II. EXPERIMENTAL

II-A. Synthesis of ^{14}C Labeled Compounds

As part of the experimental program to complete the radiotracer study of the role or promoters in iron based Fischer-Tropsch catalysts, a number of labeled ^{14}C alcohols, alkenes, and alkanes had to be synthesized. With the exception of a few cases, $Ba^{14}CO_3$ is the most convenient and economical commercially available source of ^{14}C.

One of the widely used methods for the introduction of ^{14}C into organic compounds is by the addition of ^{14}C-labeled carbon dioxide to the Grignard Reagent followed by acid hydrolysis (equation II-1).

$$RMgX + {}^{14}CO_2 \longrightarrow R^{14}C\,O_2MgX \longrightarrow R\text{-}{}^{14}C/O_2H \qquad [II\text{-}1]$$

In turn this acid can be reduced by means of $LiAlH_4$ to give an alcohol (equation II-2).

$$R\text{-}{}^{14}CO_2H + LiAlH_4 \longrightarrow R\text{-}{}^{14}CH_2OH \qquad [II\text{-}2]$$

The radioactive labeled alcohol ($R\text{-}{}^{14}CH_2OH$) can be used in the following three ways:

a) direct injection into the reactor.

b) conversion to an alkyl halide which in turn can be used for the synthesis of higher carbon number compounds (equation II-3).

$$R\text{-}{}^{14}CH_2OH \xrightarrow{PBr_3} R\text{-}{}^{14}CH_2Br \xrightarrow{Mg} R\text{-}{}^{14}CH_2MgBr \xrightarrow{R'C(=O)H} R\text{-}{}^{14}CH_2C(OH)\text{-}R' \qquad [II\text{-}3]$$

c) conversion of the alcohol to alkenes or alkanes (equation II-4).

$$R\text{-}CH_2\text{-}{}^{14}CH_2OH + (Ac)_2O \longrightarrow R\text{-}CH_2\text{-}{}^{14}OAc \xrightarrow{400^{\circ}C} R\text{-}CH = {}^{14}CH_2 \xrightarrow{H_2,\ Cat.} R\text{-}CH_2\text{-}{}^{14}CH_3 \qquad [II\text{-}4]$$

A typical reaction of CO_2 with a Grignard reagent is carried out with large excess of CO_2 (ca. 200%) and at low temperature to prevent side reactions. Obviously, this excess of CO_2 is not practical when ^{14}C-labeled carbon dioxide being used. However, all of $^{14}CO_2$ can be

generated at once and then introduced over the Grignard Reagent. Under atmospheric pressure this would result in a great loss of $^{14}CO_2$. This problem was resolved by use of reaction vessel (figure II-1) which was kept under 100mm Hg vacuum. The unreacted $^{14}CO_2$ was kept in a closed system; a secondary reaction vessel was used to permit removal of any of the unreacted $^{14}CO_2$.

II-B. Catalyst Preparation

A series of precipitated iron oxides were prepared by adding ammonium hydroxide to iron nitrate solutions. These materials were dried at 120°C and then calcined in air at 400°C. Samples were reduced at 400°C in flowing hydrogen. While high surface area materials (greater than 200 m^2/g) could be obtained, the materials reduced at 400°C in flowing hydrogen had less than 5 m^2/g, usually less than 1 m^2/g. This method of catalyst preparation was therefore successful in attaining a high area oxide material but the material did not produce sufficient surface area following reduction. Hence, this method of preparation was not pursued.

A series of promoted iron catalysts, based on a United Catalysts, Inc. commercial iron oxide, were prepared. The unpromoted iron oxide had a high surface area (155 m^2/g) but the promoted material, following reduction at 400°C, had a surface area of less than 1 m^2/g. The preparative method was also abandoned.

Al_2O_3-, ThO_2- and ZrO_2-containing catalysts were prepared by room temperature coprecipitation from mixed nitrate solutions (135g Fe/1000 ml H_2O) with 10% NH_4OH. The NH_4OH was added quickly to the mixed nitrate solution, with vigorous stirring, until the solution reached a pH of 9. The precipitate was filtered and then washed with distilled H_2O to a pH ca. 7.4. It was then dried overnight in air at 120°C and calcined overnight in air at 350°C. The calcined cake was crushed and the -80 + 170 mesh fraction selected for use. A 29 gm samples was charged to the reaction and reduced 48 hours at 350°C with a H_2 flow of 150 ml/min. The time of reduction was sufficient to reduce the H_2O evolution to the point where the blue color of the drierite no longer changed in the outlet trap.

The SiO_2-containing catalyst could not be prepared in exactly the same way because no suitable Si compound was not available. Instead, a 34% colloidal dispersion of SiO_2 in H_2O (pH = 3), offered by Johnson Matthey, Inc. under the trade name AESAR, was added to the $Fe(NO_3)_3$ solution. Thereafter the procedure employed was the same as that described above.

A silica (Davison 923, W. R. Grace, BET = 700 m^2/g) supported iron catalyst was prepared by the so-called "double impregnation method" to provide 11.1% Fe or silica. This catalyst then was impregnated with varying amounts of potassium (KNO_3).

Most of the runs were conducted with a United Catalysts, Inc. C-73 commercial formulation.

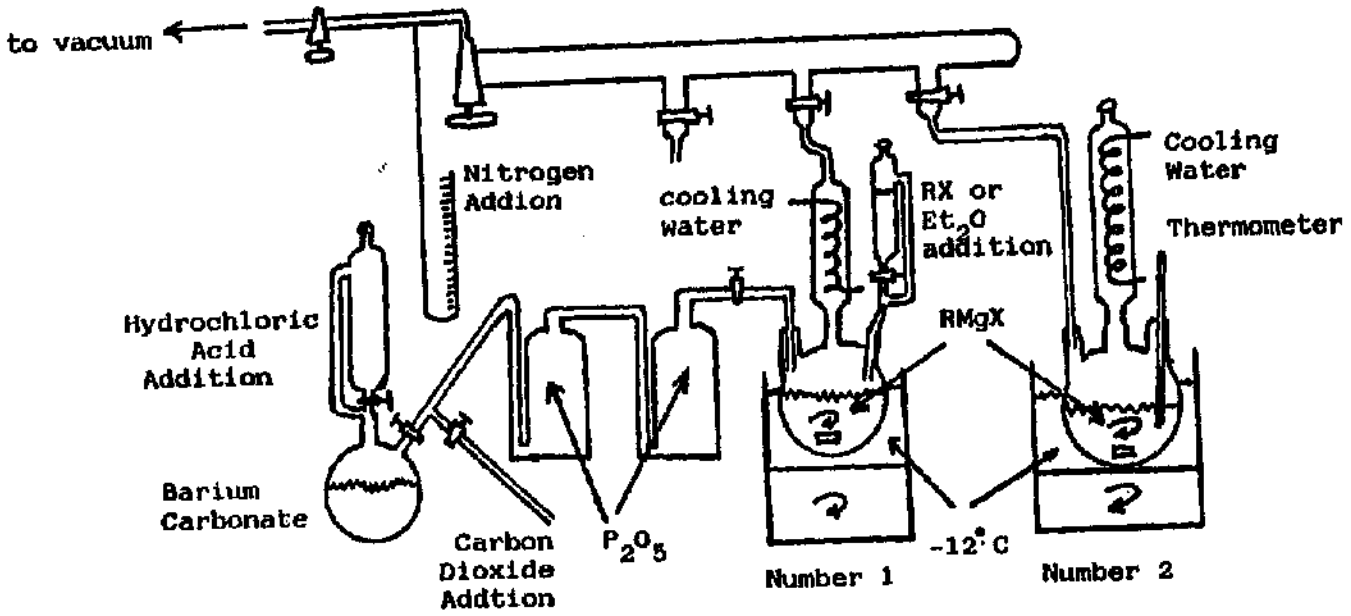


Figure II-1. Schematic for generation of $^{14}CO_2$ for Grignard synthesis of labeled acids.

