

DEVELOPMENT AND PROCESS EVALUATION OF
IMPROVED FISCHER-TROPSCH SLURRY CATALYSTS

QUARTERLY TECHNICAL PROGRESS REPORT
FOR THE PERIOD 1 JANUARY to 31 MARCH 1987

Submitted to

UNITED STATES DEPARTMENT OF ENERGY

June 9, 1987

by

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Air Products and Chemicals, Inc.

Allentown, PA 18105

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UNDER DOE CONTRACT NO. DE-AC22-85PC80011

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I. Abstract

Optimal experimental conditions for preparation of Fe/Cu/K catalysts have been identified. Using this procedure the following catalysts were prepared (100 g of each): 100% Fe, 100 Fe/0.05 K, 100 Fe/0.1 K, 100 Fe/0.2 K, 100 Fe/1.0 K and 100 Fe/2.0 Cu. Five Fe/Cu catalysts have been characterized by a temperature programmed reduction technique for their comparative reduction behaviors.

Programs for automatic peak identification of all components appearing in gas, aqueous and organic phase have been developed and tested. Response factors and retention times for organic phase components have been determined.

Shakedown runs in the fixed bed and the slurry reactor were performed with a fused iron catalyst. No major operational problems were encountered during over 140 hours of continuous operation in both systems. In general, very good mass balance closures were obtained in both reactor systems and the products were found to follow the Anderson-Schulz-Flory distribution over a wide range of carbon numbers.

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 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. These kinetic parameters will be utilized to simulate catalyst performance under actual bubble column conditions.

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. Data obtained from Tasks 2 and 3 will be used to generate a product yield structure, Fischer-Tropsch reactor residence time, and key process flow rates. These economic studies will include relative capital costs, operating costs, and required revenues for each catalyst, as well as a sensitivity study of the assigned relative values of the principal products (i.e. diesel and gasoline).

III. Summary of Progress

During the second quarter of this contract the following major accomplishments have been made:

- Optimal experimental conditions for the co-precipitation and impregnation techniques for synthesizing Fe/Cu/K catalysts have been identified. In order to achieve nearly quantitative precipitation of copper a pH value of less than 6.5 is required. Several catalysts of the following compositions 100% Fe, 100Fe/0.05K, 100 Fe/0.1K, 100Fe/0.2K, 100Fe/1.0K and 100Fe/20Cu have been prepared (100 g of each).
- A temperature programmed reduction (TPR) technique was employed to characterize the comparative reduction behaviors of five Fe/Cu catalysts. It was found that the presence of copper facilitates iron reduction, and that, under the conditions of the TPR experiments, CO is a more effective reducing agent for iron than is H₂.
- Response factors for organic phase components have been determined and software for automatic peak identification of all products (gas phase, aqueous phase and organic phase) has been developed and tested successfully.
- A fixed bed catalyst reduction unit, which will be used to reduce/activate selected catalysts prior to slurry reactor testing, has been constructed. Construction of a new fixed bed reactor (~ 15 cc) has been initiated and all components for a new 1-ℓ slurry reactor system have been received.
- Two blank runs were made to assess the reactivity of the existing slurry reactor system. One blank run was made with the reactor system completely empty. At 319°C, 400 psig, 1:1 H₂/CO feed gas at 0.6

Nl/min an average $H_2 + CO$ conversion of 13% was observed during 40 hours on stream. During the next 24 hours of testing at a lower reaction temperature of $280^\circ C$, the average $H_2 + CO$ conversion dropped to 4%. For the second reactor run the reactor was loaded with a 10 volume % slurry of alumina particles in a Fischer-Tropsch derived paraffin wax. During a 24 hours synthesis test at $280^\circ C$, 400 psig, 1:1 H_2/CO feed at 0.6 Nl/min the average $H_2 + CO$ conversion was only 0.6%.

- Shakedown runs of the fixed bed and the slurry reactor were conducted using a fused iron ammonia synthesis catalyst (United Catalyst, Inc. C73-1). Both runs were arbitrarily terminated after over 140 hours of continuous and successful operation at 200-215 psig and flow rate of 0.75 Nl/g-cat/h of 1:1 H_2/CO synthesis gas feed. Five mass balances were performed during both runs (3 at $265^\circ C$ and 1 each at 235 and $250^\circ C$).

Catalyst activity and product selectivity obtained during the slurry reactor shakedown run are in good agreement with results reported in the literature. Catalyst activity in the fixed bed reactor was somewhat lower than that obtained in the slurry reactor, but the product distributions were similar in both systems.

In general, very good mass balance closures were obtained in both reactor systems and the products were found to follow Anderson-Schulz-Flory (ASF) distribution over a wide range of carbon numbers. Negative deviations from this distribution were observed in C_6 - C_9 range, which is more than likely caused by the loss of small quantities of these components during sample handling, and at higher carbon numbers. The latter is due to the fact that

the reactor wax composition was not determined. Also, during the fixed bed run, in mass balance periods 2 and 3 some positive deviations from the ASF distribution in C_{14} - C_{21} range and C_{21} - C_{29} range, respectively, were observed. These observations are in agreement with results that have been reported previously in literature.

IV. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

TASK 1 - Project Work Plan

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

TASK 2 - Slurry Catalyst Improvement

2.1 Catalyst Preparation and Characterization

During the past quarter, we have finalized optimal experimental conditions for both the co-precipitation and impregnation techniques that will be employed throughout this project for synthesizing all Fe/Cu/K catalysts. Using this procedure, we have begun to prepare selected catalysts for initial kinetic and physical/chemical characterization studies. We have also confirmed the efficacy of the temperature-programmed reduction (TPR) technique for determining comparative reduction behaviors of precipitated iron catalysts containing varying levels of copper promoter. Detailed descriptions of experimental results are presented in the following sections.

2.1.1 Catalyst Preparation

For any quantitative co-precipitation procedure, it is essential to confirm that homogeneous precipitation of all pertinent components occurs in the same ratio as that of their respective concentrations in solution. The various species of interest may respond quite differently to factors such as solution pH, ionic strength, etc. In the present case, precipitation of FeOOH from Fe(NO₃)₃ solutions by aqueous NH₃ is essentially quantitative at all pH's greater than ~ 2. However, co-precipitation of Cu(OH)₂ is markedly influenced by solution pH, since the soluble Cu(NH₃)₄²⁺ complex forms readily at sufficiently high pH, thus

decreasing the effective Cu/Fe ratio in the precipitate. The importance of this effect has been reported by other investigators (Diffenbach and Fauth, 1986).

Using a modification of the co-precipitation procedure to be described in detail below, we prepared a series of batches at varying pH of a catalyst in which the solution concentrations corresponded to the composition Fe/Cu = 100/10. The actual Fe/Cu ratios in the final, dried catalysts were determined, following re-solution, by inductively-coupled plasma (ICP)-type atomic absorption spectroscopy. The results are summarized in Figure 1. It is clear that virtually quantitative precipitation of copper occurs at pH levels $\leq \sim 6.5$. Copper content in the final catalyst decreases markedly, however, with increasing pH, becoming $< 70\%$ of the expected value at a precipitation pH of 7.3. The effect of pH on copper precipitation appears to diminish somewhat at lower Cu/Fe ratios. When a similar series of batches was prepared from a solution having an Fe/Cu ratio of 100/0.87, the copper level in all samples prepared at a pH less than ~ 7.0 was 0.84 ± 0.05 . Based on the results of these experiments, all catalysts prepared for study in this project are being synthesized using a precipitation pH of 6.0 ± 0.2 . Details of the finalized overall catalyst preparation procedure are summarized in the following paragraphs.

2.1.2 Co-Precipitation Procedure

Desired compositions of copper-promoted iron-based catalysts are prepared by continuous co-precipitation, using an apparatus and a technique similar to that employed by previous investigators (Kolbel and Ralek, 1980; Deckwer et al., 1982). Unlike conventional batch precipitation, this approach ensures that precipitation occurs at a constant, rather than

continuously changing, pH, resulting in much more uniform and predictable particle size and pore size/structure.

In the present case, an aqueous solution containing $\text{Fe}(\text{NO}_3)_3$ (~ 0.6 M), together with a concentration of $\text{Cu}(\text{NO}_3)_2$ that corresponds to the desired Fe/Cu ratio in the final catalyst, and a second solution containing aqueous NH_3 (~ 2.7 M) are maintained in stirred vessels at $83 \pm 3^\circ\text{C}$. The two solutions are separately conveyed by fluid pumps to a stirred tubular reaction vessel that is thermostatted at $82 \pm 1^\circ\text{C}$. Precipitation (to form FeOOH and $\text{Cu}(\text{OH})_2$) occurs continuously as the two solutions are pumped upward through the vessel, while an in-line pH electrode is used to monitor the pH of the reactor effluent. The flow rate of the NH_3 solution is normally fixed at ~ 60 ml/min, while that of the $\text{Fe}^{3+}/\text{Cu}^{2+}$ solution is adjusted (typically to ~ 90 ml/min) to give a precipitation pH of 6.0 ± 0.2 . Collection of the slurried precipitate is made in ice-cooled vessels and is continued until one of the two solutions is consumed. The precipitate is then thoroughly washed by vacuum filtration to remove excess NH_3 and NO_3^- , using ~ 10 liters of deionized, distilled water per 100 g (dry weight) of final catalyst. This procedure is very time-consuming when performed on a bench scale using individual filtration flasks, due to the very small precipitate particle size and consequent slow rate of filtration. The washed precipitate is dried in a vacuum oven for 48 hrs at 50°C , to remove most of the excess water, and then for an additional 12 to 24 hrs at 120°C .

2.1.3 Impregnation Procedure

Addition of the desired levels of potassium promoter to precipitated Fe/Cu catalysts is performed by a pore-filling technique, using dried

precipitate that has been crushed to pass a 40 mesh sieve. In this method, the required amount of KHCO_3 is dissolved in a volume of water that is ~ 5% larger than that needed to just fill all of the pores of the solid. The solution is then added to a weighed sample of catalyst, resulting in the so-called "incipient wetness" condition. This procedure ensures uniform and complete distribution of the potassium salt throughout the catalyst pore structure. For a typical batch of precipitated FeOOH , for example, prepared by the method described in the preceding section, ~ 40 ml of water per 100 g (dry weight) of catalyst is required to achieve incipient wetness. Excess solvent is then removed by vacuum-aided evaporation, with continuous rotational agitation. The final product is dried further in a vacuum oven for 16 hrs at 120°C .

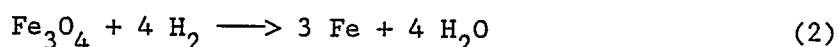
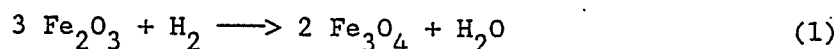
Table 1 summarizes the catalyst compositions that are scheduled for synthesis during this project using the above procedure. We will prepare 100 g of each $\text{FeOOH}/\text{Cu}(\text{OH})_2/\text{KHCO}_3$ composition; those catalysts designated by an asterisk have already been prepared at the time of this report. We are currently initiating detailed characterization of each of these materials, involving TPR, surface area, and pore volume distribution measurements. These results will be provided in future reports as they become available.

2.1.4 Catalyst Characterization

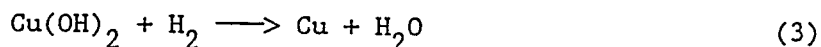
In order to establish the efficacy of the TPR technique for characterizing the comparative reduction behaviors of the various catalysts being investigated, we synthesized small (10 g) batches of catalysts having five different Fe/Cu compositions. These materials, together with their BET

surface areas before and after treatment in H_2 for three hrs at $250^\circ C$, are listed in Table 2. TPR profiles obtained using H_2/N_2 ($12 \text{ cm}^3/\text{min}$ flow rate) reductant are shown for each of the five materials in Figure 2.

As reported by previous investigators for both supported and bulk iron oxides (Unmuth et al., 1980; Brown et al., 1982), we observed that reduction in H_2 of uncalcined $FeOOH$ (essentially hydrated Fe_2O_3) occurs in two steps:



The peak at $340^\circ C$ in the TPR profiles of the two catalysts containing 0 and 0.5 parts Cu is due to the reduction step of Eq. 1 above. Subsequent reduction of Fe_3O_4 to metallic Fe (Eq. 2) occurs over a wide temperature range in the TPR experiments and gives rise to the very broad "peak" that is observed at $400-800^\circ C$ in each of the five profiles shown in Figure 2. It is clear that the first reduction step occurs at progressively lower temperature with increasing copper content, the peak at $340^\circ C$ eventually shifting to $< 290^\circ C$ in the cases of the two catalysts containing 5 and 10 parts of Cu. Copper-induced shifts in the broad peak due to the second stage of reduction also occur, but are less pronounced. The peak at $240^\circ C$ that increases in intensity, but does not shift position, with increasing copper content is due to reduction of $Cu(OH)_2$ (or CuO):



It is the presence of this reduced copper that facilitates dissociation and consequent reactivity of H_2 and decreases the temperature required for reduction of the iron component.

Corresponding TPR profiles for the same five catalysts using CO/He (12

cm³/min flow rate) as the reduction mixture are shown in Figure 3. It can be seen that, under the conditions of the TPR experiments, CO is a more effective reducing agent for iron than is H₂. The peak corresponding to the first step of FeOOH reduction (Eq. 1) occurs here at only 200°C and again shifts to lower temperature with increasing copper content, eventually merging with the Cu(OH)₂ reduction peak which occurs at 160-180°C. In further contrast with the results observed with H₂ as reducing agent, the TPR peak due to reduction of Fe₃O₄ to metallic Fe is more intense, much more well-defined, and occurs at a lower temperature, viz., ~ 350°C vs. ~ 600°C. It is not yet clear, however, whether these effects are due to greater reduction ability of CO or to insufficiently rapid removal of the water that is generated during reduction in H₂.

These TPR data will not be discussed in greater detail, since the five catalysts shown were not prepared using the eventually finalized catalyst synthesis procedure and will not be used for actual catalytic reactor studies. They do serve to demonstrate, however, the usefulness of the TPR technique for characterization of the comparative reduction behaviors of copper-promoted precipitated iron catalysts. It is important to note that reduction profiles obtained using the TPR method must be viewed in a comparative, rather than an absolute, sense. The use of temperature ramping, together with vastly different gas flow rates, sample sizes, etc. from those employed in actual catalytic reactors prevent absolute correlations between observed TPR peak positions, for example, and the corresponding temperatures that would be required for the same reaction occurring under isothermal conditions. The principal benefit of the TPR data is that

of rapid, comparative evaluations of reduction behaviors for catalysts having a wide range of compositions.

2.2 Product Analysis

2.2.1 Carle AGC 400 Modifications

Modifications to the internal valve/column configuration of the Carle AGC 400 chromatograph have been performed. Originally, two injections of the same sample were required for a complete analysis. One sample was analyzed using a flame ionization detector (FID) for C_1 to C_5 hydrocarbons, while the second sample was analyzed by a thermal conductivity detector (TCD) for CO , CO_2 , H_2 , CH_4 , C_2H_4 and C_2H_6 . The complete analysis was then constructed using tie components. Past experience in our laboratory has demonstrated that a more accurate analysis is obtained when a given sample is analyzed for all components. Thus, the Carle chromatograph was modified so as to allow for analysis of all components (permanent gases and hydrocarbons) from one sample injection.

These modifications involved replacing a 10 port sample valve with a six port switching valve, and minor changes in the column configuration. The sample analysis is first routed through the TCD, then through the FID. The TCD is non-destructive, and thus allows for the sample to be analyzed by either detector. In this arrangement, the TCD is used to determine gas phase concentration of CO , CO_2 , H_2 and CH_4 , while the FID analyzes C_2 - C_5 hydrocarbons. A GC trace of the actual F-T product obtained with this new configuration is shown in Figure 5.

2.2.2 Response Factors for the Organic Phase Components

Response factors and retention times for organic phase components of interest expected in a Fischer-Tropsch product were obtained using a

Sigma 1 chromatograph equipped with an FID. These components include C₆-C₃₀ N-paraffins, C₆-C₂₀ α-olefins, C₄-C₁₀ N-alcohols and C₆-C₈ aromatics.

Response factors for these components were determined from the following equations:

$$RF'_i = \frac{AREA_i}{(mole\ %) _i N_i} \quad (4)$$

$$RF_i = \frac{RF'_i}{RF'_{ref}} \quad (5)$$

where: RF'_i is the response factor relative to the sample; AREA is the peak area of integration; Mole % is the concentration of component i in the standard; N is the number of carbon atoms in component i; RF'_{ref} is the response factor of a reference component and RF_i is the calculated, normalized response factor.

The reference response factor, RF'_{ref} , is determined relative to N components in the mixture (1-olefins and normal paraffins)

$$RF'_{ref} = \frac{1}{N} \sum_{i=1}^N RF'_i \quad (6)$$

Typically, all N-Paraffins and 1-olefins present in the calibration sample whose RF'_i value was ±10% of the average were used in calculation of RF'_{ref} .

Calibration standards were prepared by mixing known quantities of pure components. Component separation was achieved by using a 30 m x 0.32 mm fused silica capillary column coated with 0.25 μm DB-5 under conditions given in Table 4a. The response factors of all components are listed in Table 3, together with values reported by Dietz (1967). Response factors for hydrocarbons from C₇ up to C₂₀ were found to be approximately equal to 1.0, which is in excellent agreement with values obtained by Dietz. A loss

in detector response for hydrocarbons greater than C_{20} , and the concentration dependence of response factors of higher hydrocarbons were observed. The latter is reflected in greater values of standard deviation for these components. In addition, a lower than expected response at C_6 was also observed. This is probably due to high volatility of these components. Reproducibility in detector response was typically very good, and relative deviations of about 5% or less from the mean value were obtained for most components.

Response factors for C_6 to C_8 aromatics were determined relative to N-paraffins. Response factors for these components were found to be ~ 1.0 . Response factors for C_4 to C_{10} N-alcohols were determined relative to N-paraffins and they are 20-30% less than those obtained by Dietz.

2.3 Data Acquisition and Reduction

2.3.1 Anderson-Schultz-Flory (ASF) Plotting Programs

Two programs have been written to produce ASF plots for the distribution of normal paraffins, 1 and 2 olefins, hydrocarbon isomers, oxygenates, and the total product. The first program, written for an IBM-PC or compatible, takes its results from the HP-9000 mass balance routine. The program produces an ASF plot on the screen and allows the user to interactively include or exclude stray data points from the analysis. It has also been observed that Fischer-Tropsch product may be characterized by more than one chain growth probability (Huff and Satterfield, 1984; Egiebor and Cooper, 1985). To account for this, the program allows multiple lines to be fit to the data. A second program was written on the HP-9000 to produce hard copy outputs of the ASF plots results. Existing software is used for the transfer of data between the two computer systems. The ASF

plots for the shakedown runs with a fused iron catalyst are shown in Figures 10 to 14, and 16 to 20. Data points indicated by open circles were not included in fitting the ASF line because the analytical methods have not been optimized for these product ranges. This will be discussed in more detail later in this report.

2.3.2 Peak Identification Software

Peak identification software, used for identification of peaks appearing in GC traces of Fischer-Tropsch products, have been written and successfully tested. These programs identify gas and liquid phase Fischer-Tropsch product composition on the basis of the retention times of the components. By using this software the product analysis is done automatically. After data processing the output is checked for possible errors in identification.

The peak identification routine for the aqueous phase components was described in the previous Quarterly report (October 17, 1986-January 31, 1987). The chromatogram of the aqueous F-T product from the fixed bed reactor shakedown run FA-01-1147 (period 4) is shown in Figure 4 and results from the peak identification routine are given in Table 5. The GC operating conditions for aqueous phase analysis are listed in Table 4b. An excellent separation of all normal 1-alcohols was achieved (Fig. 4) and all components were identified correctly. The positive identification of peaks by GC/MS is currently in progress.

Gas phase components analyzed on the Carle AGC 400 chromatograph are identified based on their retention times using the Sigma 15 console. The chromatographic output provided by the console is then upgraded and converted to an output file which is compatible with the material balance subroutines via an identification interface routine, IDGAS.F. The interface routine was necessary, as the Sigma identification algorithm has flaws which could lead to inaccurate material balance/data reduction. The pur-

pose of IDGAS.F is to remove these shortcomings and provide a component identification for both the user and the material balance routine. Upgrading of the Sigma 15 output involves deleting of peaks due to valve switching and background air, and treating unidentified peaks appearing in the C_4 and C_5 hydrocarbon region as C_4 and C_5 isomer paraffins, respectively. In addition to the identification upgrading, IDGAS.F. determines the molar composition of the gas stream, percent contraction, and conversions of CO , H_2 and $CO + H_2$. Sample output from IDGAS.F is reported in Table 6. This output corresponds to an actual F-T tail gas analysis during the shakedown run in the fixed bed reactor. The GC trace of this sample is shown in Figure 5 and the GC conditions are listed in Table 4c. Note that an excellent separation of all components is obtained and that all peaks are correctly identified. Currently, IDGAS.F will identify twenty peaks, ranging from CO to C_5 hydrocarbons. The listing of these components is reported in Table 6.

Gas phase components analyzed on the Sigma 1B chromatograph equipped with a 6' Porapak Q column are identified based on their retention times using the Sigma 1B console. The chromatographic output provided by the console is then upgraded and converted to an output file which is compatible with the material balance routine via an identification interface routine, IDGAS2.F. The purpose of IDGAS2.F is to remove shortcomings of the Sigma identification algorithm and to provide a component identification to both the user and the material balance routine. IDGAS2.F is similar to IDGAS.F used in upgrading the Carle gas phase identification. Upgrading of the Sigma 1B output involves removal of repeated labeled peaks

(i.e., more than one peak with the same identification) and provides a means of treating unidentified peaks. For example, identified peaks appearing between $N-C_6$ and $N-C_7$ are treated as C_7 paraffin isomers. A sample output from IDGAS2.F is reported in Table 7. These data correspond to an actual Fischer-Tropsch tail gas analysis (mass balance period 4 during the shakedown run in the fixed bed reactor). All peaks are correctly identified. Currently, an identification search for all C_1-C_8 N-paraffins and C_2-C_8 N-terminal olefin is attempted. GC column conditions for this type of analysis are given in Table 4c. The chromatogram of this sample is shown in Figure 6, which indicates that small amounts of C_6-C_8 hydrocarbons are present in the tail gas. Note also from this figure that a good separation of olefins and paraffins in this carbon number range is not achieved. Work to improve this separation will be conducted during the next quarter.

