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Performance Testing with a Gas-Liquid-Solid System in a Mechanically-Stirred Reactor: The Fischer-Tropsch Synthesis

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ABSTRACT

Careful attention to reactor operating procedures and methods of product trapping and analysis is required to obtain accurate and reliable data on selectivity and kinetics when a wide variety of products are formed. Useful methods are discussed in detail. The focus of attention is on use of iron-based Fischer-Tropsch catalysts studied in a well-mixed slurry reactor, but many of the findings apply to other catalysts and reactor systems used for Fischer-Tropsch synthesis or to other reactions in which a complex mixture of products is formed.

Some apparent discrepancies in the literature regarding catalyst activity and selectivity in Fischer-Tropsch synthesis are explained by analysis of the pertinent experimental systems.

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INTRODUCTION

A mechanically-stirred, slurry reactor is frequently used in experimental studies of the Fischer-Tropsch synthesis (1-19). These reactors offer excellent temperature control and flexibility in operating conditions. Since the internal composition of such reactors is uniform, they facilitate development of kinetic models without the complications involved in analysis of integral data obtained in a fixed-bed reactor.

Regardless of the type of reactor, it is necessary to design flow, temperature, and pressure control systems that allow steady-state operation. It is also necessary to collect and analyze a wide range of condensable and non-condensable products to analyze hydrocarbon and oxygenate distributions. Gas chromatography offers considerable flexibility in analyzing hydrocarbon and oxygenated products over a wide range of molecular weights, but care must be taken in developing analytical algorithms. Care must also be taken to avoid mass transfer limitations. In slurry reactors, low-density catalysts may be entrained by exit vapors, and finely divided catalyst particles may also be difficult to separate from slurry waxes.

DESCRIPTION OF REACTOR SYSTEM

Our experimental system has been in operation for more than ten years. The original configuration has been described in some detail elsewhere (1,20,21,22). Since our earlier publications, we have made some modifications both to the reactor system and to

our analytical methods, which we document here. We also summarize the previous descriptions here as background for later discussion.

Experiments are performed in either of two one-liter continuous-flow stirred autoclave units, previously loaded with a hydrocarbon having a high boiling point, plus a finely-divided solid catalyst. Figure 1 is a schematic diagram of the reactor system. Gas flow into the reactor is controlled by Brooks 585Ø mass flow meters operated by a Brooks 5878 mass flow controller. These controllers can each feed up to 2.Ø liters per minute (at STP) of either CO (CP grade) or H_2 (pre-purified grade). Gases are passed through activated carbon beds to remove possible metal carbonyls. Drier units are used to effect water removal. 1Ø µm frits are installed upstream of the mass flow meters to remove any solid impurities. Condensible product is collected in two traps in series.

Feed, reactor, and condensed product trap pressures are controlled by Grove back pressure regulators. Relief valves are installed on all feed lines and set to 5.2 MPa. Pressure gauges are installed on the feed section, the reactor inlet, and on the hot and cold traps. The hot trap is maintained at reactor pressure and the cold trap at Ø.Ø2 MPa.

Gas enters the reactor through heated tubing at the bottom of the autoclave. The slurry is mixed and the catalyst suspended by a combination of a flat-bladed impeller and a propeller on the same shaft, driven by a packless Magnedrive. Huff and

Satterfield (1) have observed that this combined agitation system is a more effective means of suspending catalyst than either type alone. The flat-bladed impeller alone required 500 RPM to suspend a 15 weight % slurry of a reduced magnetite catalyst, while the combined system required only 200 RPM for the same task. The reactor is baffled by two vertical bars spaced 180° apart. Exit gases pass through a frit (7 to 20 μm) on an alonized outlet tube. Alonizing deposits aluminum on the interior of a stainless steel tubing, which deactivates the surface. The inertness of both reactors has been tested in "blank runs", with liquid carrier but no catalyst present and no hydrocarbon products were detected by our chromatographic techniques.

The liquid temperature in the reactor is controlled by an LFE series 2000 controller, backed up by a Jewell limit controller. The furnace limit is set at 400°C to prevent excessive boiling of slurry wax, as well as runaway reaction. Temperatures are measured by type "J" thermocouples. The lines running into the reactor, from the reactor to the hot trap,and from the hot trap to the cold trap are heated by heating tape, with temperatures controlled by Variacs.

Condensable aqueous and organic products are collected in two sequential stainless steel bombs, referred to as hot and cold traps. Back pressure regulator temperatures for these traps are controlled by heating tapes an Variacs. The hot trap is contained in a heated enclosure, maintained at 80 to 90°C and

controlled by a Variac. The cold trap is immersed in a water bath maintained at 2 to 4°C by a Blue M refrigeration unit.

The hot and cold trap systems have similar configurations. In each case, a 1000 ml trap is used most of the time, but during material balances, flow is directed through a 75 ml trap. The 75 ml traps are blown clean with helium before each material balance and are cleaned periodically with either toluene, for the hot trap, or n-pentane, for the cold trap. Non-condensable products pass through both traps during material balances. The composition of the non-condensables is determined by on-line sampling with a chromatograph described below.

DESCRIPTION OF ANALYTICAL SYSTEM

We analyze the products of the synthesis using a series of three gas chromatographs (GCs), which are described in table 1. Huff et al. (20) described the system in detail. Modifications for detailed wax analysis were described by Stenger et al. (23) and by Matsumoto (24). The analyses are carried out on five phases: organic and aqueous liquids in each of two traps and non-condensable gases. Oxygenated organic products are distributed between the liquid phases in each trap, with the majority solubilized in the aqueous phase. A Hewlett-Packard 5880 equipped with a capillary dimethyl silicone column (HP 19091Y-105) and a flame ionization detector (FID) is used for hydrocarbon analyses of non-condensable gas, as well as the organic liquids from both traps. Water, oxygenated hydrocarbons,

and aqueous liquids from the hot and cold traps are analyzed in a Hewlett Packard 5710 equipped with a three meter 60/80 mesh Tenax packed column and a thermal conductivity detector (TCD). In both the HP 5880 and the HP 5710, 1.0 ml samples are used for gases and 0.1 µl samples for liquids.

The liquid accumulated in the reactor, which includes waxy products, is analyzed in the HP 5880, after being dissolved in an equal volume of carbon disulfide. Stenger et al. (23) used a 2.4 meter packed dimethyl silicone column to effect the separation of waxy products. Matsumoto (24) reports improved techniques, using a bonded methyl silicone capillary column. We inject a 0.15 to 0.20 µl sample, which allows for the dilution of wax by CS_2. Toluene has been used instead of carbon disulfide, but CS_2 provides the advantages of eluting rapidly from the column and having a low response in the FID. Toluene elutes among other hydrocarbon products and care must be taken to avoid interfering with other peaks.

The third chromatograph is a Carle Model 111-H Refinery Gas Analyzer (RGA) and is used exclusively for light gas analysis. Some modifications have been made to the RGA, since Huff et al. (20) described it. The RGA is equipped with a series of 4 columns and a separate hydrogen transfer system (HTS), with eluent detection provided by a TCD. The columns are described in table 1. The HTS is a palladium thimble which uses nitrogen as a carrier to separate H_2 from He. The HTS circumvents the problems caused by the similar responses of helium and hydrogen in a TCD,

including negative peaks, nonlinearity, and poor sensitivity. The RGA is used to determine concentrations of CO, CO_2, H_2, CH_4, and C_2 and C_3 hydrocarbons.

Methane, C_2 and C_3 hydrocarbons, and CO_2 are used as tie-components to match the outputs of the three chromatographs. Fortran codes are used to match the outputs of the GCs and to generate hydrocarbon and oxygenated hydrocarbon distributions for C_1 to C_{30} products. In general, no oxygenates are detected at carbon numbers above 8 or 10. Isomer distributions are generated for terminal and internal alkenes up to about C_{10}. Analysis of volatile products can be matched to wax analyses for comparison of chain growth probabilities in different carbon number ranges (25).

