daily calibrations of standard gas mixtures containing H_2, CO, CO_2 and C_1–C_4 hydrocarbons, revealed significant variations in response factors of components determined by thermal conductivity detector (H_2, CO, CO_2 and CH_4). As a result, in several mass balances, the atomic closures have been below our self imposed standard for acceptance of results (i.e. 100±3%). Nevertheless, in eleven of the eighteen balances both the total and carbon atomic closures were within ±3% limit and results from these balances are considered reliable. Also, we have performed sensitivity analysis for some of the balances in which these conditions have not been met, and found that hydrocarbon selectivities were not strongly affected by changes in atomic closures.

A typical carbon number product distribution is shown in Figure 3 in form of Anderson-Shulz-Flory (ASF) plot. With exception of a few data points (C_5, C_8, C_9, C_{14}-C_{16}) the entire carbon number distribution (C_1-C_{50}) is well represented by a three parameter model of Huff and Satterfield (1984)

$$x_n = \beta(1-\alpha_1)\,\alpha_1^{n-1} + (1-\beta)\,(1-\alpha_2)\,\alpha_2^{n-1}$$

where: x_n is the mole fraction of products containing n carbon atoms, β is fraction of type 1 sites, and α_1 and α_2 are chain growth probabilities associated with the type I and type II sites, respectively.

Hydrocarbon selectivity shifted gradually towards lower molecular weight products with time-on stream. The average hydrocarbon product distribution during the first 500 h on stream (250°C, SV = 2 or 1.3 N*l*/g-cat/h) was: 6.8 (CH_4), 21.0 (C_2–C_4), 31.3 (C_5–C_{11}) and 40.9 wt% (C_{12}^{+}). Upon increasing the reaction temperature to 258°C (520-1020 h) the hydrocarbon selectivity shifted towards lower molecular weight products, both due to higher temperature and longer time on stream. For example, methane selectivity varied between 8 and 11 wt%, and increased with TOS. Upon reestablishment of the baseline conditions (250°C, 2 N*l*/g-cat/h) in the final portion of the test (balances 17 and 18) the yield of methane and light gases (C_2-C_4) was higher than at the beginning of the run, due to catalyst aging and deactivation.

In summary, during this test the Ruhrchemie catalyst had met the target performance in terms of activity (85-89% (H_2+CO) conversion at 258°C, 2.5 N*l*/g-Fe/h), and stability during the first 1020 h on stream (deactivation rate less than 1% per day). However, the catalyst did not meet the selectivity target of less than 7 wt% of (C_1+C_2) hydrocarbons at the process conditions employed in this run.

Comparison with the Run FB-99-1588

The Ruhrchemie catalyst was tested previously in our laboratory in the run designated FB-99-1588 under the same process conditions as those used initially in the current run (250°C, 200 psig, 2 Nl/g-cat/h, $H_2/CO = 0.67$). In the Run FB-99-1588 the catalyst was reduced in situ with CO at 280°C for 12 h and the results were reported in Quarterly Technical Progress Report for the period April 1 – June 30, 1988 (DOE Contract DE-AC22-85PC80011). The (H_2+CO) conversion in the Run FB-99-1588 decreased with TOS from 60% at 40 h to 54% at about 340 h, whereas in the present run it increased with time on-stream (60-69% over the same period of time). Overall, the catalyst activity of the H_2 reduced catalyst (current run) was higher than that of the CO reduced catalyst (Run FB-99-1588). Also, the WGS activity of the CO reduced catalyst was lower than that of the H_2 reduced catalyst, e.g. (H_2/CO) usage ratio in the Run FB-99-1588 was about 0.8 vs. 0.6 in the current run.

Hydrocarbon product distribution was very stable in the Run FB-99-1588 during the first 360 h on stream (Balances 1-4), and the average selectivity was: 5.5 (CH_4), 22.3 (C_2–C_4), 19.4 (C_5–C_{11}), and 52.8 wt% (C_{12}^+). The CO reduced catalyst produced less methane (5.5 vs. 6.8%) and more C_{12}^+ products (52.8 vs. 40.9%) than the H_2 reduced catalyst, but the yield of C_5^+ products was exactly the same in both runs (72.2 wt%).

III-1.2 Run SB-99-0440 with the Ruhrchemie LP 33/81 Catalyst

The objective of this run was to evaluate the Ruhrchemie catalyst in the slurry reactor under the same reduction and process conditions as those employed in the fixed bed reactor test (Run FA-99-3509). The catalyst was crushed and sieved to 270/325 mesh (44-53 μm) and loaded into a fixed bed reactor unit for hydrogen reduction. During the reduction a hot spot was noticed at the bottom of the reactor (T_{max} = 270°C), and the reaction was quenched by introducing helium flow. After that the hydrogen content in the helium stream was gradually increased, and the reduction was completed in pure hydrogen at 220°C for 1 h. The entire reduction period lasted about 3 h.

Following the reduction, the bed was cooled to ambient temperature in flowing helium and the catalyst was transferred to a slurry reactor.

The catalyst was tested initially (first 420 h) at 250°C, 200 psig, 2 N*l*/g-cat/h using the synthesis gas feed with (H_2/CO) molar ratio of 0.67 (nominal composition, which varied slightly during the run). During the last 130 h on stream (421-550 h) the catalyst was tested at higher temperature (258°C) and lower gas space velocity (1.3 N*l*/g-cat/h), while keeping the reaction pressure and feed composition constant. The run was terminated voluntarily after 550 h on stream. Results from seven mass balances conducted during this period of time are summarized in Table 2.

Catalyst Activity and Stability

As shown in Figures 4 and 5 the catalyst activity, measured by (H_2+CO) conversion or volumetric gas contraction, passed through a maximum at about 50 h on stream, and remained essentially constant during the time period between 200 and 420 h on stream. After the change in process conditions, the catalyst activity increased as expected and then started to decrease with time.

The (H_2+CO) conversions during the slurry bed reactor test, were about 50% lower than the corresponding values obtained in the fixed bed reactor test (FA-99-3509). This lower than expected activity in the slurry reactor may be ascribed, in part, to problems experienced during the reduction. Also, the WGS activity of the catalyst during the slurry reactor test was lower than that observed in the fixed bed reactor test, as can be seen by comparing ratios of partial pressures in Tables 1 and 2.

In summary, the catalyst had good stability but its activity at Mobil's conditions for the high wax mode of operation (258°C, 200 psig, 2.5 N*l*/g-Fe/h, H_2/CO = 0.67) was significantly lower than the target activity, i.e. (H_2+CO) conversion of 89%.

Wax (Slurry) Withdrawals during Run SB-99-0440

Two methods of wax (slurry) withdrawal were employed during this run, i.e. wax withdrawal through a cylindrical filter element and slurry withdrawal to an external settler followed by wax removal and return of concentrated slurry to the reactor. Both of these methods have been described in our previous DOE reports (e.g. Bukur et al., 1989b). Results from all wax (slurry) withdrawals are summarized in Table 3, whereas other major events during the run are listed in Table 4.

Following the catalyst transfer to the slurry reactor the excess wax was removed through a vertical filter element. The amount withdrawn (181.3 g) was higher than expected (the slurry static volume below the filter element or a dipleg tube was 550 cm^3), and therefore 7 hours later about 110 g of wax was returned to the reactor. At 102 h on stream another wax withdrawal (385.8 g) was made through the filter. The amount withdrawn was again higher than expected, and 275 g of wax was returned to the reactor at 105 h. At this point it was decided to discontinue this method of wax withdrawal, and switch to slurry withdrawal through a dipleg tube immersed in the reactor (at the reactor static height of 550 cm^3). Prior to the first mass balance 53.5 g of wax was withdrawn through the dipleg via an external slurry settler (TOS = 108 h), and after that eight additional slurry withdrawals were made during the run (see Table 3 and Figure 5). The wax production rates during the first 420 h on stream were erratic and varied between 0.5 and 2.8 g/h, whereas the catalyst activity did not vary much during this period of time. This indicates that the slurry withdrawals may have not been quantitative (complete) in all cases. This was confirmed at the end of the run, when the excess of 327 g of wax was found in the reactor. The average wax production rate, based on the amount of wax withdrawn throughout the run and the excess wax in the reactor, was 1.5 g/h.

The wax withdrawn throughout the run was filtered to collect catalyst which might have been removed with the wax. The solids remaining on the filter after washing with Varsol were first dried and then oxidized in air on a Bunsen burner, and any remaining solids material following this procedure was assumed to be an iron oxide. The total amount of catalyst lost during the slurry withdrawals was 1.55 g (i.e. 3% of the amount charged). The amount of the catalyst recovered from the reactor was 41.2 g, and the total catalyst recovery was 75% only. This indicates that some of the catalyst was lost during filtration or was carried over into the refluxer and the high pressure product trap.

The wax recovery was +212% (excess wax), which is much higher than expected. In our prior slurry reactor runs (DOE Contract DE-AC-85PC80011) the wax recovery ranged between 89.4 and 105% (Bukur et al., 1989b).

Catalyst Selectivity

Hydrocarbon selectivities shown in Table 2 are based on actual data without any corrections (i.e. actual wax production rates were used in each of the balances and no allowance was made for the excess wax found in the reactor at the end of the run). The results vary significantly between mass balances. This is due to errors in estimation of the wax production rate and several other factors such as: (1) Evaporation of products in (C_5–C_{11}) range due to improper handling; (2) Loss of products in (C_5–C_{11}) range due to condensation in the exit line following the installation of water vapor removal line (balances 4-7); (3) wax overflow into the high pressure trap in balance 7; and (4) possible errors in quantification of methane on Carle gas chromatograph (balances 2-7).

As a result of these problems the hydrocarbon plus oxygenates yields were either too low (Balances 1-4, 6) or too high (Balance 7). Hydrocarbon product distribution and product yields after adjustments in the wax production rate are listed in Table 5. These results were obtained by assuming the constant wax production rate of 1.5 g/h in all seven balances. (This rate takes into account the excess wax found in the reactor at the end of the run).

Table 6 shows results after adjustments of the wax production rate and methane concentration. The latter was obtained from GC analysis on the Sigma 1B chromatograph using a flame ionization detector, whereas the results shown in Tables 2 and 5 are based on gas analysis done on Carle 400 Series GC using TCD. Methane selectivities determined from Sigma 1B GC were fairly stable during the entire run (6-9%), and they are consistent with values obtained in our previous tests of the Ruhrchemie catalyst. Results for balance 7 in Table 6 were obtained by subtracting the wax overflow which had entered the high pressure trap during this mass balance.