A routine for identification of species present in a Fischer-Tropsch organic phase product has been written and successfully tested. Currently, the routine identifies N-paraffins, N- α and β -olefins from C_5 to C_{30} , and C_4 to C_{10} N-alcohols. Peaks are identified based on their retention times relative to the previous N-paraffin. Table 8 reports a sample output from this routine. The data in this table correspond to an actual Fischer-Tropsch organic phase product analysis collected during the shakedown run in the fixed bed reactor (mass balance period #4).

The chromatogram of this sample is shown in Figure 7. Note that excellent separation of 1-olefin, N-paraffin and c,t-2 olefin is achieved past C_{20} . Also note that a very good separation of N-alcohols is achieved. All peaks have been correctly identified. Positive identification of peaks

by GC/MS is currently in progress.

The peak identification software developed for this project requires minimal human intervention and alleviates the need for a tedious manual identification and transfer of data to the mass balance program.

2.4 Design and Construction of Reactor Systems

2.4.1 Catalyst Reduction Unit

A catalyst reduction unit, which may be used to reduce/activate selected catalysts prior to slurry testing, has been constructed. A schematic of this system is shown in Figure 8.

Reducing gas enters the system via a mass flow meter and passes through a trap filled with 5A molecular sieve to remove water. An electrically heated preheater is used to bring the reducing gas up to reduction temperature before entering the reactor. The gas then enters the reactor, and passes over the catalyst bed. After leaving the reactor, the gas flows through a bed of indicating drierite, used to visually monitor the course of reduction, and passes through a wet test meter which measures the gas exit flowrate.

The reactor itself, Figure 9, is made of 3/4" x 12" SS tube, fitted at both ends with SS reducing unions to bring the tube diameter down to 3/8". One end is left open and serves as the top, through which reducing gas enters the reactor. The gas exits the reactor through the other end, which is closed with a SS sintered metal plate backed by pyrex wool. The sintered plate/pyrex wool are used to support the catalyst bed and prevent entrainment of catalyst particles in the flowing gas.

During operation, the reactor is placed in an electrically heated aluminum block to ensure a uniform temperature in the reactor. Thermo-

couples, located along the bed, are used to monitor the axial temperature profile of the reactor. The effective heated volume of the reactor is 63 cm³.

Following reduction/pretreatment, the unit is cooled to ambient temperature under a helium purge. The reactor is sealed in helium, and removed from the system, and weighed to determine the catalyst weight loss upon reduction. The catalyst is transferred through a 3/8" charging port located in the head of the slurry reactor. Prior to transfer, the slurry system is purged with helium to remove all oxygen. The reduction reactor is inverted and attached to the loading port of the slurry reactor. The catalyst is transferred to the slurry reactor pneumatically with helium. After the transfer is complete, the reduction reactor is removed and weighed and the slurry reactor sealed. The weight of catalyst transferred to the slurry reactor is determined by the difference in weights before and after the transfer is made.

2.4.2 Fixed Bed Reactor Apparatus

Construction of the second fixed bed reactor system is underway. Details regarding the design and flow diagram of this system were given in the previous quarterly report (October 17, 1986-January 31, 1987). All components necessary for construction of this system have been received. Construction will be completed during the month of May.

2.4.3 Slurry Reactor Apparatus

A detailed description, including the flow diagram, of the second slurry reactor system, was given in the previous quarterly report (October 17, 1986-January 31, 1987). All components necessary for the construction of the 1-2 Autoclave reactor system have been recieved. Construction will

be initiated during the next quarter.

2.5 Testing of the Existing Slurry Reactor System

2.5.1 Blank runs

Two blank runs were made to assess the reactivity of the existing slurry reactor system. One blank run was made with the reactor completely empty. The system was first pretreated using pure H_2 at ambient pressure with a flow-rate of 0.3 Nl/min for 24 hours. The reactor temperature was maintained at 377°C during this time. Following pretreatment, a synthesis test was made at 319°C, 400 psig, 1:1 H_2 /CO feed gas at 0.61 Nl/min. These conditions were held for approximately 42 hours and an average H_2 + CO conversion of 13% was observed. Measureable quantities of C_1 - C_6 hydrocarbons were observed in the reactor outlet gas stream. This high level of activity was not expected and further testing was conducted under less severe operating conditions.

Immediately following the test at 319°C, the reactor temperature was lowered to 280°C. All other conditions remained the same. During 24 hours of testing, the average H_2 + CO conversion observed at these conditions dropped to 4%. The system was tested further by discontinuing the heating of the reactor feed and exit lines, and the reflux condenser, while holding the reactor temperature at 280°C. No significant change in conversion was observed, which indicates that the bulk of the background activity of the system is confined to the reactor.

For the second blank run, the reactor was loaded with a 10 volume % slurry of alumina particles (<325 mesh) in a Fischer-Tropsch derived paraffin wax (FT-300 wax with the average molecular weight of 730 purchased from

Durachem). This test was made to check the activity of the slurry reactor system in a more realistic environment, and to evaluate the integrity of the liquid medium under synthesis conditions. The reactor was again pretreated with pure H_2 flowing at 0.3 NL/min. Since the wax was present in the reactor, the pretreatment temperature was decreased to 280°C and the system pressure increased to 400 psig. No measurable quantities of either reactor wax or hydrocarbon products were observed in the reactor outlet during the 24 hour pretreatment. Following pretreatment, the feed was switched to a 1:1 H_2 /CO feed at 0.6 NL/hr. During a 24 hour synthesis test, the average H_2 + CO conversion measured was 0.6%. This low level of activity is acceptable, since high conversions are expected at these operating conditions in the presence of a catalyst.

2.5.2 Wax Withdrawal Experiments

During actual operation of the reactor accumulated F-T wax in the reactor produced by the synthesis must be removed at the end of each material balance period in order to obtain accurate total and atomic mass closures. Several methods have been experimented with using slurries simulated by iron oxide or alumina as solids and hydrocarbon solvent (tradename Varsol), toluene, or FT-300 wax as liquids.

The first method used a dipleg (1/8" stainless steel tube) placed in the reactor at the desired slurry level. A 1/2" shield was placed around the dipleg in order to allow the solids to settle out of the wax before withdrawal. The reactor content was agitated with a mechanical stirrer at 1,000 rpm. The shield, however, did not prevent excessive amounts of solids to be removed with the liquid.

Another method of wax withdrawal was employed by placing a 5- μ m filter

in the reactor to separate the solids from the liquid. When this method was tested, the filter quickly plugged with solids, preventing the removal of any material from the reactor. Similar difficulties with this method have been reported in the literature (Ledakowicz et al., 1985; Brian et al., 1983, 1984).

Finally, a dipleg was employed with no shielding or filter. Prior to wax withdrawal, the reactor stirrer was stopped and any feed was bypassed around the reactor. After allowing the solids to settle for 15-20 minutes, it was possible to withdraw nearly clear liquid from the reactor. This method is currently used to withdraw accumulated wax from the reactor during synthesis.

2.5.3 Catalyst Separation from Slurry Samples

When wax is withdrawn from the reactor through the dipleg, there is a possibility that small amounts of solid catalyst will also be removed with the wax. It is important to quantify the amount of catalyst removed in order to accurately determine the weight of catalyst remaining in the reactor, upon which catalyst activity and space velocity are based, as well as to improve mass closures. Two methods have been tested for catalyst separation from a slurry sample. In the first method the wax was placed in a 500 cc Soxhlet extraction apparatus. Methylene chloride and toluene were both tested as solvents, but in either case the solvent became saturated with wax before the extraction was complete. This method was also found to be very slow. For the second method, the wax sample was dissolved in a large quantity of hot hydrocarbon solvent (Varsol). After all the wax dissolved, the solution was filtered in a Buchner funnel to separate the catalyst from the solution. The amount of clear wax withdrawn is given by

activation and was held at this temperature for the next 24 hours. Following this the temperature was raised to 400°C and maintained at this temperature for 24 hours. During the final stage of reduction, the bed was kept at 430°C for additional 24 hours. Pressure drop across the bed was initially 300 psi. It decreased steadily during the activation and stabilized at about 80 psi after 60 hours. The weight loss of catalyst was about 25%, and 43.6 g of reduced catalyst was transferred to the slurry reactor which contained 322 g of FT-300 wax, giving 15.3 wt% slurry (unreduced catalyst basis). The loading port on the reactor head was resealed after the catalyst transfer and the reactor was pressurized to 200 psig and its temperature raised to 150°C in flowing helium at a stirring speed of 1,000 rpm. After 3 hours at these conditions the synthesis gas ($H_2/CO = 1:1$) was introduced and the temperature was increased gradually to 265°C over a period of 4 hours, using manual control to stabilize the reactor temperature at a desired value.

The fixed bed reactor (~15 cc) was charged with 3.6 g (1.6 cc) of 32-60 mesh (0.25-0.50 mm) size fused magnetite particles mixed with 6.4 cc of silica (99.9% SiO_2 from Alpha Products) of the same particle size. The catalyst bed was first heated to 150°C at a rate of 2°C per minute with pure H_2 at atmospheric pressure and a flow rate of 10,000 h^{-1} . This temperature was maintained for 2 hours. The bed temperature was then raised to 370°C at a rate of 2°C/minute. This temperature was maintained for 24 hours, followed by 24 hours at 400°C, followed by 24 hours at 430°C. Pressure drop across the bed was less than 5 psi. Following reduction, the catalyst was cooled to room temperature in flowing helium. Then, the

reactor was sealed and pressurized to 200 psig and left in helium atmosphere for 90 hours to prevent the catalyst reoxidation. This unexpected delay in the start of the run was caused by malfunctioning of a H_2 mass flow meter and the Carle gas chromatograph. After these instruments were repaired, the bed temperature was raised to 265°C at a rate of 2°C/min in flowing helium at a gas hourly space velocity of $2,340\text{ h}^{-1}$ (based on the volume of unreduced catalyst) at atmospheric pressure. Once at this temperature the syngas feed was introduced ($H_2/CO = 1:1$), and the pressure was gradually increased to 215 psig.

2.6.2 Shakedown Run in the Slurry Reactor

The slurry shakedown run designated SA-01-0817 (SA = slurry reactor A; 01 = catalyst designation; 0817 = run starting date, 81st day of 1987) with the fused iron catalyst was arbitrarily terminated after 155 hours of continuous and successful operation. During this period five mass balances, each of at least 8 hours duration, were performed. The run was conducted using the synthesis gas feed of 1:1 H_2/CO molar ratio, at 200 psig (1.5 MPa), the space velocity of $0.75\text{ l(STP)/g-cat (unreduced)/h}$ (i.e. $GHSV = 97\text{ h}^{-1}$ based on the unexpanded slurry volume of 450 ml) and the stirring speed of 1,000 rpm. The temperature was varied between 235°C and 265°C. A detailed description of the operating procedures and results obtained during this run is given below.

(a) Operating Procedure

Following the catalyst transfer and adjustments to achieve the desired process conditions (265°C and 200 psig) the system was allowed to run undisturbed for 40 hours. Then, stirring was discontinued and the feed gas was directed to bypass the reactor. After waiting 15 minutes for the

catalyst to settle, the excess wax was withdrawn through the 1/8" dipleg which maintains the slurry volume at 450 ml. A negligible amount of catalyst, determined by separation (section 2.5.3), was withdrawn with 39.6 g of wax.

In general, after the wax withdrawal, stirring at 1,000 rpm and synthesis gas feed are resumed and the system is allowed to reach a steady state. After about 16 hours the product trap is drained and the mass balance period begins. During the mass balance period, exit gas flowrates are measured and exit gas samples are taken periodically. At the end of about 8 hours of operation, stirring is discontinued, the feed is bypassed around the reactor, and the synthesis products are drained from the product trap and weighed. While the feed is bypassed around the reactor, the feed flowrate is measured volumetrically and a feed sample is taken. After the catalyst has been allowed to settle for about 15 minutes, the accumulated wax is withdrawn from the reactor. The weight of wax collected is averaged over the time since the last withdrawal to estimate the weight of wax produced during the mass balance period. When the wax withdrawal is complete, stirring and synthesis gas feed are resumed, any changes in process conditions are made, and the procedure repeats itself. When following this procedure, one 8 hour mass balance may be performed per day.

(b) Discussion of Results

Selected results from the five mass balance periods are summarized in Table 9. A detailed sample output from the mass balance program for period 5 is given in Appendix I. As shown in Table 9, poor mass balance closures were obtained for the first two mass balance periods (91.2% and 87.1%), whereas the mass balance closures for the remaining three balances were

much better (95.8-99.7%).

Three mass balances were made at 265°C (Periods 1, 2, and 5) and their comparison provides check on data reproducibility. Similar conversions ($\text{CO} + \text{H}_2$ conversions: 75.2-78.6%) and space-time-yields ($\text{STY} = 0.024\text{-}0.025$ mols $\text{H}_2 + \text{CO}/\text{g} - \text{cat}/\text{h}$) were obtained in all three balances. Hydrocarbon selectivities for periods 1 and 5 are very similar for both the individual components and products lumped according to carbon numbers. The product selectivities for the second mass balance period are different than for the other two balances mainly due to the fact that during this balance no wax was withdrawn from the reactor. The chain growth probability factor, α , in the ASF distribution determined from selected points (dark squares in Figures 9, 10 and 13) was nearly the same for all three balances. The $\text{H}_2 + \text{CO}$ conversion increased with temperature: 39.3, 73.5 and 78.6% at 235, 250 and 265°C respectively. The small change in conversion between 250 and 265°C may have been caused by the reaction becoming limited by CO depletion at higher temperatures. The CO conversion at 265°C is 93.7%, while at 250°C it is 87.9%. The product distribution shifts to lighter fractions as temperature increases, which is as expected. For example, the hydrocarbon selectivity in $\text{C}_2\text{-C}_{11}$ range is 63.2% at 265°C, whereas it is only 39.8% at 235°C. On the other hand the products which accumulate in the reactor during the run and are removed at the end of the mass balance period (reactor wax) comprise 39.4% of hydrocarbons at 235°C vs. 14% at 265°C. The carbon number distribution of products in the reactor wax was not determined. Methane selectivity varied from 10.7% at 250°C to 14.6% at 265°C.

The Anderson-Schulz-Flory plots (logarithm of mole fraction vs. carbon

number) for all the five balances are shown in Figures 10 to 13. Some features that are common to all balances are as follows: (1) Concentrations of components in the C_6 - C_9 range are too low; and (2) The products of high carbon number ($n > 16$) deviate below the theoretical line. Both of these deviations are fairly common and have been reported in literature (Satterfield and Huff; 1982; Satterfield *et al.* 1982). Hydrocarbons in the C_6 - C_9 range are probably lost by volatilization in handling, whereas the concentrations of high molecular weight components are too low due to their accumulation in the reactor. Alpha values do not vary much with temperature, e.g. $\alpha = 0.71$ at 265° whereas $\alpha = 0.73$ at 235°C . This is in agreement with results reported by Satterfield and Huff (1982) who obtained $\alpha = 0.67$ at 263°C and $\alpha = 0.71$ at 234°C under the following operating conditions: $H_2/CO = 1.3$, $P = 0.79$ MPa and GHSV = $93 - 107\text{ h}^{-1}$.

Results obtained during the shakedown run are in good agreement with results obtained previously in our laboratory (Brown, 1986) with the same catalyst under the same conditions, as well as with those of Huff (1982) obtained under similar conditions. For example the $H_2 + CO$ conversion of 78.6% at 265°C obtained during the shakedown run is in good agreement with 81.6%-conversion reported by Brown (1986) under the same set of operating conditions. Product selectivities are also similar. Huff (1982) reported the following values of $H_2 + CO$ conversion for experiments conducted at $H_2/CO = 0.90$, 1.48 MPa and 0.96 l (STP)/g-cat/h: 74% at 248° and 82% at 263° . Again, these values are comparable to the ones obtained in the present study. A detailed comparison between the results obtained in our laboratory (Brown, 1986) and at M.I.T. (Huff, 1982) is presented in our

forthcoming paper (Bukur and Brown, 1987).

The above results indicate that our analytical methods for product analysis, catalyst activation and operating procedures as well as data reduction procedure are working very well. Additional improvements in methods and procedures will be continuously made during the course of the project.

2.6.3 Shakedown Run in the Fixed Bed Reactor

The fixed bed reactor shakedown run designated FA-01-1147 (FA=fixed bed reactor A; 01 = catalyst designation; 1147 = run starting date: 114th day of 1987) with the fused iron catalyst lasted over 140 hours of continuous operation. No major operational problems were encountered during the run and, in particular, nearly isothermal conditions were achieved even at high syngas conversions (up to 78%). The maximum axial temperature difference was less than 4.4°C at the average bed temperature of 266°C (MB period 4). Five mass balances were conducted during this run, each of at least 8 hours duration. Mass balance closures were excellent, within ±3%, with the exception of the last balance which had 94.4% closure.

The process conditions were nearly the same as the ones employed in the slurry reactor shakedown run, i.e. $H_2/CO = 1$ (premixed gas), $P = 215$ psig (1.6 MPa), $SV = 0.75$ l (STP)/g-cat (unreduced)/h (GHSV = $1,690$ h⁻¹ based on the volume of catalyst only) and the temperature varied between 236°C and 266°C.

(a) Operating Procedure

After the catalyst reduction and establishment of the desired operating conditions (266°C, 215 psig, 0.75 Nl/g·cat/h) the system was allowed to run at these conditions for 33 hours (unsteady state period) before the

first mass balance was performed over a period of 8 hours. After each mass balance period the gas flow rate was checked by directing the gas feed through the reactor bypass line. After any changes in operating conditions the next material balance was performed after about 16 hours of operation at the new set of conditions. Products formed during this unsteady state period were collected in a waste trap maintained at 0°C and atmospheric pressure. Following these unsteady state periods the material balances were performed over periods 8-13 hours in length, during which the liquid products were collected in a tared collection trap at 0°C and atmospheric pressure. After equilibration to room temperature the trap was removed and weighed to determine the total amount of products collected during the material balance period. The contents of the trap are then drained and separated into an aqueous and organic layer. The products which remain in the trap after drainage of the liquid are referred to as the reactor wax, and their mass fraction is determined by subtracting the weight of the liquid fraction from that of the entire contents. During the mass balance period the tail gas flow rate was recorded and a minimum of three gas samples were collected and analyzed on the Carle 400 and Sigma 1B gas chromatographs.

In mass balance periods 3 to 5, the product trap was heated electrically to about 100°C, and additional product was drained into a vial which contained the organic phase liquid collected at the room temperature. This product was solid at room temperature but it would almost completely dissolve in CS₂, which is used to dilute organic phase samples before injection into the capillary column. Even after heating to 100°C some products would still remain in the trap. This solid material was finally

removed by adding hot toluene to the trap and draining. The reactor wax was not analyzed to determine its carbon number distribution.

Some minor operational problems were encountered during the shakedown run. Fluctuations in reactor pressure of ± 10 psi were observed occasionally. This was attributed to condensation of heavy molecular weight products and their partial blocking of lines and the back pressure regulator. Gas flow rates were stable with the exception of short periods (15-30 minutes) when the pressure was fluctuating. A hot ($\sim 100^\circ\text{C}$), high pressure trap will be installed upstream of the back pressure regulator to alleviate this problem. The temperature at the entrance to the catalyst bed was about $15\text{-}20^\circ\text{C}$ below the average bed temperature. A preheater will be installed upstream of the reactor to solve this problem.

b) Results and Discussion

Selected results from all five balances are summarized in Table 10, and the ASF plots are shown in Figures 16 to 20.

The plot of synthesis gas conversion as a function of time and temperature is shown in Figure 15. The gas phase composition was measured often during first 40 hours on stream. A drop in conversion from 78% to 70% occurred during the first 16 hours. After this, the $\text{H}_2 + \text{CO}$ conversion remained fairly constant at about 70%. It is interesting to note that the initial conversion was nearly the same as the one obtained in the slurry reactor under similar conditions (Table 9, periods 1, 2 and 5), but it could not be maintained over a long period of time. The drop in conversion might have been caused by rapid wax formation and coking of the catalyst. After the catalyst was exposed to lower reaction temperatures (236°C between 41 and 66 hours on stream, and 251°C between 66 and 81 hours on

stream), the reaction temperature was again raised to 266°C and during the mass balance period 4 the $H_2 + CO$ conversion was 76.5%, i.e. almost as high as during the first few hours on the stream. However, during the next 24 hours on the stream at the same conditions (Period 5) the $H_2 + CO$ conversion dropped to 66%, which is lower than the value obtained during the first mass balance period. Reasons for this unexpected behavior are not obvious. The synthesis gas conversions obtained at 236°C and 251°C, 32.1% and 53.2% respectively, were lower than the corresponding values obtained in the slurry reactor (39.3% at 234°C and 73.5% at 251°C). A possible explanation might be that the catalyst was partially deactivated during the first few hours on the stream. Satterfield *et al.* (1985) in the study with the fused iron catalyst, found that the catalyst activity in the fixed bed reactor was moderately greater (~20%) than that in the slurry reactor at temperatures of 233 and 248°C. In this study the catalyst employed in the fixed bed reactor was crushed to 170-230 mesh (63-88 μm) and was reduced under slightly different conditions at much higher hydrogen flow rate (20,000 h^{-1}), than used in the present study. It is also worth noting that at the reaction temperature of 269°C axial temperature differences as large as 15°C were observed, even with the use of highly diluted bed (10:1 dilution by volume with silica sand of the same particle size).

Even though, in the present study, the catalyst in the slurry reactor was more active than in the fixed bed, the product selectivities at all three temperatures were similar. Methane selectivity (wt% of hydrocarbons) in the fixed bed was generally lower than in the slurry reactor which is somewhat unexpected. This was particularly pronounced at 235°C, where the methane selectivity was 5.9% in the fixed bed compared to 13.2% obtained in

the slurry reactor. In both reactors the reactor wax selectivity increased as temperature decreased, which is as expected. Values of α in the fixed bed reactor (0.71-0.77) were somewhat greater than those obtained in the slurry reactor (0.68-0.73). This is probably due to the fact that a larger fraction of products was collected and analyzed in the former than in the latter type of reactor.

The Anderson-Schulz-Flory plots for the five mass balance periods (Figures 16 to 20) show some similarities as well as differences in comparison to data obtained in the slurry bed reactor (Figures 10-14). As in the slurry reactor, the mole fractions of C_6 - C_9 components are in general lower than expected and negative deviations from the ASF distribution appear at higher carbon numbers. However, these deviations are not as large as those observed in the slurry reactor. This may be attributed to differences in the product collection employed in these two reactor systems and improved sample handling during the fixed bed run to minimize the loss of material by volatilization. A portion of the reactor wax formed during the mass balance periods 3-5 in the fixed bed run was combined with the organic phase sample and analyzed on the GC which resulted in the better fit over the wider range of carbon numbers. For example in mass balance periods 4 and 5 the predicted and experimental values are in agreement up to C_{27} - C_{28} (with the exception of products in C_6 - C_9 range).