FLOW, TRAPPING, AND PRESSURE CONSIDERATIONS

Carrier Liquid and Line Plugging

The use of high-melting wax as a slurry medium for the Fischer-Tropsch synthesis occasionally leads to plugging of the inlet or outlet lines, and associated pressure buildup. This problem is not generally mentioned in the literature and it bears a brief discussion.

We have occasionally experienced upstream plugging in our reactors. This problem may result from several sources. First, the outlet line of the reactor and the inlet and outlet of the hot trap must be heated sufficiently to avoid solidification of the outlet stream, which can contain small amounts of entrained

slurry wax as well as product hydrocarbons. If the outlet line becomes plugged and the flow controller on the feed continues to supply gas, pressure control in the reactor may be lost. This would cause significant flow disturbances.

A similar effect occurs if power is lost, because mass flow controllers are generally "power-to-open", which means that no gas is fed during a power failure. Once again, major flow disturbances may result. The impact of such flow disturbances can be minimized by installing a check valve on the reactor feed section, near the inlet to the reactor. While these valves are not completely effective, they do prevent most backflow problems, so that upstream disturbances will be isolated from the reactor.

Downstream plugging can be caused by high reactor temperatures, which increase wax volatility, and by high space velocities, which increase wax entrainment. Both of these conditions lead to increased carry-over of slurry wax in the reactor effluent stream. This wax may solidify, particularly in the cold trap. When this occurs, the drain to the trap must be heated and, frequently, the trap must be pressurized to 0.7 MPa (100 psi) or more to force the plug out. In these cases, excessive loss of products usually occurs during trap draining and the material balance is unreliable.

Using a lower molecular weight wax as a slurry medium can cause several problems. First, the carry-over of low molecular weight products in the overhead stream is much greater than that of a high-boiling wax, such as octacosane ($C_{28}H_{58}$). This carry-

over affects the amount and composition of trapped products. Second, some waxes, such as Parowax or Krupp wax, have a wide range of molecular weights, making it difficult to distinguish products from wax carry-over. Use of such waxes has led some researchers (7) to analyze only lighter products of the synthesis.

The disadvantages of using a high molecular weight wax, such as potential plugging and difficulty in separating catalyst from the slurry wax, are outweighed by the relative ease of chromatographic analysis of products and the low carry-over of wax into the trapped products.

Wax Purification

We usually initiate a run by partially filling the reactor with n-octacosane. This provides significant benefits for product analysis, which are discussed later. The octacosane available is made by the coupling of bromo-tetradecane via the Wurtz reaction and this produces a slight bromine impurity in the wax. Bromine and other impurities can be successfully removed by recrystallization in tetrahydrofuran (THF). Madon and Taylor (26), Stenger and Satterfield (27), and Matsumoto and Satterfield (28), among others, have addressed the topic of sulfur poisoning of Fischer-Tropsch catalysts. If paraffin wax is used, sulfur may be present in small quantities and it is important to remove it to avoid affecting the catalyst performance.

Wax produced via the Fischer-Tropsch synthesis is generally

very low in poisons and, from this point of view, is very good as a carrier liquid. Waxes with a distribution of molecular weights and relatively low levels of impurities include FT-200 and FT-300, which are hydrotreated SASOL fixed-bed waxes, used by Mobil (13,14); Amoco Parowax, used by Dictor and Bell (7,8); and Krupp wax, used by Calderbank, et al. (29). The major drawback is the complication of chromatographic analyses.

Trapping

Product Splitting:

Products are divided between the outlet vapor stream and the slurry liquid. Those which leave as vapors are collected in a trapping system, often with two or three traps kept at different temperatures (1,5). It is usually impractical to collect all products in a single trap, although Schulz et al. (30) trapped all hydrocarbon products except methane from a fixed-bed reactor in one trap at $-190^{\circ}C$. Anderson (31) recommends the use of a two-trap system, which Huff and Satterfield (1), among others, have adopted. However, the use of multiple traps introduces several difficulties.

As a result of products splitting between traps, accurate carbon number distributions are difficult to generate. This is mostly caused by the small quantities of liquid products relative to gas flow at synthesis gas conversions less than about 60 or 70%. For example, when 50 % of a 1:1 H_2/CO feed fed at 1 liter/min, is converted over a period of eight hours, the

combined hot and cold trap organic-phase yields are between 10 and 40 grams, representing 2 to 10 wt% of the material fed to the reactor. The hot trap, held at 80 to 90°C, generally condenses C_{10} and heavier products, while the cold trap, 2 to 4°C, condenses C_5 to C_{12} products, with light gases remaining uncondensed. A Schulz-Flory diagram typically shows two C-number distributions, with a "breakpoint" in the region of C_7 to C_{13}. Any loss of liquid products in either trap by splatter or by adhesion to the trap wall may lead to "bumps" or "dips" on the Schulz-Flory diagram in the region of the break point.

Figures 2a, b and c show irregularities that have occurred from time to time with each of several experimental systems. Figure 2a shows the C_1-C_{20} distribution from a run with a bubble column used at Mobil and a run by Bukur, et al. (32). Figure 2b shows product from one of our studies. The C_{25}-C_{40} distribution is shown on Fig. 2c for product from an Exxon fixed-bed unit (26), and the Mobil bubble column. Bukur et al. (32) suggest that the dip they observed near C_6 in this run was due to product evaporation. Mobil did not attempt to explain the irregularities they observed in the volatile products or in the wax fraction; however, their analysis was carried out by field-ion mass spectroscopy (FIMS), and Kuo (14) reports that response factors were unknown for the hydrocarbons analyzed. Madon and Taylor (26) indicated that they were unable to explain the bump they observed in the wax products, but they detected no deviations from linearity in the response factors of C_{30}^+ hydrocarbons in

their chromatograph.

We have performed a sensitivity analysis on flow and trapping conditions to determine if they affect the size or location of irregularities. We have been unable to account for the bumps by parametrically varying the amounts of collected hot or cold aqueous or organic phases, or by varying the outlet gas flow rates to account for possible inaccuracies in our measurements. We believe that only a small portion of the bumps may be caused by the flow conditions. We suggest that a larger contribution is made by the effects of changing reactor conditions. If sufficient time is not allowed to ensure steady-state composition of outlet vapors before a material balance is made, products volatilized by a drop in reactor pressure or increase in temperature may cause bumps to appear. A dip can be caused by a change in the opposite direction.

Loss of products while draining traps presents an additional problem because the viscosities and densities of the aqueous and organic phases in the cold trap are markedly different (33). This can result in a sudden rush of products into the collection container when the aqueous/organic interface is reached during product draining.

One additional consequence of product splitting between traps is that the molecular weights of hydrocarbons added to the feed or to the reactor, for example to study secondary reactions of 1-alkenes, should be chosen to minimize such splitting. Hanlon and Satterfield (34) report that components which split

between hot and cold traps or between the cold trap and the non-condensable stream are difficult to account for in the subsequent analysis. They added several 1-alkenes to a slurry reactor and observed little incorporation of the alkene into growing carbon chains, except for 1-hexene. They attributed the seemingly anomalous behavior of 1-hexene to an experimental artifact; its division between the cold trap and the vapor stream.

Trap Temperature Limits

Both hot and cold traps have limits on the highest and lowest temperature at which they can be maintained without causing flow problems. Too low a temperature in either trap causes solidification of condensed products and plugging of the trap drains. Too high a temperature results in vaporization of components, which may then condense in unheated lines downstream. The carry-over of products from the cold trap into the non-condensable stream is the major problem here, because these products could be trapped downstream in an on-line gas chromatograph.

Slurry Sampling

Slurry wax withdrawal has been reported to be difficult by Bukur et al. (32). It appears from another report (5) that their slurry sampling loop is similar to that devised by Huff and Satterfield (1). Figure 3 is a schematic diagram of this sampling loop. To withdraw a sample, the reactor is pressurized with helium through valve 1 and flow in and out are halted. The slurry sample section is a short section of tube attached to the

reactor by a port on the reactor head. To withdraw wax, the impeller is turned off and the contents allowed to settle for 10 to 15 minutes. Then valve 2, between the reactor and slurry tube, is opened and the pressure difference forces a sample into the tube. The valve is closed and valve 3 on the other end of the slurry sample tube and open to the atmosphere is opened and the sample expelled. The short tube section can be purged with helium to remove traces of previous slurry samples.