III-1.3 Run FB-99-0750 with the Ruhrchemie LP 33/81 Catalyst

This test was conducted to study the effect of pretreatment conditions (H_2 reduction at 280°C, ambient pressure, superficial gas velocity of 1.5 m/s for 1 h) on the catalyst performance in a fixed bed reactor. Throughout this test average reaction temperature, pressure and space velocity were maintained at 250°C, 200 psig and 2 Nl/g-cat/h, respectively. The synthesis gas with H_2:CO molar ratio of 1:1 was used during the first 140 h on stream, whereas H_2:CO = 2:3 feed gas was used from 140 to 330 h on stream. Results from six mass balances are summarized in Table 7.

The (H_2+CO) conversion was fairly stable during the first 100 h on stream at about 70%, but decreased substantially to about 60% at 133 h on stream (Figure 6). The (H_2+CO) conversion declined further after the change in the feed composition, but after 200 h on stream it leveled at about 50%.

Methane selectivity was unusually high in all six mass balances (26-44%), which may be caused by hot spots in the reactor. The existence of hot spots was not detected, but the temperature was not recorded according to our standard procedures . The chart recorder was not used during the first 200 h on stream, and the temperature was not monitored regularly during the initial period (20-40 h on stream) of the test.

The carbon number distribution followed the ASF distribution except for CH_4, whose concentration was well above the model predictions as shown in Figure 7. The run was terminated after 330 h on stream due to poor catalyst selectivity. We plan to repeat this test at some later time.

III-2. Task 3. Improved Iron/Silica Catalysts

The work on this task has been initiated on March 1, 1990 as per contract schedule. During the last month several activities have been undertaken as described below.

III-2.1 Catalyst Synthesis

All the necessary parts for catalyst synthesis apparatus (glassware, pump and pH electrode) have been obtained, and the apparatus has been assembled in a ventilated hood. Initial tests with water indicated that both pumps are functioning properly.

III-2.2 Equipment Installation and Testing

During the past quarter we received all remaining capital equipment items: (1) Hewlett Packard GC integrator; (2) Ametek quadrupole mass spectrometer, and (3) two mass flow meters and the dual channel readout from Brooks. A new Varian 3400 GC was received at the end of the last quarter, and work on development of methods for the aqueous phase and gas phase analysis on this gas chromatograph has been initiated.

Varian 3400 Analysis of Aqueous Liquid and Gaseous Hydrocarbon Samples

The new Varian GC has both FID and TCD detectors, and is equipped for capillary and packed column operation. This instrument is intended to be used as an alternative means of analyzing aqueous liquid samples and gas phase hydrocarbons. These two analyses are currently performed on the existing Perkin-Elmer Sigma 1 GC.

Two different columns have been tested for the aqueous analysis: an RSL-300 (1.2 µm film thickness), 10-m x 0.53-mm capillary (phenylmethyl silicone, Alltech Associates), and a 6' x 1/4" C1500 on 80/100 Graphac GC packed column (Alltech), which is the same column used in the existing Sigma 1. The aqueous analysis on the capillary column initially looked promising. After adjusting flows, temperature program, and injection technique, injections of aqueous standard gave relative deviations ranging between 0.3-4.0% on the FID, which is acceptable but slightly higher than the deviations on the Sigma 1, which ranged between 0.2-1.3%. Injections of actual aqueous phase products from fixed bed run FA-99-3509, balance 7, showed good agreement between the new Varian analysis and the Sigma 1, which are compared in Table 8. The largest absolute differences between the two analyses were for 1-pentanol and 1-hexanol, -16.8 and 193%, respectively. However, these two species are present in the aqueous phase in minute quantities, and are not clearly resolved in either of the analyses (higher alcohols partition strongly to the organic liquid sample, which is analyzed on a separate GC). Products present in significant quantities (C_1–C_4) showed much better agreement, and the differences between the two analyses ranged from -4.1 to 3.1%. Further attempts to improve the analysis were unsuccessful, but the column broke before all work on the analysis was completed. The cause of the breakage was probably due to too rapid oven cooling between injections, a flaw in the procedure which has since been corrected.

The packed column was tested using the FID detector in series downstream of the TCD in an attempt to analyze the water content of the sample directly on the GC. Using this column with actual sample showed that methanol and water elute at approximately the same time, so a water analysis was not possible. Using the packed column gave relatively good results with a standard solution. The relative deviations were 0.5-2.8% using the FID, and 0.4-3.0% using the TCD. However, there were some separation problems in analysis of actual product samples, and comparison between the Varian analysis to the Sigma 1 was poor. Work on the aqueous phase analysis using the packed column, and a second capillary column, is continuing.

Some preliminary work has been completed using a packed column (6' x 1/8" Poropak Q) for the gas phase analysis. This is the same column used for the existing analysis on the Sigma 1 GC. The FID and TCD detectors were again used in series, and the TCD gives peaks for CO, CO_2, and H_2, in addition to hydrocarbons (the FID detects exclusively hydrocarbons). Injections of calibration gas which contains CO, CO_2, and C_1–C_4 hydrocarbons gave deviations ranging from 0.3-2.4%. Injections of synthesis gas (H_2+CO), however, shows poor separation between H_2 and CO using this column. Furthermore, H_2 is detected as a small negative peak on the TCD using helium carrier, due to the similar thermal conductivities of He and H_2. Nitrogen carrier is used to analyze H_2 on the Carle GC, but it is not suitable for the remaining gas phase species. Using tail gas samples from fixed bed run FB-99-0750, balance 4, injections were made on the Varian, Sigma 1, and Carle GC's. A comparison of results between the Varian and Sigma 1 is made in Table 9. There are large differences between the two analysis. Smaller peaks which appear on the Sigma 1 analysis (C_6^+) are either not detected or correctly analyzed on the Varian. Also, for larger peaks, the differences are also large, for example, propylene shows 13.2 and 17.9% differences on the FID and TCD, respectively. Comparison with the Carle (Table 10) on an H_2-free basis also shows large differences in results. Ethylene, propylene, and propane show unacceptably large differences, and the C_4^+ species were not analyzed properly on the Varian. Work on the Varian gas phase analysis is continuing. Larger samples and/or higher sensitivities are required to improve the analysis of the C_4^+ products. Also, peak separation is poor for C_4^+ on both the Varian and Sigma 1. A capillary column, which gives better separation than the packed column for higher hydrocarbons (including *cis*- and *trans*-2-olefins as well as paraffin and 1-olefin) will be tested for the gas phase analysis.

Status of Carle 400 Gas Chromatograph

As mentioned in the previous Quarterly Technical Progress Report, and elsewhere in this report, the performance of Carle 400 GC has been erratic. The response factors of components determined by TCD (CH_4, CO, CO_2 and H_2) varied considerably from one calibration to another. Several adjustments had been made such as: baseline adjustments, replacement of molecular sieve column and change in hydrogen transfer tube temperature. Following these adjustments the instrument would work properly for a few days, but then changes in TCD baselines would occur gradually leading to wrong area calculations for these components.

According to our in-house expert, Dr. C. V. Philip, it appears that nothing is wrong with the hardware but that our problems are caused by integration errors. These may be corrected through changes in the computer software. We are planning to continue working on this problem during the next quarter.

IV. References

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Table 1. Summary of results for fixed bed run FA-99-3509 .

Catalyst: $3.56\ g^a$, Ruhrchemie
Catalyst volume: $5.60\ cc$

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

Period	1	2	3	4	5	6
Date	12/20/89	12/23/89	12/26/89	12/30/89	01/03/90	01/06/90
Time on Stream (h)	95.8	152.7	225.2	324.2	416.7	490.7
Balance Duration (h)	12.0	6.0	6.0	6.0	6.0	7.0
Average Temperature (°C)	250.	250.	250.	250.	250.	250.
Maximum Δ Temperature (°C)[b]	1.00	2.00	1.00	1.00	1.00	2.00
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48	1.48
H_2/CO Feed Ratio	.672	.672	.672	.672	.672	.672
Space Velocity (Nl/g–cat·h)[a]	2.00	2.00	2.00	2.00	2.00	1.31
Space Velocity (Nl/g–Fe·h)	3.81	3.81	3.81	3.81	3.81	2.50
GHSV (h^{-1})[c]	231.	231.	231.	231.	231.	151.
CO Conversion (%)	64.2	63.8	69.1	75.9	78.6	85.1
H_2+CO Conversion (%)	62.2	61.8	67.4	68.8	69.4	77.8
H_2/CO Usage	.620	.619	.631	.514	.477	.529
STY ($mols$ H_2+CO/g–cat·h)[a]	.053	.053	.060	.061	.062	.046
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	5.24	7.58	6.56	13.1	23.1	22.1
Weight % of Outlet						
H_2	1.90	2.00	1.63	2.08	2.26	1.63
H_2O	2.64	1.92	2.47	1.92	1.37	1.67
CO	34.6	36.3	29.6	24.7	22.6	15.2
CO_2	44.2	46.4	51.8	52.3	55.6	60.3
Hydrocarbons	7.81	7.51	9.07	12.8	11.9	13.4
Oxygenates	.469	.900	.470	.978	1.02	1.25
Wax[d]	8.36	5.04	4.95	5.25	5.18	6.59
Yield (g/Nm^3 H_2 + CO *Converted*)						
CH_4	8.57	8.73	10.6	13.7	13.4	12.8
C_2–C_4 Hydrocarbons	23.1	23.6	41.3	40.0	38.3	39.0
C_5–C_{11} Hydrocarbons	27.4	46.3	45.3	65.8	56.5	62.4
C_{12}+ Hydrocarbons	142.	73.1	65.1	72.0	66.2	73.8
Wax[d]	104.	60.9	57.3	55.7	52.7	62.1
Oxygenates	5.84	10.9	5.44	10.4	10.4	11.8
Total	207.	163.	168.	202.	185.	200.
1+2 Olefins/n–Paraffin Ratio						
C_2	1.17	1.17	.815	.604	.576	.458
C_3	5.69	5.69	5.04	4.94	4.80	4.69
C_4	4.49	4.49	4.16	3.92	3.92	3.74
C_8	3.41	2.59	2.96	2.43	2.08	2.05
C_{10}	2.10	1.98	1.81	1.66	1.63	1.46

[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 FA-99-3509 .