On the other hand, in runs where the collection trap was not heated to remove some of the high molecular weight products (MB periods 1 and 2) a typical tailing of the products was observed around C_{20} . The latter was quite common in all slurry bed reactor runs, where the heavy molecular

weight products (reactor wax) accumulate in the reactor as discussed earlier.

Some positive deviations from the ASF distribution were observed during the second (Figure 17, C_{14} - C_{21} range) and the third balance period (Figure 18, C_{21} - C_{29} range). It is quite conceivable that if the composition of the reactor wax were determined this type of behavior would be observed for all balances and that the deviations would be more pronounced. This type of behavior (positive deviations from the ASF distribution in a higher carbon number range) has been observed by other investigators (e.g. Bauer *et al.*, 1983; Kuo *et al.*, 1983; Satterfield, 1983; Huff and Satterfield, 1984; Egiebor and Cooper, 1985) and in our laboratory (Bukur and Brown, 1986).

In summary, the shakedown run demonstrated that nearly isothermal conditions can be maintained in an integral fixed bed reactor even at relatively high $H_2 + CO$ conversions (up to 78%). Sample handling and analysis techniques are sound, as evidenced by excellent material balance closures and the fact that products follow the ASF distribution over the wide range of carbon numbers. Further modifications in the hardware, operating procedures and analytical methods, which will lead to improved accuracy and reliability of results, will be made continuously during the course of the project.

Task 3 - Process Evaluation Research

This task is scheduled to begin December 1, 1987

TASK 4 - Economic Evaluation

This task is scheduled to begin June 1, 1988.

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Table 1

Summary of Catalyst Compositions to be Synthesized¹

<u>Fe</u>	<u>Cu</u>	<u>K</u>	<u>Prepared to Date</u>
100	0	0	*
100	0	0.01	
		0.02	
		0.05	*
		0.1	*
		0.2	*
		0.5	
		1.0	*
		2.0	
↓	↓		
100	0.1	0	
100	0.3	0	
		0.05	
		0.2	
		1.0	
↓	↓		
100	1	0	
100	3	0	
		0.05	
		0.2	
		1.0	
↓	↓		
100	10	0	
		0.05	
		0.2	
		1.0	
↓	↓		
100	20	0	*

¹ All compositions are given in parts by weight.

100 g. of each listed catalyst will be prepared.

Table 2

Fe/Cu Catalysts Prepared for TPR Study

<u>Fe/Cu</u> <u>Composition</u> ¹	Surface Area (m ² /g)	
	<u>As Prepared</u>	<u>After 3 hrs.</u> <u>in H₂ at 250°C</u>
100/0	258	19
100/0.5	203	17
100/2	284	21
100/5	280	20
100/10	264	19

¹ Parts by weight

Table 3
Response Factors for Organic Phase Components

<u>Component</u>	<u>Response Factor</u>
1-Hexene	0.91±0.160
N-Hexane	0.81±0.054
1-Heptene	0.98±0.050
N-Heptane	1.00±0.061
1-Octene	0.92±0.064
N-Octane	0.96±0.064
1-Nonene	1.00±0.047
N-Nonane	1.00±0.076
1-Decene	1.05±0.023
N-Decane	1.00±0.015
1-Undecene	1.01±0.027
N-Undecane	1.00±0.043
1-Dodecene	0.93±0.060
N-Dodecane	1.04±0.032
1-Tridecene	0.99±0.102
N-Tridecane	1.03±0.090
1-Tetradecene	1.02±0.040
N-Tetradecane	0.99±0.040
1-Pentadecene	1.01±0.060
N-Pentadecane	1.01±0.020
N-Hexadecane	0.97±0.040
N-Heptadecane	1.01±0.023
N-Octadecane	0.98±0.018
N-Nonadecane	0.97±0.033
N-Eicosane	0.94±0.036
N-Docosane	0.86±0.082
N-Tetracosane	0.78±0.088
N-Hexacosane	0.77±0.077
N-Octacosane	0.67±0.055
N-Triacontane	0.60±0.046

A response factor of 1.00 was used for all hydrocarbons up through C₂₈ by Huff (1982). Dietz (1967) reports response factors of approximately 1.00 for all hydrocarbons through C₉.

Table 3 (Continued)
Response Factors for Organic Phase Components (con't)

<u>Component</u>	Response Factor	Response Factor
	<u>This Study</u>	<u>Dietz</u>
Benzene	0.95±0.060	1.03
Toluene	0.89±0.053	1.00
Ethylbenzene	1.00±0.028	0.98
Xylenes	1.00±0.028	1.02
Butanol	0.57±0.055	0.87
Pentanol	0.54±0.076	
Hexanol	0.68±0.059	0.90
Heptanol	0.78±0.040	
Octanol	0.76±0.044	0.99
Nonanol	0.78±0.060	
Decanol	0.62±0.052	0.95

Response factors obtained using Sigma 1 chromatograph, DB-5 column, FID. All response factors are determined relative to C₈ to C₁₄ hydrocarbons.

Table 4A
Chromatographic Conditions for Organic Phase Analysis

Chromatograph:	Sigma 1
Column:	30m. x 0.32mm, 25 μ DB-5
Temperature Program:	35°C for 10 min, heat to 110°C at 6°C/min, heat to 275°C at 4°C/min, hold for 15 minutes
Analysis Time:	80 minutes
Column Pressure:	8 psig
Carrier Gas:	1.0ml/min Helium
Make-up Gas:	25.0ml/min Helium
Detector:	FID, 350°C
Injection:	On-column, 35°C
Sample Dilution:	30 to 50:1 in CS ₂
Sample Size:	0.8 μ l

Table 4B
Chromatographic Conditions for Aqueous Phase Analysis

Chromatograph:	Sigma 1B
Column:	6' x 2mm Carbowax 1500 on Carbosieve G
Temperature Program:	50°C for 2 min, heat to 90°C at 20°C/min, heat to 160°C at 10°C/min, hold for 10 minutes
Analysis Time:	26 minutes
Carrier Gas:	20.0ml/min Helium
Detector:	FID, 250°C
Injection:	Splitless, 250°C
Sample Dilution:	None
Sample Size:	0.2 μ l

Table 4C
Chromatographic Conditions for Gas Phase Analysis

Analysis:	C ₁ -C ₅ Hydrocarbons, CO, CO ₂ , H ₂
Chromatograph:	Carle AGC 400
Temperature Program:	57°C Isothermal
Analysis Time:	60 minutes
Carrier Gas:	20.0ml/min Helium
Detector:	FID, TCD
Sample Size:	250 μ l

Analysis:	C ₆ + Hydrocarbons
Chromatograph:	Sigma 1B
Column:	6' x 1/8" Porapack Q
Temperature Program:	50°C for 0 min, heat to 170°C at 15°C/min, hold for 30 minutes
Analysis Time:	38 minutes
Carrier Gas:	18.0ml/min Helium
Detector:	FID, 250°C
Injection:	Splitless, 250°C
Sample Size:	1.0 - 2.0 ml

TABLE 5
Peak Identification of Aqueous Fischer-Tropsch Product, Sigma
1B Chromatograph. Fixed bed reactor shakedown run FA-01-1147,
material balance period 4.

PEAK IDENTIFICATION
MATERIAL BALANCE 4-28-87

PEAK FILE: 57
INPUT FILE: FB01.AQU.428A
OUTPUT FILE: AQU.OUT.428A

NUMBER	TIME	AREA	NAME
1	.8300	1.8673	METHANOL
2	2.1100	17.6889	ETHANOL
4	2.5900	.6362	ACETONE
5	3.6800	.8845	2-PROPANOL
6	4.6800	5.9385	PROPANOL
7	5.3700	.0446	BUTYRALDEHYDE
8	6.3100	.2611	2-BUTANONE
9	6.6700	.2408	2-BUTANOL
11	7.6200	2.2461	BUTANOL
12	8.1800	.0786	unknown C5
13	8.5700	.1502	VALERALDEHYDE
14	9.6100	.1905	2-PENTANOL
15	9.7700	.1043	unknown C5
16	10.0400	.2113	3-PENTANOL
17	10.7900	.9832	PENTANOL
18	11.3000	.1440	unknown C6
19	12.2200	.2871	unknown C6
20	13.1600	.1433	unknown C6
21	13.4700	.0759	unknown C6
22	13.8800	.0506	unknown C6
23	14.7900	.2704	HEXANOL
25	17.8700	.0300	HEPTANOL

	AREA
sum of unknown C1:	.0000
sum of unknown C2:	.0000
sum of unknown C3:	.0000
sum of unknown C4:	.0000
sum of unknown C5:	.3942
sum of unknown C6:	.7009
sum of unknown C7:	.0000

TABLE 6
Peak Identification Output of Tail Gas Analysis,
Carle AGC 400 Chromatograph. Fixed bed reactor
shakedown run FA-01-1147, material balance period 4.

CARLE PEAK IDENTIFICATION
MATERIAL BALANCE 4-28-87

PEAK FILE: 23
INPUT FILE: FB01.GASI.428C
OUTPUT FILE: GASI.OUT.428C

NO.	RT	AREA	MOL PCT	IDENTIFICATION
1	4.4400	121.6000	.5375	C6 BKFLSH
4	7.2500	77.4195	37.1268	HYDROGEN
8	9.0300	38.9299	.3441	PROPANE
9	10.0200	170.3424	1.5058	PROPYLENE
10	12.6200	18.4819	.1225	ISOBUTANE
11	14.4200	28.8908	.1915	N-BUTANE
12	16.6900	104.4377	.6924	1-BUTENE
13	17.2600	19.7926	.1312	ISOBUTYLENE
14	18.5400	9.4688	.0628	T-2-BUTENE
15	19.9400	8.9100	.0591	C-2-BUTENE
16	23.7000	5.9580	.0316	ISOPENTANE
17	26.8800	24.3840	.1293	N-PENTANE
18	32.0000	71.8515	.3811	1-PENTENE
19	34.6800	3.0964	.0205	UNKNOWN C5
20	35.6900	3.7270	.0198	T-2-PENTENE
21	37.4600	3.7868	.0201	C-2 PENTENE
22	42.7200	581.6729	40.6471	CO2
23	45.0800	63.0502	.8360	ETHYLENE
24	47.0000	61.5270	.8158	ETHANE
25	51.6800	39.7670	3.6822	METHANE
26	52.7400	157.8496	12.6467	CO

	AREA	
SUM OF UNKNOWN C4:	.0000	.0000 mole pct
SUM OF UNKNOWN C5:	3.0964	.0821 mole pct

INLET FLOW RATE (Nml/min):	45.2100
OUTLET FLOW RATE (Nml/min):	22.1500
PERCENT CONTRACTION:	51.0064
CO CONVERSION (PCT):	87.7789
H2 CONVERSION (PCT):	63.1039
CO + H2 CONVERSION (PCT):	75.6142

C2 OLEFIN/PARAFFIN RATIO:	1.0248
C3 OLEFIN/PARAFFIN RATIO:	4.3756
H2/CO TAIL GAS RATIO:	2.9357

TABLE 7
Peak Identification Output of Tail Gas Analysis,
Sigma 1B Chromatograph. Fixed bed reactor shake-
down run FA-01-1147, material balance period 4.

PEAK IDENTIFICATION
MATERIAL BALANCE 4-28-87

PEAK FILE: 25
INPUT FILE: FB01.GAS2.428C
OUTPUT FILE: GASII.OUT.428C

NO.	RT	AREA	IDENTIFICATION
2	.5900	64.3916	METHANE
3	1.5200	29.2441	ETHYLENE
4	1.9200	30.3488	ETHANE
5	3.9700	73.9276	PROPYLENE
6	4.2200	23.2051	PROPANE
7	5.2500	.3961	UNKNOWN C4
8	6.2100	16.6867	UNKNOWN C4
9	6.3700	71.0553	1-BUTENE
11	7.7600	1.2167	UNKNOWN C5
12	8.2300	3.6480	UNKNOWN C5
13	8.6100	36.9049	1-PENTENE
14	8.8800	8.5545	N-PENTANE
15	10.1900	.3764	UNKNOWN C6
16	10.9200	3.6612	UNKNOWN C6
17	11.5600	20.5024	1-HEXENE
18	13.3100	.0165	UNKNOWN C7
19	14.2600	.0766	UNKNOWN C7
20	15.8800	1.6887	UNKNOWN C7
21	17.1700	6.9721	1-HEPTENE
22	22.9400	.0128	UNKNOWN C8
23	25.7700	.1123	UNKNOWN C8
24	28.8600	.7624	1-OCTENE

	AREA
SUM OF UNKNOWN C4:	17.0828
SUM OF UNKNOWN C5:	4.8647
SUM OF UNKNOWN C6:	4.0376
SUM OF UNKNOWN C7:	1.7818
SUM OF UNKNOWN C8:	.1251

Table 8
Peak Identification of Organic Phase Fischer-Tropsch
Product, Sigma 1 Chromatograph. Fixed bed reactor
shakedown run FA-01-1147, material balance 4.

PEAK IDENTIFICATION
MATERIAL BALANCE 4-28-87

PEAK FILE: 50
INPUT FILE: FB01.ORG 428A
OUTPUT FILE: ORG.OUT.428A

NO.	RT	AREA	IDENTIFICATION
1	3.6900	2.3170	C 5 1-OLEFIN
3	5.0400	19.8905	C 6 1-OLEFIN
4	5.0600	5.1150	C 6 N-PARAFFIN
5	5.2800	.1313	C 6 T-2-OLEFIN
6	5.3600	1.1657	C 6 C-2-OLEFIN
11	7.6800	49.3593	C 7 1-OLEFIN
14	8.0300	20.5971	C 7 N-PARAFFIN
15	8.4000	1.0900	C 7 T-2-OLEFIN
25	14.0400	79.8712	C 8 1-OLEFIN
28	14.6600	19.1583	C 8 N-PARAFFIN
29	14.8400	.1072	C 8 T-2-OLEFIN
30	14.8600	.0764	C 8 C-2-OLEFIN
39	19.2300	99.3945	C 9 1-OLEFIN
40	19.5000	33.1686	C 9 N-PARAFFIN
41	19.6800	2.7152	C 9 T-2-OLEFIN
42	19.9200	2.8377	C 9 C-2-OLEFIN
51	22.3100	100.5363	C10 1-OLEFIN
52	22.5300	36.5760	C10 N-PARAFFIN
53	22.6700	5.3801	C10 T-2-OLEFIN
54	22.7900	5.2924	C10 C-2-OLEFIN
66	25.0900	85.8931	C11 1-OLEFIN
67	25.3100	33.1417	C11 N-PARAFFIN
68	25.4200	5.9097	C11 T-2-OLEFIN
69	25.6700	3.9452	C11 C-2-OLEFIN
79	27.9400	64.8294	C12 1-OLEFIN
80	28.1800	27.6070	C12 N-PARAFFIN
81	28.3000	4.3544	C12 T-2-OLEFIN
82	28.5700	3.0617	C12 C-2-OLEFIN
89	30.9300	47.1449	C13 1-OLEFIN
90	31.1700	24.1612	C13 N-PARAFFIN
91	31.2800	2.8758	C13 T-2-OLEFIN
92	31.5900	2.0479	C13 C-2-OLEFIN
96	33.9900	34.3987	C14 1-OLEFIN
97	34.2300	22.2604	C14 N-PARAFFIN
98	34.3600	2.1568	C14 T-2-OLEFIN
99	34.6700	1.1790	C14 C-2-OLEFIN
101	37.0600	25.0790	C15 1-OLEFIN
102	37.3000	19.6883	C15 N-PARAFFIN
103	37.4100	1.6951	C15 T-2-OLEFIN
104	37.7500	.6230	C15 C-2-OLEFIN
105	40.0700	18.2624	C16 1-OLEFIN
106	40.3000	19.7772	C16 N-PARAFFIN
107	40.4000	1.3890	C16 T-2-OLEFIN
108	40.7600	.1623	C16 C-2-OLEFIN

Table 8 (Continued)

NO.	RT	AREA	IDENTIFICATION
109	43.0000	13.4764	C17 1-OLEFIN
110	43.2100	15.1353	C17 N-PARAFFIN
111	43.3100	.4676	C17 T-2-OLEFIN
112	43.6700	.0323	C17 C-2-OLEFIN
113	45.8000	9.9622	C18 1-OLEFIN
114	46.0000	13.2345	C18 N-PARAFFIN
115	46.1000	.2373	C18 T-2-OLEFIN
116	48.5000	7.1510	C19 1-OLEFIN
117	48.6800	11.1955	C19 N-PARAFFIN
118	48.7700	.1299	C19 T-2-OLEFIN
120	51.0800	5.4076	C20 1-OLEFIN
121	51.2600	9.1734	C20 N-PARAFFIN
122	51.3400	.1045	C20 T-2-OLEFIN
123	53.5600	3.4364	C21 1-OLEFIN
124	53.7200	7.8848	C21 N-PARAFFIN
125	53.8100	.0192	C21 T-2-OLEFIN
126	55.9300	2.0228	C22 1-OLEFIN
127	56.0800	6.7564	C22 N-PARAFFIN
128	56.6700	.0250	C22 T-2-OLEFIN
129	58.2100	.9251	C23 1-OLEFIN
130	58.3500	5.3152	C23 N-PARAFFIN
131	58.6200	.0236	C23 T-2-OLEFIN
132	58.8700	.0157	C23 C-2-OLEFIN
133	60.3900	.1473	C24 1-OLEFIN
134	60.5100	4.1889	C24 N-PARAFFIN
135	60.8000	.0300	C24 T-2-OLEFIN
136	62.4900	.0258	C25 1-OLEFIN
137	62.6000	3.3211	C25 N-PARAFFIN
138	62.8900	.0225	C25 T-2-OLEFIN
139	64.6400	1.8076	C26 N-PARAFFIN
140	65.1900	.0159	C26 T-2-OLEFIN
141	66.6100	.0518	C27 1-OLEFIN
142	66.8500	.3368	C27 N-PARAFFIN
143	67.1500	.0329	C27 T-2-OLEFIN
144	67.5100	.0264	C27 C-2-OLEFIN
145	69.3800	.0292	C28 1-OLEFIN
146	69.6900	.0472	C28 N-PARAFFIN
147	70.3400	.4143	C28 T-2-OLEFIN
10	6.6800	8.5579	1-BUTANOL
21	11.9700	4.7891	1-PENTANOL
36	18.0700	12.5832	1-HEXANOL
43	21.7600	11.9340	1-HEPTANOL
61	24.0700	6.4451	1-OCTANOL
77	27.0900	1.9184	1-NONANOL
88	30.3800	1.4162	1-DECANOL

Table 8 (Continued)

	AREA
SUM OF UNKNOWN C 6 ISOMERS:	.0000
SUM OF UNKNOWN C 7 ISOMERS:	.1788
SUM OF UNKNOWN C 8 ISOMERS:	9.7183
SUM OF UNKNOWN C 9 ISOMERS:	14.6684
SUM OF UNKNOWN C10 ISOMERS:	16.8138
SUM OF UNKNOWN C11 ISOMERS:	15.0903
SUM OF UNKNOWN C12 ISOMERS:	7.0401
SUM OF UNKNOWN C13 ISOMERS:	1.3453
SUM OF UNKNOWN C14 ISOMERS:	.3069
SUM OF UNKNOWN C15 ISOMERS:	.0236
SUM OF UNKNOWN C16 ISOMERS:	.0000
SUM OF UNKNOWN C17 ISOMERS:	.0000
SUM OF UNKNOWN C18 ISOMERS:	.0000
SUM OF UNKNOWN C19 ISOMERS:	.0000
SUM OF UNKNOWN C20 ISOMERS:	.0182
SUM OF UNKNOWN C21 ISOMERS:	.0000
SUM OF UNKNOWN C22 ISOMERS:	.0000
SUM OF UNKNOWN C23 ISOMERS:	.0000
SUM OF UNKNOWN C24 ISOMERS:	.0000
SUM OF UNKNOWN C25 ISOMERS:	.0000
SUM OF UNKNOWN C26 ISOMERS:	.0000
SUM OF UNKNOWN C27 ISOMERS:	.0000
SUM OF UNKNOWN C28 ISOMERS:	.0000
SUM OF UNKNOWN C29 ISOMERS:	.0000
SUM OF UNKNOWN C30 ISOMERS:	.0000

Table 9. Summary of results for slurry run SA-01-0817.

Catalyst: United Catalyst C-73-1, 57.9 g (a)

Liquid: FT-300, 322 g

Unexpanded slurry volume: 450 cc

Period	1	2	3	4	5
Date	03/24/87	03/25/87	03/26/87	03/27/87	03/28/87
Time on Stream (h)	54.0	74.0	99.0	123.0	147.0
Balance Duration (h)	8.0	9.0	8.0	8.0	8.0
Reactor Temp (C)	264	265	234	251	265
Reactor Pres (MPa)	1.48	1.48	1.48	1.48	1.48
H ₂ /CO Molar Feed Ratio	1.04	1.04	1.04	1.04	1.04
Space Velocity (NI/g-cat·h) (a)	.72	.72	.70	.75	.74
Space Velocity (NI/g-Fe·h) (a)	1.08	1.08	1.04	1.11	1.11
GHSV (1/h) (b)	91.8	91.8	89.3	95.6	94.4
Weight Closure (%)	91.2	87.1	99.7	99.7	95.8
H ₂ Conversion (%)	62.5	57.8	28.1	59.7	64.1
CO Conversion (%)	92.3	93.3	51.0	87.9	93.7
H ₂ +CO Conversion (%)	77.1	75.2	39.3	73.5	78.6
H ₂ /CO Molar Usage	.705	.645	.574	.707	.712
STY (mols H ₂ +CO/g-cat·h) (a)	.025	.024	.012	.024	.026
Chain Growth Probability Factor (Based on selected points)	.70	.68	.73	.72	.71
[P-CO ₂]/[P-H ₂]/[P-CO]/[P-H ₂ O]	24.1	28.5	9.1	19.8	27.9
Wt % of Outlet					
H ₂	2.87	3.38	5.03	2.82	2.61
H ₂ O	5.28	6.01	2.29	4.24	5.72
CO	7.90	7.18	45.74	11.29	6.09
CO ₂	61.57	63.99	33.51	59.08	65.39
Hydrocarbons	18.49	18.82	7.48	13.86	17.17
Reactor Wax (c)	3.31	.00	4.86	8.14	2.53
Oxygenates	.58	.63	1.08	.57	.49
Yield (g/Nm ³ -Syngas converted)					
C1	20.88	22.32	27.22	21.07	23.11
C2-C4	63.52	74.69	43.42	45.29	55.38
C5-C11	43.31	34.17	38.60	43.46	44.83
C12-C17	13.13	11.80	15.07	13.65	13.41
C18+ (d)	3.14	.44	.59	.29	.93
Reactor Wax (c)	25.80	.00	81.22	72.71	20.30
Oxygenates	4.52	4.77	18.06	5.06	3.91
Total	174.29	148.19	224.18	201.54	161.87

(a) Based on unreduced catalyst weight; (b) Based on unexpanded slurry volume
(c) Liquid accumulated in the reactor; (d) Does not include reactor wax

Table 9 (Cont'd). Summary of results for slurry run SA-01-0817.