Unfortunately, the pressure difference which is used to drive the sample into the slurry loop also disturbs the stagnant fluid in the reactor. This can cause catalyst particles to be entrained by the slurry sample leading to uncertainty about the amount of catalyst remaining in the reactor. We have avoided this problem by using a long-stem Pasteur pipet to withdraw wax samples through an open port on the head of the reactor. Helium is bubbled slowly through the reactor during this procedure to avoid diffusion of air into the slurry, as this could cause re-oxidation of the catalyst.

Runs lasting more than one hundred to two hundred hours may cause sufficient high molecular weight products to accumulate to fill the reactor. The frit through which the outlet vapor stream passes extends about 2 cm down into the one-liter reactor. If it becomes submerged in slurry wax, extremely high rates of wax carry-over and high pressure drops are observed.

CONTROL CONSIDERATIONS

Reactor temperature, pressure, and space velocity are controlled by the operator. While pressure control is fairly straightforward, flow and temperature control merit some discussion.

For uniform temperatures throughout the reactor, it is important to control the slurry temperature directly, rather than by controlling the heating mantle temperature. A steady-state temperature difference exists between the heating mantle and the reactor contents, and at low slurry temperatures (232 to 248^{o}C) this difference can be much as 60^{o}C (24). Matsumoto indicates that temperature differences between the heating mantle and reactor contents decrease to about 20^{o}C when the contents are kept at temperatures near 300^{o}C.

Our temperature controllers (LFE 2000) generally require about 20 to 30 minutes to adjust the liquid temperature. We have observed some oscillation around the set-point or temperature drift if the jacket temperature, rather than the liquid temperature is the controlled variable.

Another temperature control consideration is the reflux of volatile products caused by condensation on the reactor head. Autoclave heating mantles do not generally extend to the top of the reactor, but leave several centimeters unheated. Studies performed in our laboratory (33,35) showed temperature differences of 40 to 100^{o}C between the liquid contents and the vapor in the reactor head space, with liquid temperatures between

232 and 263°C. This suggests that heavier products which might otherwise leave as vapors condense and are returned to the slurry liquid.

The other controlled variable of interest is flow rate, or space velocity. Mass flow controllers offer significant advantages over most other methods. In particular, the response of mass flow meters is linear with flow rate. Control by a pneumatic control valve in conjunction with a differential pressure (DP) cell (1) requires calibration curves for each synthesis gas composition.

CATALYST-RELATED CONSIDERATIONS

Catalyst Sizing

Diffusional Limitations:

The temperatures of interest in the Fischer-Tropsch synthesis are up to about 300°C. In general, we use ASTM mesh 170 to 270 particles (53 to 90 μm in diameter). Thiele modulus calculations for United Catalysts C-73 fused magnetite, Ruhrchemie precipitated iron, PETC unalkalized precipitated iron, and several cobalt catalysts indicate no internal diffusional limitations at these conditions. Higher temperature experiments, such as those reported by Matsumoto and Satterfield (21), may require use of ASTM 270 to 325 mesh particles, 45 to 53 μm in diameter.

Mass transfer limitations result in erroneous kinetic models and apparent activation energies are typically about one-half

those reported for kinetically controlled reaction (36). For example, a recent study by Fujimoto and Kajioka (37) reports an activation energy of 50 kJ/mol on a 150 mesh ruthenium catalyst slurried in ethylcyclohexane at 220 to 270°C. Their activation energy may be compared to a value of 117 kJ/mol, reported by Kellner and Bell (38), among others. Because of the high activity of ruthenium relative to iron, and because their experiments were conducted at temperatures up to 270°C, it is likely that some diffusional resistance was encountered by Fujimoto and Kajioka.

Entrainment and Plugging:

Finely divided catalyst particles may be entrained by the gas flowing through the reactor. To prevent this, we recommend that the outlet stream be passed through a stainless steel frit, 10 to 60 μm, before entering the trapping system. Such frits may be plugged by small catalyst particles or by small carbon particles formed via the Boudouard reaction (33).

$$2\ CO \longrightarrow C\ (s) + CO_2 \qquad (1)$$

Plugging of the outlet frit can be observed by measuring the pressure drop across the reactor. Reactors should have pressure gauges both at the reactor inlet and outlet. If these gauges indicate the same pressure while the reactor is operating, plugging of the frit can be assumed to be insignificant. We have observed the pressure drop to increase to as much as 70 kPa with increasing time-on-stream and with increasing space velocity (33). Plugging problems may be accentuated in larger frits,

since the pores in such frits are large enough to accommodate catalyst particles. Huff (33) suggests that use of alonized tubing minimized occurrence of the Boudouard reaction on stainless steel surfaces, preventing some free carbon formation.

It is, therefore, important to consider the trade-off between use of large and small particles. Small particles do not cause diffusional limitations but may cause downstream plugging. In contrast, larger particles will probably not cause plugging, but may be subject to mass transfer limitations, particularly at high temperatures.

It is also necessary to suspend the catalyst in the slurry medium and to separate the catalyst from slurry wax, which may be withdrawn as a product stream. These considerations are treated in the following section.

Catalyst Density

Precipitated catalysts are generally of somewhat lower density than fused magnetite catalysts. We consider bulk density to be the density of powdered catalyst in air, measured, for example, by comparing the weights of a volumetric flask full of catalyst and empty. Solid density may be measured by filling a volumetric flask with catalyst, then adding water dropwise until the catalyst pores are filled. The known weight and volume of the added water allow determination of the catalyst solid density, as well as the porosity of the catalyst. Our measurements indicate bulk densities of crushed precipitated Ruhrchemie and PETC catalysts, 53 to 90 μm, near 0.7 grams/cm^3

and solid densities near 2.7 grams/cm^3. The bulk-density value is very close to that of Fischer-Tropsch wax at reaction conditions, which Stern et al. (39) estimate to be about Ø.68 grams/cm^3 using a correlation reported by Calderbank et al. (29) for Krupp wax. For high melting waxes, catalyst separation may be difficult because of high viscosity. Separation may be either continuous, to remove wax from the reactor and prevent flooding, or batchwise, to allow analysis of used catalyst.

Catalyst Concentration Gradients in Bubble-Column Reactors:

In a mechanically-stirred autoclave, the slurry composition, including catalyst concentration, may be held constant by operating at sufficiently high impeller speed. In contrast, in a bubble column, in which agitation is provided only by sparged gas, a vertical catalyst concentration gradient may develop at low agitation rates or high viscosities.

Mobil experienced catalyst settling in their bubble-column reactor (13,14). Typically, Mobil started-up with about 2Ø wt% of catalyst in their slurry. Significant catalyst concentration gradients were observed during several of their experiments. At the top of the reactor, about 5 to 1Ø wt% of the slurry was catalyst, while at the bottom of the reactor as much as 25 wt% of the slurry was catalyst. In extreme cases, these gradients caused termination of the run. The high concentration of catalyst near the bottom of the bubble-column led to temperature gradients of 8 to 1Ø^{o}C vertically in the reactor. When these problems occurred, experiments were ended prematurely, sometimes

after only 200 to 300 hours-on-stream. Mobil reported the solid density of their catalyst was 2.6 grams/cm^3 and estimated their wax density as 0.67 grams/cm^3 using a correlation reported by Deckwer et al. (40).

Matsumoto (24) also reports a 10 to 12°C temperature gradient for experiments conducted in a mechanically-stirred slurry reactor at 285 and 310°C, using a fused magnetite catalyst with a solid density of 3.2 grams/cm^3. The carrier fluid for these studies was octacosane with an estimated density of 0.68 grams/cm^3. Matsumoto found that, in a one liter stirred autoclave, it was necessary to increase the impeller speed from 620 to 860 RPM to remove the temperature gradient when 15 wt% of catalyst was suspended in the slurry medium.