Period	1	2	3	4	5	6
Weight % of Hydrocarbons						
CH_4	4.26	5.75	6.54	7.14	7.06	6.79
Ethane	1.71	2.31	3.90	3.36	3.62	3.76
Ethylene	1.87	2.53	2.96	1.89	1.95	1.61
Propane	.628	.849	1.57	1.37	1.47	1.43
Propylene	3.41	4.61	7.55	6.44	6.71	6.39
n–Butane	.682	.922	1.77	1.55	1.63	1.55
1+2 Butenes	2.96	4.00	7.09	5.87	6.16	5.59
C_4 Isomers	.235	.318	.587	.425	.443	.423
n–Pentane	.728	.984	1.75	1.68	1.76	1.53
1+2 Pentenes	3.77	5.17	7.99	5.47	6.05	6.15
C_5 Isomers	.160	.216	.461	.211	.235	.202
n–Hexane	.511	.785	1.34	1.19	1.09	1.56
1+2 Hexenes	1.37	1.80	3.70	3.00	3.26	2.84
C_6 Isomers	.0572	.0460	.0811	.263	.481	.492
n–Heptane	.318	.523	1.14	.809	.929	1.17
1+2 Heptenes	.789	1.31	2.00	1.74	1.94	2.36
C_7 Isomers	.0387	.0904	.0525	.119	.244	.355
n–Octane	.143	.638	.541	.890	.991	1.17
1+2 Octenes	.480	1.62	1.58	2.12	2.02	2.35
C_8 Isomers	.0912	.0622	.147	.169	.376	.311
n–Nonane	.294	1.62	.616	1.62	1.49	1.66
1+2 Nonenes	.757	3.39	1.24	2.91	2.63	2.71
C_9 Isomers	.0247	.116	.0373	.126	.142	.394
n–Decane	.667	2.38	.959	2.39	1.84	1.88
1+2 Decenes	1.38	4.66	1.71	3.91	2.96	2.71
C_{10} Isomers	.0843	.283	.169	.227	.184	.190
n–Undecane	.645	1.71	.868	2.24	1.58	1.41
1+2 Undecenes	1.14	2.90	1.35	3.15	2.09	1.62
C_{11} Isomers	.160	.226	.216	.147	.103	.126
C_2–C_4	11.5	15.5	25.4	20.9	22.0	20.7
C_5–C_{11}	13.6	30.5	27.9	34.4	32.4	33.2
C_{12}+	70.6	48.2	40.1	37.6	38.0	39.3
Wax[d]	51.7	40.2	35.3	29.1	30.2	33.0

[d] Unanalyzed products collected from hot trap

Table 1 (cont'd). Summary of results for fixed bed run FA-99-3509 .

Catalyst: 3.41 g^a, Ruhrchemie
Catalyst volume: 5.60 *cc*

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

Period	7	8	9	10	11	12
Date	01/09/90	01/14/90	01/15/90	01/16/90	01/17/90	01/18/90
Time on Stream (*h*)	573.2	665.7	695.2	741.3	766.5	788.7
Balance Duration (*h*)	12.0	12.0	12.0	10.0	12.0	12.0
Average Temperature (°C)	258.	258.	258.	258.	258.	258.
Maximum Δ Temperature (°C)[b]	2.00	2.00	1.80	1.70	2.00	2.00
Pressure (*MPa*)	1.48	1.48	1.48	1.48	1.48	1.48
H_2/CO Feed Ratio	.672	.672	.672	.672	.672	.672
Space Velocity (Nl/g–cat·h)[a]	1.31	1.31	1.31	1.31	1.31	1.31
Space Velocity (Nl/g–Fe·h)	2.50	2.50	2.50	2.50	2.50	2.50
GHSV (h^{-1})[c]	151.	151.	151.	151.	151.	151.
CO Conversion (%)	91.5	94.0	93.6	92.4	92.7	92.4
H_2+CO Conversion (%)	85.3	89.5	88.6	87.4	87.8	86.7
H_2/CO Usage	.558	.592	.584	.582	.583	.570
STY (*mols* H_2+CO/g–cat·h)[a]	.050	.052	.052	.051	.051	.051
$P_{CO_2} \cdot P_{H_2}/P_{CO} \cdot P_{H_2O}$	42.4	101.	98.5	67.5	80.6	89.7
Weight % of Outlet						
H_2	1.19	.798	.860	.901	.898	1.02
H_2O	1.13	.581	.597	.754	.655	.599
CO	8.69	5.73	6.08	7.07	6.90	7.43
CO_2	61.7	73.9	73.1	70.2	71.3	69.0
Hydrocarbons	20.6	13.8	14.1	15.2	15.2	16.9
Oxygenates	.648	.318	.344	.545	.357	.329
Wax[d]	6.13	4.90	4.92	5.26	4.72	4.78
Yield (g/Nm^3 $H_2 + CO$ *Converted*)						
CH_4	20.1	13.1	13.8	15.5	16.5	17.6
C_2–C_4 Hydrocarbons	57.3	34.1	35.4	38.4	44.3	45.4
C_5–C_{11} Hydrocarbons	85.3	62.0	67.4	74.8	64.2	75.3
C_{12}+ Hydrocarbons	65.1	54.1	52.4	60.1	54.2	53.3
Wax[d]	52.3	42.8	43.8	48.5	42.4	42.3
Oxygenates	5.53	2.78	3.06	5.02	3.21	2.91
Total	233.	166.	172.	194.	182.	195.
1+2 Olefins/*n*–Paraffin Ratio						
C_2	.319	.356	.353	.343	.322	.324
C_3	4.13	4.27	4.32	4.19	4.10	4.04
C_4	3.44	3.54	3.58	3.53	3.46	3.42
C_8	1.56	1.33	1.31	1.79	1.73	1.48
C_{10}	1.17	1.21	1.25	1.26	1.25	1.24

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

Table 1 (cont'd). Summary of results for fixed bed run FA-99-3509 .

Period	7	8	9	10	11	12
Weight % of Hydrocarbons						
CH4	8.83	8.01	8.17	8.19	9.22	9.19
Ethane	4.86	3.95	3.95	3.97	4.71	4.50
Ethylene	1.45	1.31	1.30	1.27	1.42	1.36
Propane	1.94	1.55	1.56	1.56	1.92	1.88
Propylene	7.65	6.31	6.41	6.23	7.51	7.25
n–Butane	2.02	1.65	1.64	1.57	1.99	1.91
1+2 Butenes	6.72	5.65	5.66	5.35	6.65	6.30
C_4 Isomers	.519	.440	.433	.419	.516	.488
n–Pentane	2.12	1.81	1.67	1.71	2.03	1.96
1+2 Pentenes	8.02	6.99	6.48	6.35	7.52	6.89
C_5 Isomers	.247	.209	.196	.189	.232	.221
n–Hexane	1.69	1.12	2.31	1.94	1.65	1.99
1+2 Hexenes	2.79	1.96	4.23	3.28	2.69	3.25
C_6 Isomers	.537	.420	1.15	.637	.501	.640
n–Heptane	1.67	1.48	1.41	1.50	1.36	1.68
1+2 Heptenes	2.58	2.31	2.35	2.63	2.30	2.53
C_7 Isomers	.369	.404	1.09	.377	.348	.433
n–Octane	1.76	2.66	2.44	1.49	1.42	1.94
1+2 Octenes	2.69	3.48	3.13	2.62	2.41	2.82
C_8 Isomers	.634	.433	.431	.173	.204	.919
n–Nonane	1.77	2.13	1.83	2.37	1.87	1.90
1+2 Nonenes	2.45	3.06	2.67	3.45	2.72	2.76
C_9 Isomers	.428	.180	.193	.336	.347	.503
n–Decane	2.00	2.38	2.08	2.62	2.05	2.17
1+2 Decenes	2.30	2.84	2.55	3.25	2.52	2.65
C_{10} Isomers	.177	.242	.217	.278	.221	.322
n–Undecane	1.63	1.93	1.71	2.17	1.69	1.83
1+2 Undecenes	1.44	1.72	1.59	2.07	1.58	1.71
C_{11} Isomers	.138	.200	.163	.202	.179	.197
C_2–C_4	25.2	20.9	20.9	20.4	24.7	23.7
C_5–C_{11}	37.5	38.0	39.9	39.6	35.8	39.3
C_{12}+	28.5	33.2	31.0	31.8	30.2	27.8
Wax[d]	23.0	26.2	25.9	25.7	23.7	22.1

[d] Unanalyzed products collected from hot trap

Table 1 (cont'd). Summary of results for fixed bed run FA-99-3509 .

Catalyst: 3.41 g^a, Ruhrchemie
Catalyst volume: 5.60 cc

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

Period	13	14	15	16	17	18
Date	01/20/90	01/21/90	01/23/90	01/28/90	01/30/90	02/02/90
Time on Stream (h)	815.5	839.5	909.7	1009.0	1077.7	1149.7
Balance Duration (h)	12.0	12.0	12.0	12.0	12.0	12.0
Average Temperature (°C)	258.	258.	258.	258.	250.	250.
Maximum Δ Temperature (°C)[b]	2.00	2.00	2.00	2.00	2.00	2.00
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48	1.48
H_2/CO Feed Ratio	.67	.67	.67	.67	.67	.67
Space Velocity (Nl/g–cat·h)[a]	1.31	1.31	1.31	1.31	2.00	2.00
Space Velocity (Nl/g–Fe·h)	2.50	2.50	2.50	2.50	3.81	3.81
GHSV (h^{-1})[c]	151.	151.	151.	151.	231.	231.
CO Conversion (%)	92.7	91.1	91.6	92.0	48.5	46.6
H_2+CO Conversion (%)	87.5	85.4	86.6	87.2	51.8	46.3
H_2/CO Usage	.579	.567	.581	.586	.787	.662
STY ($mols$ H_2+CO/g–cat·h)[a]	.051	.050	.051	.051	.046	.041
$P_{CO_2} \cdot P_{H_2}/P_{CO} \cdot P_{H_2O}$	73.3	100.	89.1	106.	9.61	8.67
Weight % of Outlet						
H_2	.946	1.13	.957	.908	1.89	2.46
H_2O	.717	.486	.532	.447	.835	1.04
CO	7.11	9.02	7.97	7.56	46.5	50.2
CO_2	69.4	68.2	69.4	69.6	34.8	32.3
Hydrocarbons	16.5	16.6	16.5	16.7	13.7	11.9
Oxygenates	.425	.435	.459	.258	.832	.756
Wax[d]	4.85	4.10	4.18	4.58	1.55	1.32
Yield (g/Nm^3 $H_2 + CO$ $Converted$)						
CH_4	18.3	19.7	20.4	20.6	28.0	35.0
C_2–C_4 Hydrocarbons	45.6	49.9	52.6	50.6	67.9	70.0
C_5–C_{11} Hydrocarbons	69.7	66.1	65.3	65.3	109.	85.8
C_{12}+ Hydrocarbons	54.3	43.8	50.3	56.1	39.1	36.0
Wax[d]	42.7	35.5	38.1	41.5	24.7	22.7
Oxygenates	3.74	3.76	4.18	2.34	13.3	12.9
Total	192.	183.	193.	195.	257.	240.
1+2 Olefins/n–Paraffin Ratio						
C_2	.309	.292	.287	.302	.884	.746
C_3	3.95	4.02	3.59	3.62	4.88	4.58
C_4	3.37	3.37	3.34	3.35	3.88	3.65
C_8	1.40	1.52	1.72	1.59	2.16	2.77
C_{10}	1.05	.993	1.05	.789	1.88	1.95

[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 FA-99-3509 .