II-C. Catalyst Characterization

II-C-1. ESCA

Our ESCA equipment includes probes constructed following the design of Professor David Hercules. This probe permits the reduction of a catalyst pellet at elevated temperature, sealing off the pellet in hydrogen at atmospheric pressure while cooling to room temperature, insertion of the sample into a vacuum chamber and then, after evacuation, insertion into the ESCA. This should permit us to insert the sample without reoxidation of the sample. We have verified that supported Group VIII metals, Pt or Rh, could be reduced to the metal and inserted into the ESCA without reoxidation. Under similar conditions, neither the tin nor the rhenium component of bimetallic catalysts was completely reduced to the metallic state.

II-C-2. XRD

In-situ X-ray diffraction studies were effected using a Picker X-ray Diffractometer instrument. The sample could be reduced in the counting chamber so that the XRD data could be collected without exposure to air.

II-C-3. Mossbauer

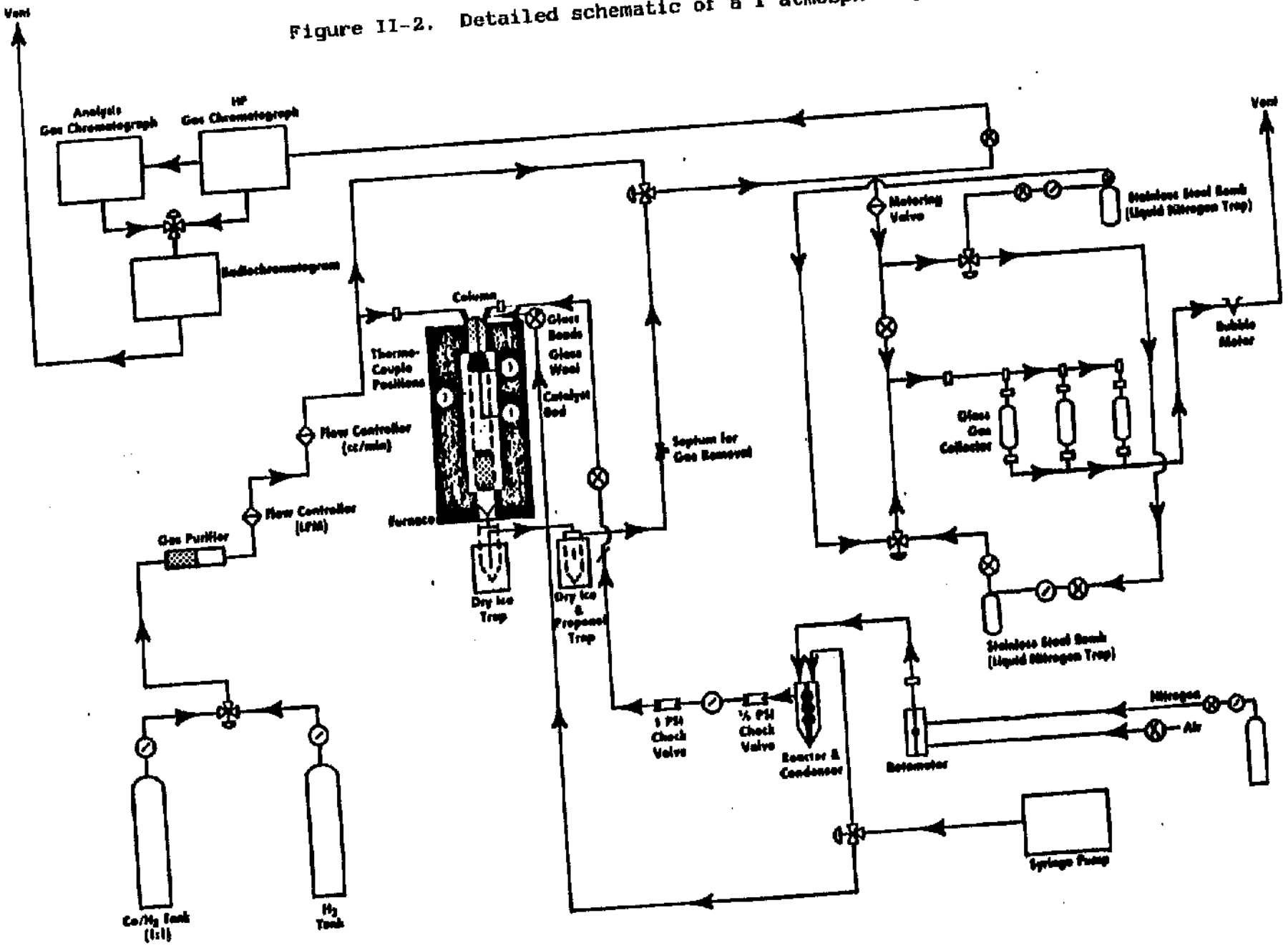
Mossbauer spectra were obtained for some of the catalysts when they were in the reduced state as well as for samples following use as a catalyst. Transmission spectra is obtained in the constant-acceleration mode with an Elscinct Mossbauer Spectrometer. The entire system is coupled with a multi-channel analyzer (MCA) and data from MCA is dumped onto an IBM p.c. The whole system can be operated at 10K.

II-D. Catalytic Conversions

II-D-1. Atmospheric Pressure Reactor

A detailed schematic drawing of the fixed-bed, atmospheric-pressure unit is shown in figure II-2. Gas flows are regulated by Brooks flow controllers. The reactor is a glass tube 1.25 inches in diameter and 24 inches long, with a central thermocouple well containing two thermocouples. Liquid products are condensed in a series of traps chilled with dry ice and liquid nitrogen. The liquid nitrogen traps are made of stainless steel and rated for operation at 200 psi to withstand the gas pressure developed when they are warmed to room temperature without venting. The non-condensable gases are analyzed by an on-line gas chromatograph. Ethanol or pentanol have been added to the feed using a liquid metering pump. Ethylene addition has been accomplished by dehydration of a metered stream of ethanol over a basic Al_2O_3 catalyst operating at 300°C. Catalysts were reduced with H_2 in-situ for 48 hours at 450°C at a space velocity of about 180 $(hr)^{-1}$. Following reduction, the gas feed was then changed to synthesis gas and the test started. The test conditions chosen are 260°C, one atmosphere total pressure, $CO/H_2 = 1$, space velocity = 120 $(hr)^{-1}$ for supported catalysts and 60 $(hr)^{-1}$ for unsupported catalysts.

Figure II-2. Detailed schematic of a 1 atmosphere process unit.



II-D-2. Continuous Stirred Tank Reactor (CSTR) System

A schematic of the experimental apparatus is shown in figure II-3. The flows of CO and H_2 are controlled by separate mass-flow-controllers (MFC). CO and H_2 are thoroughly mixed by passing through two 300 ml bombs before it enters the slurry reactor. Details of the slurry reactor are discussed later. Products from the slurry reactor are condensed in two traps, one operated at about 65°C and the second at about 5°C. Non-condensable gases that pass through these traps are analyzed by dedicated gas chromatographs that utilize an on-line sampling value. The flow rate of this non-condensable gases can be measured by either a wet-test-meter (WTM) or soap-film flowmeter.

A fixed-bed reactor is installed parallel to the slurry reactor. Two three-way valves allows one to select between the fixed-bed and slurry reactors. A high pressure liquid pump is mounted in front of reactors. A desired liquid reactant can be pumped into the reactor with a flow rate as low as 1 cc/hr.

II-D-2-a. Slurry Reactor

Synthesis is carried out in a one-liter stainless-steel permanent magnetic-drive agitated reactor (PPI), as shown in figure II-4, it is basically of the same design as the one employed in earlier studies at PETC (ref. II-1). A level adjustment line, fitted with a J-micron filter, is position to maintain within the reactor a slurry volume (unexpanded) of about 500 ml at any operating temperature.

II-E. Product Analysis

The non-condensable gases are analyzed with three on-line gas chromatographs. Combining the output from these three g.c.'s, the following gases are determined: H_2, CO, CO_2, H_2O and hydrocarbons from carbon number one to eleven, with most individual isomers separated through carbon number six. The products collected in the "hot" and "cold" traps can be analyzed separately, or following their mixing according to the masses produced, by a capillary g.c. (60 meter, DB5). The heavy hydrocarbons from the reactor is also analyzed using this capillary column. A typical product distribution for the products using an UCI fused-iron catalyst is shown in figure II-5.