Catalyst Recovery:

Pot liquid withdrawal during experiments is often performed to prevent reactor over-filling (32,33). Mobil reports in detail on their bubble-column reactor, which included an external wax-filtration assembly (13,14). This unit was intended to remove catalyst from the wax which was produced in the synthesis. This wax was then fed to a second-stage ZSM-5 reforming unit. Initial designs of this filtration unit were unsuccessful. Modifications to the equipment were necessary to prevent severe plugging of the filter by wax and catalyst and excessive entrainment of catalyst in the filtrate. Several techniques were attempted to improve the separation of catalyst in the filtration unit. The most successful were magnetic separation, the addition of a lower

molecular weight alkane (hexadecane) as a "thinner", and the use of higher temperatures during filtration.

Catalyst separation from end-of-run slurries by a combination of hot-filtration and Soxhlet extraction has been reported by Pennline et. al. (10) at PETC. They report more than 90 % recovery of an iron/manganese catalyst from their slurry.

Because of the high molecular weight and corresponding high melting point of octacosane (MP = 64.5^{o}C), hot filtration of octacosane slurries can be difficult. However, the benefits of using octacosane, as compared to lower molecular weight wax, are substantial.

High-density catalysts are relatively easy to separate from slurry wax. The United Catalysts C-73 fused magnetite catalyst has a solid density of about 3.2 grams/cm^{3}, as compared to a wax density of about 0.68 grams/cm^{3}. Much of the recovery of this catalyst can be achieved simply by allowing the magnetite to settle in the molten wax, before draining from the reactor. Further separation is accomplished by toluene extraction in a Soxhlet thimble.

Catalyst Pretreatment

A number of studies have shown the importance of pretreatment to catalyst performance, among others, Shultz et al. on precipitated and fused iron and on cobalt (41); Pennline et al. (10) on iron/manganese oxides; Zarochak et al. (9) on precipitated iron; and Bukur et al. (32) on precipitated iron. Pretreatment is a complex process and is difficult to perform

repeatably.

Huff and Satterfield (1) have described a reduction unit for United Catalysts C-73 fused magnetite ammonia synthesis catalyst. This is a fluidized-bed reactor kept at a maximum temperature of about 400°C. If the temperature goes above about 410°C, the catalyst sinters and shows low activity. Such a temperature increase can occur readily because of the highly exothermic nature of the reduction. At the end of reduction, the pyrophoric iron is charged under inert gas to a slurry reactor through a side port.

Mobil (14) has reported that their iron/copper/potassium type I-B catalyst could be activated in synthesis gas in situ, but that the same catalyst added to the reactor after several hundred hours-on-stream could not be activated at the same conditions. This suggests that some poorly understood start-up phenomena are involved in iron catalyst pretreatment and is additional evidence that pretreatment should be described completely and followed exactly to ensure repeatability of catalyst performance.

Donnelly and Satterfield (22) and Zimmerman et al. (6) performed detailed studies of a precipitated iron Ruhrchemie catalyst and observed different stability behavior depending on the method of pretreatment. Pretreatment of the precipitated iron Ruhrchemie catalyst may require adapting fixed-bed reduction protocols to a slurry reactor. The major advantages offered by in situ reduction are improved temperature control and the

elimination of the procedure for charging a reduced catalyst to the slurry reactor after external reduction.

The high reduction temperatures required for some cobalt catalysts and fused magnetite make it impractical to reduce these catalysts in the slurry reactor, as significant volatilization of the slurry wax would occur at these conditions.

Measurements at Steady-State

To determine the effects of operating conditions on catalyst performance, data at steady-state are needed. Satterfield et al. (42) report that the oxidation state of a fused magnetite ammonia synthesis catalyst introduced to the reactor as reduced α-iron does not reach steady-state for several days.

Data on deactivation of the catalyst with time-on-stream are also needed as part of any evaluation of performance characteristics. Changes in both activity and selectivity of precipitated iron catalysts has been observed by Donnelly and Satterfield (22). Such changes may be caused either by changes in the catalyst oxidation state and surface composition or by loss of surface area by coking or sintering.

A second facet of ensuring steady-state behavior is allowing adequate time after reactor conditions are changed to ensure that the volatile product stream is representative of the current reaction conditions. Huff and Satterfield (3,43) report that several days may be required to assure such performance. Decrease in reactor pressure or increase in temperature result in flashing of products to the overhead stream, which will give

misleading data.

Accumulation of heavy products in slurry wax also constrains the carbon number range of volatile products that is useful for data analysis. If insufficient time is allowed, data for high carbon numbers in the overhead product will "tail off" on a Schulz-Flory diagram, due to the solubilization of heavy products in the slurry medium. For typical conditions only about ten hours may be required after reactor start-up to ensure that gaseous products, below C_{10}, are accurately measured overhead; however, about 300 hours may be required for the overhead stream to include representative concentrations of products up to C_{20}.

Catalyst Performance Gradients in Fixed-Bed Reactors

The integral nature of fixed-bed reactors may cause an activity profile along the catalyst bed. The gases leaving the reactor, particularly the H_2O component, are much more oxidizing than the gas at the inlet. As a result, the oxidation state of the catalyst may vary along the reactor, the catalyst being more reduced at the inlet and more oxidized at the outlet. With an iron catalyst activity is decreased and product selectivity may be somewhat altered.

In a fixed-bed reactor, sulfur compounds in synthesis gas adsorb onto the catalyst by a chromatographic effect, resulting in a concentration profile (26). Catalyst performance can be markedly affected by sulfur, (26,27,28) so data from a fixed-bed reactor with a sulfur gradient are very difficult to analyze.

PRODUCT ANALYSIS

We have found that gas chromatography (GC) is an appropriate technique to analyze carbon number distributions of products up to about carbon number 50, and isomer distributions of lighter products. Schulz and co-workers (30,44) and Egiebor et al. (45) use mass spectroscopy to analyze for isomer distributions, as well as some carbon number distributions.

Heavier products, up to about carbon number 100, have been analyzed by Stenger et al. (23) using gel permeation chromatography (GPC). Detailed discussions of the use of GPC, high-performance liquid chromatography (HPLC), mass spectrometry (MS), and nuclear magnetic resonance (NMR) for characterization of Fischer-Tropsch waxes are given by Sturm et al. (46), Shah et al. (47), and Kuo (48).

Shah's group at UOP tested Arge fixed bed wax, Mobil wax from their bubble column pilot plant, and waxes produced by Air Products and Union Carbide using cobalt catalysts. They found that GPC and NMR analyses of wax composition agreed well up to C_{90}. They also report that either electron-impact mass spectroscopy (EIMS) or field-ion mass spectroscopy (FIMS) were good techniques for products up to about C_{55}, but that it was difficult to solubilize heavier products for analysis by these techniques. In addition, they report that fractionation of waxes into discreet boiling point ranges by distillation caused thermal cracking, which affected the apparent compositions. UOP was able to analyze products up to about C_{250} using a combination of

techniques.

Kuo (14) reports that GPC was found not to be a good method for wax analysis because of problems in choosing appropriate column packings. Using a modified GC technique, Mobil characterized waxes up to about C_{60}. They also used FIMS to analyze products in that range and found good agreement between the two techniques. Mobil was able to analyze products up to about C_{90} using FIMS.

Oil and Wax Analysis

Our analytical techniques have already been described. We obtain similar chromatograms for volatile organic products and for waxes withdrawn from the slurry, although different chromatographic techniques are used. Most of the issues discussed below are applicable to both analyses, but those which mention carbon numbers greater than 20 are restricted to wax analysis.

There are several salient points to consider in interpreting the carbon number distributions. First, it is very difficult to determine isomer distributions of heavy products. The boiling points of isomers of heavier products tend to be very close to each other. Table 2 lists the boiling points of C_8 products, typically observed in the Fischer-Tropsch synthesis. The boiling points of cis- and trans-2-octene are indistinguishable from that of octane. In addition, the polarities of these components, and hence their retention times by the liquid stationary phase (dimethyl silicone) in the GC column are nearly identical. Thus,

2-octenes and octane elute from the column at essentially the same time. This results in poor resolution, in spite of the high number of theoretical plates in the column (about 190,000 for a 50 meter HP 19091Y-105 column). Care must be taken in developing chromatographic protocols to ensure maximum resolution of the compounds of interest.

