A Stirred Autoclave Apparatus
for Study of the Fischer-Tropsch
Synthesis in a Slurry-Bed

II.   Analytical Procedures

George A. Huff, Jr. and Charles N. Satterfield
Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, MA 02139

and

Martin H. Wolf
Cambridge Analytical Associates
Watertown, MA 02172

MASTER

Abstract

A procedure is presented that provides a complete quantitative analysis of Fischer-Tropsch products from an iron or a cobalt catalyst including oxygenates and hydrocarbons. Notably hydrogen and water are also determined, so that complete material balances can be obtained on all elements.

&   &   &

INTRODUCTION

The wide range of products that can be formed by Fischer-Tropsch synthesis, with respect to both molecular type and molecular weight, sets a difficult problem of quantitative analysis. This is especially so for the products formed by certain catalysts, such as those based on iron, which may contain substantial quantities of oxygenated species in addition to olefins and paraffins, and if it is desired to determine H_2 and H_2O in the products as well as CO and CO_2. For some purposes, a fast and simplified quantitative procedure may suffice, even if a complete material balance is not obtained and certain compounds or groups of compounds may not be specifically identified. Several papers describing procedures

of varying degrees of detail have been published and are referred
to in the recent paper by Nijs and Jacobs (1981) who also present
a fast and inexpensive method they developed for on-line analysis.
This gives detailed information on hydrocarbons, and includes CO
and CO_2, but not H_2 and H_2O. They state that their procedure also
separates lower alcohols but their typical chromatogram shows no
alcohols except for a trace of n-propanol. We present here a pro-
cedure that allows specific oxygenated products as well as CO,
H_2, CO_2 and H_2O and hydrocarbons up to C_{30} to be determined
quantitatively in detail, such that complete material balances can
be achieved.

EXPERIMENTAL

The trapping system is detailed in Part I of this paper. Con-
densable products are collected in a wax trap (heated to 70°C)
followed by a cold trap (cooled to 2°C). Each generally separates
into two phases - an aqueous layer which contains water and light
oxygenates and an oil layer which contains mostly hydrocarbons.
Three gas chromatographic systems are employed to analyze these four
fractions and the residual gas. Components in the oil phase of the
material condensed in either the cold trap or the wax trap are
separated on a capillary column inside a Hewlett-Packard gas
chromatograph and detected by flame ionization (F.I.D.). Aqueous-
phase material from each of the two traps is analyzed with a Perkin-
Elmer gas chromatograph using a conventional packed column with a
thermal conductivity detector (T.C.D.). The gaseous sample contains
significant quantities of hydrocarbons greater than C_5 in addition
to water vapor. It is analyzed on-line by a Carle refinery gas
analyzer. The water and hydrocarbons are determined by injection
into the Perkin-Elmer and Hewlett-Packard equipment.

Care must be taken to protect the samples during storage or
they can lose more volatile components. Ideally they should be
stored under an inert nitrogen blanket to avoid oxidation of aldehydes

to organic acids that can occur in the presence of air at room temperature. One puncture of a septum seal, for instance, is usually enough to allow volatiles to escape and air to infiltrate.

Light Gases: Hydrogen, carbon monoxide, carbon dioxide, and C_1 to C_4 hydrocarbons are separated over three columns used in conjunction with a multifunction gas-sampling/backflush-to-vent valve and two column switching valves in a Carle Model 111-H refinery gas analyzer (RGA) with a T.C.D. This analyzer is used primarily to determine H_2, CO and CO_2. The column/valve arrangement is depicted in Figure 1 and the operating sequence given in Table I. Valve 1 is air-actuated and provides on-line sampling while Valves 2 and 3 are electrically operated. The sequencing routine is controlled by the microprocessing ability of the Hewlett-Packard 3385A integrating chart recorder. A fresh sample is automatically taken after 45 minutes has elapsed following completion of the last chromatogram. This allows sufficient time to backflush heavier hydrocarbons from the first column.

Fischer-Tropsch gases contain a considerably larger fraction of hydrogen, carbon monoxide, and carbon dioxide than do typical refinery gases, so the columns were modified here to optimize the separation. Furthermore, Valve 1, originally an 8-port valve, was replaced with a 10-port Valco valve that allows backflushing of the C_5+ material to vent without interrupting other separations and contains a 1.0 cc sample loop.

Since the thermal conductivity of hydrogen is very similar to that of helium, which is used as the carrier gas, gas chromatographic determination of hydrogen until recently was troublesome with such inherent problems encountered as negative peaks, nonlinearity and poor sensitivity. However, this gas chromatograph employs a hydrogen

transfer system (HTS) which provides a linear and sensitive method of hydrogen measurement while not sacrificing sensitivity to other sample components. Hydrogen is transferred from the helium carrier gas stream by diffusion through the wall of a palladium alloy that is heated at 600°C, into a nitrogen carrier gas stream for measurement. The alloy remains impenetrable to other gases.