Gas chromatograph-mass spectrometric analyses were performed on a Hewlett-Packard 5985A capillary g.c./quadrupole mass spectrometer system. G.C. separation was carried out on an OV1 WCOT column and mass spectra were recorded every two seconds. The spectrometer was operated in the EI mode at 70V electron energy and a source temperature of 150°C. Component identification was aided by search of a mass spectral library.

The i.r. spectra were obtained using Capillary G.C./Matrix Isolation-FTIR (GC/MI-FTIR). A commercially available system (Cryolect, Mattson Instruments Madison, WI) was used. The system consists of a Varian 3700 GC equipped with a split/splitless injector, a Sirius 100 FTIR spectrometer, a Matrix Isolation interface and a Starlab computer. The configuration of the system is shown in figure II-6. Helium doped with 1.2% argon is used as the carrier gas. As the effluent exits the capillary column (DB-5, J & W Scientific) approximately 20%

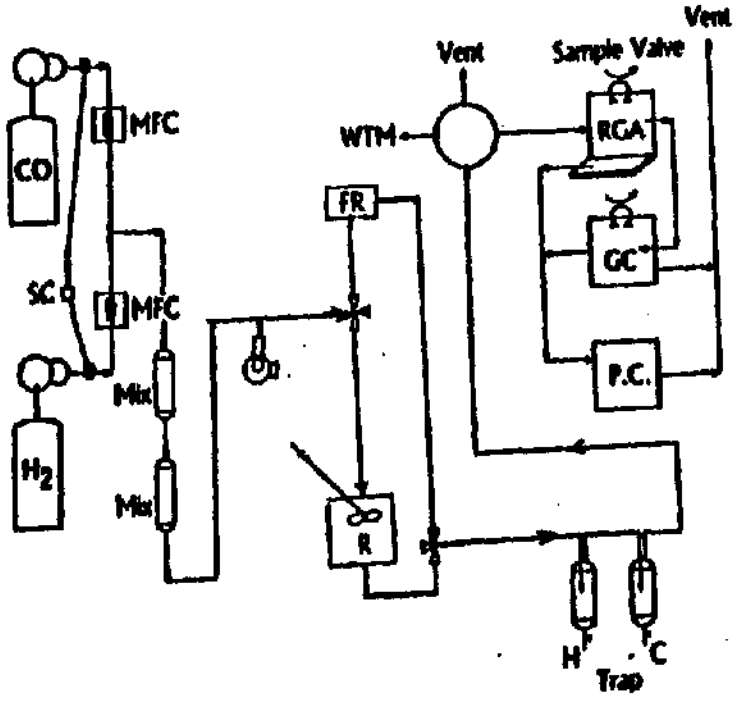


Figure II-3. Schematic of the reactor system showing the fixed bed reactors (FR) and the stirred tank autoclave reactor (R) as well as the hot (H) and cold (C) traps and the on-line gas analysis by gas analyzer (RGA) or chromatograph (GC) and the ^{14}C proportional counter (PC)

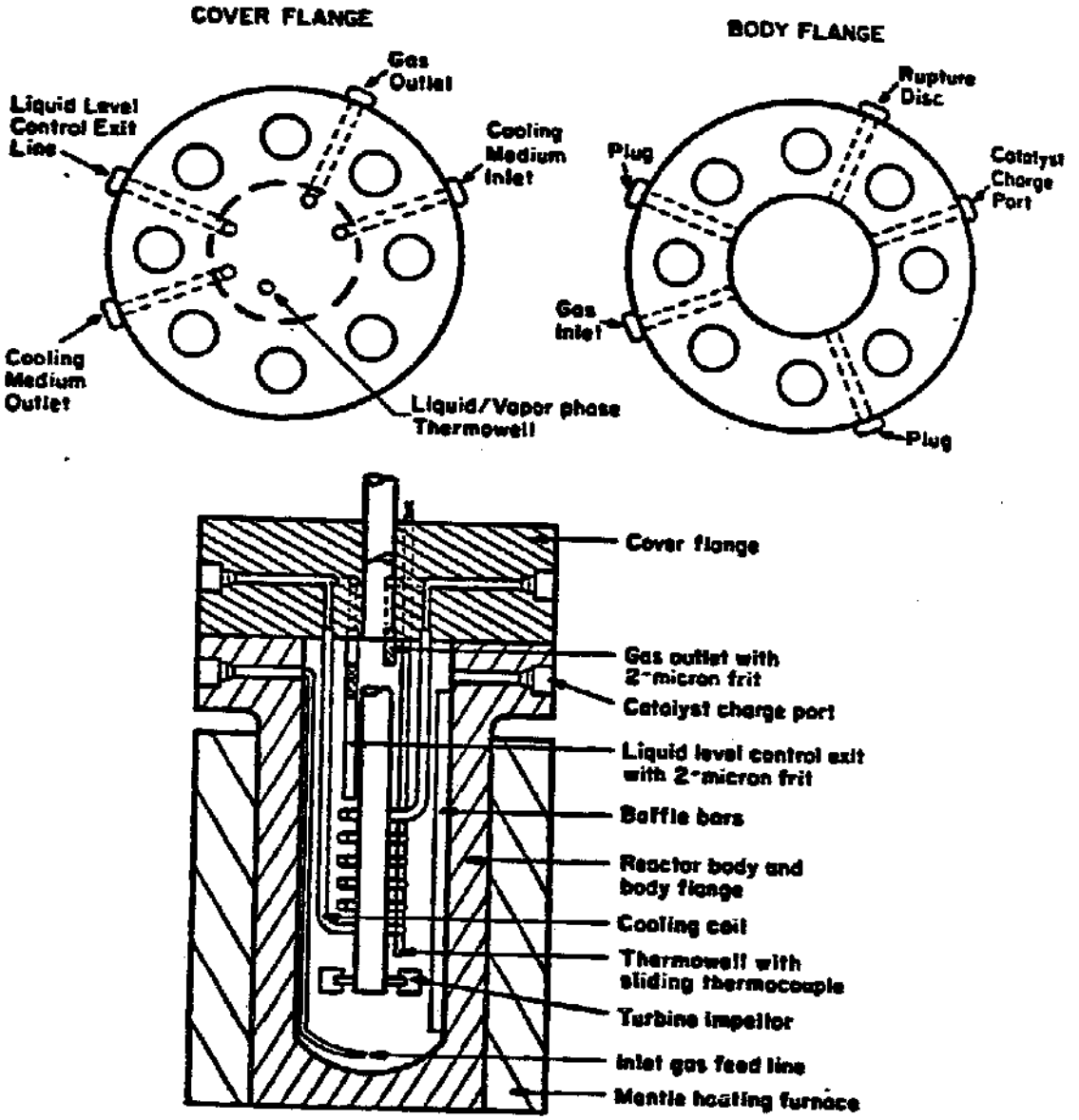


Figure II-4. Drawing of three phase one-liter slurry reactor.