A second difficulty in determining intrinsic isomer distributions is the occurrence of secondary reactions in the reactor, including hydrogenation, isomerization, and, possibly, secondary incorporation of primary products into growing carbon chains. Heavier products remain in the slurry longer and, therefore, may be more likely to undergo secondary reactions. These reactions lead to decreases in the 1-alkene/alkane ratio and increases in the 2-alkene/1-alkene ratio at higher carbon numbers (22). This means that, at high carbon numbers, it is not possible to decouple products formed by primary Fischer-Tropsch synthesis from those formed by secondary reactions. The lower residence times of light products may make it possible to determine selectivity of the primary synthesis more readily for them.

Matsumoto (24) has discussed some of these issues. Some peaks "cross" the alkane peak at high carbon numbers. At low carbon numbers, a particular isomer may elute after the n-alkane has eluted, while at higher carbon numbers the analogous isomer will elute before the n-alkane. Matsumoto indicates that this makes resolution of isomers in the region C_{36} to C_{38} intractable

and that the apparent yield of n-alkanes in this region are higher than should be observed. Consideration of the issues discussed above suggests that it is unwise to treat any isomer distributions above about C_{10} or C_{12} as representative of the primary synthesis.

Slurry wax analysis presents an additional challenge. The use of a paraffin wax with a distribution of molecular weights as a start-up medium poses a problem in detecting carbon number distributions of products. For our studies, we have generally used octacosane as the initial charge. The carrier thus elutes as a single peak on the chromatogram, which is readily excluded from further analysis. However, waxes such as FT-200 or FT-300 have a broad distribution of hydrocarbons, each eluted as a separate peak on the GC. It is extremely difficult to decouple the products of the synthesis from the slurry charge when such a wax is used as the start-up medium.

This problem may also affect volatile products, if a low boiling paraffin wax is used as a slurry wax. Dictor and Bell (7,8) used Parowax (C_{20} to C_{45} linear alkanes) as a carrier and report that traces of C_{16} to C_{19} alkanes were present. These lighter components restrict the range of carbon numbers which can be used in GC analysis and limit the temperatures which can be used for the synthesis. At high temperatures, some of the light ends of the Parowax would be carried over in the volatile products, confusing the analysis.

Waxes produced at high temperature synthesis may cause

additional difficulties. Matsumoto (24) reports that the GC baseline for high temperature waxes is much less stable than that for low temperature waxes. Figure 4 shows a large degree of noise in the baseline in the range C_{28} to C_{38} for the wax produced at 310°C, relative to that produced at 232 to 263°C.

Non-Condensable Gas Analysis

In GC analyses, ethene and ethane, and propene and propane are difficult to split from each other. These components all elute rapidly from the GC column, and it is important to maintain a combination of carrier gas flow rate and column temperature which can separate all components. If the peaks do not resolve correctly, the apparent alkene/alkane ratios will be incorrect.

Hydrogenation and isomerization of 1-butene proceed quickly on reduced fused magnetite (49). It is possible that, for very high rates of secondary reactions, the selectivity of the light products might be determined by diffusional limitations, rather than by kinetic considerations. It is also important to remember that equilibrium isomer distributions constrain selectivity. The approach to equilibrium should be shown when secondary reactions are being considered.

In addition to hydrocarbons, CO, CO_2, H_2, and H_2O are analyzed by GC. We will consider the analyses of CO, CO_2, and H_2 in this section, and deal with aqueous products separately. Non-dispersive infra-red spectroscopy (NDIR) is a good alternative to chromatography for determining CO and CO_2 concentrations. Mobil (13,14) used NDIR to monitor start-up activity of their

catalysts, demonstrating that transient behavior can be monitored by this type of analysis. If such a system is available, it provides a good method to supplement GC data.

Hydrogen analysis by chromatography offers some special features of interest. Particularly, the response of H_2 in a thermal conductivity detector (TCD) may be a "negative peak", if helium is used as a carrier. Huff et al. (20) discuss this matter in detail and show that a palladium hydrogen transfer system with a nitrogen carrier can be used in a refinery-gas analysis chromatograph to resolve hydrogen and produce a valid response.

Aqueous Components

It is critical that the amount of water produced by the synthesis be determined accurately if kinetic models are to be developed. A recent study (50) showed that superior kinetic models can be developed to include synthesis inhibition by water in a system which allows chromatographic analysis of aqueous components. It is, however, not easy to measure water concentration accurately. We use a Hewlett-Packard 5710 gas chromatograph with a 3 meter Tenax packed column to analyze our aqueous phases, which are predominantly water with small amounts of alcohols, aldehydes, and ketones. Water is detected in the non-condensable gas and in both hot and cold trap aqueous phases. Unfortunately, the water peak tends to tail somewhat, and this makes water analysis more difficult than hydrocarbon analyses, which give very sharp peaks on our HP 5880 chromatograph.

MATERIAL BALANCE CRITERIA

There is perhaps no more subjective problem in experimental design than choosing criteria for acceptability of data. In particular, the criteria for closure of a material balance over the reactor varies from laboratory to laboratory. Our procedure is to accept as valid material balances in which 97 to 103 wt% of the oxygen fed to the reactor as CO is recovered as CO, CO_2, H_2O, and oxygenated hydrocarbons. Typically, oxygen closure is better than that of hydrogen or carbon, because some hydrocarbon products accumulate in the slurry wax (4,33). These criteria are not rigid. Some empirical knowledge and the judgement of the researcher is occasionally used to discard a material balance that meets this criterion or to accept a material balance that fails marginally.

Only at very high conversions do the products condensed in the hot and cold traps affect the closure of a material balance on oxygen. Low water-gas-shift activity makes the amount of water trapped off considerably more important in closing an oxygen balance.

CONCLUSIONS

We present here a detailed examination of experimental considerations in the slurry-phase Fischer-Tropsch synthesis. Decisions regarding catalyst sizing and pretreatment, slurry medium, duration of experiments, and analytical techniques may all affect reported kinetic and selectivity data. We suggest

that some of the differences observed in catalyst performance as reported in the literature may be resolved in the light of careful examination of the associated experimental systems.

Table 1

Chromatograph Information

Chromatograph	Detector	Column(s)
HP 5880	FID	Gas and oils: HP 19011Y, 50 meter dimethyl silicone capillary Wax: Supelco SPB-1 30 meter methyl silicone capillary
HP 5710	TCD	3 meter 60/80 mesh Tenax packed in glass
Carle 111-H	TCD	1A: 4.6 meter 28 % bis(2-ethoxyethyl) adipate + 4.7 % squalene + 2 % carbowax 1540 on Chromosorb PAW 1B: 1.8 meter 3.1 % Carbowax 1540 on Porasil C 2: 1.4 meter HayeSep Q 3: 2.1 meter molecular sieve 13X 4: 1.8 meter 20 % SF96 on Chromosorb PAW HTS palladium cylinder used to separate H_2 from helium carried

Table 2

Normal Boiling Points of C_8 Compounds

Compound	Normal Boiling Point, °C
octane	125.7
1-octene	121.3
2-cis-octene	125.6
2-trans-octene	125
2-methylheptane	117.6
3-methylheptane (d)	115 - 118
3-methylheptane (dl)	119
3-methylheptane (l)	117 - 118
4-methylheptane (l)	117.7

Source: CRC Handbook of Chemistry and Physics, 62nd Edition, R.C. Weast, ed., CRC Press, Inc., Boca Raton, Florida (1981).