Period	1	2	3	4	5
Wt % of Hydrocarbons					
Methane	12.30	15.56	13.21	10.72	14.63
Ethane	6.62	8.19	2.25	5.12	6.09
Ethylene	3.97	4.76	4.08	2.30	3.21
Propane	4.08	19.14	1.96	2.23	1.93
Propylene	11.06	4.41	6.36	6.93	12.80
n-Butane	2.38	2.92	1.58	1.57	2.02
1+2 Butenes	8.22	11.37	4.20	4.38	8.06
C4 Isomers	1.09	1.30	.63	.52	.96
n-Pentane	1.86	3.19	1.64	1.56	2.23
1+2 Pentenes	5.93	7.88	3.44	3.80	5.89
C5 Isomers	1.71	.43	.27	.21	.31
n-Hexane	.01	.04	.00	1.09	.06
1+2 Hexenes	4.86	.15	3.69	2.41	4.70
C6 Isomers	.00	.00	.00	.00	.00
n-Heptane	.71	.13	.65	.74	.77
1+2 Heptenes	1.92	.35	1.59	1.41	2.03
C7 Isomers	.01	.01	.00	.06	.01
n-Octane	.58	.47	.34	.75	.78
1+2 Octenes	1.20	.87	.82	1.11	1.66
C8 Isomers	.00	.02	.01	.32	.06
n-Nonane	.68	1.02	.45	.97	.93
1+2 Nonenes	1.08	1.67	.70	1.11	1.64
C9 Isomers	.02	.12	.01	.24	.48
n-Decane	.99	1.43	.79	1.40	.75
1+2 Decenes	1.46	2.15	1.33	1.57	1.61
C10 Isomers	.20	.39	.39	.27	1.26
n-Undecane	1.01	1.32	.79	1.43	1.06
1+2 Undecenes	1.10	1.74	1.57	1.42	1.47
C11 Isomers	.17	.44	.22	.26	.68
C2+ (d)	72.51	84.44	47.39	52.27	72.52
C2-C4	37.41	52.08	21.06	23.05	35.06
C5-C11	25.51	23.82	18.72	22.12	28.38
C12-C17	7.73	8.23	7.31	6.95	8.49
C18+ (d)	1.85	.31	.29	.15	.59
Reactor Wax (c)	15.20	.00	39.40	37.01	12.85

(c) Liquid accumulated in the reactor; (d) Does not include reactor wax

Table 10. Summary of results for fixed bed run FA-01-1147.

Catalyst: United Catalyst C-73-1, 3.61 g (a)

Diluent: Alpha Products SiO₂, 6.9 g

Catalyst volume: 1.6 cc

Diluent volume: 6.4 cc

Period	1	2	3	4	5
Date	04/25/87	04/26/87	4 /27/87	04/28/87	4/49/87
Time on Stream (h)	33.3	58.5	81.5	110.0	131.0
Balance Duration (h)	8.0	8.0	12.7	8.0	9.0
Average Reactor Temp (C)	266	236	250	266	266
Max Reactor Temp Gradient (C) (b)	3.4	2.7	2.7	4.4	3.0
Reactor Pres (MPa)	1.58	1.58	1.58	1.58	1.58
H ₂ /CO Molar Feed Ratio	.97	.97	.97	.97	.97
Space Velocity (NI/g-cat*h) (a)	.74	.75	.75	.75	.75
Space Velocity (NI/g-Fe*h) (a)	1.10	1.12	1.12	1.12	1.12
GHSV (l/h) (c)	1670	1690	1690	1690	1690
Weight Closure (%)	97.1	101.8	99.4	102.1	94.4
H ₂ Conversion (%)	61.5	34.5	47.6	63.6	54.6
CO Conversion (%)	79.1	29.8	58.7	89.0	77.0
H ₂ +CO Conversion (%)	70.4	32.1	53.2	76.5	66.0
H ₂ /CO Molar Usage	.756	1.126	.788	.695	.690
STY (mols H ₂ +CO/g-cat*h) (a)	.023	.011	.018	.026	.022
Chain Growth Probability Factor (Based on selected points)	.74	.70	.76	.75	.77
[P-CO ₂]/[P-H ₂]/[P-CO]/[P-H ₂ O]	11.8	4.6	8.0	26.8	17.2
Wt % of Outlet					
H ₂	2.59	4.21	3.45	2.33	3.14
H ₂ O	3.40	1.63	2.64	2.87	2.52
CO	20.11	64.49	38.85	10.07	22.74
CO ₂	54.57	19.94	41.84	58.34	55.13
Hydrocarbons	14.79	5.73	8.31	16.64	12.77
Wax (d)	3.63	3.81	4.03	8.84	2.85
Oxygenates	.91	.19	.88	.91	.85
Yield (g/Nm ³ -Syngas converted)					
C1	17.04	12.07	15.78	17.62	18.36
C2-C4	48.58	49.18	34.62	57.52	48.19
C5-C11	49.37	43.15	32.26	51.58	33.90
C12-C17	20.64	15.51	15.14	16.97	15.48
C18+ (e)	2.55	3.34	7.35	6.94	8.03
Wax (d)	33.92	81.93	51.03	80.04	27.67
Oxygenates	8.53	3.98	11.12	8.28	8.23
Total	180.63	209.15	167.30	238.94	159.87

(a) Based on unreduced catalyst; (b) Maximum axial temperature difference; (c) Based on catalyst volume
 (d) Solid products remaining after trap is drained; (e) Does not include wax

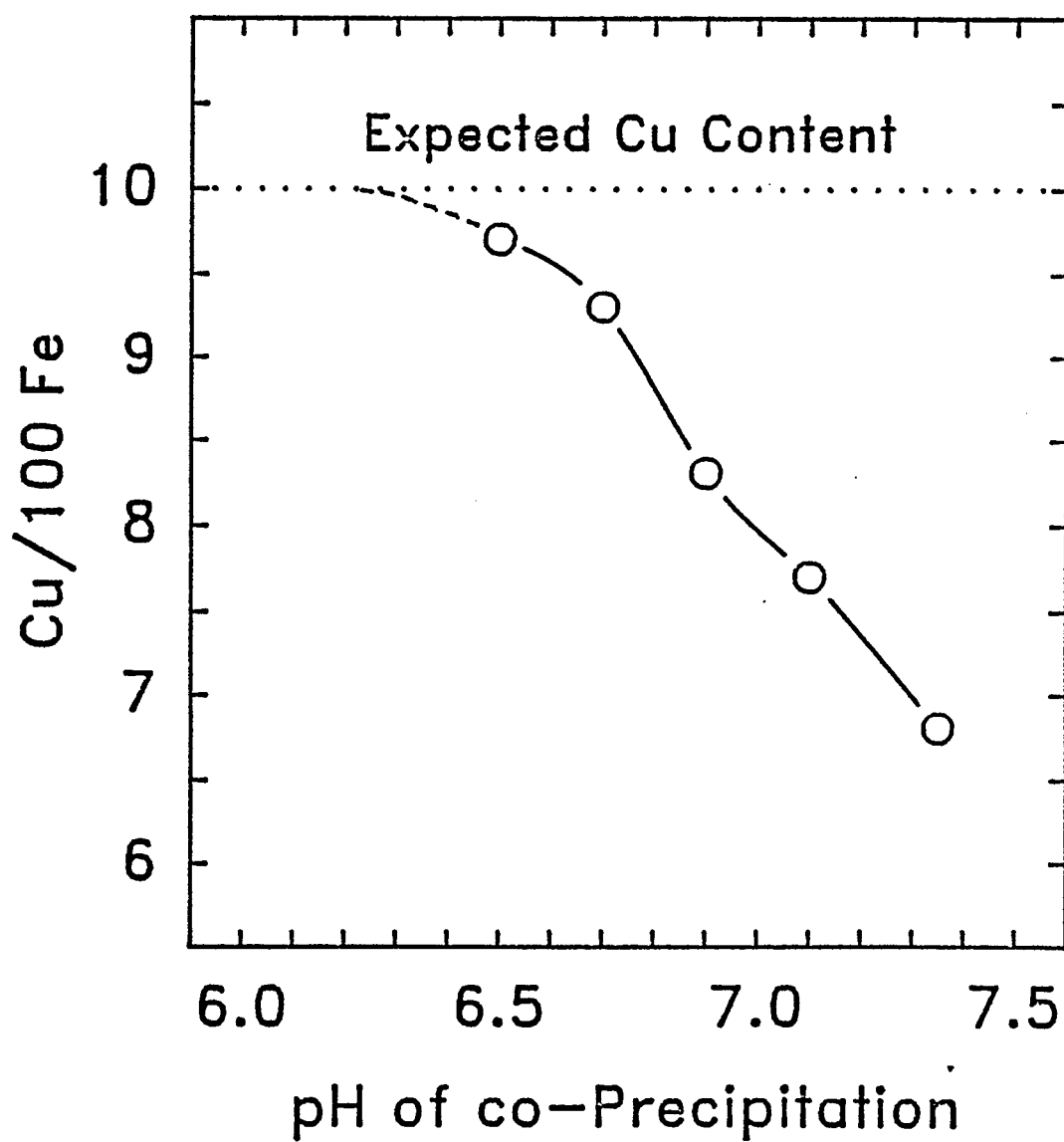
Table 10 (Cont'd). Summary of results for fixed bed run FA-01-1147.

Period	1	2	3	4	5
Wt % of Hydrocarbons					
Methane	9.90	5.88	10.10	7.64	12.11 *
Ethane	4.50	4.06	2.69	3.26	4.66
Ethylene	4.36	4.99	3.62	3.00	4.77
Propane	2.27	2.33	2.05	1.87	2.60
Propylene	9.01	6.47	7.11	8.07	10.31
n-Butane	1.46	1.31	1.30	1.38	1.69
1+2 Butenes	5.97	4.33	4.86	5.65	6.98
C4 Isomers	.65	.49	.54	1.72	.76
n-Pentane	1.57	1.26	1.25	1.33	1.70
1+2 Pentenes	4.26	5.21	3.35	3.66	5.16
C5 Isomers	.46	.79	.33	.42	.55
n-Hexane	.33	.45	.00	.12	1.32
1+2 Hexenes	2.79	3.35	2.47	2.67	2.06
C6 Isomers	.49	.81	.46	.45	.74
n-Heptane	.31	.19	.07	.31	.14
1+2 Heptenes	2.35	.79	1.43	1.88	1.36
C7 Isomers	.26	.13	.23	.24	.18
n-Octane	.73	.19	.36	.51	.36
1+2 Octenes	2.58	1.09	1.39	1.87	1.15
C8 Isomers	.19	1.13	.07	.29	.10
n-Nonane	.99	.50	.72	.59	.54
1+2 Nonenes	2.89	1.26	2.08	1.85	1.46
C9 Isomers	.42	.01	.10	.38	.19
n-Decane	.99	.53	.78	.64	.65
1+2 Decenes	2.89	1.52	2.32	1.90	1.74
C10 Isomers	.46	.04	.28	.40	.31
n-Undecane	.90	.42	.66	.60	.61
1+2 Undecenes	2.45	1.37	2.09	1.67	1.70
C11 Isomers	.38	.01	.20	.57	.34
C2+ (e)	70.39	54.19	57.22	57.66	69.64
C2-C4	28.23	23.97	22.16	24.94	31.78
C5-C11	28.69	21.03	20.65	22.36	22.36
C12-C17	11.99	7.56	9.69	7.36	10.21
C18+ (e)	1.48	1.63	4.70	3.01	5.30
Wax (d)	19.71	39.93	32.68	34.70	18.25

(d) Solid products remaining after trap is drained; (e) Does not include wax

Figure 1

Effect of pH on Copper Precipitation



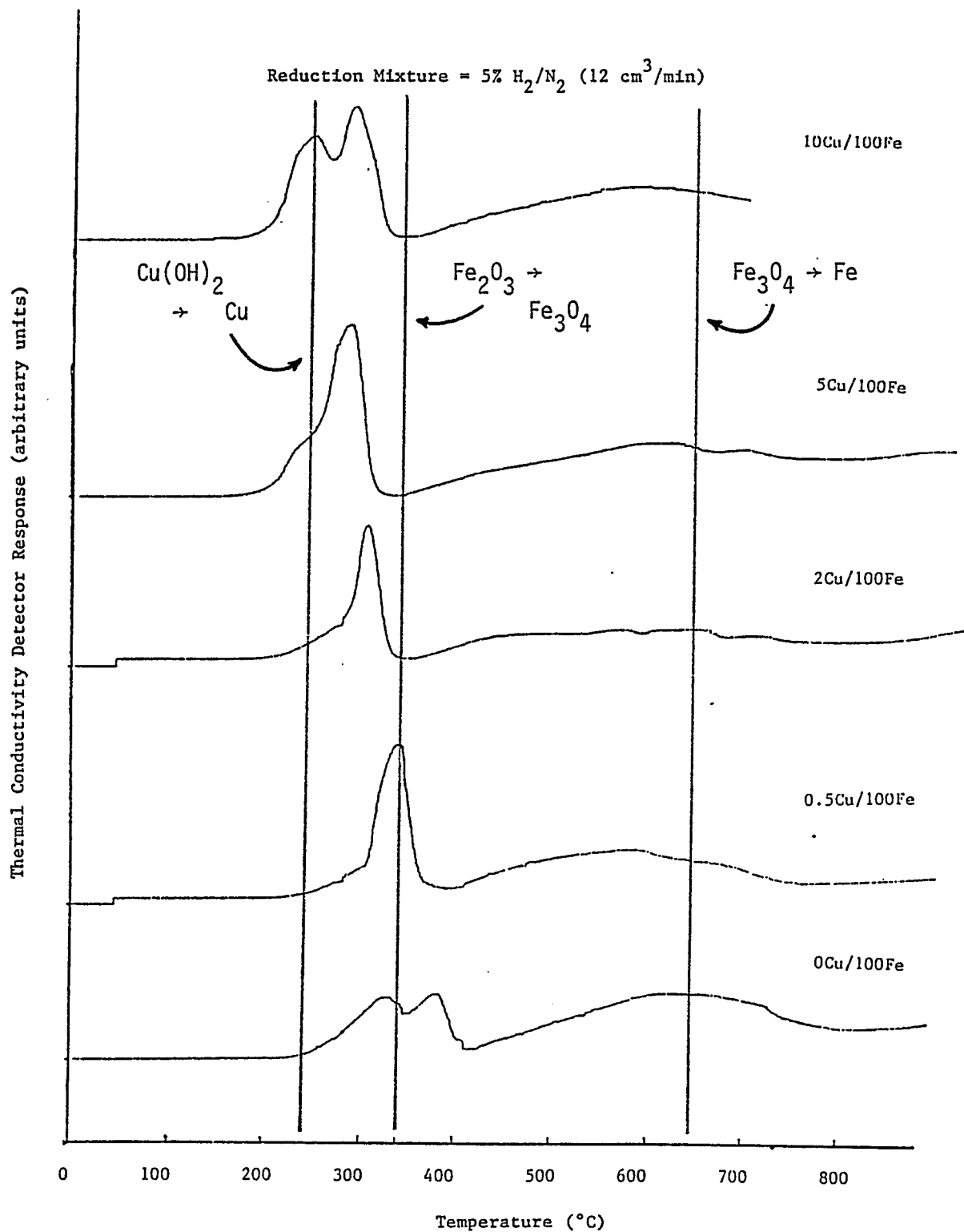


Figure 2. Temperature programmed reduction of Fe/Cu catalysts in H₂.

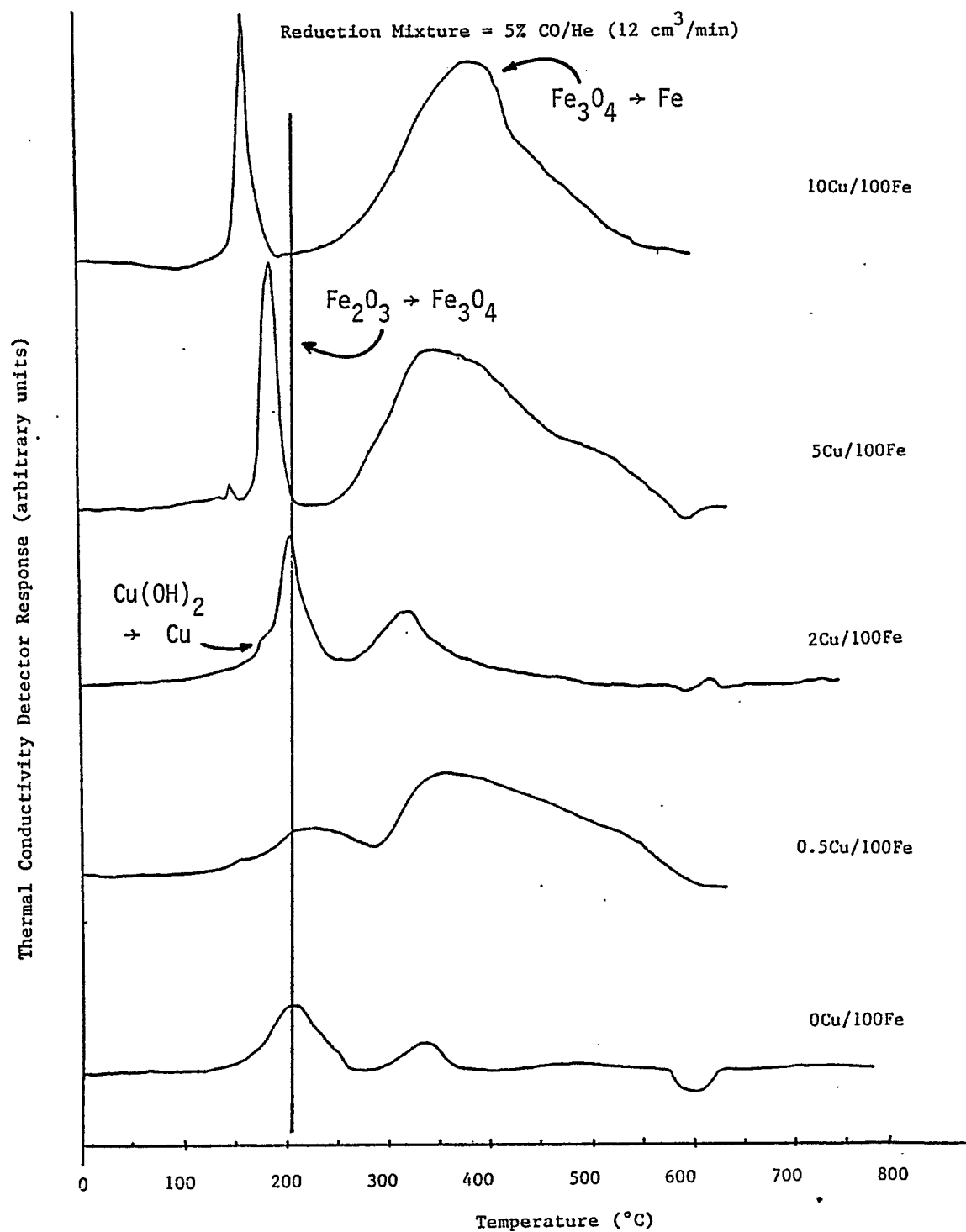


Figure 3. Temperature programmed reduction of Fe/Cu catalysts in CO.

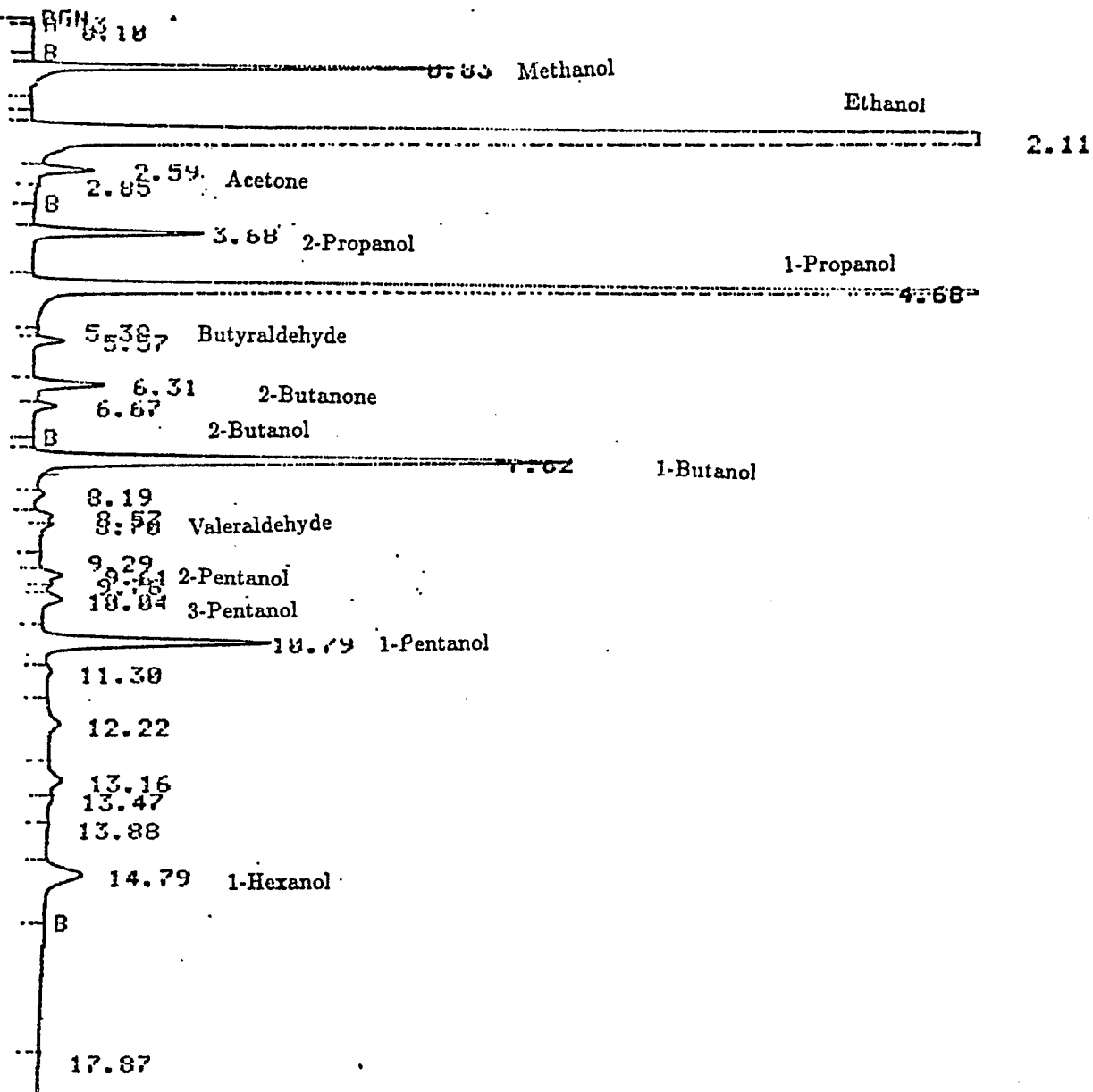


Figure 4: Chromatogram of aqueous Fischer-Tropsch product, Sigma 1b chromatograph. Fixed bed reactor shakedown run FA-01-1147, material balance period 4.