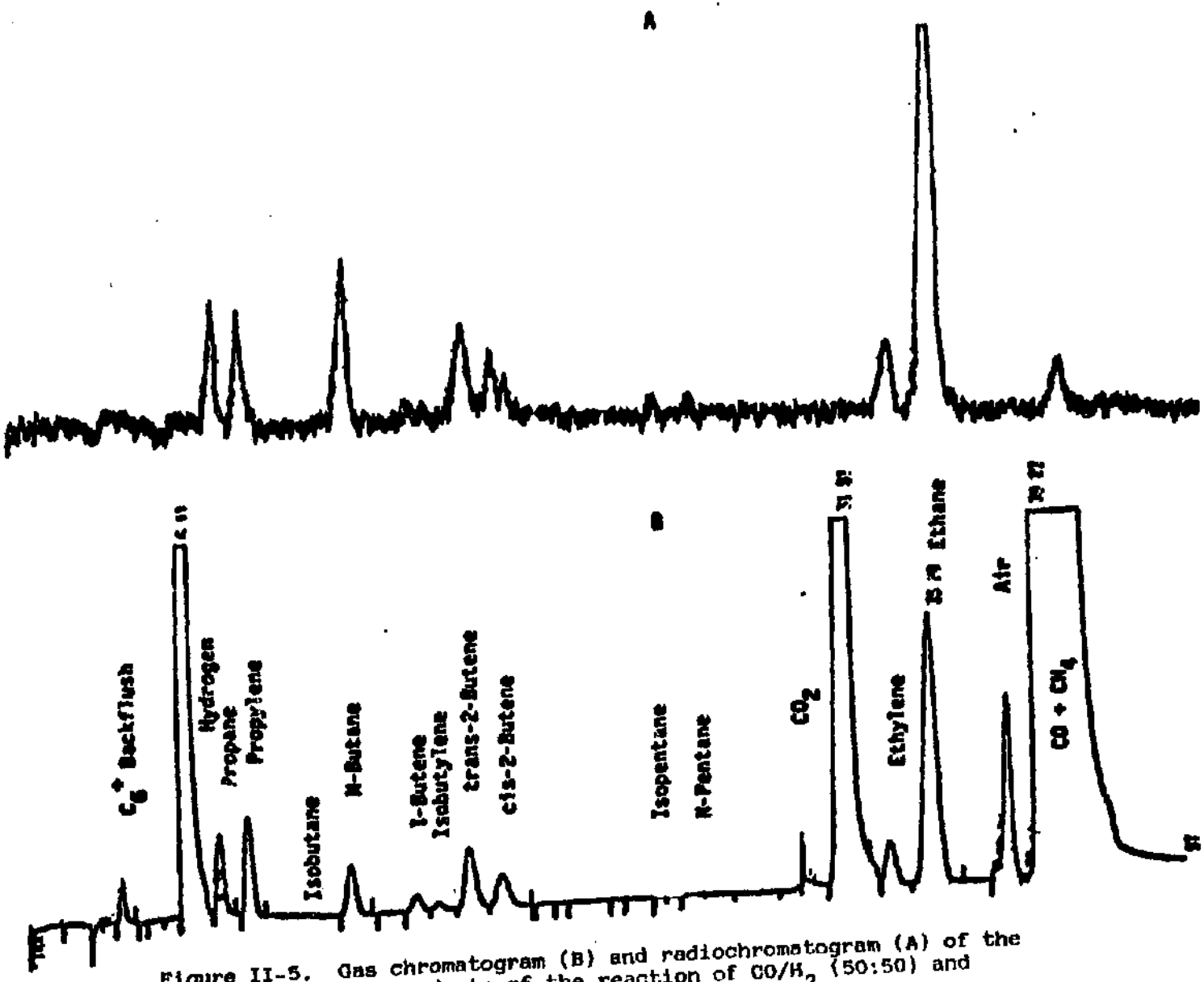


Figure II-5. Gas chromatogram (B) and radiochromatogram (A) of the gas products of the reaction of CO/H_2 (50:50) and $^{14}CH_3$-CH_2OH at 260 + 2°C, LHSV 231/hr.

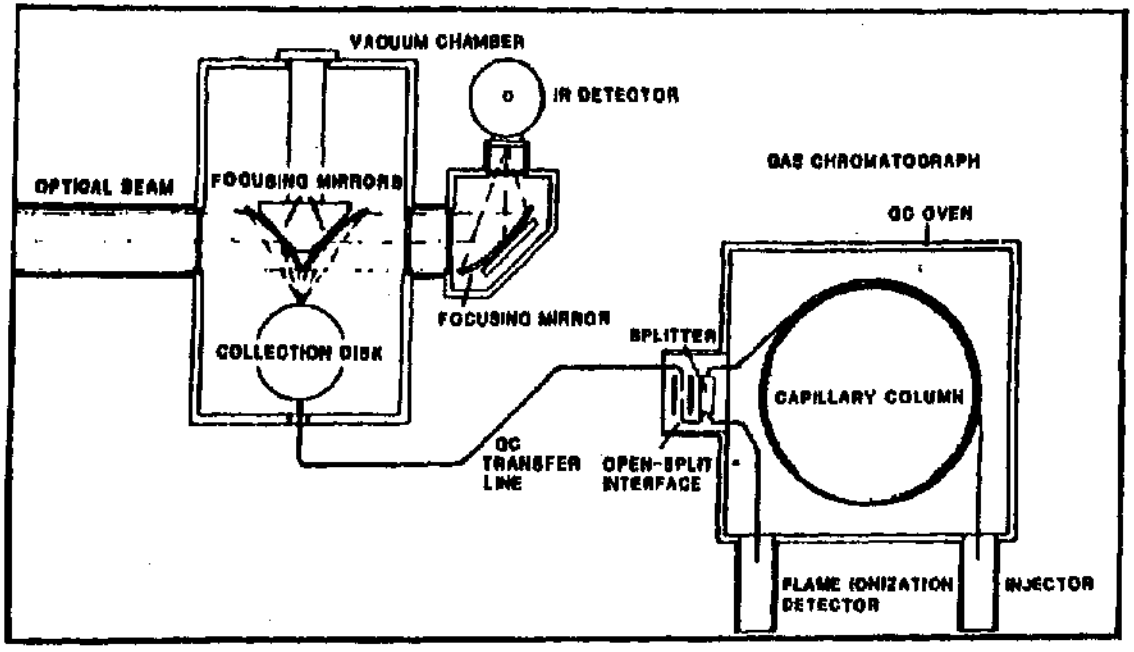


Figure II-6. Schematic of the capillary gas chromatograph/Matrix Isolation/FTIR instrument (from reference II-2).

is diverted to the FID. The remainder is directed to the collection disk via a capillary transfer line. The collection disk, which is plated with optically polished gold, is cooled to 13K by a closed cycle He compressor and cryogenic cold finger. A precision compumotor is used to rotate the disk during deposition. The Ar freezes the components of the sample on the disk as they elute from the column. The FID tracing is then used to locate the peaks on the disk after the GC run is complete. By positioning the peaks of interest in front of the focusing mirrors, IR spectra may be obtained (III-15). Because the components are frozen in a fixed position that may be accurately positioned by the precision computer, an optimum number of scans may be taken and averaged to increase the S/N ratio. The spectra used in this paper were taken using 32 scans at 4 cm^{-1} resolution.

II-F. Product Separations

II-F-1. Alkane, Alkene and Alcohol Separation

In order to have sufficient sample for counting in the proportional counter, it has been necessary to use a packed g.c. column rather than a more efficient capillary column. Sufficient resolution cannot be attained with the packed column to effect separation of alkanes and alkenes. Thus, these compound classes had to be separated prior to analysis for g.c. proportional counter analysis.

The dry column silica gel chromatography procedure utilized to effect the separation is outlined in figures II-7, II-8. Four grams of a wax sample obtained from PETC is added to the top of the silica column and then isopropanol is used to elute the sample. The first three fractions eluting from the column are composed of pure alkanes. Fractions 3 through 17 are enriched in olefins but still contain some alkanes. Thus, fractions 3 through 17 are combined and mixed with 2 g of isooctane. The combined fractions-isooctane mixture is added to a second dry silica column and eluted with isopropanol. The first fractions (20-25) are mixtures containing isooctane but fractions 26 through 36 contain alkenes essentially free of alkanes. Fraction 37 contains isopropanol plus some oxygenates that were present in the sample. Figure II-9 shows a high resolution capillary column (DB-5) chromatograph of the original sample and an alkane fraction; note the absence of the three large olefin peaks for each carbon number corresponding to 1-alkene, trans-2-alkene and cis-2-alkene. In figure II-9 the upper curve (A) is again the g.c. of the original sample, the middle curve (B) is the g.c. of an alkene fraction from the first separation and the bottom curve (C) shows the alkene fraction after a second fractionation. Figure II-10 shows a g.c. of an oxygenate fraction and the original sample.

The total recovery for both fractionations was 88%; much of this loss was during the collection of the lowest boiling alkane and alkene fractions. With careful cooling during collection of the initial samples, this was improved to 95% or greater.