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Figure Captions

Figure 1 Mechanically-Stirred Reactor System

Figure 2 Irregularities on Schulz-Flory Diagrams: (a) Volatile products from Mobil precipitated iron catalyst in bubble column (+) and Texas A&M precipitated iron catalyst in fixed-bed (■) (b) Volatile products from iron/manganese catalyst studied at MIT. (c) Wax products from Mobil precipitated iron catalyst in bubble column (+) and Exxon precipitated iron catalyst in fixed-bed. (■)

Figure 3 Schematic of Slurry Sampling Loop on Mechanically Stirred Slurry Reactor at MIT

Figure 4 Baseline Noise for Chromatograms of Wax Produced at High Temperature (Matsumoto and Satterfield, Energy & Fuels, 3 (1989) 249

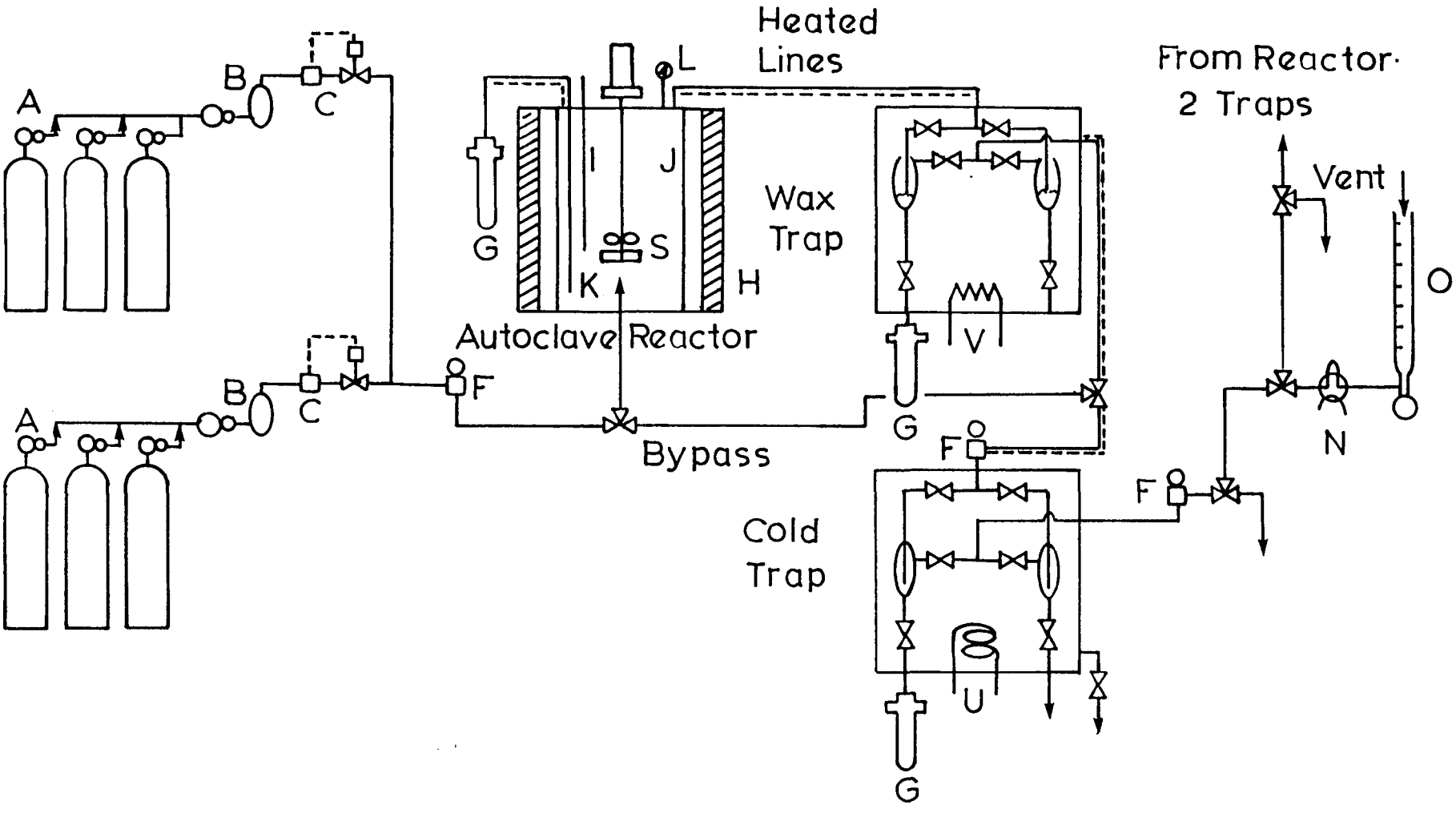
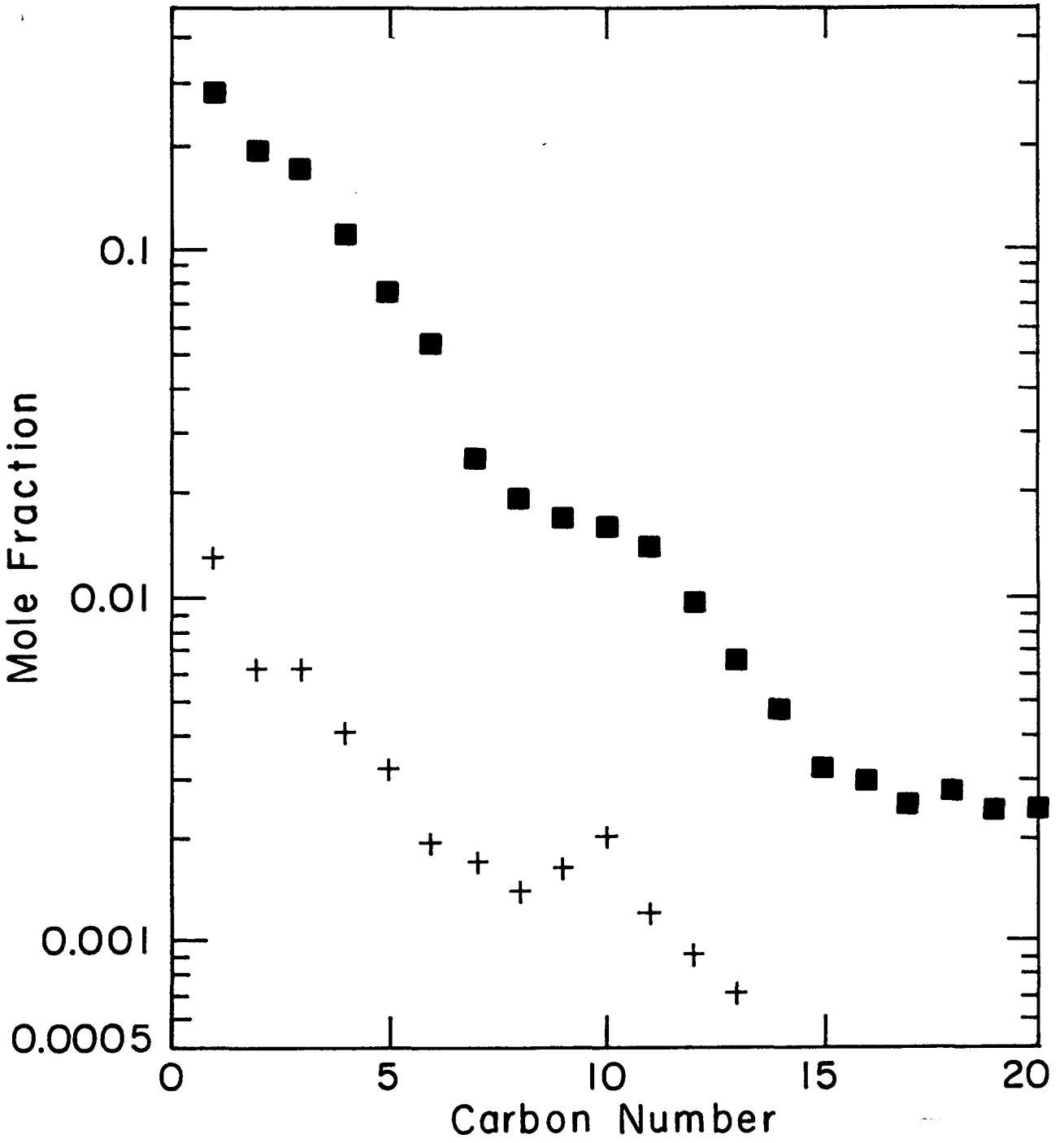
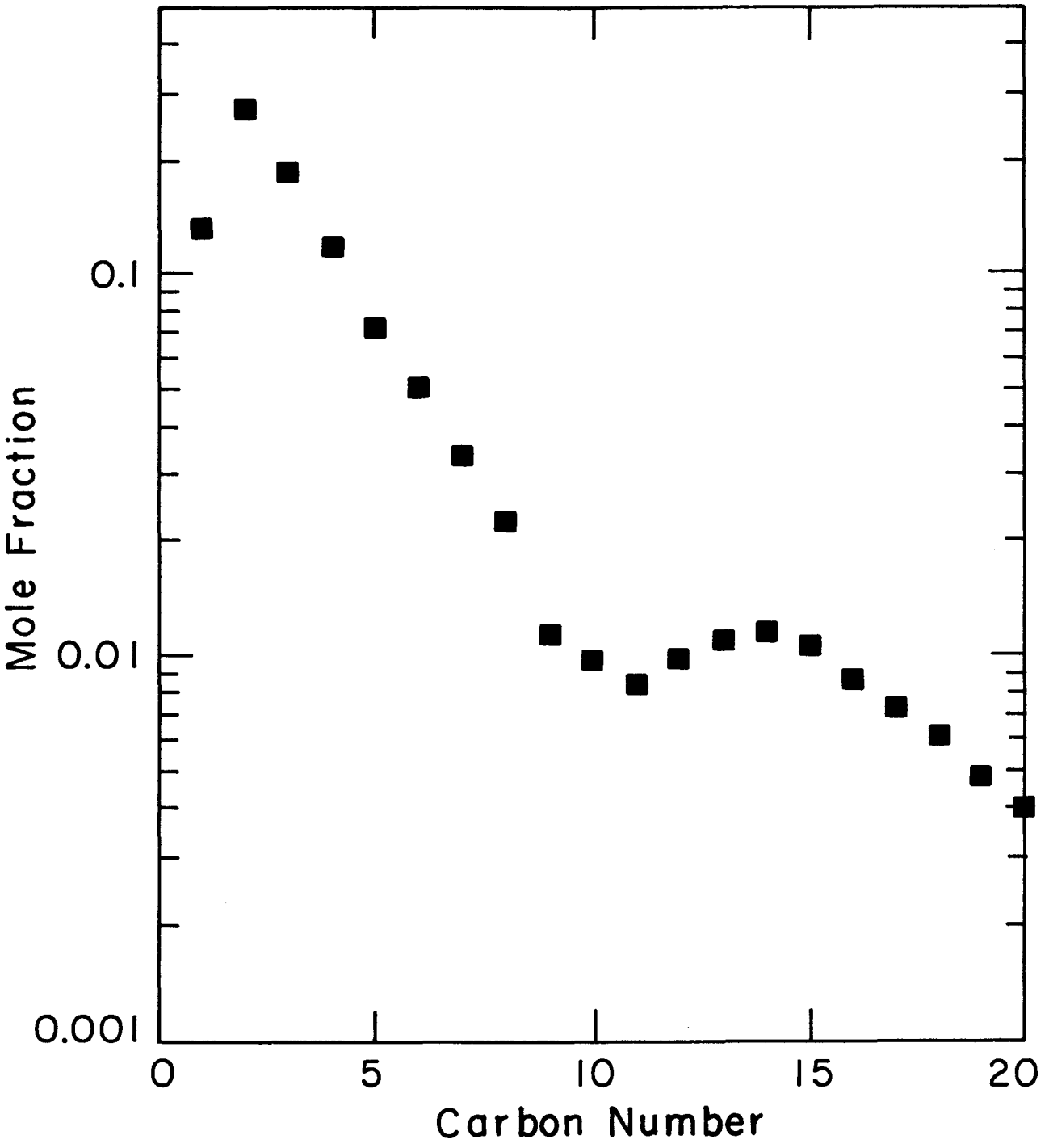