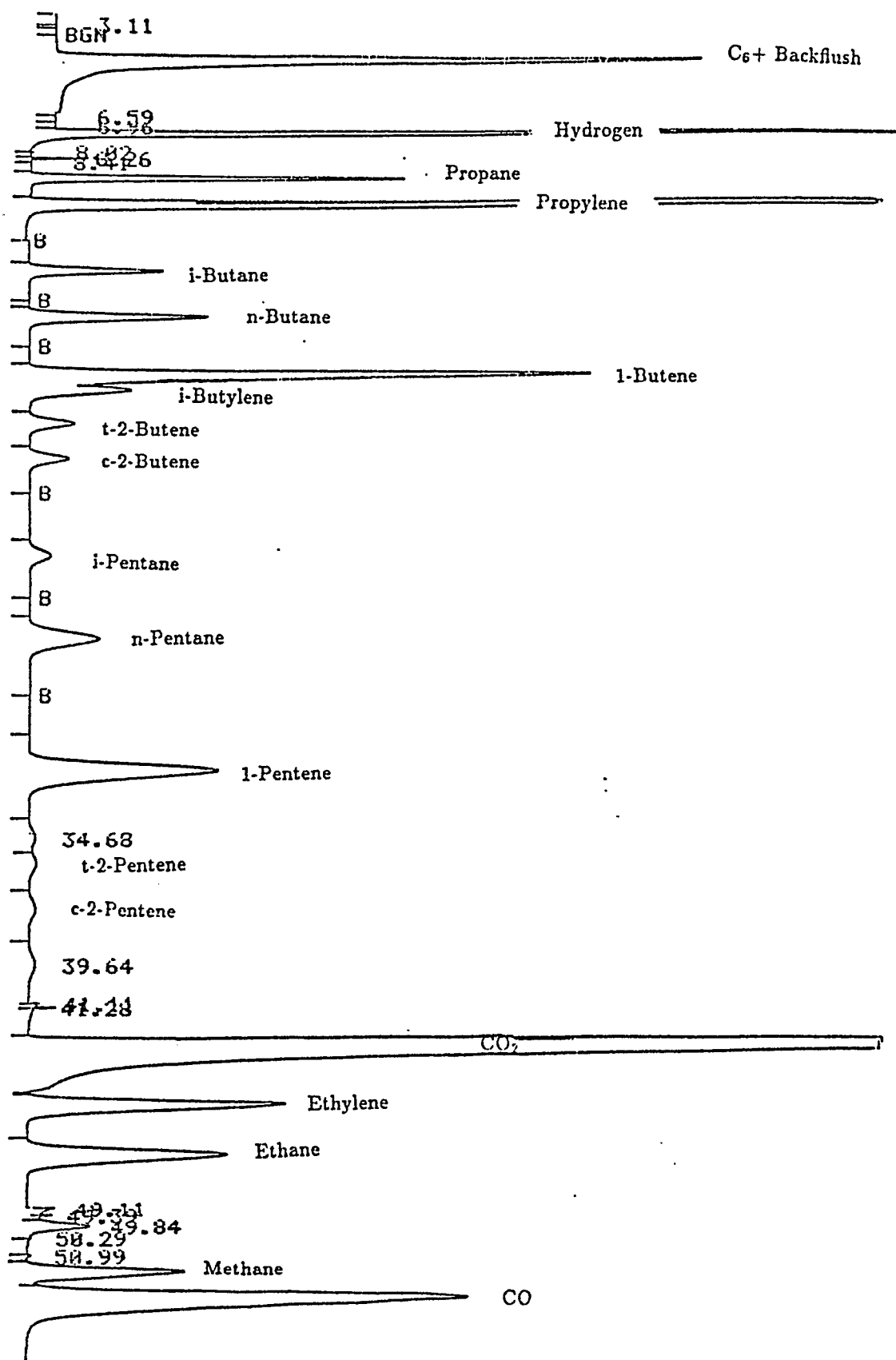


Figure 5: Chromatogram of Fischer-Tropsch tail gas, Carle AGC 400 chromatograph. Fixed bed reactor shakedown run FA-01-1147, material balance period 4.

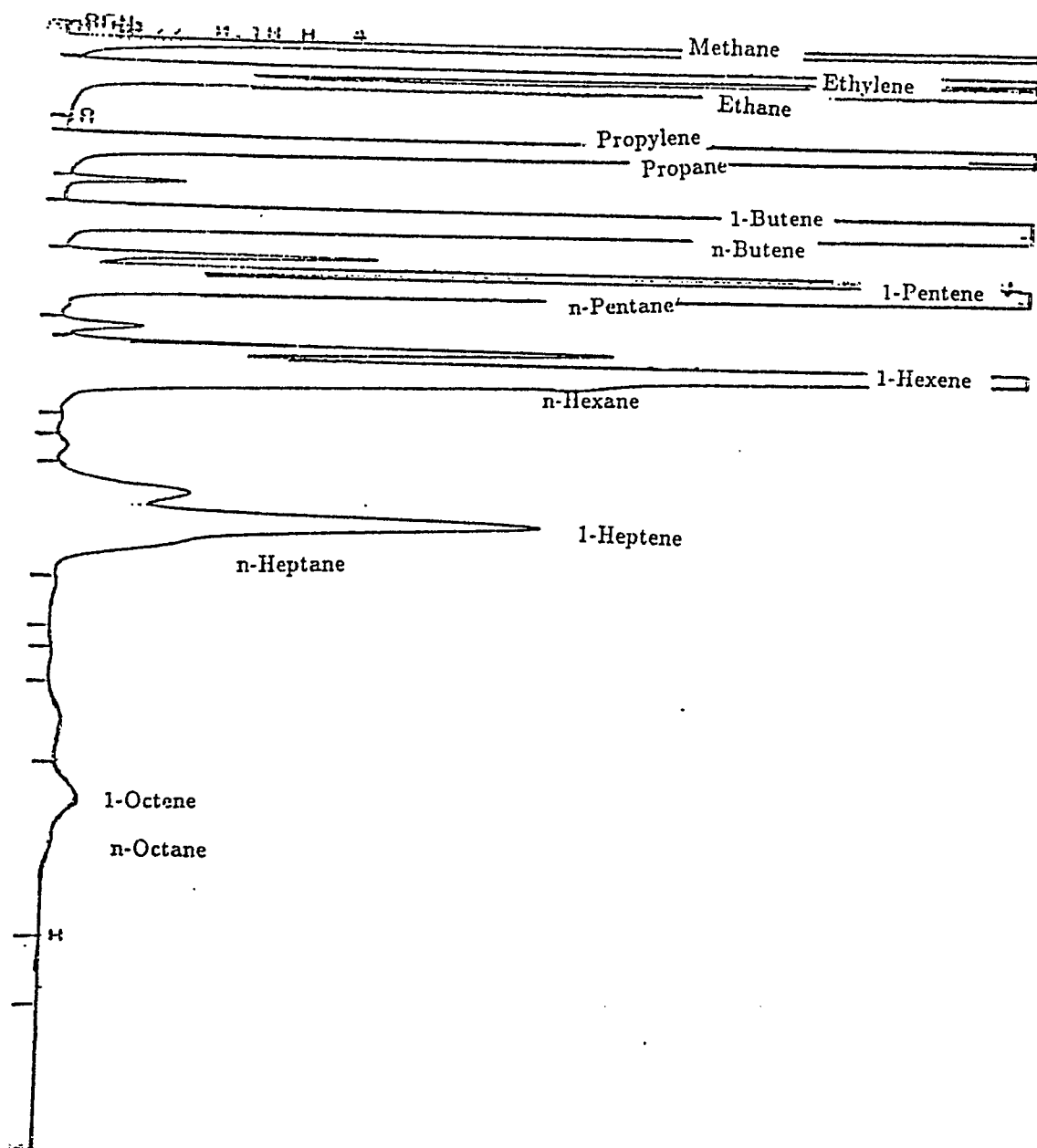
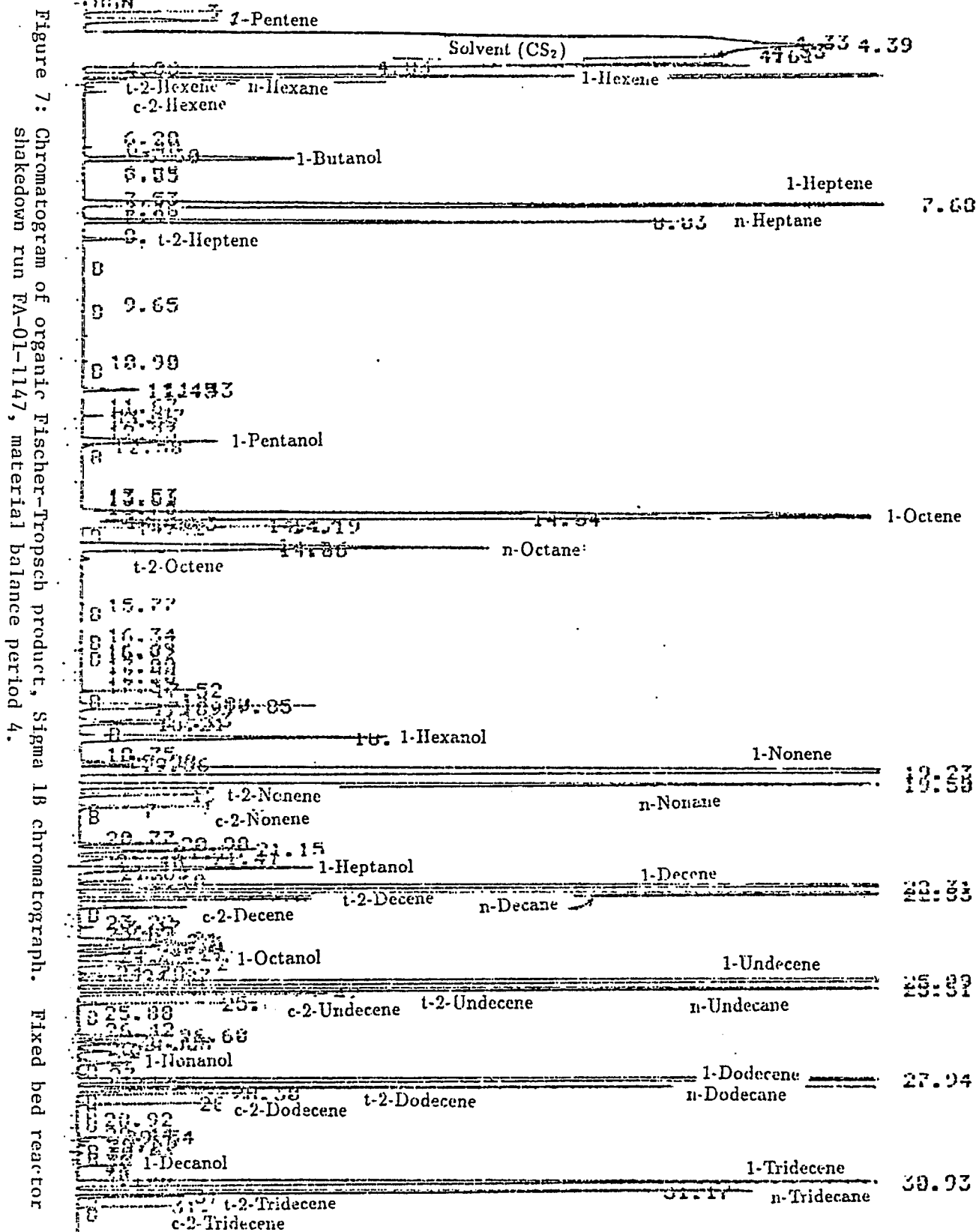


Figure 6: Chromatogram of Fischer-Tropsch tail gas, Sigma 1B chromatograph. Fixed bed reactor shakedown run FA-01-1147, material balance period 4.



34.2	1-Tetradecene
34.2	n-Tetradecane
37.5	1-Pentadecene
37.5	n-Pentadecane
40.7	1-Hexadecene
40.7	n-Hexadecane
43.9	1-Heptadecene
43.9	n-Heptadecane
47.3	1-Octadecene
47.3	n-Octadecane
50.7	1-Nonadecene
50.7	n-Nonadecane
54.1	1-Eicosene
54.1	n-Eicosane
57.5	1-Unicosane
57.5	n-Unicosane
60.9	1-Docosene
60.9	n-Docosane
64.3	1-Tricosane
64.3	n-Tricosane
67.7	1-Tetracosene
67.7	n-Tetracosane
71.1	n-Pentacosane
74.5	n-Hexacosane
77.9	n-Heptacosane
81.3	n-Octacosane
84.7	
88.1	
91.5	
94.9	
98.3	
101.7	
105.1	
108.5	
111.9	
115.3	
118.7	
122.1	
125.5	
128.9	
132.3	
135.7	
139.1	
142.5	
145.9	
149.3	
152.7	
156.1	
159.5	
162.9	
166.3	
169.7	
173.1	
176.5	
179.9	
183.3	
186.7	
190.1	
193.5	
196.9	
200.3	
203.7	
207.1	
210.5	
213.9	
217.3	
220.7	
224.1	
227.5	
230.9	
234.3	
237.7	
241.1	
244.5	
247.9	
251.3	
254.7	
258.1	
261.5	
264.9	
268.3	
271.7	
275.1	
278.5	
281.9	
285.3	
288.7	
292.1	
295.5	
298.9	
302.3	
305.7	
309.1	
312.5	
315.9	
319.3	
322.7	
326.1	
329.5	
332.9	
336.3	
339.7	
343.1	
346.5	
349.9	
353.3	
356.7	
360.1	
363.5	
366.9	
370.3	
373.7	
377.1	
380.5	
383.9	
387.3	
390.7	
394.1	
397.5	
400.9	
404.3	
407.7	
411.1	
414.5	
417.9	
421.3	
424.7	
428.1	
431.5	
434.9	
438.3	
441.7	
445.1	
448.5	
451.9	
455.3	
458.7	
462.1	
465.5	
468.9	
472.3	
475.7	
479.1	
482.5	
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669.5	
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686.5	
689.9	
693.3	
696.7	
700.1	
703.5	
706.9	
710.3	
713.7	
717.1	
720.5	
723.9	
727.3	
730.7	
734.1	
737.5	
740.9	
744.3	
747.7	
751.1	
754.5	
757.9	
761.3	
764.7	
768.1	
771.5	
774.9	
778.3	
781.7	
785.1	
788.5	
791.9	
795.3	
798.7	
802.1	
805.5	
808.9	
812.3	
815.7	
819.1	
822.5	
825.9	
829.3	
832.7	
836.1	
839.5	
842.9	
846.3	
849.7	
853.1	
856.5	
859.9	
863.3	
866.7	
870.1	
873.5	
876.9	
880.3	
883.7	
887.1	
890.5	
893.9	
897.3	
900.7	
904.1	
907.5	
910.9	
914.3	
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1148.9	
1152.3	
1155.7	
1159.1	
1162.5	
1165.9	
1169.3	
1172.7	
1176.1	
1179.5	
1182.9	
1186.3	
1189.7	
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1196.5	
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1204.3	
1207.7	
1211.1	
1214.5	
1217.9	
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1224.7	
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1231.5	
1234.9	
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1248.5	
1251.9	
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1258.7	
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1272.3	
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1279.1	
1282.5	
1285.9	
1289.3	
1292.7	
1296.1	
1299.5	
1302.9	
1306.3	
1309.7	
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1316.5	
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1326.7	
1330.1	
1333.5	
1336.9	
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1343.7	
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1350.5	
1353.9	
1357.3	
1360.7	
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1367.5	
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1374.3	
1377.7	
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1391.3	
1394.7	
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1571.5	
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1795.9	
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1819.7	
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1833.3	
1836.7	
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1846.9	
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1853.7	
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1860.5	
1863.9	
1867.3	
1870.7	
1874.1	
1877.5	
1880.9	
1884.3	
1887.7	
1891.1	
1894.5	
1897.9	
1901.3	
1904.7	
1908.1	
1911.5	
1914.9	
1918.3	
1921.7	
1925.1	
1928.5	
1931.9	
1935.3	
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1945.5	
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1959.1	
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1986.3	
1989.7	
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2004.3	
2007.7	
2011.1	
2014.5	
2017.9	
2021.	

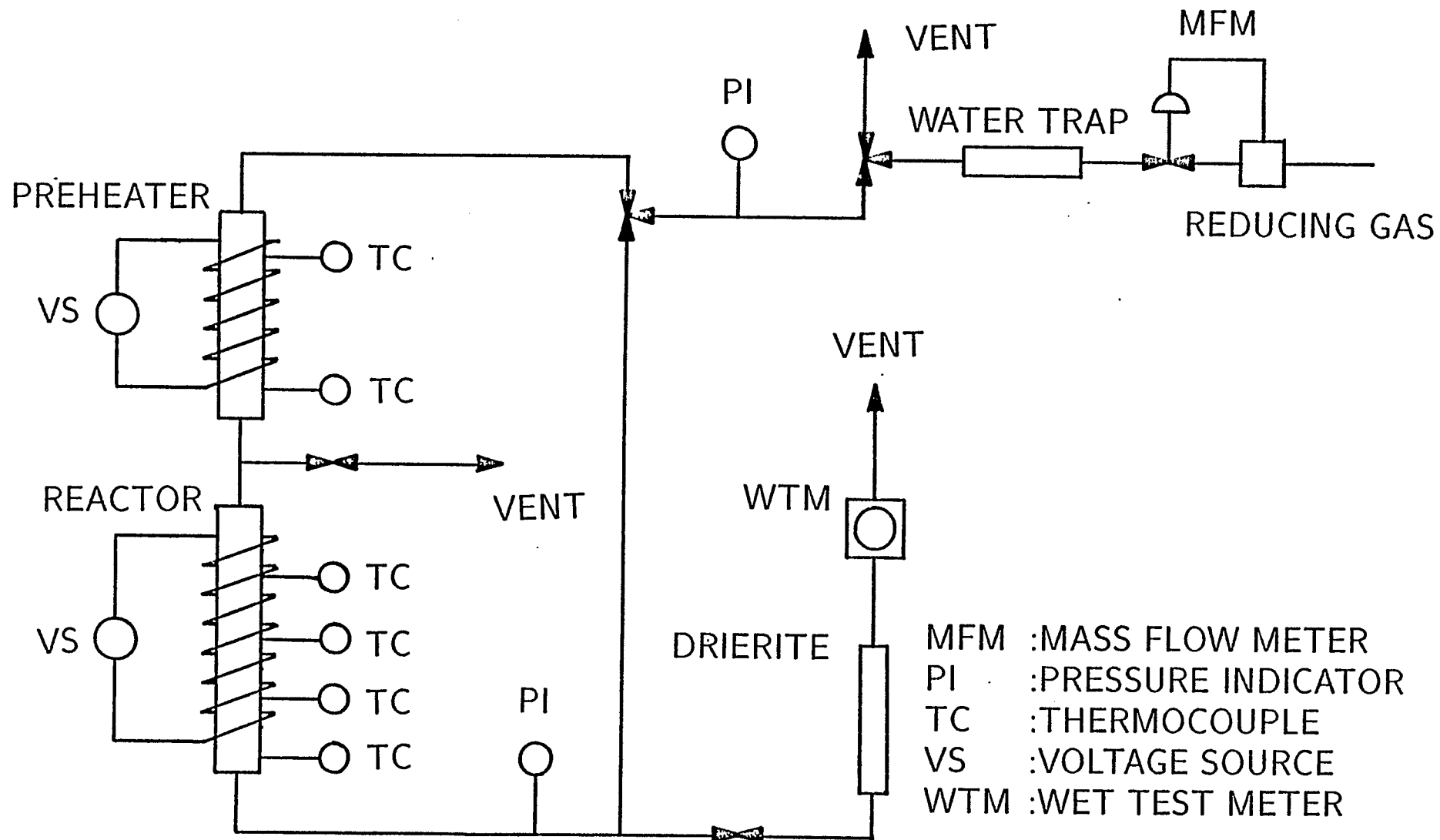


Figure 8. Process schematic of the catalyst reduction unit.