The flow rate of helium carrier is 27 cc/min and the inlet pressure is methodically maintained at 120.0 psig. Balanced flow to eliminate baseline shift when columns are bypassed is provided by needle valves which act as adjustable restrictors. The inlet nitrogen pressure for the hydrogen transfer system is held at 60 psig. The isothermal column oven is at 80°C, and the hydrogen transfer tube is maintained at 600°C by a Valco Model ITC-K-10 temperature controller with a type "K" thermocouple. The columns are removed from the gas chromatograph about every six months and conditioned at an elevated temperature overnight with helium flowing at 30 cc/min to remove accumulated impurities.

Water and Light Oxygenates: A Perkin-Elmer (P-E) 900B gas chromatograph with a T.C.D. is employed to analyze the aqueous phase of the material condensed in each of the two traps and to determine the amount of water carried out in the gaseous effluent. The components are separated on a 2-mm I.D. glass column that is 10-ft long and packed with 60/80 mesh Tenax-GC. With a stainless steel column water samples tailed badly and were irreproducible. As the Tenax-GC column ages, gaps appear in the packing which result in poorer resolution although they do not affect the quantitative analysis. With continuous usage, the column is repacked about every month.

The injector and detector temperatures of the gas chromatograph are set at 250°C and 300°C, respectively. Bridge current of the

thermal conductivity cell is 175 ma. The carrier gas is helium flowing at 30 cc/min with an inlet pressure of 60 psig. For the gaseous effluent samples, the oven is initially held at 30°C for 4 minutes and then heated at 12°C/min to 225°C where it is kept for 4 minutes. Temperature programming is the same for liquid samples except that the initial temperature is 55°C and not 30°C. Injection of both samples is by syringe - 1.0 cc for light gases and 0.1 ul for aqueous components.

Hydrocarbons and Oxygenates: A Hewlett-Packard (H-P) 5880A gas chromatograph with a F.I.D. is employed to analyze the oil-phase components from each of the two traps and to determine the amount of light hydrocarbons in the residual gas smaple. Flame ionization provides high sensitivity detection and simpler data reduction since the weight-response factors for hydrocarbons are essentially the same and thus only those for oxygenates need be determined. The components are separated on a fused-silica capillary column (Hewlett-Packard part 19091-60050) that is coated with dimethyl silicone fluid and surface deactivated with Carbowax 20M. The column is 50-m long and 0.2-mm I.D., and it contains 225,000 theoretical plates. The sample is split (200:1 ratio) to avoid overloading the column. The glass split liner is a Jennings tube (see Schomburg et al., 1977) that is packed with a small amount of 10% OV-1 on 80/100 mesh Chromosorb W HP to homogenize the sample.

Injection of quantitative standards revealed that to avoid split-discrimination effects and condensation of higher-boiling components in the injection port, an injector temperature of about 375°C was required. It is cooled two minutes after injection to 275°C without any loss in accuracy and in this manner lessens the rate of

septum deterioration. The detector is maintained at 325°C. We also found that the sample injection technique can influence accuracy and reproducibility. In particular, after the desired amount of sample has been drawn into the syringe with a needle plunger, it is removed from the sample bottle and about 0.05 µl of air is drawn into the syringe. Upon piercing the chromatogram's septum, the needle is allowed to heat for about three to five seconds before injection with a quick smooth motion, and then about ten seconds are allowed to elapse before removal of the syringe. This technique is known as "hot-needle injection," and care must be taken not to delay sample injection too long or doublets for each peak will result.

The syringe is rinsed with carbon disulfide and acetone and then placed in a Hamilton syringe cleaner which heats the needle while a vacuum is pulled on the needle. Liquid sample sizes are 0.15 µl by syringe for cold trap material and 0.30 µl by syringe for components collected in the wax trap, which have been previously solubilized with 50% carbon disulfide. Carbon disulfide was chosen because it readily dissolves hydrocarbons while not being detected by flame ionization.

With a 19 psig column head pressure, helium carrier flows at 0.6 cc/min through the column. Part of the carrier sweeps the septum and is vented to minimize ghost peaks caused by septum bleed. However, the flow is slow enough (2 cc/min here) to avoid split discrimination, as a small portion of the sample is lost to this continuous purge. Helium make-up, air and hydrogen flow rates to the detector are 30 cc/min, 450 cc/min, and 30 cc/min, respectively. For cold trap and wax trap samples, the oven temperature is held at 35°C for 8 minutes before heating to 280°C at 4°C/min where it is held for 30 minutes. On the other hand, residual

gas samples (1 cc syringe injection) are separated by holding the oven at -25°C for 3 minutes (by cooling with liquid nitrogen). Subsequent heating at 4°C/min to 175°C is sufficient to elute the sample.