Figure 1: Slurry Reactor System: A, Pressure regulator; B, Filter/drier; C, Mass flow controller; F, Back pressure regulator; G, Sample bottle; H, Electric furnace; I, Thermocouple; J, Baffle; K, Magnedrive stirrer; L, Pressure gauge; N, Gas sample valve; O, Soap bubble meter; U, Refrigeration coil; V, Strip heater (after Huff and Satterfield, 1982).



2a


Mole Fraction
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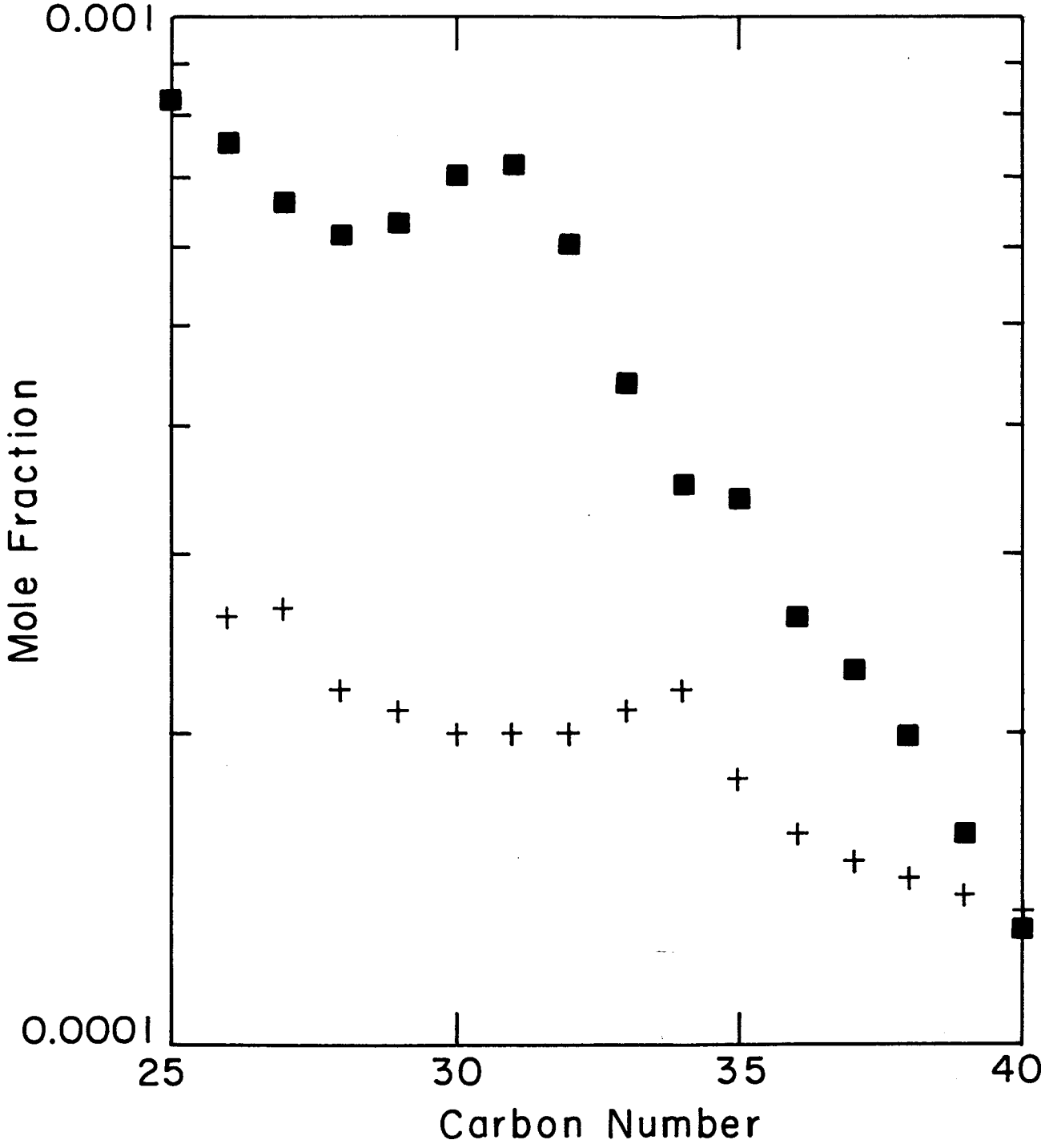
0.01
0.001
0
5
10
15
20
Carbon Number