Figure II-11 shows the n-alkane/isoalkane ratio calculated from the alkane fraction and for the whole sample assuming all peaks except the n-alkane and the 1-, t-2 and C-2 alkene peaks are isoalkanes. It is clear that, in the alkane fraction, the n-alkane/isoalkane ratio remains constant over the C_9-C_{17} carbon range. Reacting the PETC sample with Br_2 did not alter

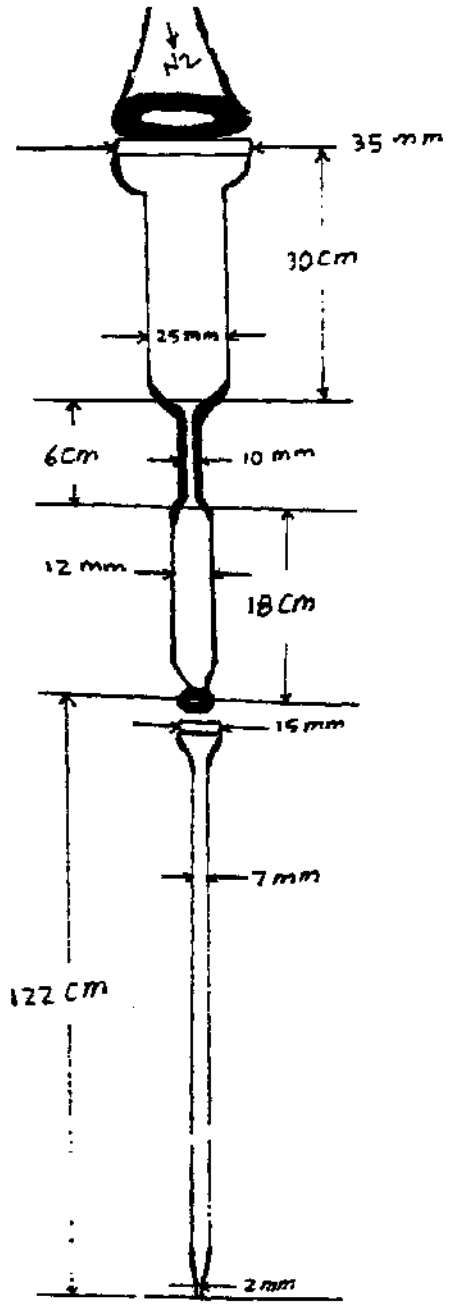


Figure II-7. Schematic of the column used for silica gel chromatography for alkane and alkene separation.

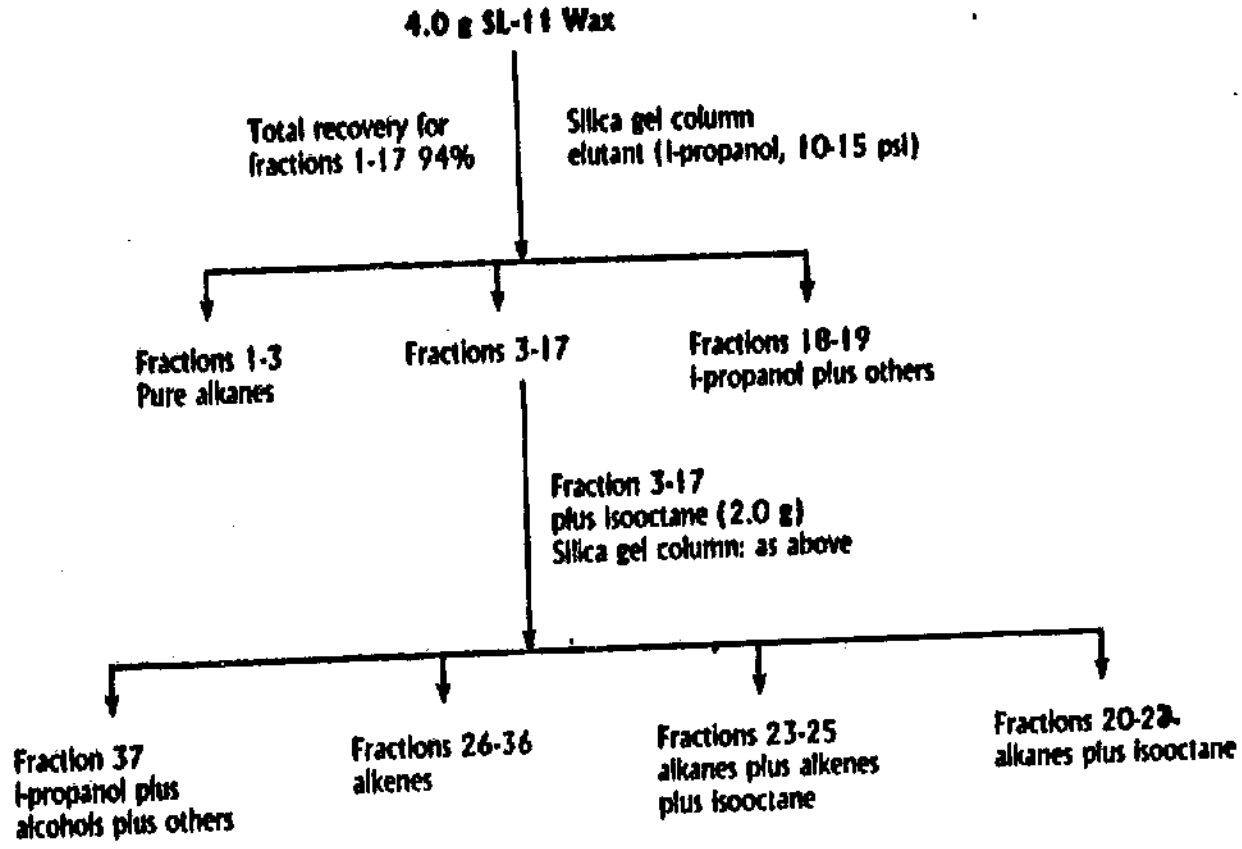


Figure II-8. Outline for the separation of Fischer-Tropsch products into a pure alkane fraction (fractions 1-3), alkene fraction (fractions 26-36) and oxygenate fractions (fractions 18-19 and 37).