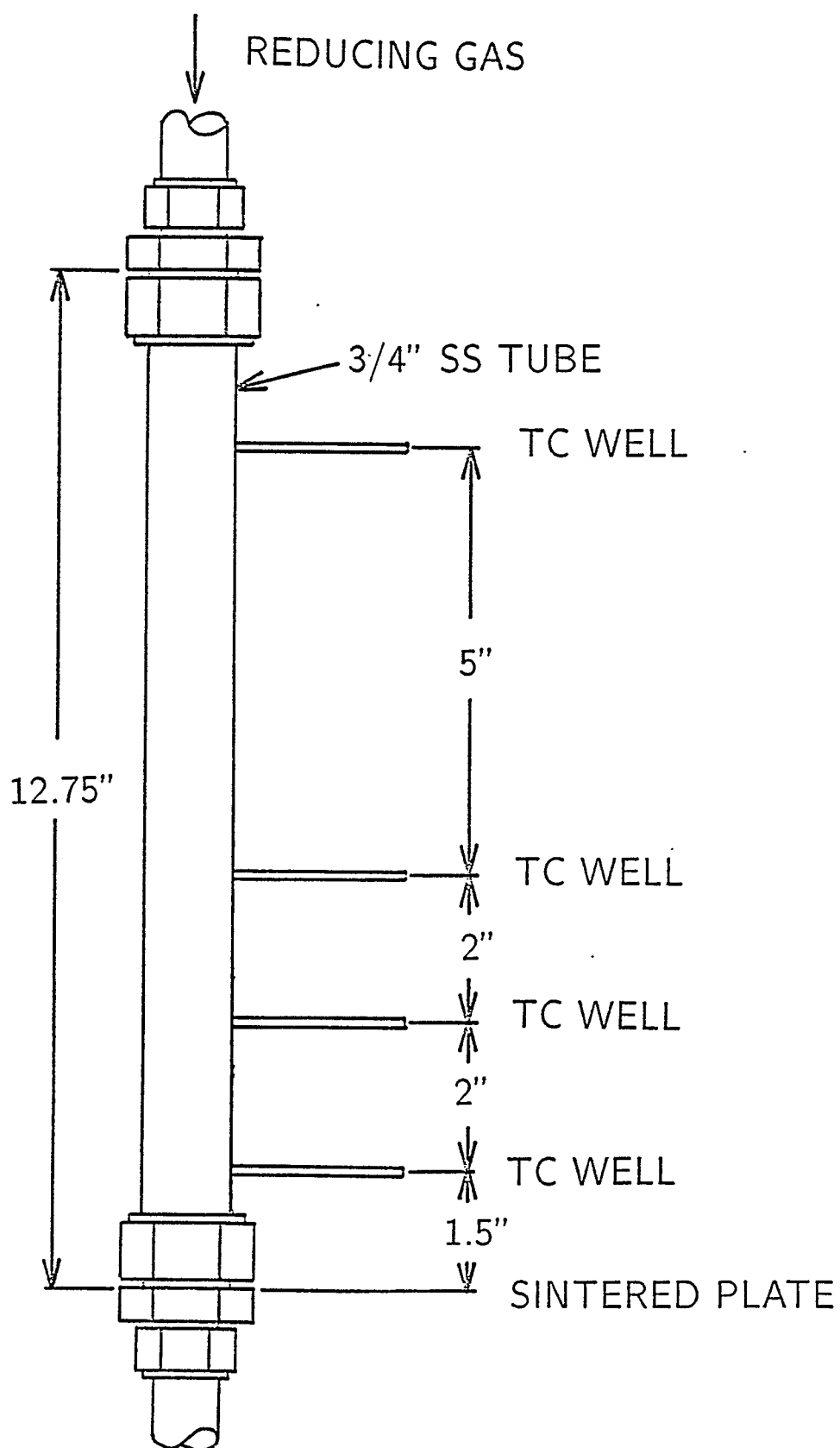


Figure 9. Schematic of the catalyst reduction reactor.

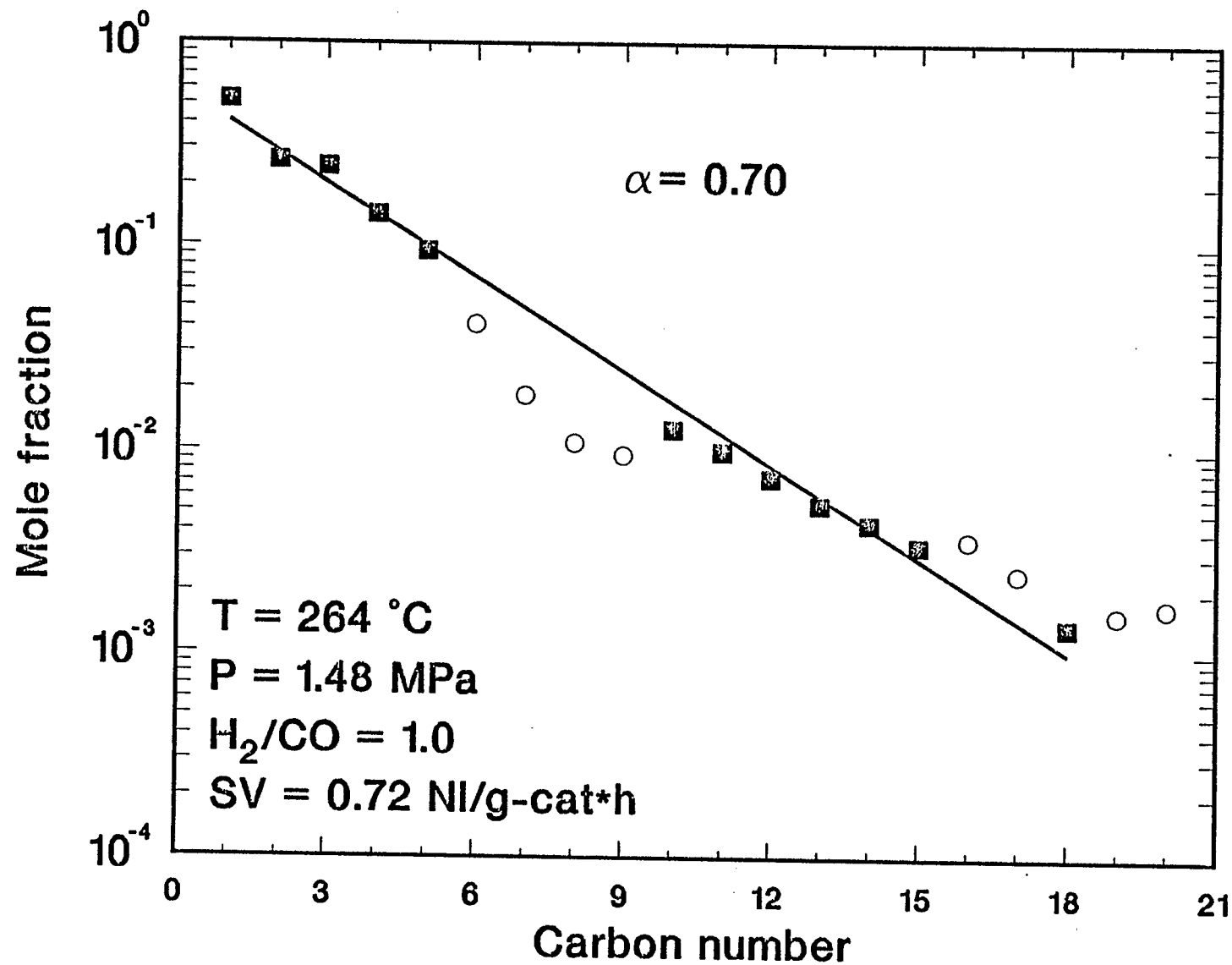


Figure 10. Anderson-Schulz-Flory plot for Run SA-01-0817-1.

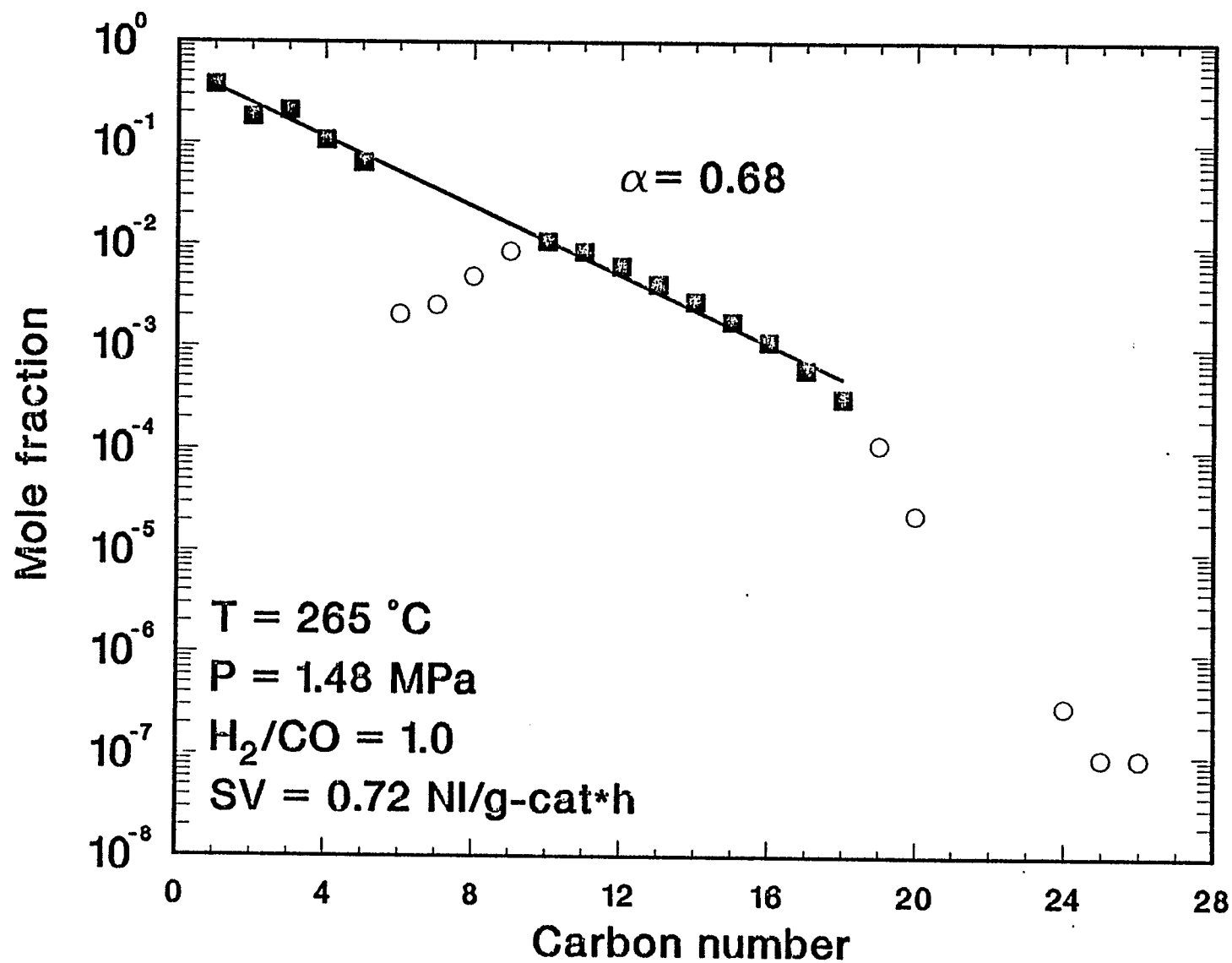


Figure 11. Anderson-Schulz-Flory plot for Run SA-01-0817-2.

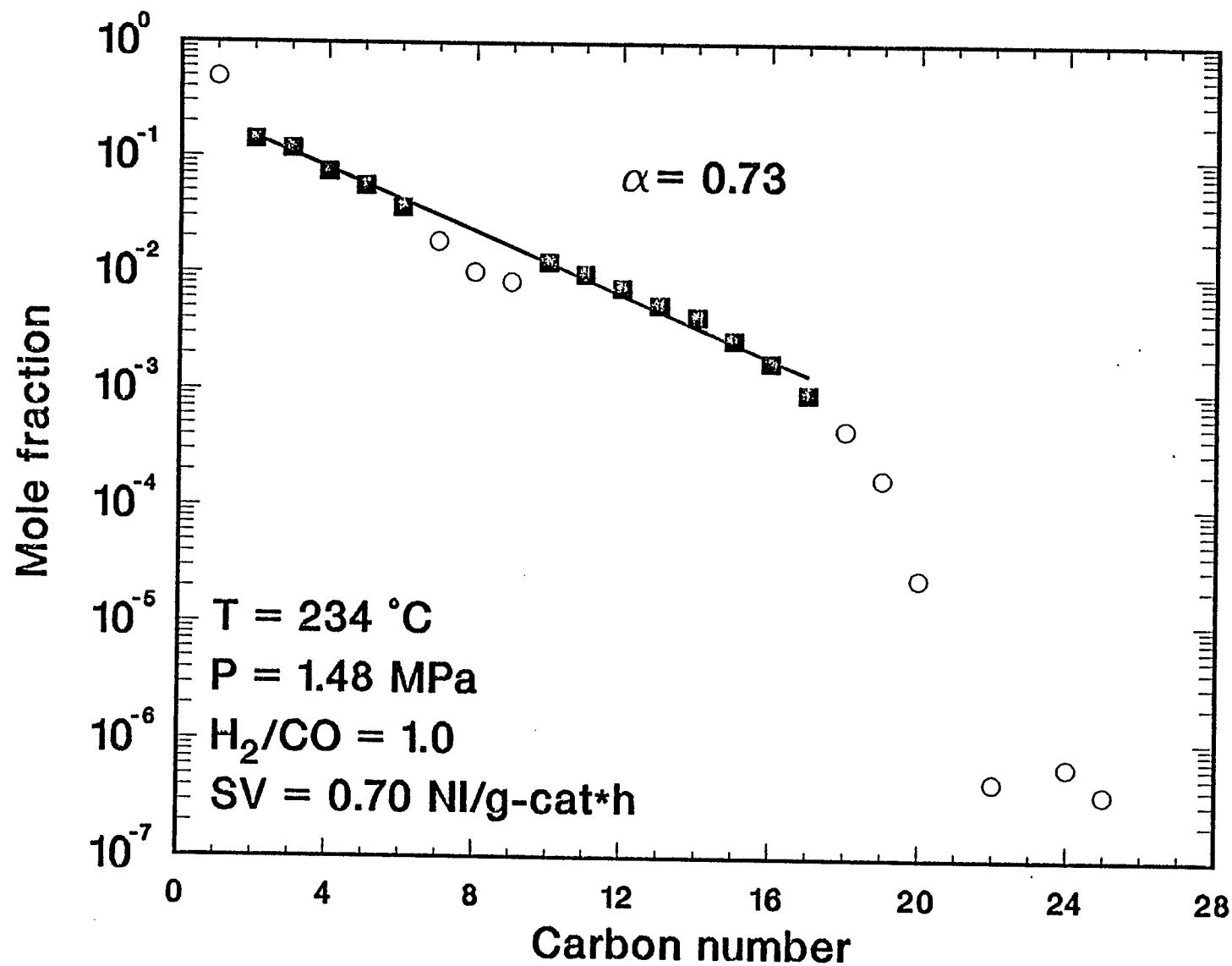


Figure 12. Anderson-Schulz-Flory plot for Run SA-01-0817-3.

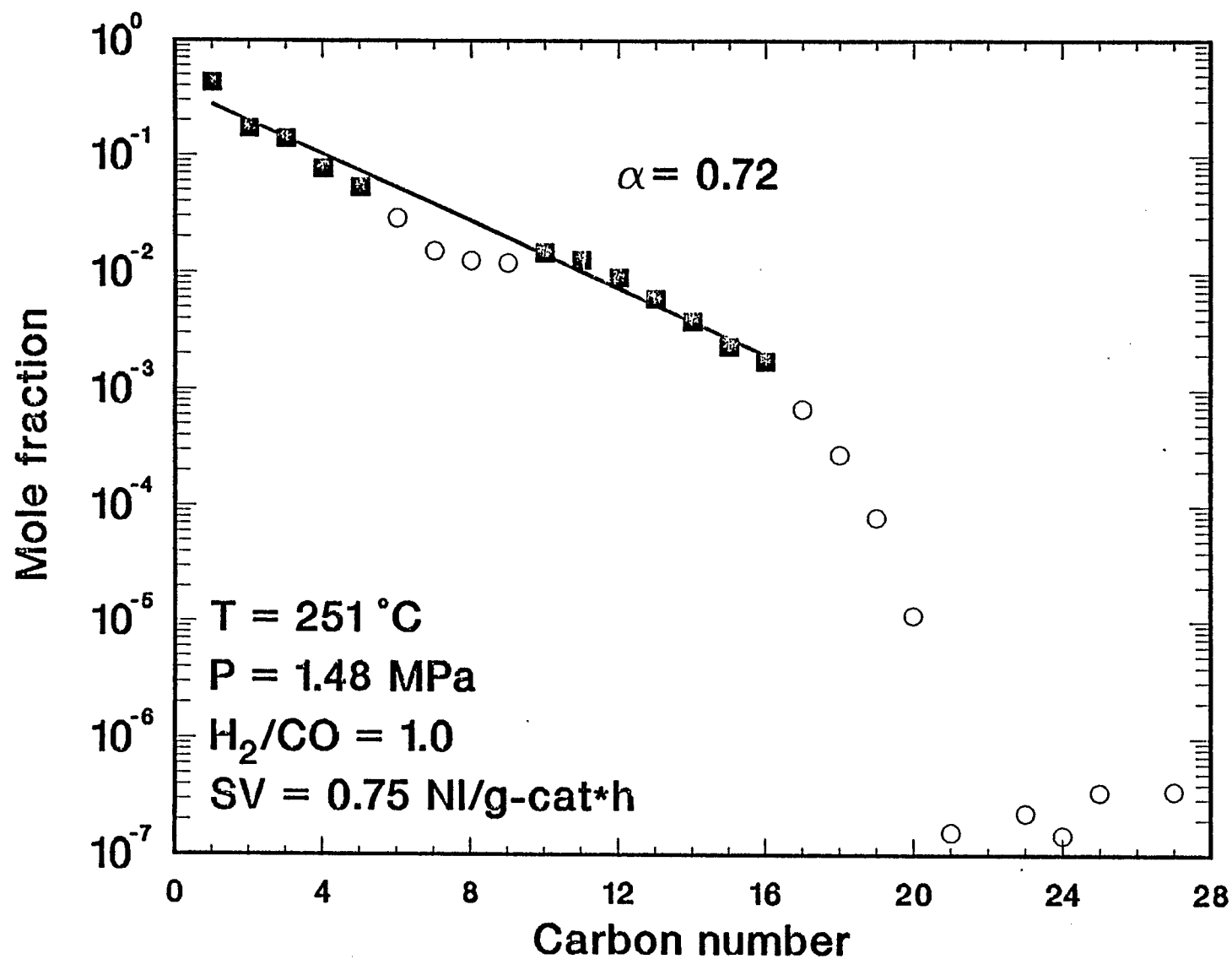


Figure 13. Anderson-Schulz-Flory plot for Run SA-01-0817-4.

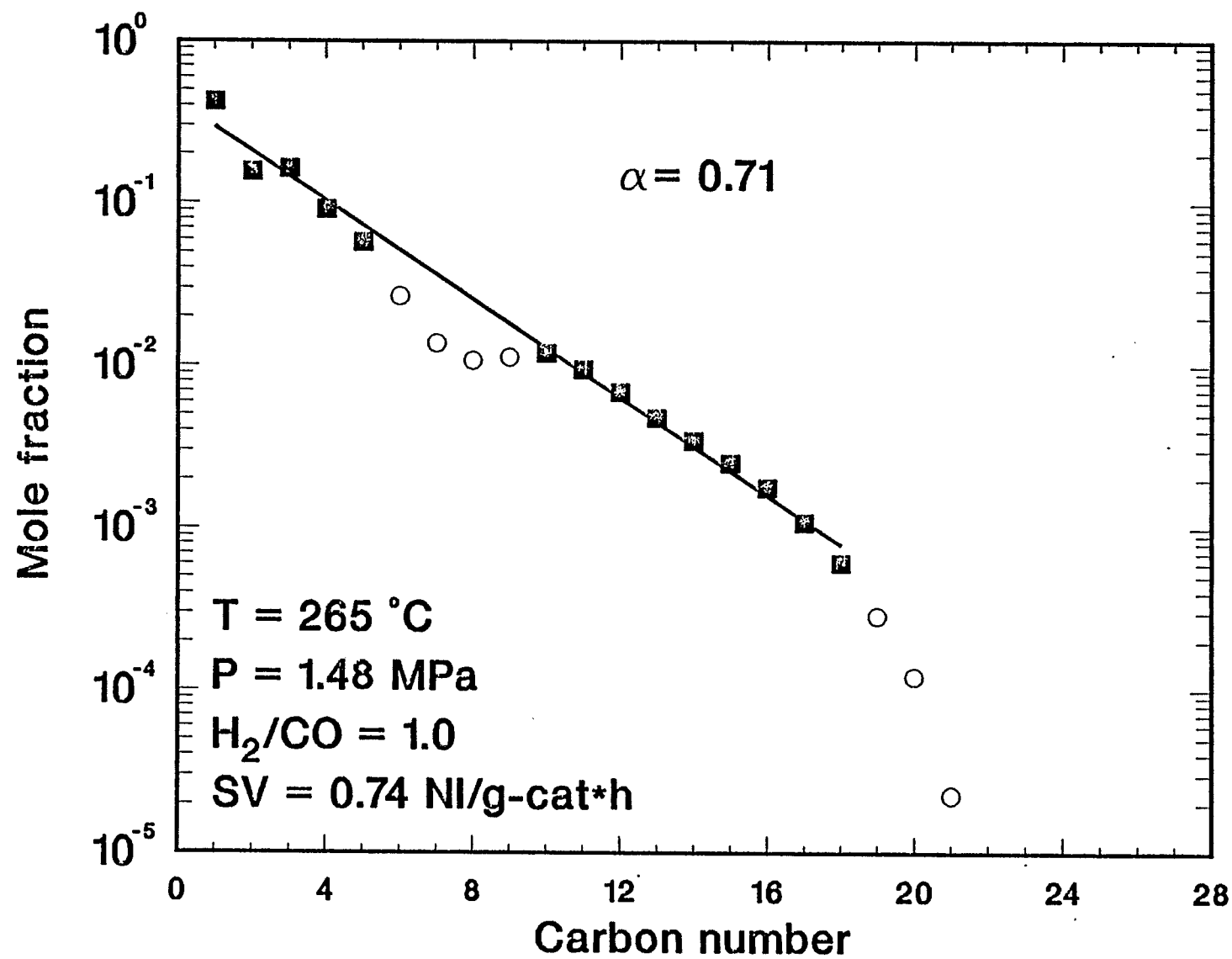


Figure 14. Anderson-Schulz-Flory plot for Run SA-01-0817-5.