2c

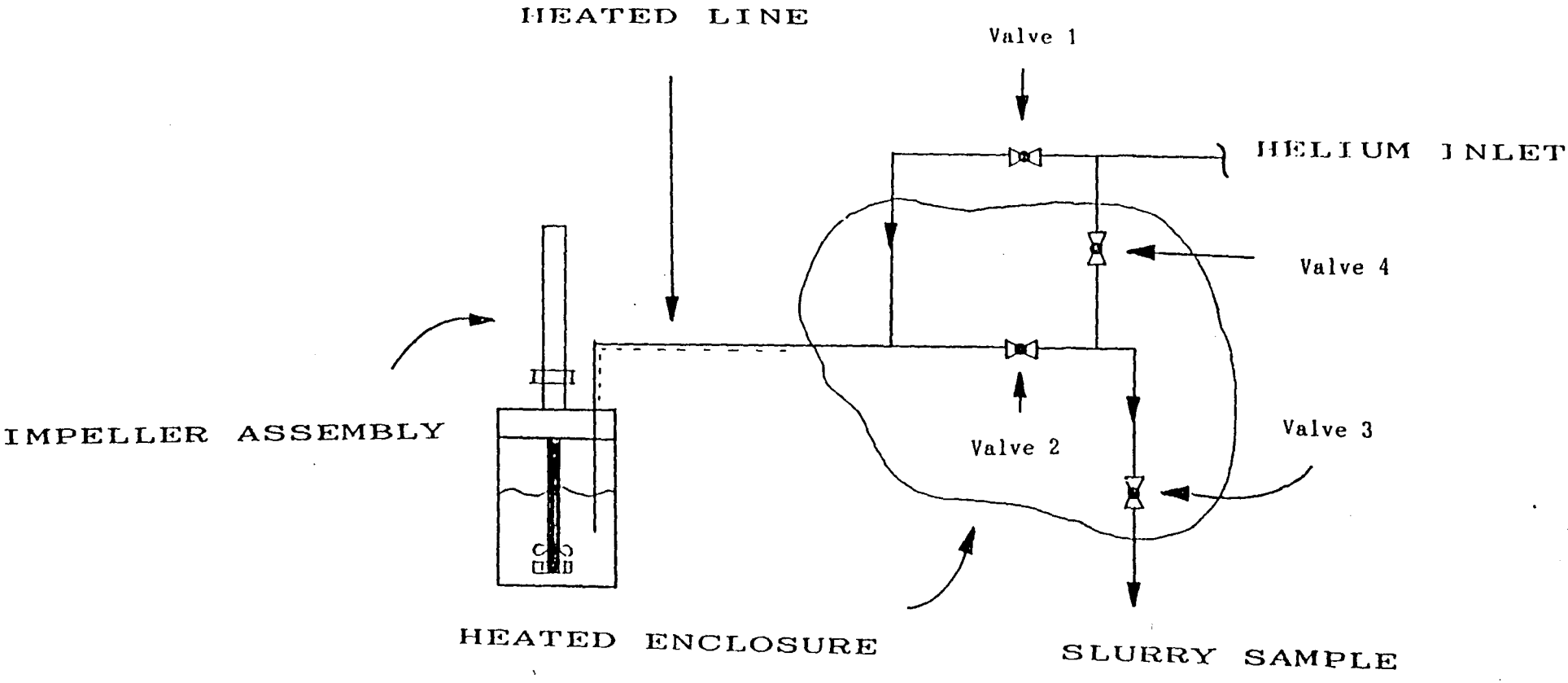

HEATED LINE
Valve 1
HELIUM INLET
Valve 4
IMPELLER ASSEMBLY
Valve 2
Valve 3
HEATED ENCLOSURE
SLURRY SAMPLE

Fig 3

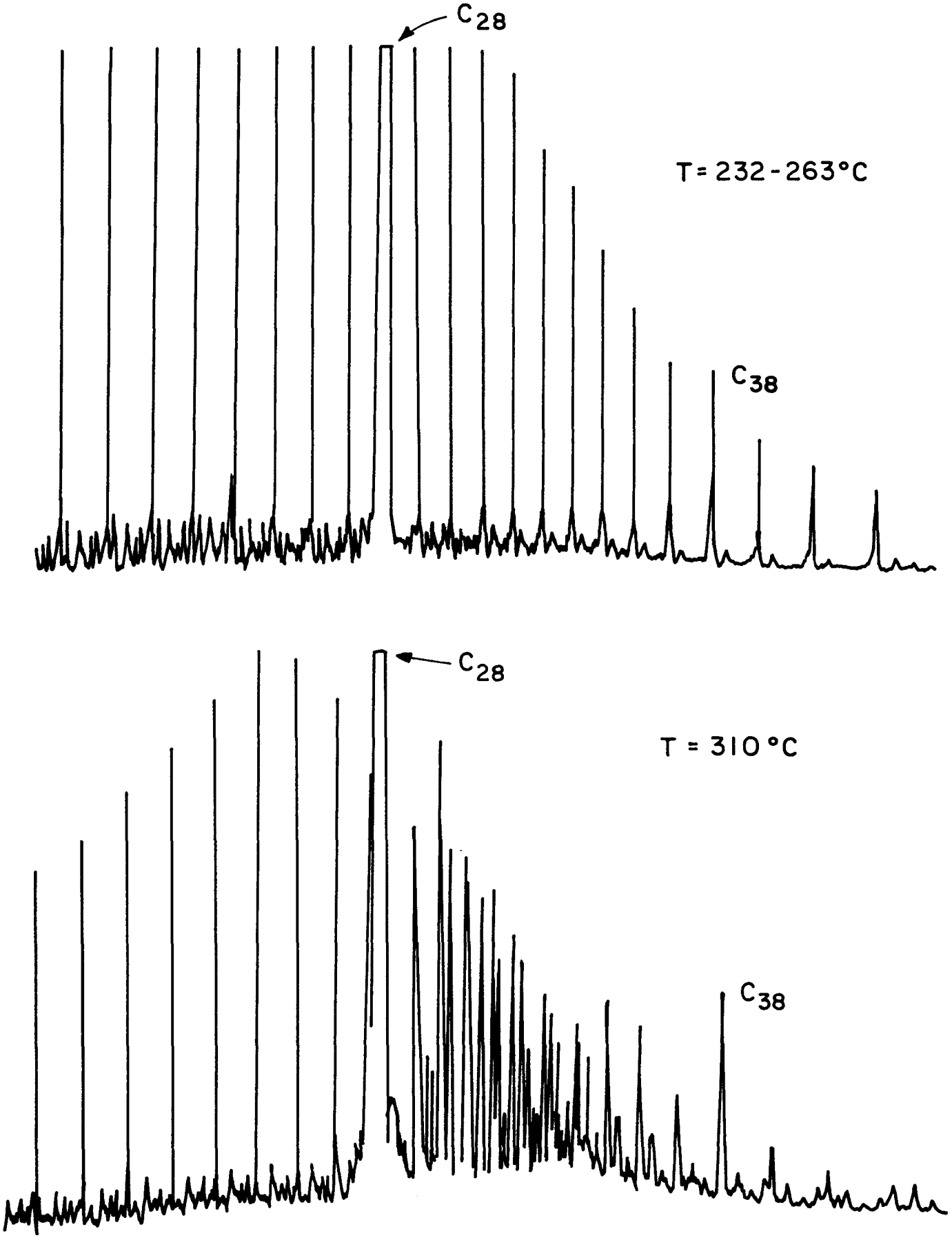


FIG. 4