Period	13	14	15	16	17	18
Weight % of Hydrocarbons						
CH4	9.71	11.0	10.8	10.7	11.5	15.4
Ethane	4.78	5.34	5.46	5.40	4.37	5.63
Ethylene	1.38	1.45	1.46	1.52	3.60	3.92
Propane	1.97	2.21	2.31	2.16	1.81	2.10
Propylene	7.42	8.47	7.93	7.48	8.43	9.18
n–Butane	1.94	2.29	2.40	2.16	1.89	2.06
1+2 Butenes	6.30	7.45	7.74	7.00	7.09	7.25
C_4 Isomers	.499	.583	.613	.551	.650	.734
n–Pentane	1.98	2.39	2.65	2.20	1.94	1.98
1+2 Pentenes	6.73	7.01	7.72	6.73	7.12	6.99
C_5 Isomers	.220	.268	.278	.244	.350	.307
n–Hexane	2.10	1.91	1.72	1.85	2.42	1.88
1+2 Hexenes	3.37	3.24	2.98	3.16	5.36	4.01
C_6 Isomers	.765	.659	.103	.744	1.11	.783
n–Heptane	1.06	1.38	.607	.00000	2.74	1.80
1+2 Heptenes	1.69	2.30	1.18	.00000	5.78	3.42
C_7 Isomers	.141	.283	.00000	.00000	1.86	1.58
n–Octane	1.88	1.55	1.25	1.49	2.29	2.71
1+2 Octenes	2.58	2.32	2.11	2.34	4.87	7.38
C_8 Isomers	.599	.313	.107	.00000	.599	.233
n–Nonane	2.24	1.94	1.97	2.58	.567	.250
1+2 Nonenes	2.88	2.36	2.54	2.70	1.29	.551
C_9 Isomers	.188	.150	.160	.158	.0416	.0246
n–Decane	2.41	2.51	2.35	3.01	1.06	.629
1+2 Decenes	2.51	2.46	2.44	2.34	1.96	1.21
C_{10} Isomers	.216	.181	.236	.303	.299	.130
n–Undecane	1.92	1.99	2.12	2.29	1.15	.815
1+2 Undecenes	1.45	1.45	1.88	1.55	1.61	1.02
C_{11} Isomers	.194	.176	.205	.208	.205	.128
C_2–C_4	24.3	27.8	27.9	26.3	27.8	30.9
C_5–C_{11}	37.1	36.8	34.6	33.9	44.6	37.8
C_{12}+	28.9	24.4	26.7	29.1	16.1	15.9
Wax[d]	22.7	19.8	20.2	21.5	10.1	10.0

[d] Unanalyzed products collected from hot trap

Table 2. Summary of results for slurry run SB-99-0440 .

Catalyst: 52.23 g^a, LP 33/81 Slurry liquid: 361.0 g, n-C28

Reactor volume: 550. cc^b

Period	1	2	3	4	5	6	7
Date	02/19/90	02/22/90	02/26/90	02/28/90	03/01/90	03/05/90	03/08/90
Time on Stream (h)	123.5	193.5	290.5	338.0	374.0	457.5	537.5
Balance Duration (h)	6.0	6.0	6.0	6.0	12.0	6.0	6.0
Average Temperature (°C)	250.	250.	250.	250.	250.	258.	258.
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48	1.48	1.48
H_2/CO Feed Ratio	.637	.636	.639	.690	.644	.706	.700
Space Velocity (Nl/g–cat·h)[a]	2.00	2.00	2.00	2.00	2.00	1.30	1.30
Space Velocity (Nl/g–Fe·h)	3.81	3.81	3.81	3.81	3.81	2.47	2.47
GHSV (h^{-1})[b]	209.	209.	209.	209.	209.	136.	136.
CO Conversion (%)	35.3	25.2	29.3	33.4	29.7	41.0	39.2
H_2+CO Conversion (%)	31.1	27.9	31.0	32.2	31.8	42.6	40.2
H_2/CO Usage	.443	.812	.733	.629	.760	.775	.744
STY ($mols$ H_2+CO/g–cat·h)[a]	.028	.025	.028	.029	.028	.025	.023
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	1.03	.904	1.11	2.80	1.86	2.38	2.54
Weight % of Outlet							
H_2	3.92	3.15	3.09	3.33	2.93	2.72	2.62
H_2O	3.38	3.35	3.40	2.58	2.46	3.09	2.50
CO	73.3	75.9	71.4	64.3	68.5	57.3	54.2
CO_2	11.4	12.8	15.3	24.4	18.7	27.3	23.1
Hydrocarbons	4.88	3.57	5.04	4.21	6.41	8.25	16.0
Oxygenates	.330	.316	.316	.248	.335	.333	.321
Wax[c]	2.75	.827	1.44	.917	.624	.977	1.22
Yield (g/Nm^3 H_2 + CO *Converted*)							
CH_4	9.97	14.5	26.0	17.0	17.9	16.0	17.5
C_2–C_4 Hydrocarbons	22.4	23.1	35.9	28.4	40.6	43.7	45.1
C_5–C_{11} Hydrocarbons	30.9	17.5	33.5	11.9	24.5	44.3	92.4
C_{12}+ Hydrocarbons	102.	63.7	62.1	64.7	89.5	59.2	198.
Wax[c]	59.6	22.3	35.0	21.8	15.3	17.3	25.1
Oxygenates	7.15	8.53	7.68	5.90	8.22	5.89	6.60
Total	173.	127.	165.	128.	181.	169.	360.
1+2 Olefins/n–Paraffin Ratio							
C_2	2.05	1.94	1.93	1.95	1.90	1.46	1.41
C_3	4.15	3.00	4.58	5.34	5.38	5.38	5.29
C_4	3.19	4.61	6.70	.995	6.47	4.76	5.13
C_8	.820	.741	1.000	.956	4.18	3.14	3.14
C_{10}	3.90	4.79	3.65	3.49	2.41	2.01	2.01

[a] Based on unreduced catalyst

[b] Based on static slurry volume

[c] Unanalyzed wax withdrawn from reactor

Table 2 (cont'd). Summary of results for slurry run SB-99-0440 .

Period	1	2	3	4	5	6	7
Weight % of Hydrocarbons							
CH4	6.02	12.2	16.5	14.0	10.4	9.77	4.96
Ethane	1.39	1.19	2.49	3.33	2.26	3.02	1.33
Ethylene	2.66	2.16	4.48	6.07	4.01	4.10	1.75
Propane	.838	1.67	.998	1.19	.921	1.27	.695
Propylene	3.32	4.79	4.36	6.07	4.73	6.51	3.05
n–Butane	.626	.998	.894	1.14	.986	1.26	.597
1+2 Butenes	1.93	4.44	5.78	1.19	6.16	5.79	2.96
C_4 Isomers	2.77	4.22	3.78	4.39	4.47	4.85	2.48
n–Pentane	.641	1.04	.921	1.05	.995	1.18	.646
1+2 Pentenes	3.24	4.31	3.78	4.40	.0817	4.23	2.98
C_5 Isomers	.0922	.145	.123	.130	.149	.158	.0922
n–Hexane	.986	.418	3.59	.111	.0111	.00121	1.94
1+2 Hexenes	2.70	2.91	3.51	.150	.139	14.3	6.84
C_6 Isomers	.365	.357	.390	.0332	.00000	.0618	.00000
n–Heptane	.560	.266	2.02	.0265	.0283	.0410	.0779
1+2 Heptenes	1.72	.181	1.98	.263	.205	.110	.209
C_7 Isomers	.273	.187	.414	.182	.0513	.00000	.00000
n–Octane	3.41	.775	1.25	.0516	.111	.157	.298
1+2 Octenes	2.75	.564	1.22	.0485	.454	.484	.918
C_8 Isomers	.0495	1.17	.190	.00000	.00315	.00785	.0149
n–Nonane	.0307	.0447	.0266	.0547	.525	.460	.873
1+2 Nonenes	.169	.282	.114	.252	1.59	1.12	2.14
C_9 Isomers	.0120	.00866	.0146	.00962	.0291	.0391	.0742
n–Decane	.112	.122	.116	.211	1.25	.739	1.40
1+2 Decenes	.429	.574	.417	.727	2.97	1.47	2.78
C_{10} Isomers	.00653	.0118	.0445	.0613	.0733	.0603	.115
n–Undecane	.297	.309	.285	.526	1.84	1.02	1.94
1+2 Undecenes	.808	1.05	.778	1.36	3.59	1.39	2.64
C_{11} Isomers	.0193	.0136	.0625	.123	.114	.103	.195
C_2–C_4	13.5	19.5	22.8	23.3	23.5	26.8	12.8
C_5–C_{11}	18.7	14.7	21.2	9.77	14.2	27.2	26.2
C_{12}+	61.8	53.6	39.5	53.0	51.9	36.3	56.1
Wax^c	36.0	18.8	22.2	17.9	8.87	10.6	7.10

^{c} Unanalyzed wax withdrawn from reactor

Table 3. Wax and Solids inventory for run SB-99-0440

TOS (h)	Event
-12	Reactor charged with: 361g n-octacosane
-2	52.2g catalyst
-1	Wax removed using internal filter: 181.3g
6	Wax returned to reactor: 110.6g
102	Wax removed using internal filter: 385.8g
105	Wax returned to reactor: 275g
108	Wax removed to external settler: 535g
108	Total amount of solids collected during 108h on stream: 0.94g
131	Wax removed to external settler: 61.8g
203	Wax removed to external settler: 44.0g
247	Wax removed to external settler: 30.6g
299	Wax removed to external settler: 58.2g
390	Wax removed to external settler: 46.1g
419	Wax removed to external settler: 28.8g
	Total amount of solids collected between 131 and 419 h on stream: 0.52 g
464	Wax removed: 22.8, solids removed: 0.049g
544	Was removed: 49.7g, solids removed: 0.05g
549	End of run: 617.7g-wax, 41.3 g-solids removed; wax recovery: +212%; catalyst recovery: 75%.