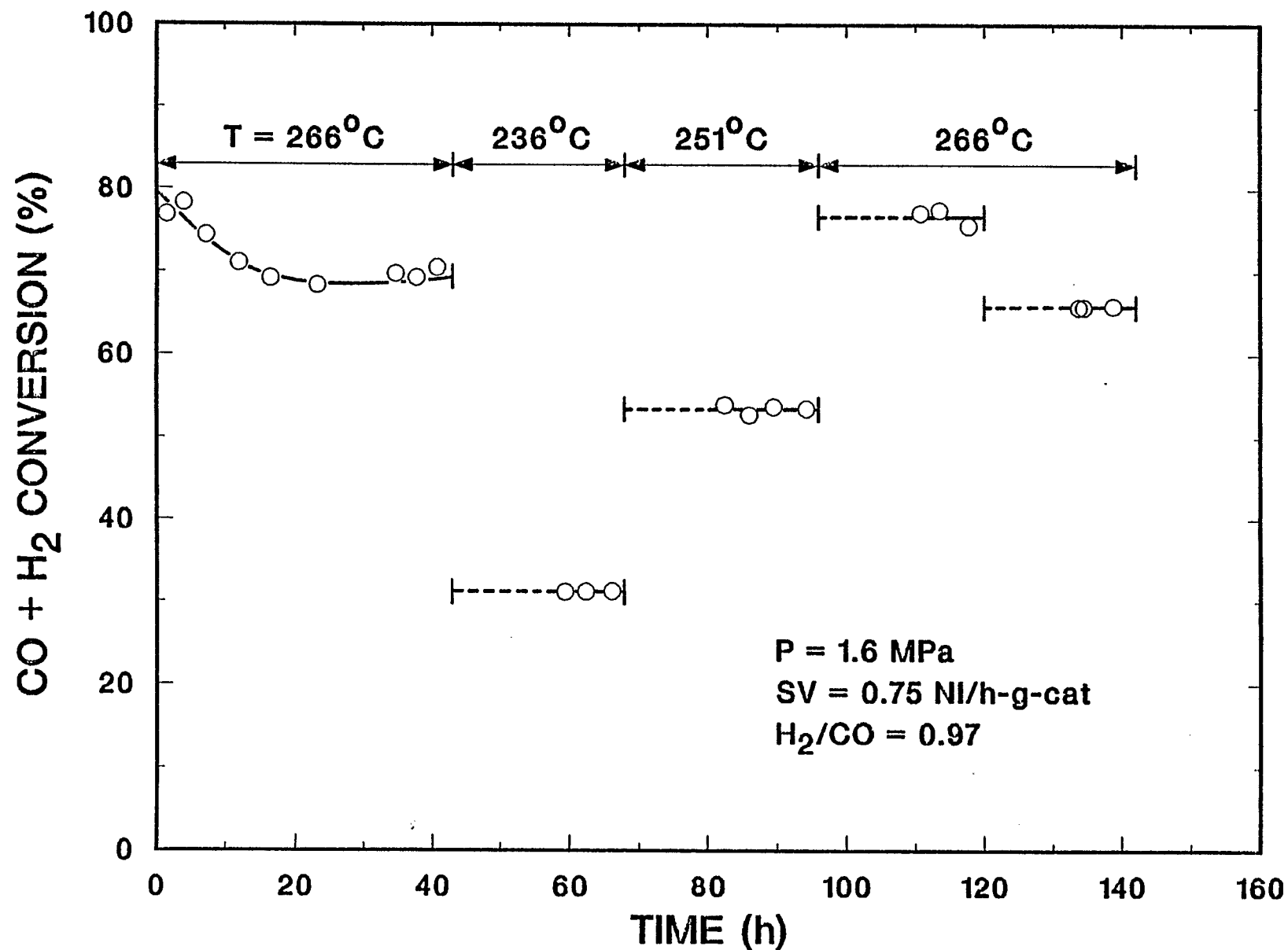


Figure 15. Synthesis gas conversion as a function of time and temperature. Fixed bed reactor run FA-01-1147.

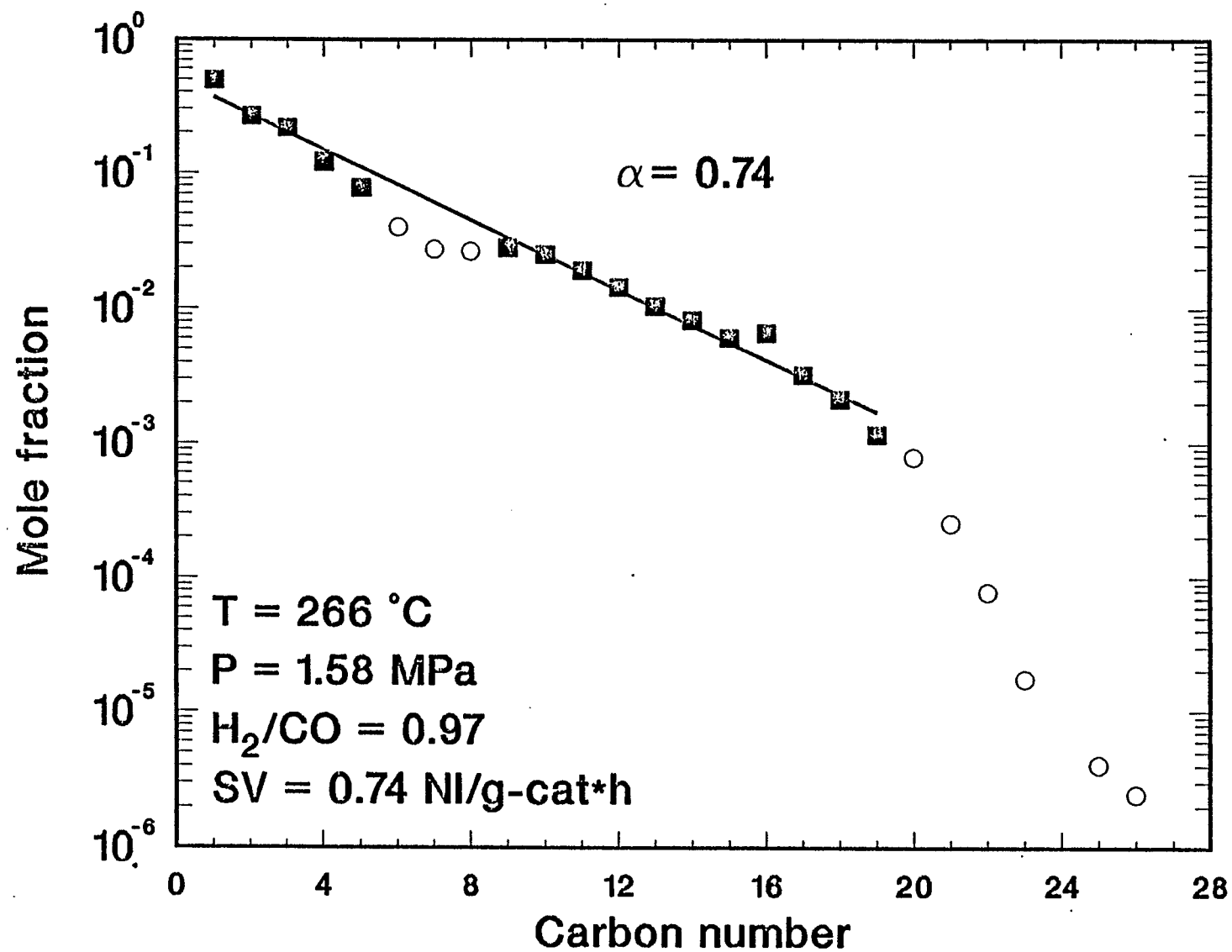


Figure 16. Anderson-Schulz-Flory plot for Run FA-01-1147-1.

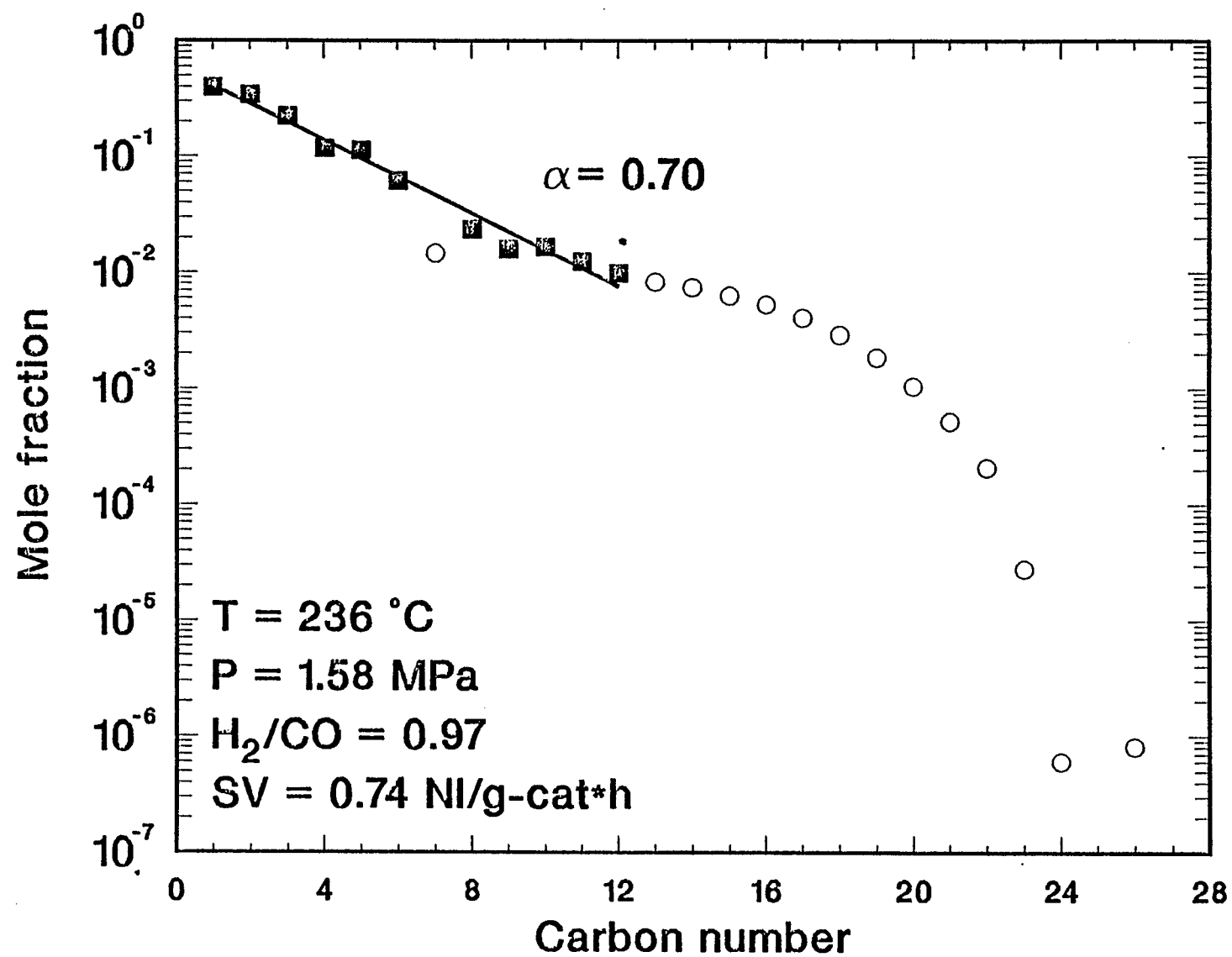


Figure 17. Anderson-Schulz-Flory plot for Run FA-01-1147-2.

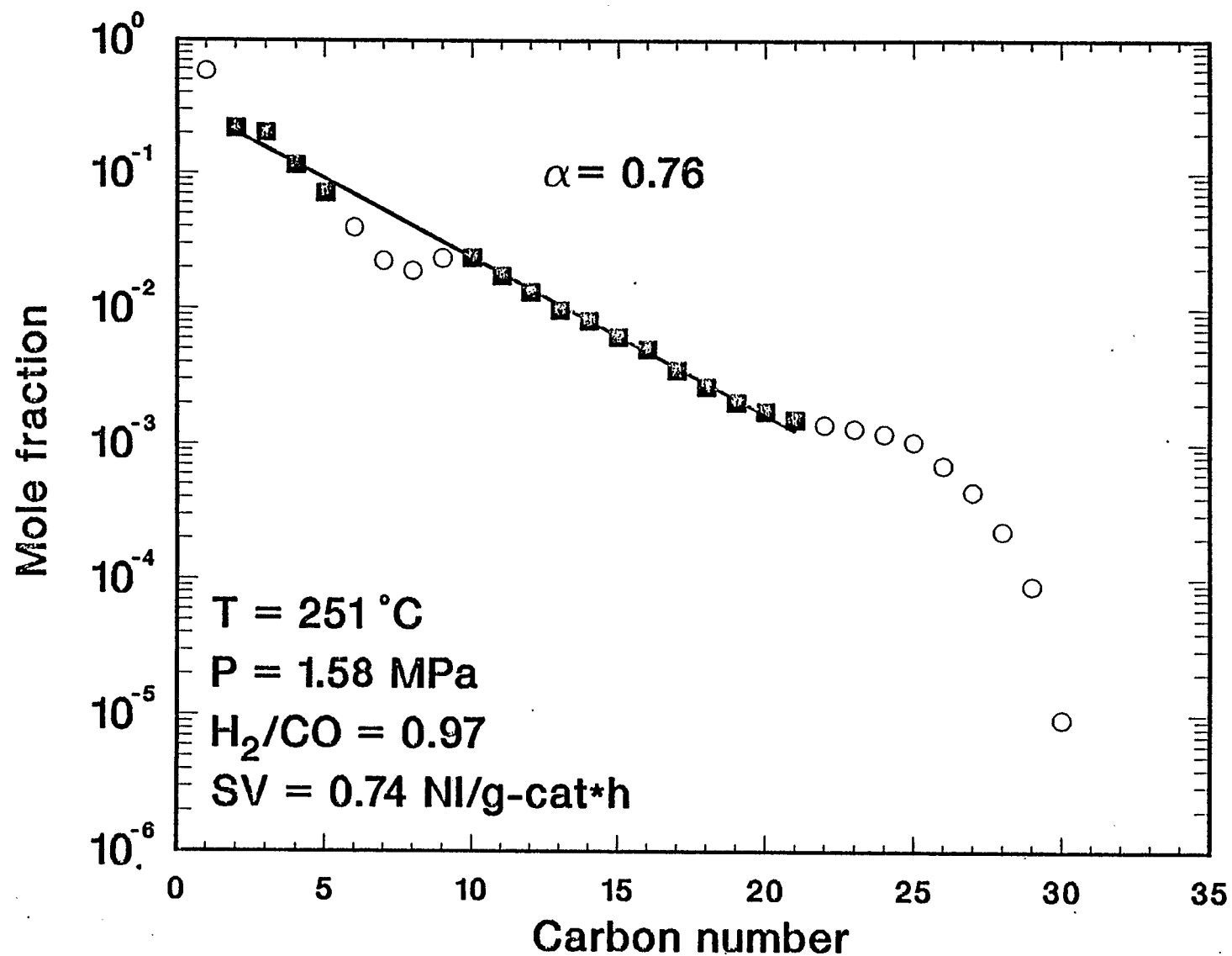


Figure 18. Anderson-Schulz-Flory plot for Run FA-01-1147-3.

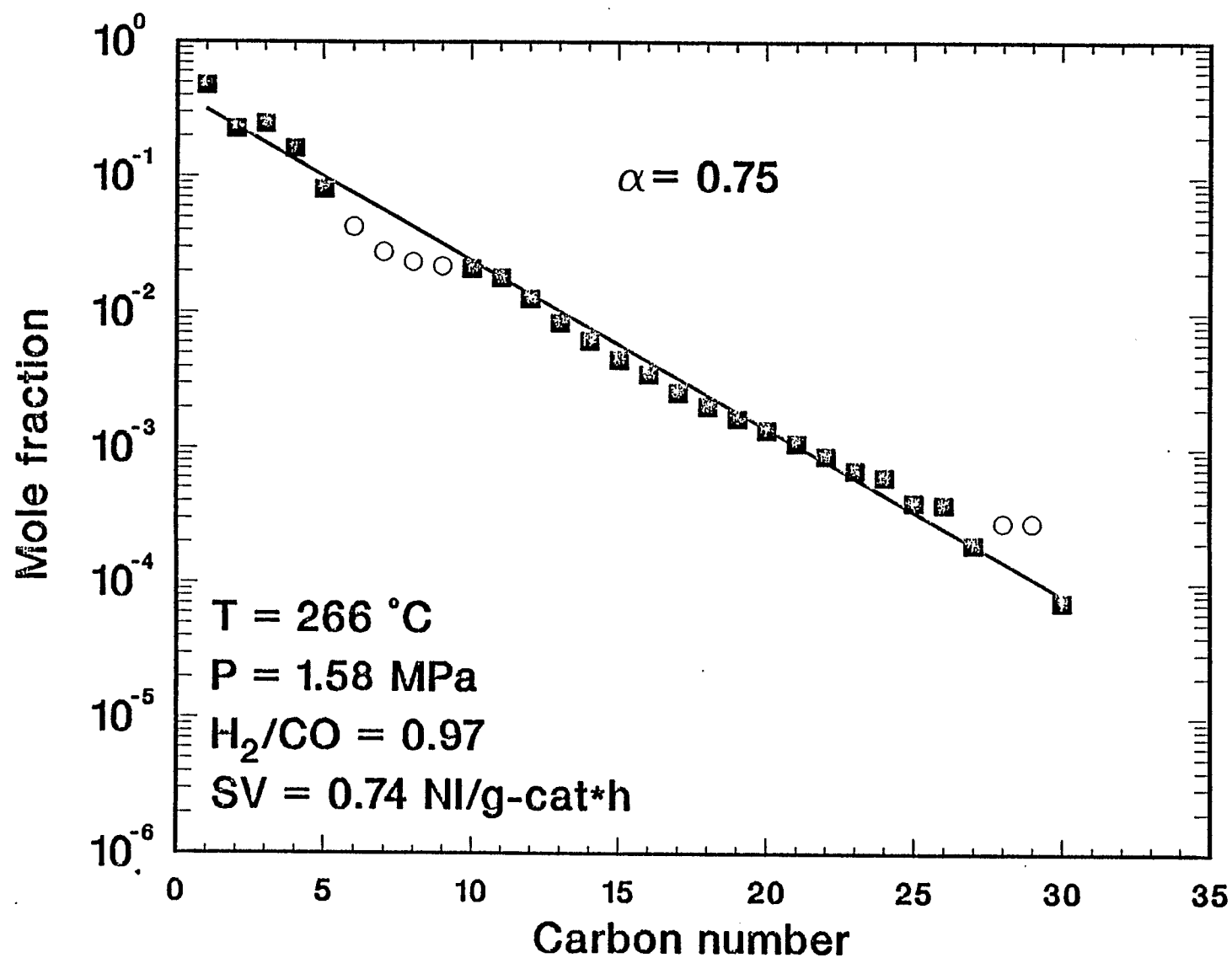


Figure 19. Anderson-Schulz-Flory plot for Run FA-01-1147-4.

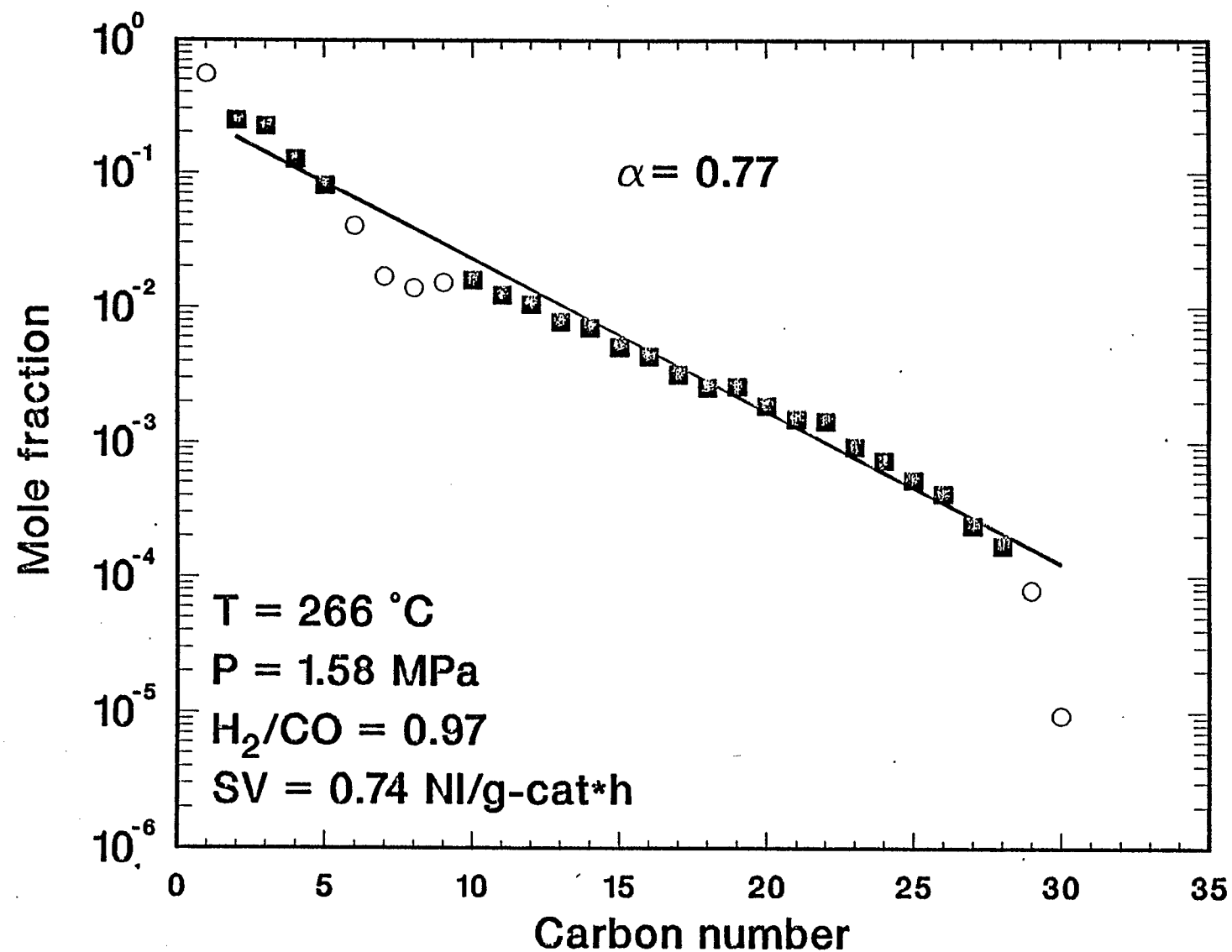


Figure 20. Anderson-Schulz-Flory plot for Run FA-01-1147-5.