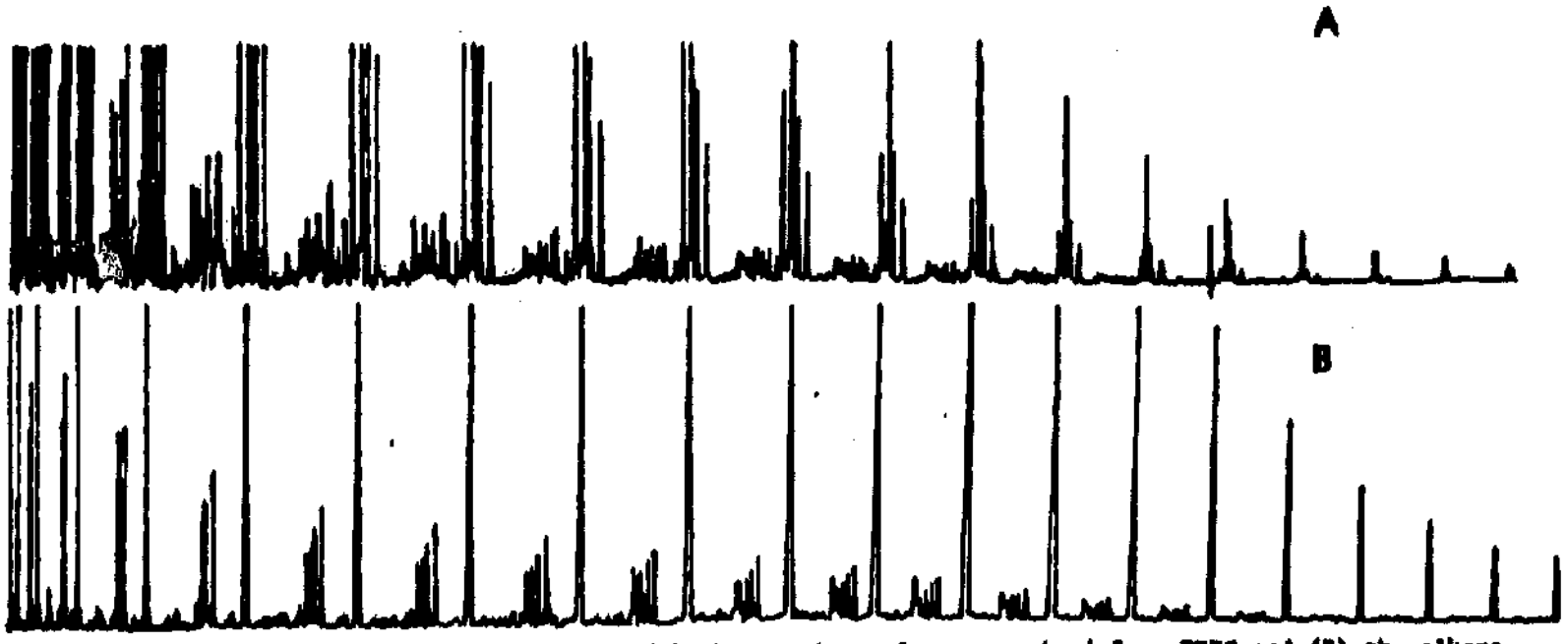


Figure II -9.Capillary gas chromatographs of (A) the total sample as-received from PETC and (B) the alkane fraction after separation by the scheme outlined in figure 11.

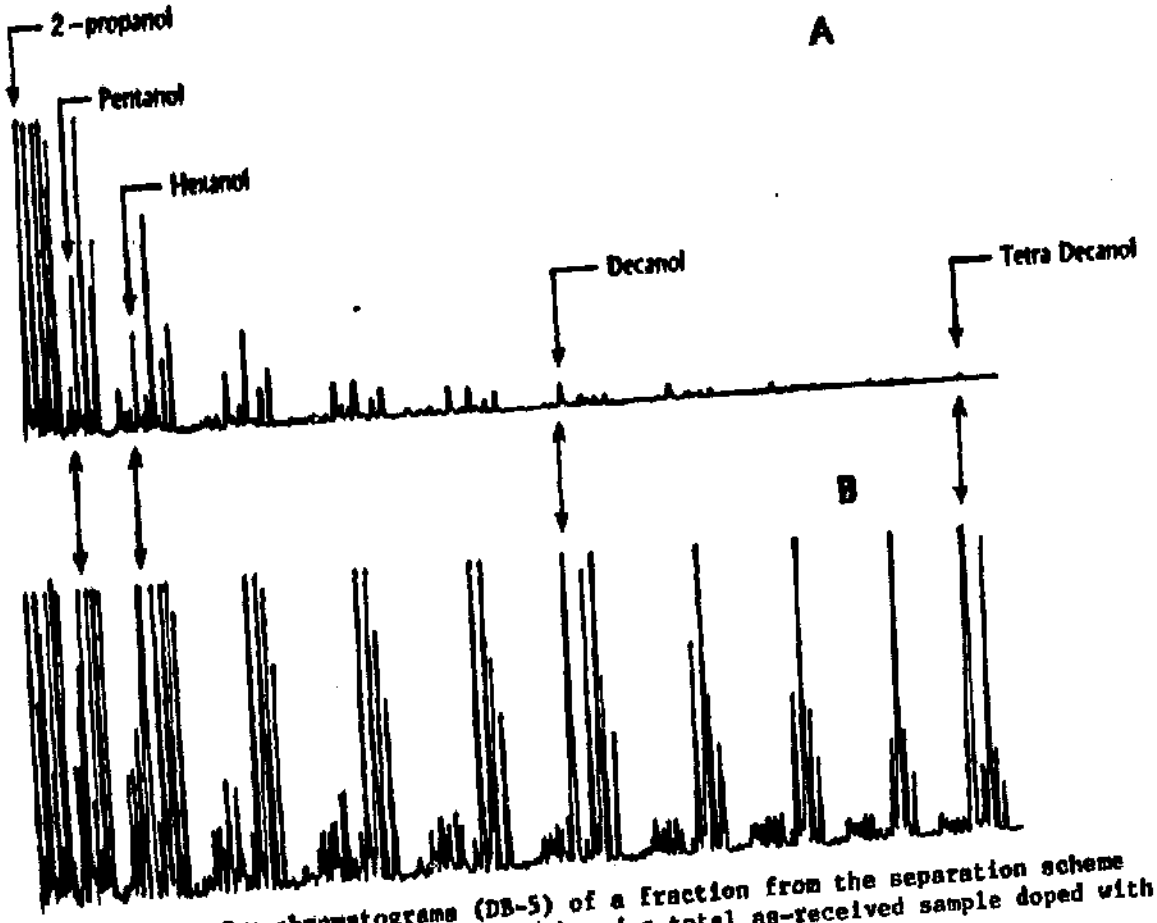


Figure II-10. Gas chromatograms (DB-5) of a fraction from the separation scheme outlined in figure 11 (A) and a total as-received sample doped with the alcohols indicated (B).

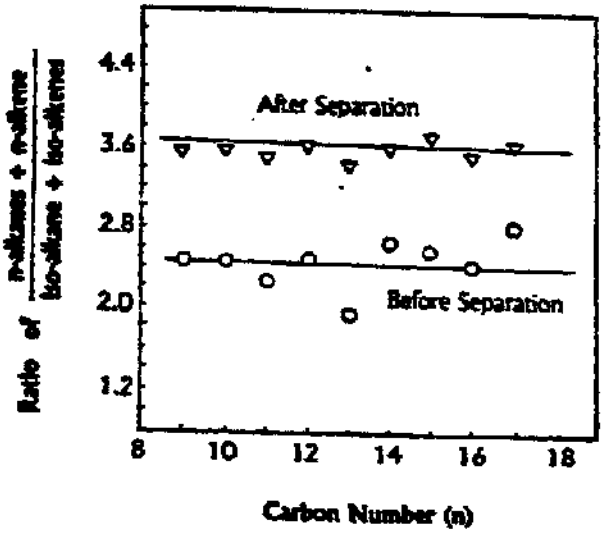


Figure II-11. n-Alkane/isoalkanes ratio for increasing carbon number for the sample before separation and the sample after separation using the scheme in figure 11.

the n-alkane/isoalkene ratio significantly even though the normal alkenes (1, t-2 and C-2 isomers) were brominated and shifted to higher carbon numbers. Considering the n-alkane/isoalkene ratio before and after separation, it is calculated that approximately half of the compounds other than n-alkane and 1- plus t-2 plus C-2 alkenes, are oxygenates.

Normal alkanes and alkenes have been separated from the sample by sorption into 5A zeolite pellets. Since the zeolite separation can be carried out for alkane or alkene fractions, it has been possible to obtain pure isoalkene and isoalkene fractions. It has not been possible to completely recover the normal alkane or alkene fraction from the zeolite by back-extractions.

II-F-2. HPLC Procedures for Fischer-Tropsch Reaction Products

The HPLC set-up used consisted of a solvent delivery system (Waters 6000A pumps), a valve-loop injector and an RI detector (Waters 401). An analytical column 25cm x 4.6mm ID, Supelcosil LC-18 (5 micron) used in the HPLC procedures was packed with octadecyldimethylsilyl-bonded packing with minimum dead volume. A 4" guard column with the same stationary phase as that of analytical column was used in order to avoid chocking of the column. Methanol and its mixtures with water and tetrahydrofuran (THF) were used as mobile phases. The methanol and THF were of HPLC grade (commercially available) and were used as received. However, mobile phases were always degassed through a wall vacuum system just before their use. Although several mobile phases were tried for separations of paraffins and olefins, the following ones were found to be most suitable:

a) for paraffins:

(i) $C_6 - C_{14}$; $CH_3OH:H_2O$, 90:10, 1ml/min.

(ii) $C_{12} - C_{24}$; neat CH_3OH, 1 ml/min.