Table 4. Major events occuring in run SB-99-0440

TOS (h)	Event
-8	Catalyst pretreatment in fixed bed according to Ruhrchemie procedure (H_2, 220°C, 0.1 MPa, 9.7 Nl/min) Hot spot observed at the fixed bed outlet 270°C
-2	Transfer of reduced catalyst to slurry reactor
0	Initiated synthesis gas ($H_2/CO=0.67$)
3	Achieved desired operating conditions: 250°C, 1.48 MPa, $H_2/CO=0.67$, 2.0 nl/g-cat/h
26	Conditions stable, (H_2+CO)-conversion: 32.2%, contraction: 27.9%
129	Conditions stable, (H_2+CO)-conversion: 31.3%, contraction: 26.1%
195	Conditions stable, (H_2+CO)-conversion: 28.7%, contraction: 22.9%
292	Conditions stable, (H_2+CO)-conversion: 30.7%, contraction: 23.1%
385	Conditions stable, (H_2+CO)-conversion: 28.5%, contraction: 22.8%
420	Changed process conditions: 258°C, 1.48 MPa, $H_2/CO=0.67$, 1.3 Nl/g-cat/h
459	Conditions stable, (H_2+CO)-conversion: 42.7%, contraction: 30.2%
539	Conditions stable, (H_2+CO)-conversion: 38.9%, contraction: 28.5%
549	Termination of run SB-99-0440

Table 5. Summary of results for slurry run SB-99-0440 after adjustments in the wax production rate[a] .

Catalyst: 52.23 *g*, LP 33/81 Slurry liquid: 361.0 *g*, n-C28

Reactor volume: 550. *cc*

Period	1	2	3	4	5	6	7
CO Conversion (%)	35.3	25.2	29.3	33.4	29.7	41.0	39.2
H_2+CO Conversion (%)	31.1	27.9	31.0	32.2	31.8	42.6	40.2
H_2/CO Usage	.443	.812	.733	.629	.760	.775	.744
Yield (g/Nm^3 $H_2 + CO$ *Converted*)							
CH_4	9.97	14.5	26.0	17.0	17.9	16.0	17.5
C_2–C_4 Hydrocarbons	22.4	23.1	35.9	28.4	40.6	43.7	45.1
C_5–C_{11} Hydrocarbons	30.9	17.5	33.5	11.9	24.5	44.3	92.4
C_{12}+ Hydrocarbons	89.5	93.6	74.1	88.1	120.	94.5	229.
Wax[b]	46.9	52.2	46.9	45.2	45.7	52.5	55.8
Oxygenates	7.15	8.53	7.68	5.90	8.22	5.89	6.60
Total	160.	157.	177.	151.	211.	204.	390.
Weight % of Hydrocarbons							
CH4	6.52	9.73	15.3	11.7	8.81	8.04	4.56
C_2–C_4	14.7	15.6	21.2	19.5	20.0	22.0	11.7
C_5–C_{11}	20.2	11.8	19.7	8.20	12.1	22.3	24.1
C_{12}+	58.6	62.9	43.7	60.5	59.1	47.6	59.6
Wax[b]	30.7	35.1	27.7	31.1	22.5	26.5	14.5

[a] Constant wax production rate of 1.5 g/h in each mass balance

[b] Unanalyzed wax withdrawn from reactor

Table 6. Summary of results for slurry run SB-99-0440 after adjustments in the wax production rate and methane concentration

Catalyst: 52.23 *g*, LP 33/81

Slurry liquid: 361.0 *g*, n-C28

Reactor volume: 550. *cc*

Period	1	2	3	4	5	6	7*
CO Conversion (%)	35.3	24.9	28.8	33.2	29.5	40.8	38.9
H_2+CO Conversion (%)	31.1	27.7	30.5	32.0	31.6	42.5	39.9
H_2/CO Usage	.443	.814	.735	.628	.761	.775	.745
Yield (g/Nm^3 $H_2 + CO$ *Converted*)							
CH_4	9.97	8.82	12.7	12.6	12.0	12.4	11.9
C_2–C_4 Hydrocarbons	22.4	23.4	36.8	28.7	41.0	44.1	45.6
C_5–C_{11} Hydrocarbons	30.9	17.7	34.3	12.0	24.7	44.6	57.1
C_{12}+ Hydrocarbons	89.5	94.3	75.4	88.6	121.	94.9	101.
Wax[a]	46.9	52.6	47.8	45.5	46.1	52.8	56.1
Oxygenates	7.15	8.59	7.81	5.93	8.28	5.91	3.93
Total	160.	153.	167.	148.	207.	202.	219.
Weight % of Hydrocarbons							
CH4	6.52	6.12	7.99	8.89	6.06	6.31	5.53
C_2–C_4	14.7	16.2	23.1	20.2	20.7	22.5	21.2
C_5–C_{11}	20.2	12.3	21.5	8.47	12.4	22.8	26.5
C_{12}+	58.6	65.4	47.4	62.4	60.8	48.4	46.8
Wax[a]	30.7	36.5	30.0	32.1	23.2	26.9	26.1

[a] Unanalyzed wax withdrawn from reactor; * with adjustment in the amount of organic products collected

Table 7. Summary of results for fixed bed run FB-99-0750 .

Catalyst: 3.50 g^a, Ruhrchemie
Catalyst volume: 5.60 *cc*

Diluent: 36.08 *g*, Glass beads
Diluent Volume: 24.00 *cc*

Period	1	2	3	4	5	6
Date	03/20/90	03/21/90	03/23/90	03/26/90	03/28/90	03/30/90
Time on Stream (h)	86.2	119.5	170.2	230.3	280.0	321.2
Balance Duration (h)	12.0	14.0	12.2	6.0	6.0	6.2
Average Temperature (°C)	250.	250.	250.	250.	250.	250.
Maximum Δ Temperature (°C)[b]	2.00	5.00	3.00	6.00	18.0	2.00
Pressure (MPa)	1.48	1.48	1.48	1.48	1.48	1.48
H_2/CO Feed Ratio	1.02	1.02	.672	.686	.686	.686
Space Velocity (Nl/g–cat·h)[a]	2.00	2.00	2.00	2.00	2.00	2.00
Space Velocity (Nl/g–Fe·h)	3.81	3.81	3.81	3.81	3.81	3.81
GHSV (h^{-1})[c]	236.	236.	236.	236.	236.	236.
CO Conversion (%)	73.5	63.9	58.7	41.6	46.1	43.3
H_2+CO Conversion (%)	72.5	63.7	58.1	49.3	52.5	48.4
H_2/CO Usage	.993	1.01	.654	.996	.919	.888
STY (*mols* H_2+CO/g–cat·h)[a]	.065	.057	.052	.044	.047	.043
$P_{CO_2} \cdot P_{H_2} / P_{CO} \cdot P_{H_2O}$	6.92	2.73	2.79	1.13	1.07	1.10
Weight % of Outlet						
H_2	1.88	2.55	2.00	1.81	1.81	2.07
H_2O	3.47	5.97	4.24	4.60	5.32	5.20
CO	23.8	34.3	39.7	54.1	51.5	54.0
CO_2	53.6	38.6	41.4	27.3	28.6	26.3
Hydrocarbons	14.3	14.7	9.02	8.03	9.12	8.27
Oxygenates	.252	.307	.358	.526	.496	.543
Wax[d]	2.75	3.60	3.24	3.68	3.16	3.58
Yield (g/Nm^3 H_2 + CO *Converted*)						
CH_4	60.2	60.0	72.8	50.5	58.3	57.4
C_2–C_4 Hydrocarbons	59.1	63.1	30.6	51.7	46.2	48.3
C_5–C_{11} Hydrocarbons	14.2	24.7	14.0	25.1	28.5	26.1
C_{12}+ Hydrocarbons	28.2	38.6	46.5	62.9	48.5	58.6
Wax[d]	26.1	36.7	43.3	59.7	46.8	57.5
Oxygenates	2.39	3.14	4.78	8.55	7.33	8.72
Total	164.	190.	169.	199.	189.	199.
1+2 Olefins/n–Paraffin Ratio						
C_2	.182	.214	.267	.293	.381	.429
C_3	1.17	1.11	1.20	1.44	1.61	1.89
C_4	2.38	3.27	2.70	2.20	3.19	2.73
C_8	.134	.675	1.16	.516	5.67	.453
C_{10}	.904	2.85	2.54	3.68	3.57	3.58

[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-99-0750 .

Period	1	2	3	4	5	6
Weight % of Hydrocarbons						
CH4	37.2	32.2	44.4	26.5	32.1	30.2
Ethane	12.1	10.1	5.66	7.60	6.39	6.08
Ethylene	2.07	2.02	1.41	2.08	2.27	2.43
Propane	5.64	5.19	2.77	3.77	3.09	2.88
Propylene	6.30	5.47	3.19	5.18	4.75	5.18
n–Butane	2.42	2.20	1.21	2.01	1.73	1.69
1+2 Butenes	5.57	6.94	3.15	4.27	5.32	4.46
C_4 Isomers	2.38	1.93	1.28	2.28	1.90	2.64
n–Pentane	1.53	1.55	.888	1.56	1.39	1.40
1+2 Pentenes	1.62	1.49	1.04	1.98	2.22	2.43
C_5 Isomers	.378	.337	.143	.328	.289	.278
n–Hexane	1.00	.890	.657	1.04	1.34	1.10
1+2 Hexenes	1.39	1.19	.891	1.64	2.35	1.95
C_6 Isomers	.291	.259	.210	.350	.457	.368
n–Heptane	.738	.476	.403	.590	1.05	.546
1+2 Heptenes	.475	1.13	.810	1.24	1.97	1.54
C_7 Isomers	.0115	.0324	.0261	.111	.0579	.312
n–Octane	.671	.735	.632	.921	.258	.982
1+2 Octenes	.0881	.487	.720	.466	1.44	.436
C_8 Isomers	.00000	.0232	.00556	.00896	.00474	.0629
n–Nonane	.0617	.577	.0720	.178	.261	.268
1+2 Nonenes	.0630	1.32	.173	.520	.694	.665
C_9 Isomers	.00000	.0632	.00000	.0250	.0281	.0319
n–Decane	.124	.404	.194	.255	.231	.191
1+2 Decenes	.110	1.13	.485	.925	.813	.673
C_{10} Isomers	.00017	.134	.0324	.0639	.0507	.0583
n–Undecane	.120	.267	.260	.211	.183	.0714
1+2 Undecenes	.111	.705	.806	.749	.620	.323
C_{11} Isomers	.00000	.0473	.0815	.0388	.0245	.0177
C_2–C_4	36.5	33.9	18.7	27.2	25.5	25.4
C_5–C_{11}	8.80	13.3	8.53	13.2	15.7	13.7
C_{12}+	17.5	20.7	28.4	33.1	26.7	30.8
Wax[d]	16.2	19.7	26.4	31.4	25.7	30.2

[d] Unanalyzed products collected from hot trap

Table 8. Comparison of aqueous phase samples from run FA–99–3509, balance 7, on the Varian 3400 and Sigma 1 GC's.