Appendix 1. Sample Output of Mass Balance Program (Run SA-01-0817-5).

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*****
                        RUN SUMMARY
*****

Run:          SA-01-0817          Sample: 5
Date:         03/28/87           Reactor: Slurry A
Balance Period: 8.00 (h)         Time on Stream: 147.00 (h)
*****

Temperature:      265. (C)      538. (K)
Pressure:         215. (psia)   1.48 (MPa)
Catalyst Type:    C-73-1 Fused   Basis: Unreduced
Wt % Fe in Catalyst: 67.00      Catalyst Loading: 57.90 (g)
Liquid Type:      FT300         Liquid Loading: 322.00 (g)
GHSV:             .7438 (NI/g-cat*h) 1.1102 (NI/g-Fe*h)
SV @ RXN T,P:     .1003 (l/g-cat*h) .1498 (l/g-Fe*h)
Inlet Flowrate:   43.0670 +/- .1815 (NI/h) ( .4215 % )
H2/CO Feed Ratio: 1.0408 +/- .0595 (molar) ( 5.7161 % )
Outlet Flowrate:  21.3635 +/- .1045 (NI/h) ( .4891 % )
Impeller Speed:   1000 (rpm)
*****

Syngas Fed:       .22678E+03 (g)
Tailgas Measured: .19395E+03 (g)
Aqueous Liquid Collected: .78900E+01 (g)
Organic Liquid Collected: .88300E+01 (g)
Total Liquid Collected: .17750E+02 (g)
Loss from Separation of Phases: -.10300E+01 (g) ( -5.8028 % )
Wax Removed from Reactor: .55000E+01 (g)
Catalyst Removed from Reactor: .00000E+00 (g)
*****

Inlet Flowrates - Total: .28348E+02 (g/h) .19214E+01 (mol/h)
                      C: .11309E+02 .94150E+00
                      H: .19755E+01 .19599E+01
                      O: .15063E+02 .94150E+00

Outlet Flowrates - Total: .27150E+02 (g/h) .10170E+01 (mol/h)
                      C: .10094E+02 .84035E+00
                      H: .17903E+01 .17762E+01
                      O: .15266E+02 .95416E+00

Mass Closures - Total: 95.77 (%)
                  C: 89.26
                  H: 90.63
                  O: 101.34
*****

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*****
Conversions -      H2:    64.13 (%)
                   CO:    93.73
                   H2 + CO: 78.64
                   CO to CH4: 5.18
                   CO to CO2: 42.84

Space Time Yield:      .02610 (mol/g-cat*h)

% Contraction:        50.39
% CO2-Free Contraction: 71.39

H2/CO Usage Ratio:    .71214E+00 (molar)
H2/CO Exit Ratio:     .59583E+01 (molar)

*****

Mole Fractions -      H2:    .34614E+00
                       CO:    .58094E-01
                       CO2:   .39726E+00
                       H2O:   .84956E-01

Partial Pressures -    H2:    .74314E+02 (psia)    .51238E+00 (MPa)
                       CO:    .12473E+02          .85995E-01
                       CO2:   .85291E+02          .58806E+00
                       H2O:   .18240E+02          .12576E+00

Liquid Concentrations - H2:    .26275E-01 (mol/l-liquid)
                        CO:    .59278E-02
                        CO2:   .76161E-01
                        H2O:   .25283E-01

Reaction Rates -      H2:    -.10854E-01 (mol/g-cat*h)
                       CO:    -.15242E-01
                       H2 + CO: -.26097E-01

[(P_CO2*P_H2)/(P_CO*P_H2O)]: .27862E+02
WGS KEQ:                  .65119E+02 (Newsome, 1980)

*****

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*****
              Avg C #   H/C       Avg MW   Mol% C   Mol% H   Mol% O
n-Paraffins:      1.8688   3.0702    28.2299   24.57   75.43    .00
Total Paraffins:   2.0412   2.9798    30.6477   25.13   74.87    .00
n-Olefins:         4.1732   2.0000    58.5376   33.33   66.67    .00
Total Olefins:     4.1702   2.0000    58.4952   33.33   66.67    .00
Total Paraffins + Olefins: 2.8481   2.4361   41.2021   29.10   70.90    .00
Total Hydrocarbons: 2.8481   2.4361   41.2021   29.10   70.90    .00
  Including Wax:      2.3732
Oxygenates:        3.1241   2.6326    61.8141   25.30   66.60    8.10
Hydrocarbons + Oxygenates: 2.8532   2.4401   41.5847   29.01   70.80    .19
  Including Wax:      2.3765
Unaccounted Products:      1.8760              35.82   67.20   -3.02

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*****
Outlet              Mol %      Wt%       mol/h      g/h
Hydrocarbons:       11.1261   17.1724   .11316E+00   .46623E+01
Oxygenates:         .2104     .4872    .21400E-02   .13228E+00
H2:                 34.5582   2.6097   .35147E+00   .70854E+00
H2O:                8.4819   5.7241   .86264E-01   .15541E+01
CO:                  5.8001   6.0859   .58989E-01   .16523E+01
CO2:                39.6626   65.3884   .40338E+00   .17753E+02
Wax:                 .1606     2.5322   .16337E-02   .68750E+00

Total:              100.0000  100.0000   .10170E+01   .27150E+02

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*****
Products            Mol %      Wt%       mol/h      g/h
Hydrocarbons:       18.6549   18.8078   .11316E+00   .46623E+01
Oxygenates:         .3528     .5336    .21400E-02   .13228E+00
H2O:                14.2215   6.2692   .86264E-01   .15541E+01
CO2:                66.5015   71.6159   .40338E+00   .17753E+02
Wax:                 .2693     2.7734   .16337E-02   .68750E+00

Total:              100.0000  100.0000   .60658E+00   .24789E+02

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*****
1 + 2 Olefins/n-Paraffins      Molar      Weight
C2:                             .5647       .5269
C3:                             6.9415      6.6242
C4:                             4.1409      3.9973
C5:                             2.7159      2.6400
C6:                             86.5032     84.4797
C7:                             2.6831      2.6292
C8:                             2.1598      2.1217
C9:                             1.7837      1.7557
C10:                            2.1876      2.1566

C2 +:                           2.1236      2.1362
C2 - C4:                        2.0001      2.3972
C5 - C11:                       3.1987      2.8874
C12 - C17:                       .7184       .6767
C18 +:                           .0876       .0850

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*****
% Olefin in Hydrocarbon      Molar      Weight
C2 +:                        66.6229     64.6629
C2 - C4:                     66.9818     70.8791
C5 - C11:                    70.5726     66.9594
C12 - C17:                   36.2472     35.2783
C18 +:                        7.9512      7.7294

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Weight % Distribution Excluding Wax

C#	n-Para	1,2-Olef	Isomer	Oxy	Total
1	16.3234	.0000	.0000	.0776	16.4010
2	6.7963	3.5808	.0000	1.0718	11.4489
3	2.1555	14.2787	.0000	.3336	16.7678
4	2.2497	8.9927	1.0670	.2330	12.5425
5	2.4877	6.5676	.3463	.5135	9.9151
6	.0620	5.2411	.0035	.1404	5.4470
7	.8625	2.2677	.0079	.1477	3.2858
8	.8754	1.8573	.0627	.1494	2.9448
9	1.0409	1.8275	.5337	.0615	3.4636
10	.8355	1.8018	1.4084	.0306	4.0763
11	1.1789	1.6393	.7566	.0000	3.5748
12	1.0392	1.1834	.5884	.0000	2.8111
13	.9684	.8275	.3363	.0000	2.1322
14	.9166	.5735	.1627	.0000	1.6529
15	.8218	.3766	.0806	.0000	1.2790
16	.6826	.2634	.0210	.0000	.9670
17	.5101	.1175	.0031	.0000	.6307
18	.3320	.0417	.0001	.0000	.3738
19	.1779	.0087	.0000	.0000	.1866
20	.0738	.0004	.0086	.0000	.0828
21	.0160	.0001	.0000	.0000	.0162
2-4	11.2016	26.8523	1.0670	1.6383	40.7592
5-11	7.3430	21.2023	3.1191	1.0431	32.7075
12-17	4.9388	3.3418	1.1922	.0000	9.4728
18+	.5998	.0510	.0088	.0000	.6595
Total	40.4065	51.4474	5.3871	2.7590	100.0000

Mole % Distribution Excluding Wax

C#	n-Para	1,2-Olef	Isomer	Oxy	Total
1	42.3114	.0000	.0000	.1008	42.4121
2	9.3988	5.3078	.0000	.9674	15.6741
3	2.0327	14.1102	.0000	.2313	16.3743
4	1.6095	6.6650	.7859	.1309	9.1913
5	1.4338	3.8941	.1996	.2422	5.7697
6	.0299	2.5896	.0017	.0571	2.6784
7	.3579	.9604	.0033	.0529	1.3745
8	.3187	.6883	.0228	.0477	1.0775
9	.3375	.6020	.1730	.0177	1.1302
10	.2442	.5342	.4116	.0080	1.1980
11	.3136	.4418	.2013	.0000	.9567
12	.2537	.2924	.1437	.0000	.6897
13	.2184	.1887	.0759	.0000	.4830
14	.1921	.1214	.0341	.0000	.3477
15	.1609	.0744	.0158	.0000	.2511
16	.1254	.0488	.0039	.0000	.1780
17	.0882	.0205	.0005	.0000	.1092
18	.0542	.0069	.0000	.0000	.0611
19	.0276	.0014	.0000	.0000	.0289
20	.0109	.0001	.0013	.0000	.0122
21	.0023	.0000	.0000	.0000	.0023
2-4	13.0411	26.0830	.7859	1.3296	41.2396
5-11	3.0357	9.7103	1.0133	.4257	14.1850
12-17	1.0387	.7462	.2738	.0000	2.0587
18+	.0949	.0083	.0013	.0000	.1045
Total	59.5217	36.5478	2.0744	1.8561	100.0000

Alpha from First Ten Carbon Numbers

Alpha from Slope:	.5890	.6638	1.0131	.6834	.6520
Alpha from Intercept:	.8531	.7976	.9995	.9933	.6809
R Correlation:	-.7829	-.9349	.0116	-.8397	-.9651

Alpha from Entire Distribution

Alpha from Slope:	.7393	.5628	.7058	.6834	.6787
Alpha from Intercept:	.9372	.5044	.9901	.9933	.6879
R Correlation:	-.8541	-.9277	-.5921	-.8397	-.9705

Weight % Hydrocarbon Distribution Including Wax

C#	n-Para	1,2-Olef	Isomer	Total
1	14.6293	.0000	.0000	14.6293
2	6.0910	3.2092	.0000	9.3002
3	1.9318	12.7968	.0000	14.7287
4	2.0162	8.0594	.9563	11.0320
5	2.2295	5.8860	.3104	8.4259
6	.0556	4.6971	.0032	4.7559
7	.7730	2.0323	.0071	2.8124
8	.7846	1.6646	.0562	2.5053
9	.9329	1.6379	.4783	3.0490
10	.7488	1.6148	1.2623	3.6259
11	1.0566	1.4692	.6781	3.2038
12	.9313	1.0606	.5274	2.5193
13	.8679	.7416	.3014	1.9109
14	.8215	.5140	.1459	1.4814
15	.7365	.3375	.0723	1.1462
16	.6118	.2360	.0188	.8666
17	.4572	.1053	.0028	.5652
18	.2975	.0374	.0001	.3350
19	.1595	.0078	.0000	.1673
20	.0661	.0004	.0077	.0742
21	.0144	.0001	.0000	.0145
2-4	10.0391	24.0654	.9563	35.0608
5-11	6.5809	19.0019	2.7954	28.3782
12-17	4.4262	2.9950	1.0684	8.4896
18+	.5375	.0457	.0079	.5911
Wax				12.8510
Total	36.2130	46.1080	4.8280	100.0000

COMBINATION ANALYSIS RESULTS, TAIL GAS

Compound Name	Formula	Mol Wt	Wt Frac	Mole Frac
1 Hydrogen	H2	2.02	.29973E-01	.38220E+00
1 Carbon Monoxide	CO	28.01	.69897E-01	.64147E-01
1 Carbon Dioxide	CO2	44.01	.75099E+00	.43866E+00
1 Methane	CH4	16.04	.33107E-01	.53049E-01
\$ Ethane	C2H6	30.07	.13785E-01	.11784E-01
\$ Ethene	C2H4	28.05	.72626E-02	.66548E-02
\$ Propane	C3H8	44.10	.43719E-02	.25486E-02
\$ Propene	C3H6	42.08	.28960E-01	.17691E-01
& n-Butane	C4H10	58.12	.45629E-02	.20180E-02
1 2-Methylpropane	C4H10	58.12	.38686E-03	.17109E-03
& 1-Butene	C4H8	56.11	.15479E-01	.70917E-02
1 cis-2-Butene	C4H8	56.11	.15700E-02	.71930E-03
1 trans-2-Butene	C4H8	56.11	.11904E-02	.54539E-03
1 Methylpropene	C4H8	56.11	.17773E-02	.81428E-03
& n-Pentane	C5H12	72.15	.50456E-02	.17977E-02
1 2-Methylbutane	C5H12	72.15	.70247E-03	.25028E-03
& 1-Pentene	C5H10	70.14	.11231E-01	.41163E-02
1 cis-2-Pentene	C5H10	70.14	.10594E-02	.38830E-03
1 trans-2-Pentene	C5H10	70.14	.10303E-02	.37764E-03
2 1-Hexene	C6H12	84.16	.10290E-01	.31429E-02
2 n-Heptane	C7H16	100.21	.13707E-02	.35163E-03
2 1-Heptene	C7H14	98.19	.37209E-02	.97413E-03
2 n-Octane	C8H18	114.23	.64086E-03	.14421E-03
2 1-Octene	C8H16	112.22	.15919E-02	.36467E-03
Total		25.71	.10000E+01	.10000E+01

1 : Present in analysis I
 2 : Present in analysis II
 & : Present in both analyses
 \$: Combination species

TOTAL PHASE ANALYSIS RESULTS, AQUEOUS

/users/bukur/mass_bal/data/SA-01-0817/5/aqu.a.cal
/users/bukur/mass_bal/data/SA-01-0817/5/aqu.a.dat

/users/bukur/mass_bal/data/SA-01-0817/5/aqu.a.cal
/users/bukur/mass_bal/data/SA-01-0817/5/aqu.b.dat

Karl-Fischer Analysis: Sample Wt Frac H2O

1	.90330E+00	
2	.90400E+00	
3	.91840E+00	
4	.90480E+00	
5	.90460E+00	
	.90702E+00	Average
	.63758E-02	Std Dev
	.70294E+00	% Rel Dev

Compound Name	Formula	Mol Wt	Wt Frac	Mol Frac
Water	H2O	18.02	.90702E+00	.96696E+00
Methanol	CH4O	32.04	.35551E-02	.21309E-02
Ethanol	C2H6O	46.07	.49080E-01	.20461E-01
1-Propanol	C3H8O	60.10	.11155E-01	.35650E-02
2-Propanol	C3H8O	60.10	.31999E-02	.10226E-02
2-Propanone	C3H6O	58.08	.91996E-03	.30421E-03
1-Butanol	C4H10O	74.12	.58240E-02	.15090E-02
2-Butanol	C4H10O	74.12	.11613E-02	.30091E-03
Butanal	C4H8O	72.11	.90107E-04	.24000E-04
2-Butanone	C4H8O	72.11	.50208E-03	.13373E-03
1-Pentanol	C5H12O	88.15	.79431E-02	.17306E-02
2-Pentanol	C5H12O	88.15	.17077E-02	.37206E-03
Pentanois	C5H12O	88.15	.10968E-02	.23897E-03
1-Hexanol	C6H14O	102.18	.59582E-02	.11199E-02
1-Heptanol	C7H16O	116.20	.78706E-03	.13008E-03
Total		19.21	.10000E+01	.10000E+01

GC ANALYSIS RESULTS, ORGANIC

/users/bukur/mass_bal/data/SA-01-0817/5/org.a.cal
/users/bukur/mass_bal/data/SA-01-0817/5/org.a.dat

Compound Name	Formula	Mol Wt	Wt Frac	Mol Frac
1-Butanol	C4H10O	74.12	.41441E-02	.84401E-02
1-Pentanol	C5H12O	88.15	.11896E-01	.20373E-01
n-Hexane	C6H14	86.18	.25867E-02	.45313E-02
Hexane Isomers	C6H14	86.18	.29045E-03	.50881E-03
1-Hexene	C6H12	84.16	.66339E-02	.11899E-01
cis-2-Hexene	C6H12	84.16	.11879E-03	.21308E-03
trans-2-Hexene	C6H12	84.16	.16328E-03	.29288E-03
1-Hexanol	C6H14O	102.18	.27705E-03	.40933E-03
n-Heptane	C7H16	100.21	.79264E-02	.11941E-01
Heptane Isomers	C7H16	100.21	.12883E-03	.19408E-03
1-Heptene	C7H14	98.19	.16773E-01	.25788E-01
cis-2-Heptene	C7H14	98.19	.63447E-03	.97549E-03
trans-2-Heptene	C7H14	98.19	.79850E-03	.12277E-02
1-Heptanol	C7H16O	116.20	.52800E-02	.68594E-02
n-Octane	C8H18	114.23	.22924E-01	.30295E-01
Octane Isomers	C8H18	114.23	.32244E-02	.42612E-02
1-Octene	C8H16	112.22	.34763E-01	.46766E-01
cis-2-Octene	C8H16	112.22	.45327E-02	.60978E-02
trans-2-Octene	C8H16	112.22	.50266E-02	.67623E-02
1-Octanol	C8H18O	130.23	.60622E-02	.70273E-02
n-Nonane	C9H20	128.26	.42215E-01	.49688E-01
Nonane Isomers	C9H20	128.26	.22112E-01	.26026E-01
1-Nonene	C9H18	126.24	.51928E-01	.62096E-01
cis-2-Nonene	C9H18	126.24	.10119E-01	.12100E-01
trans-2-Nonene	C9H18	126.24	.11944E-01	.14282E-01
1-Nonanol	C9H20O	144.26	.24881E-02	.26038E-02
n-Decane	C10H22	142.29	.16893E-01	.17923E-01
Decane Isomers	C10H22	142.29	.83063E-01	.88129E-01
1-Decene	C10H20	140.27	.49890E-01	.53693E-01
cis-2-Decene	C10H20	140.27	.54273E-04	.58411E-04
trans-2-Decene	C10H20	140.27	.13442E-01	.14466E-01
1-Decanol	C10H22O	158.29	.12205E-02	.11640E-02
n-Undecane	C11H24	156.31	.48071E-01	.46426E-01
Undecane Isomers	C11H24	156.31	.30411E-01	.29370E-01
1-Undecene	C11H22	154.30	.39543E-01	.38689E-01
cis-2-Undecene	C11H22	154.30	.11768E-01	.11513E-01
trans-2-Undecene	C11H22	154.30	.15770E-01	.15429E-01
n-Dodecane	C12H26	170.34	.42387E-01	.37565E-01
Dodecane Isomers	C12H26	170.34	.24159E-01	.21411E-01
1-Dodecene	C12H24	168.33	.24769E-01	.22215E-01
cis-2-Dodecene	C12H24	168.33	.96177E-02	.86257E-02
trans-2-Dodecene	C12H24	168.33	.13958E-01	.12519E-01

Compound Name	Formula	Mol Wt	Wt Frac	Mol Frac
n-Tridecane	C13H28	184.37	.39405E-01	.32265E-01
Tridecane Isomers	C13H28	184.37	.13814E-01	.11311E-01
1-Tridecene	C13H26	182.35	.14090E-01	.11665E-01
cis-2-Tridecene	C13H26	182.35	.75627E-02	.62610E-02
trans-2-Tridecene	C13H26	182.35	.12195E-01	.10096E-01
n-Tetradecane	C14H30	198.40	.37624E-01	.28629E-01
Tetradecane Isomers	C14H30	198.40	.68098E-02	.51818E-02
1-Tetradecene	C14H28	196.38	.76267E-02	.58629E-02
cis-2-Tetradecene	C14H28	196.38	.56903E-02	.43744E-02
trans-2-Tetradecene	C14H28	196.38	.10359E-01	.79633E-02
n-Pentadecane	C15H32	212.42	.33509E-01	.23814E-01
Pentadecane Isomers	C15H32	212.42	.34903E-02	.24805E-02
1-Pentadecene	C15H30	210.41	.35044E-02	.25144E-02
cis-2-Pentadecene	C15H30	210.41	.38504E-02	.27626E-02
trans-2-Pentadecene	C15H30	210.41	.79465E-02	.57015E-02
n-Hexadecane	C16H34	226.45	.28034E-01	.18689E-01
Hexadecane Isomers	C16H34	226.45	.13838E-02	.92254E-03
1-Hexadecene	C16H32	224.43	.15024E-02	.10106E-02
cis-2-Hexadecene	C16H32	224.43	.22541E-02	.15162E-02
trans-2-Hexadecene	C16H32	224.43	.59512E-02	.40031E-02
n-Heptadecane	C17H36	240.48	.20974E-01	.13167E-01
Heptadecane Isomers	C17H36	240.48	.25186E-03	.15811E-03
1-Heptadecene	C17H34	238.46	.40956E-03	.25928E-03
cis-2-Heptadecene	C17H34	238.46	.99636E-03	.63078E-03
trans-2-Heptadecene	C17H34	238.46	.33685E-02	.21325E-02
n-Octadecane	C18H38	254.50	.13711E-01	.81329E-02
Octadecane Isomers	C18H38	254.50	.10705E-04	.63501E-05
1-Octadecene	C18H36	252.49	.19945E-04	.11925E-04
cis-2-Octadecene	C18H36	252.49	.24674E-03	.14753E-03
trans-2-Octadecene	C18H36	252.49	.15425E-02	.92229E-03
n-Nonadecane	C19H40	268.53	.73649E-02	.41404E-02
cis-2-Nonadecene	C19H38	266.51	.10997E-04	.62290E-05
trans-2-Nonadecene	C19H38	266.51	.70162E-03	.39743E-03
n-Eicosane	C20H42	282.56	.30945E-02	.16533E-02
trans-2-Eicosene	C20H40	280.54	.34328E-04	.18473E-04
n-Heneicosane	C21H44	296.58	.64386E-03	.32773E-03
1-Heneicosene	C21H42	294.57	.11248E-04	.57644E-05
Total		150.96	.10000E+01	.10000E+01