(iii) $C_{15} - C_{24}$; CH_3OH:THF, 90:10, 1 ml/min

b) for olefins:

(i) $C_5 - C_9$; $CH_3OH:H_2O$, 80:20, 0.7ml/min

(ii) $C_9 - C_{15}$; $CH_3OH:H_2O$, 90:10, 1 ml/min

It was observed that the normal alkanes (C_9 to C_{15} only) could be separated from their iso-homologs with the only mobile phase $CH_3OH:H_2O$, 90:10 with a flow rate of either 0.7ml/min or 1 ml/min. In other mobile phases such as neat CH_3OH or CH_3OH:THF, the iso-homologs of higher alkanes appeared as peak shoulders whereas sharp (single) peaks were observed for lower hydrocarbons (where every single peak was representing the total amount of both the normal and its iso-homolog). The normal and iso-alkenes also showed somewhat similar behaviors.

The performance of our HPLC system was checked by reproducing the separation of a standard mixture (provided along with the column) containing acetophenone, benzene and toluene. In this separation, 66:34 methanol:water

was used as a mobile phase with a flow rate of 0.7 ml/min. The resulting peaks were detected by using 254 manometer UV-detector.

In order to use the HPLC procedures for quantitatively separating alkane and alkene fractions of Fischer-Tropsch reaction products, it is necessary to obtain the absolute response factor (ARF) for alkanes and alkenes under the similar HPLC conditions. Therefore, two standard solutions of alkanes and one standard solution of alkenes were prepared. Each solution was prepared in a 5ml volumetric flask. Solution 1 contained n-decane, n-undecane, n-dodecane, n-tridecane, n-tetradecane and n-pentadecane in n-heptane as a solvent. Solution 2 contained n-dodecane, n-tetradecane, n-hexadecane, n-octadecane, eicosane, docosane, tricosane and tetracosane in n-nonane as a solvent. Solution 3 contained 1-octene, 1-decene and 1-tetradecene in 1-hexane as a solvent. All the three solutions were prepared by weighing accurately about 20-25mg of each component directly into the volumetric flask and then diluted with the respective solvent to 5ml.

The HPLC system was equilibrated with the desired mobile phase with a flow rate of 1ml/min. and then 50 l of standard solution was injected into the system. Two or more injections were made with each solution until at least two injections gave peak areas within 2%. The HPLC chromatograms for these separations are given in Figures II-12 to II-14. The absolute response factor for each component was obtained by dividing its amount with its peak area:

$$ARF = \frac{\text{amount in } \mu \text{ mole}}{\text{peak area}}$$

Once the ARF was obtained, one could find out the amount of each component in micromoles through direct multiplication of ARF by its peak area from a chromatogram of unknown solution under investigation.

The HPLC separations on several Fischer-Tropsch reaction product fractions were performed and the amount of each component calculated by the procedure mentioned above. The solutions of components under the peaks were collected separately in vials containing about 10ml of In stage 1 solution (provided by Packard). The ^{14}C radioactivity of these solutions were measured using Packard Liquid Scintillation Spectrometer system (Model 3330). Results are illustrated in ffgure II-15.

II-F-3. Material Balance

A computer program, obtained from PETC is used to make the material balance. The input data includes: total run time, system pressure, gas flow in, gas flow out, weight of catalyst, temperature of reaction, and the quantities of aqueous, oil and wax samples produced during the run period. The computer program will output: hydrocarbon product distribution, overall material recovery, CO and H_2 conversions, H_2/CO usage ratio, water gas shift reaction constant, etc. This computer program will also calculate the mole fraction of each species and regroup them according to carbon number, then apply a least squares fit to solve for the linear equation for the Anderson-Schulz-Flory distribution. A typical ASF plot is shown in figure II-16.

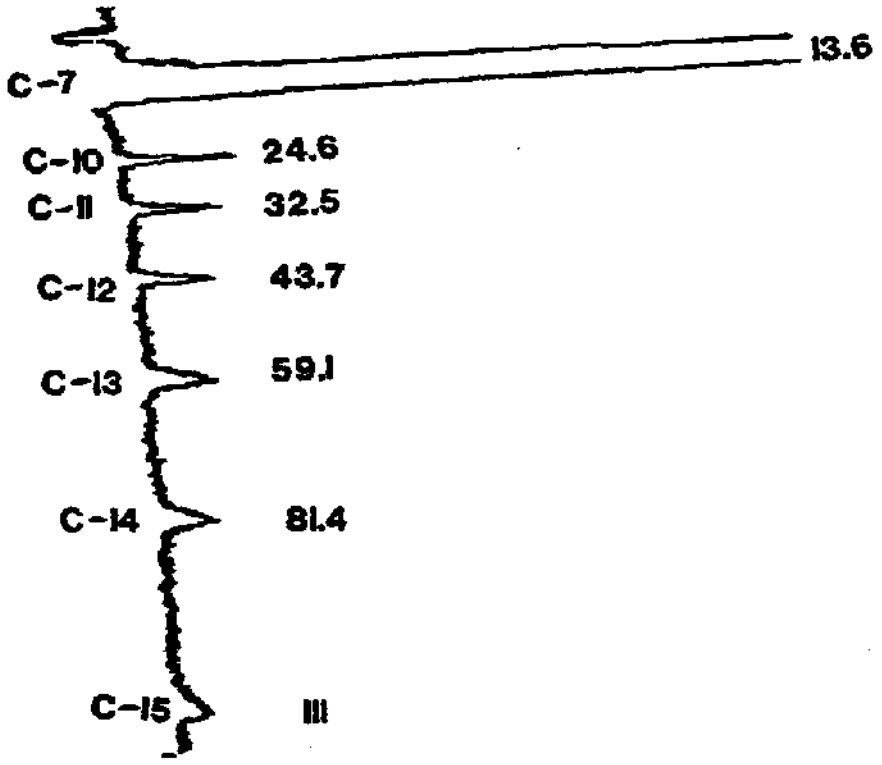


Figure II-12. HPLC chromatogram of a standard solution containing C_{10} to C_{15} normal alkanes in n-heptane as a solvent.
Mobile Phase: $CH_3OH:H_2O$, 90:10
Flow Rate: 1.0ml/min
Detector: RI

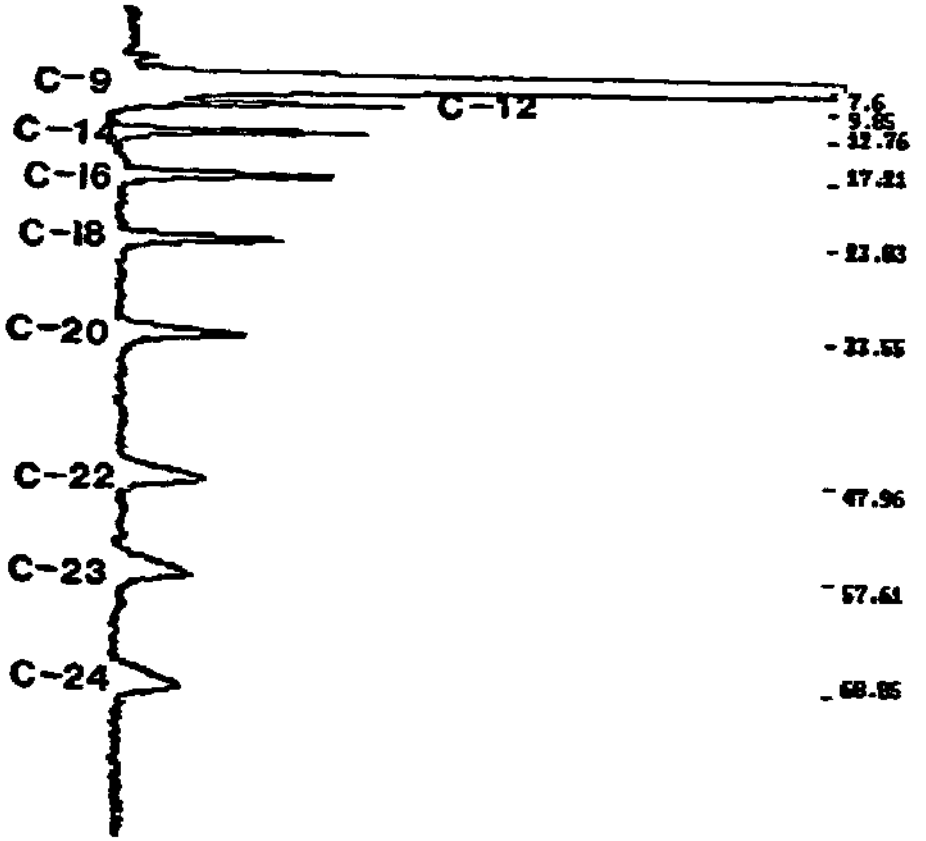


Figure II-13. HPLC chromatogram of a standard solution containing C_{12} to C_{24} normal alkanes in n-nonane as a solvent.
Mobile Phase: neat CH_3OH
Flow Rate: 1.0ml/min
Detector: RI