Species	Sigma 1[a]	Varian[b]	% Diff[c]
Methanol	29.8	29.1	−2.05
Ethanol	44.8	45.0	0.53
Isopropanol	14.0	14.4	3.13
1–Propanol	8.53	8.45	−0.93
1–Butanol	2.34	2.24	−4.15
1–Pentanol	0.53	0.44	−16.8
1–Hexanol	0.10	0.30	193

[a] C1500 on 80/100 Graphpac GC packed column

[b] RSL–300 capillary column

[c] $100\frac{\text{Varian}-\text{Sigma}}{\text{Sigma}}$

Table 9. Comparison of tail gas samples from run FB-99-0750, balance 4, on the Varian 3400 and Sigma 1 GC's using Poropak Q column.

Species	Sigma 1	Varian FID	% Diff[(a)]	Varian TCD	% Diff[(a)]
Methane	66.5	68.2	2.70	68.5	3.08
Ethylene	2.60	2.42	−6.77	2.45	−5.81
Ethane	10.4	10.8	3.91	11.1	6.29
Propylene	5.23	5.92	13.2	6.16	17.9
Propane	3.95	4.17	5.74	4.41	11.8
Isobutane	0.20	0.0	−100	0.0	−100
1-Butene	3.01	2.77	−7.86	3.15	4.91
n-Butane	3.01	2.93	−2.50	2.98	−0.79
C_5 Isomers	0.35	0.0	−100	0.0	−100
1-Pentene	1.12	1.14	1.59	1.26	12.3
n-Pentane	1.46	1.44	−1.33	0.0	−100
C_6 Isomers	0.17	0.0	−100	0.0	−100
1-Hexene	0.75	0.12	−83.6	0.0	−100
n-Hexane	0.56	0.0	−100	0.0	−100
C_7 Isomers	0.015	0.0	−100	0.0	−100
1-Heptene	0.26	0.0	−100	0.0	−100
n-Heptane	0.13	0.0	−100	0.0	−100
C_8 Isomers	0.001	0.0	−100	0.0	−100
1-Octene	0.156	0.0	−100	0.0	−100
n-Octane	0.156	0.0	−100	0.0	−100

(a) $100\frac{\text{Varian}-\text{Sigma}}{\text{Sigma}}$

Table 10. Comparison of tail gas samples from run FB–99–0750, balance 4, on the Varian 3400 (using Poropak Q column) and Carle GC's on an H_2–free basis.

Species	Carle	Varian TCD	% Diff[(a)]
CO	68.3	69.8	2.17
CO_2	21.9	20.2	7.71
Methane	6.86	6.80	−0.74
Ethylene	0.31	0.24	−20.8
Ethane	1.05	1.10	5.23
Propylene	0.51	0.61	20.0
Propane	0.36	0.44	23.3
Isobutane	0.009	0.0	−100
1–Butene	0.16	0.31	97.1
n–Butane	0.14	0.30	105
t–2–Butene	0.062	0.0	−100
c–2–Butene	0.053	0.0	−100
C_5 Isomers	0.018	0.0	−100
1–Pentene	0.012	0.13	941
n–Pentane	0.09	0.0	−100
t–2–Pentene	0.104	0.0	−100
c–2–Pentene	0.001	0.0	−100

(a) $100\frac{\text{Varian}-\text{Sigma}}{\text{Sigma}}$

2

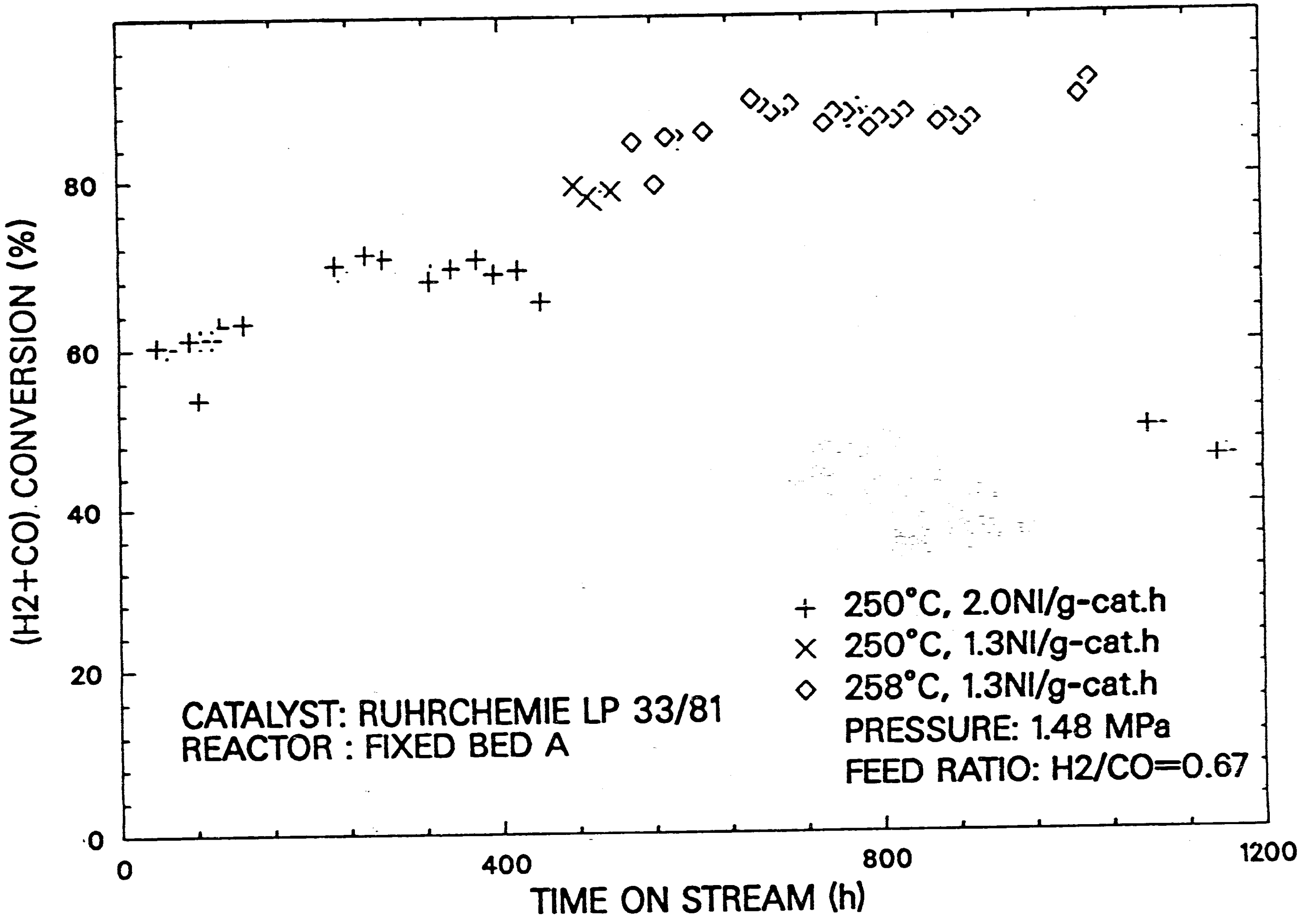

Figure 1. Stability plot, (H_2+CO) conversion versus time on stream, for run FA-99-3509.