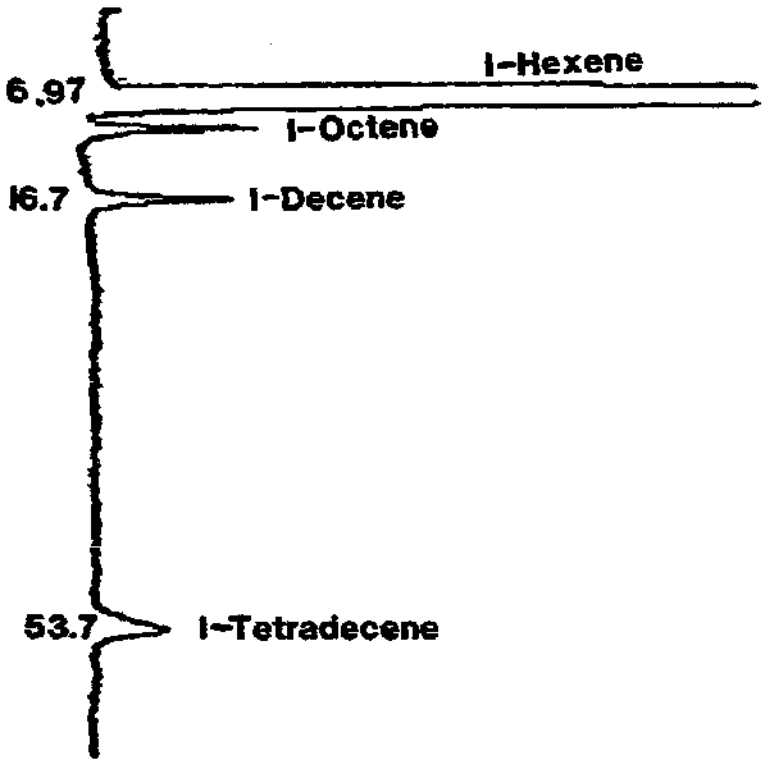


Figure II-14. HPLC chromatogram of a standard solution containing 1-octene, 1-decene and 1-tetradecene in 1-hexene as a solvent.
Mobile Phase: $CH_3OH:H_2O$, 90:10
Detector: RI

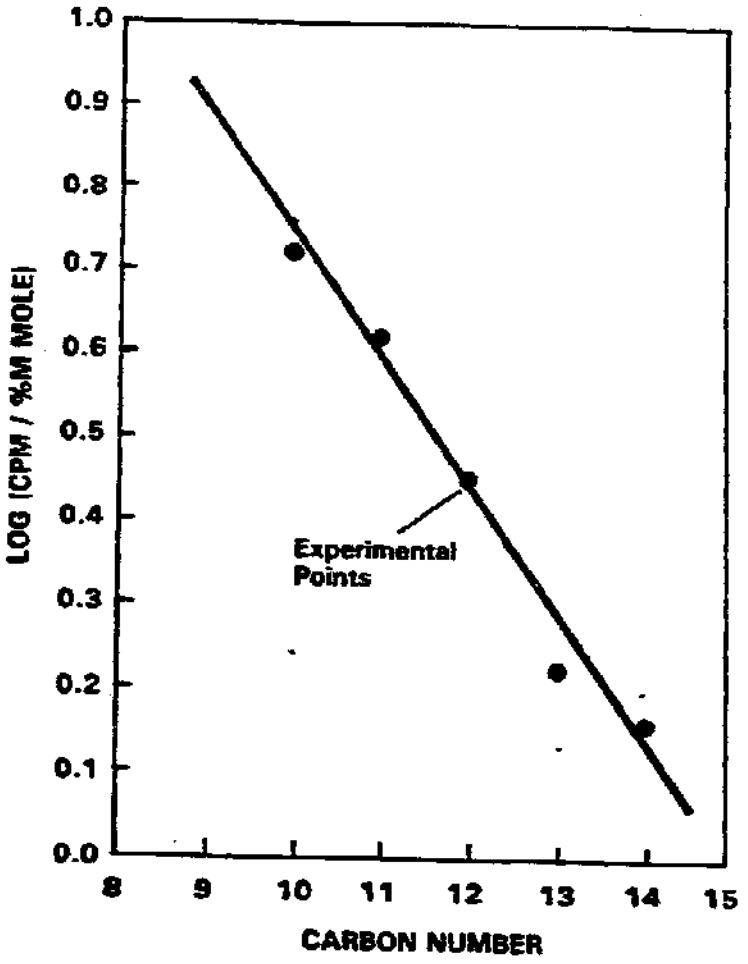


Figure II-15. Typical plot of the counts/minute per m mole % versus the carbon number for an aklane fraction.

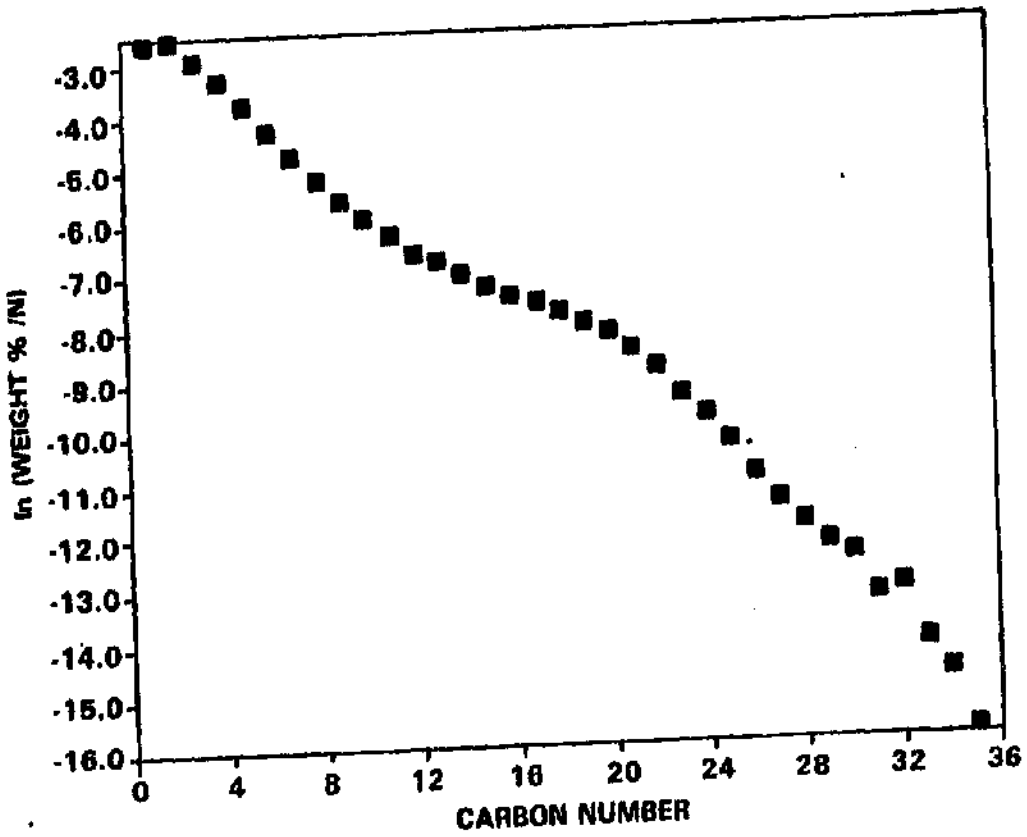


Figure II-16. A typical Anderson-Schulz-Flory plot for the products from a Fischer-Tropsch synthesis in a slurry reactor.