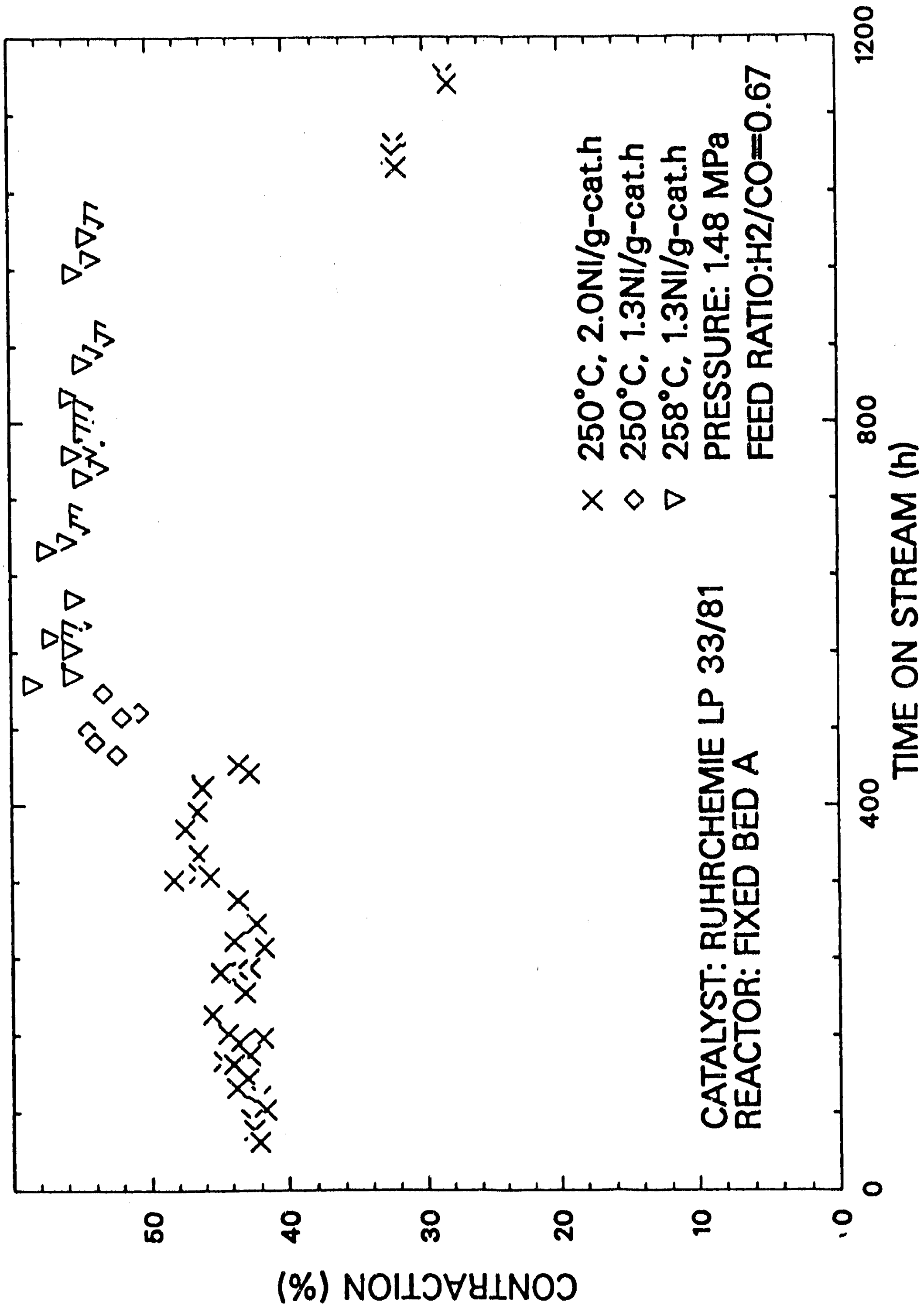

Figure 2. Volumetric contraction versus time on stream for run FA-99-3509

2

2

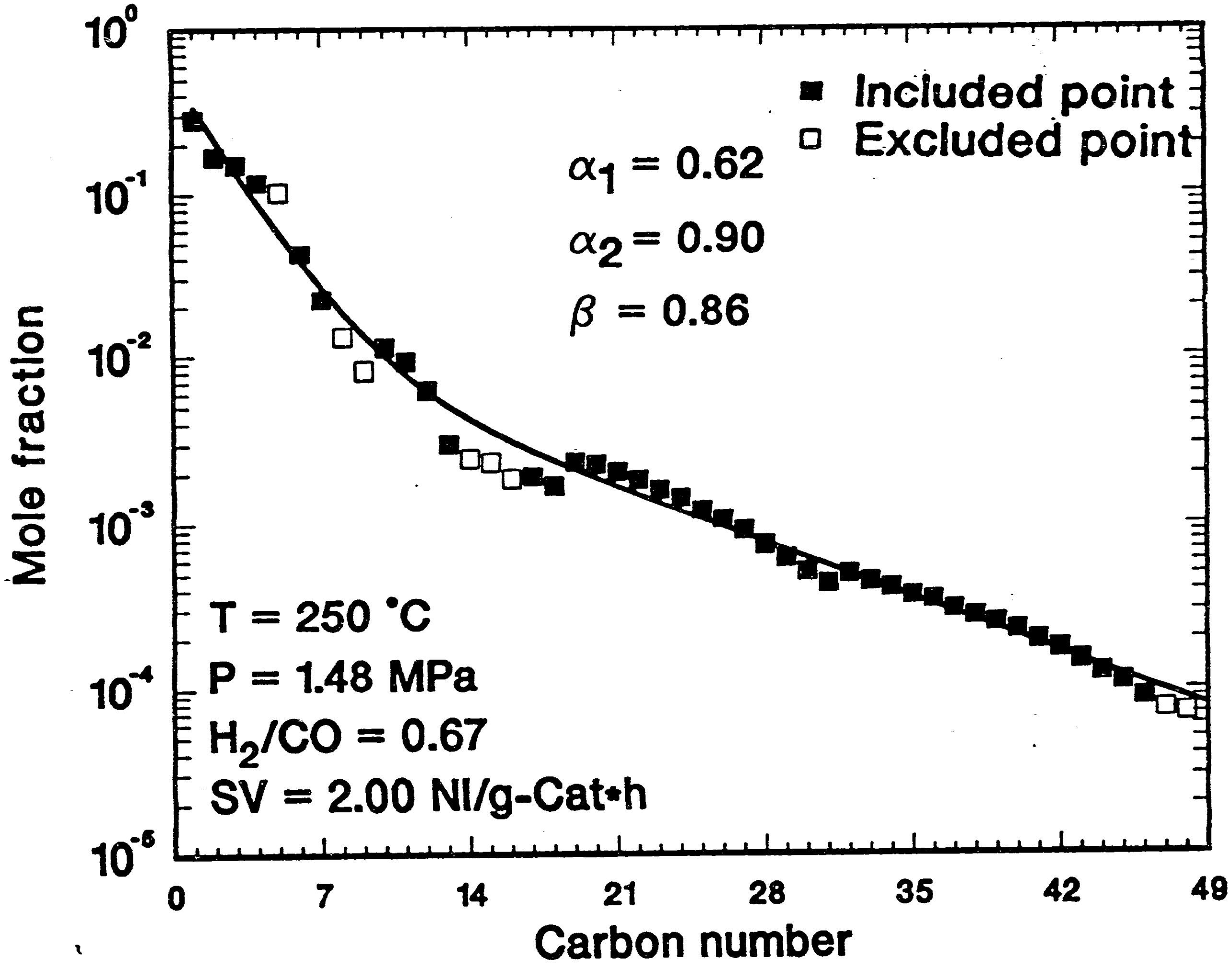

Figure 3. Anderson-Schulz-Flory plot for run FA-99-3509 (Balance #3).

2

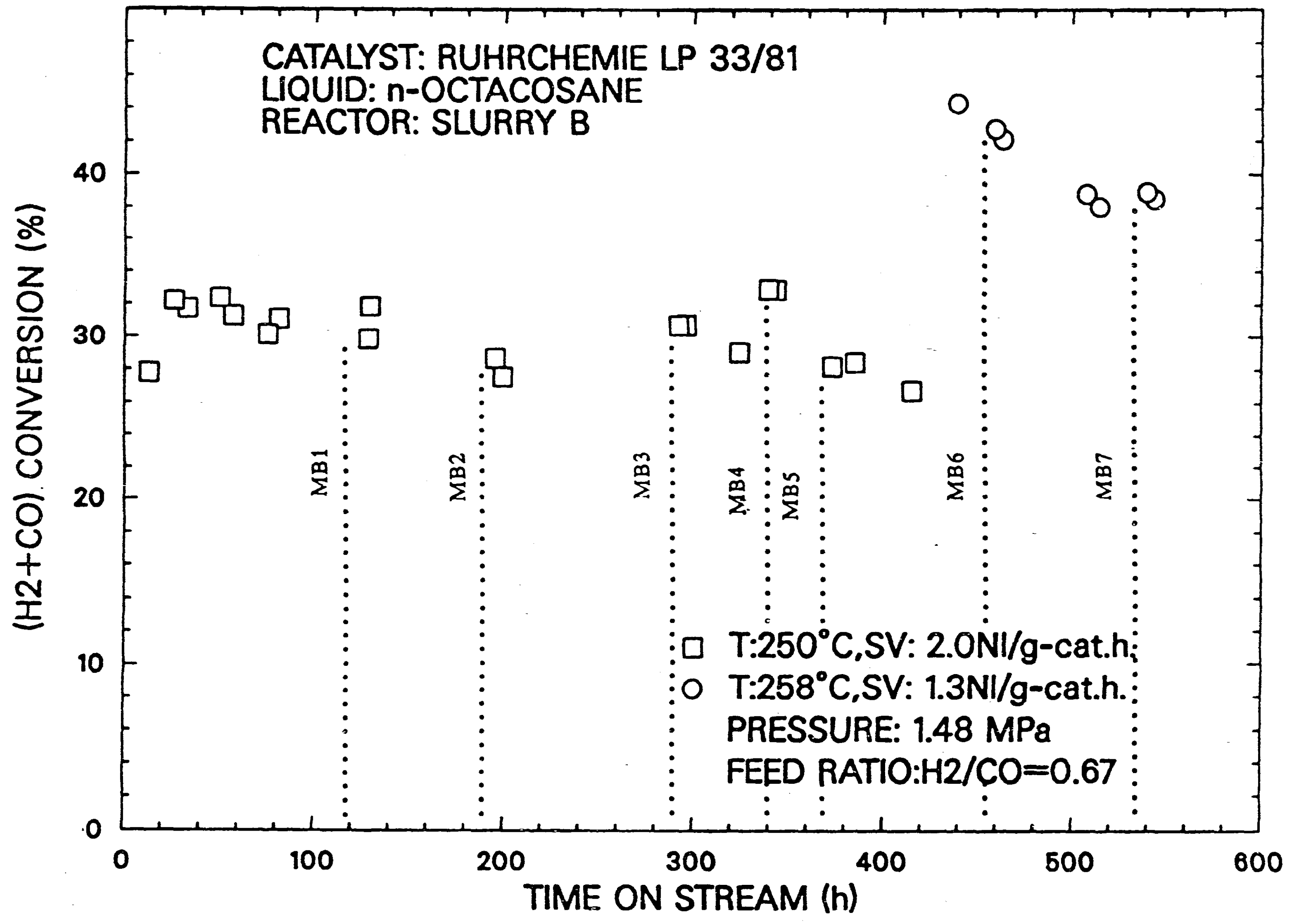

Figure 4. Stability plot, (H_2+CO) conversion versus time on strean, for run SB-99-0440.

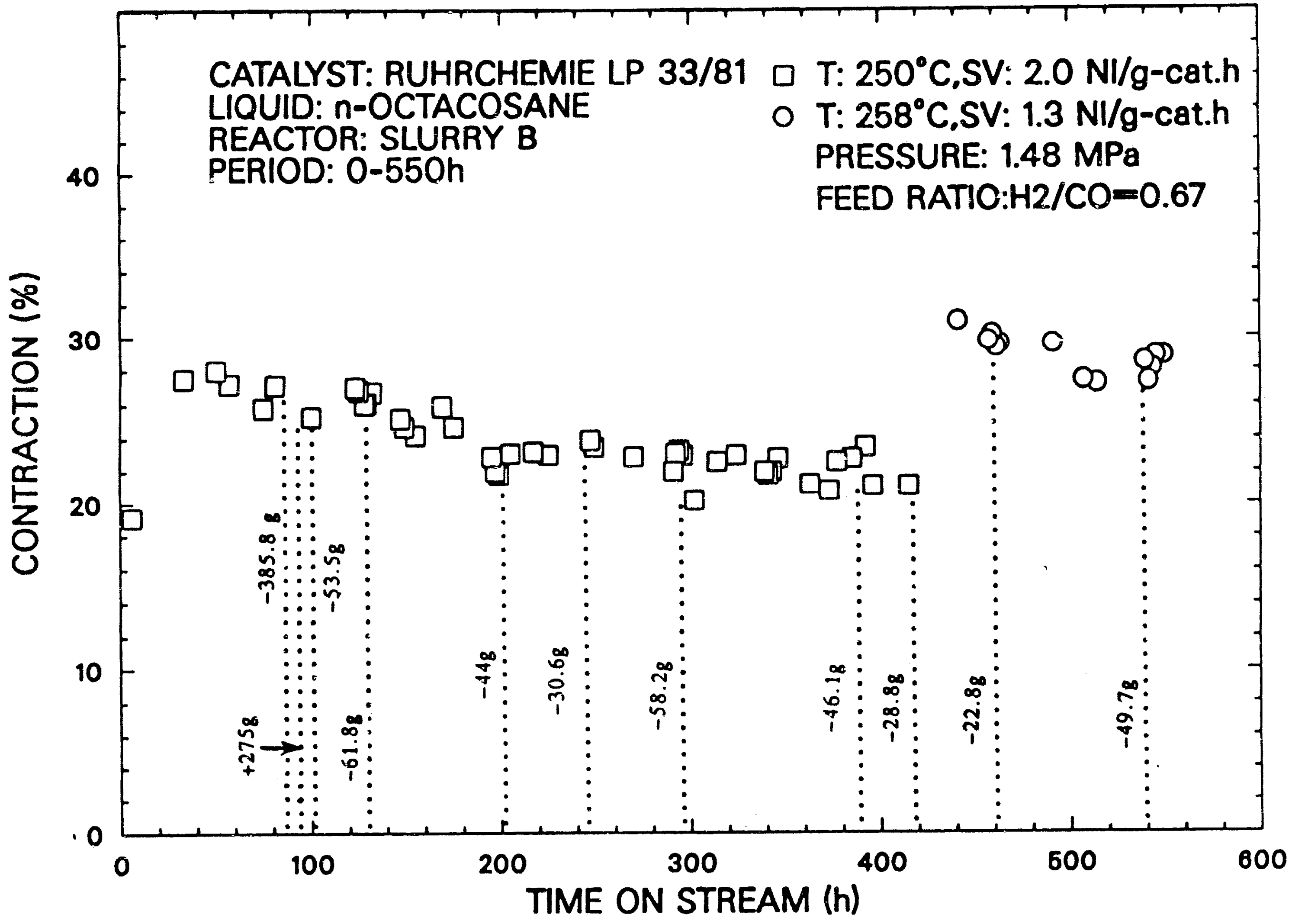

Figure 5. Volumetric contraction versus time on stream for run SB-99-0440 (weights indicate amount of wax withdrawn (-) or added (+))

2

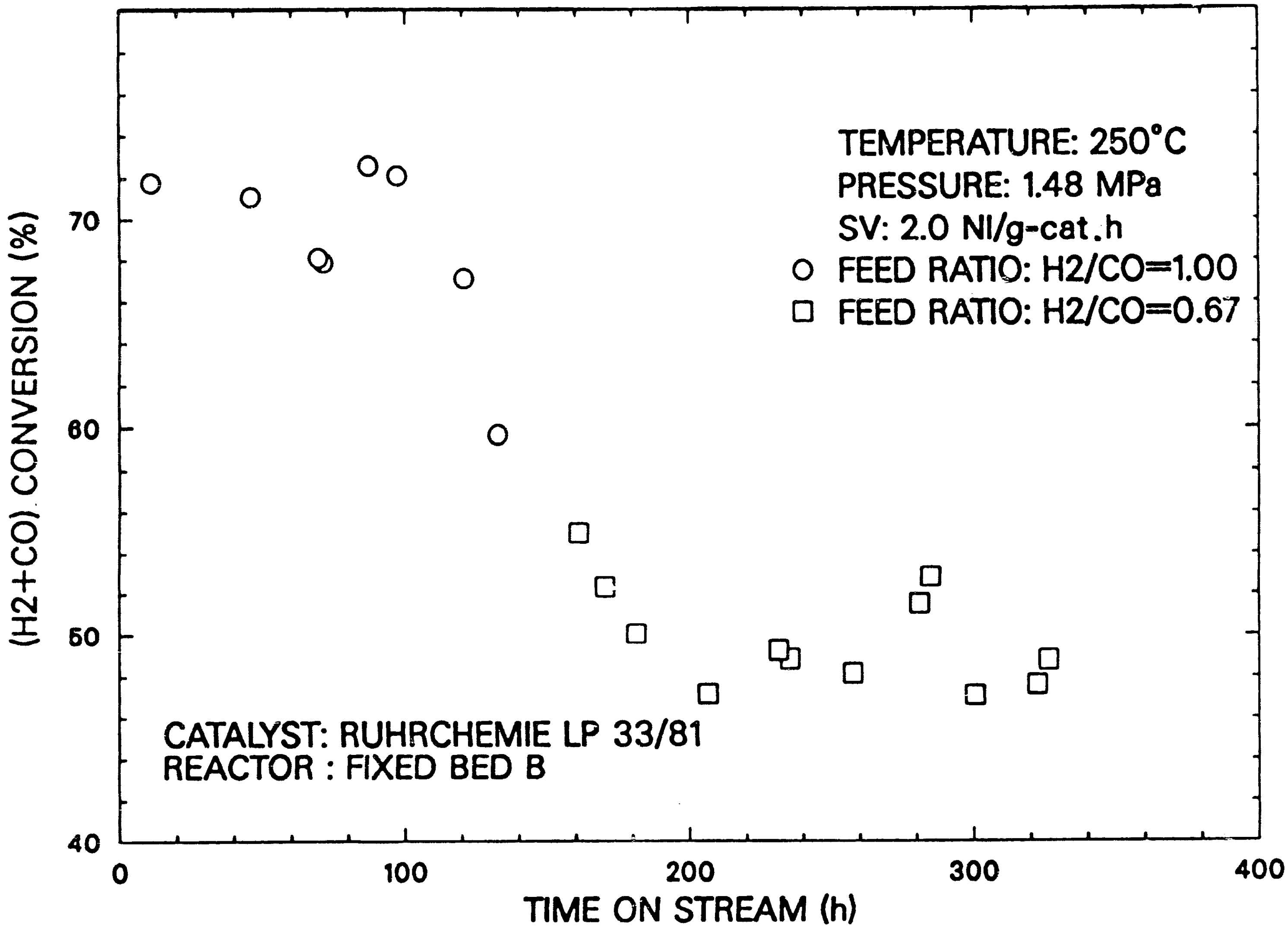

Figure 6. Stability plot, (H_2 +CO) conversion versus time on stream ,for run FB-99-0750

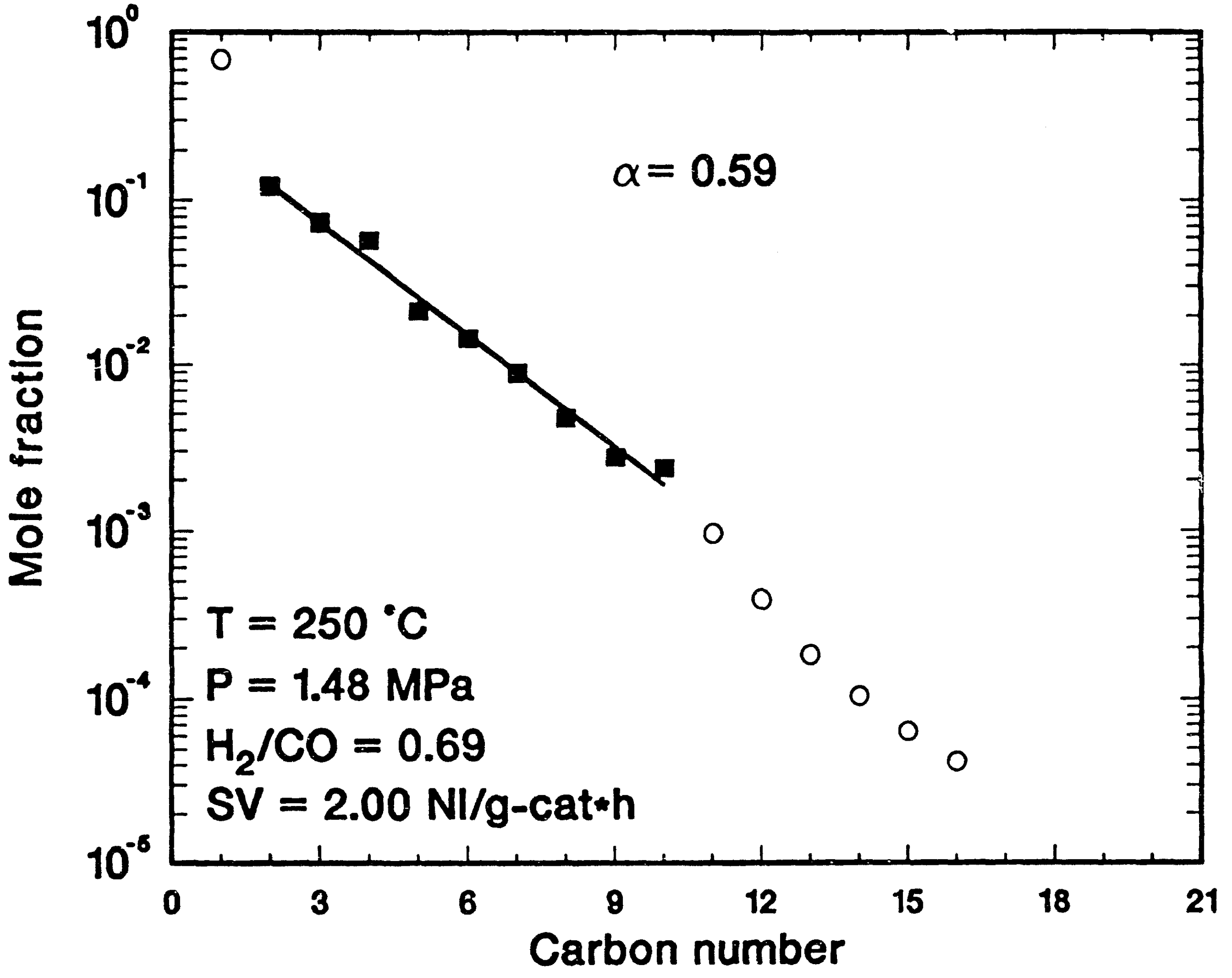

Figure 7. Anderson–Schulz–Flory plot for run FB-99-0750 (Balance #6), total products excluding wax.

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8/17/92