With column use, peaks of oxygenated species (most notably alcohols) broaden and shift their retention time relative to hydrocarbon peaks. This is most likely due to "washing" of the stationary phase from the beginning of the column with each injection, which exposes the bare silica. Since the oxygenates spend a disproportionate amount of time in the beginning of the column due to the initially low temperature, they interact with the polar deactivated surface and lose resolution. Column life is extended by removing the first coils of the column and by periodically reversing carrier flow. Even so, the column is replaced after one or two months of continuous operation. Column deterioration is undoubtedly hastened by trace amounts of water in the gas sample and by using subambient temperatures.

We tried using a dimethyl silicone gum column that was surface deactivated with siloxane, which reportedly gives a longer operating lifetime (Hewlett-Packard Publication No. 43-5953-1562). Moreover, the maximum recommended operating temperature is increased from 280°C to 350°C which shortens analysis time. However, the resolution between close boiling components was poor compared to that obtained by the dimethyl silicone fluid column.

Data Analysis: Calibration curves of peak area versus weight injected for major Fischer-Tropsch components revealed that all responses were linear and passed through the origin. Whenever a non-linear response was observed (typically concave shaped), we always found an experimental artifact such as a leaky column connection or condensation of the compound in the injection port. Thus,

the shape of the curves proved to be useful diagnostic tools. The response factors, used to correct peak area to relative weight and related to the slope of the calibration curve, agreed with those reported by Dietz (1967), and so his values for both F.I.D. and T.C.D. were employed here without correction. Since the weight response factor for hydrogen is characteristic of the analytical technique, we calculated a value of 0.29, based on Dietz's notation, for the hydrogen transfer system.

Peaks that eluted from the gas chromatographs were identified initially by peak-spiking, that is, by adding a small quantity of a known component to the unknown mixture and observing which peak increases. Pichler, Schulz and co-workers in a series of papers (see Pichler and Schulz, 1970; Schulz and Zein El Deen, 1977) have published detailed information on the analysis of Fischer-Tropsch products from iron and cobalt catalysts that provides guidance on the nature of products to be expected. DiSanzo (1981) provides an analytical method for heavy-end Fischer-Tropsch liquids and representative analyses. The identifications presented here were further checked by a combined Finnigan 9500 gas chromatograph, Finnigan 3200 Quadrupole Mass Spectrometer, and Finnigan 6000 Data System. The mass spectrometer was operated with an electron impact source. The continuous dynode electron multiplier was operated at 1250 volts, and the preamplifier sensitivity was 10^{-8} amp/volt. A scan from 11 to 450 amu was made every two seconds.

The residual gas must be analyzed by all three chromatographic systems to determine its entire composition, so it is necessary to extract the peaks of interest from each chromatogram and recombine the outputs. Hydrogen, carbon monoxide, and carbon dioxide are obtained from the Carle refinery gas analyzer. The Perkin-Elmer 900B

output provides water and C_1 oxygenates, and the remaining hydrocarbons and oxygenates come from the Hewlett-Packard 5880A gas chromatograph. The chromatograms are recombined by comparing analyses of components that are duplicated in the systems, and then standardizing the outputs relative to that from the Carle System.

Specifically, since both carbon dioxide and C_2 hydrocarbons are analyzed by the Perkin-Elmer 900B gas chromatograph and Carle refinery gas analyzer, a multiplying factor is determined to normalize the analysis to the Carle instrument, and similarly, the Hewlett-Packard output is put on the same basis as that from the Carle analyzer by methane and C_2 hydrocarbons. Although this standardization could be accomplished by using only one duplicate component, we compare two to check accuracy of the multiplying factor. With the desired peaks relative to the Perkin-Elmer gas chromatograph output, the weight percents are normalized to 100% and the molar composition of the effluent gas can be calculated since the molecular weight of the various constituents is known.

There are no duplicate chromatograms of those components con- densed in the wax trap and cold trap. For an overall material balance, the weight of material collected in the oil and aqueous layers in each trap is determined over a time interval of about 8 hours, depending on the synthesis rate. This information is combined with the residual gas analysis and a knowledge of the effluent gas flow rate.

Because of the large number of compounds produced, for most purposes we regroup them back into four categories - oxygenates, normal paraffins, alpha and beta olefins, and a "remainder" which is composed primarily of branched hydrocarbon isomers plus a few cyclic hydrocarbons. This classification of compounds is done only to

C_{11} after which we simply calculate the total organic produced at each carbon number.

RESULTS

Chromatograms from the three analytical systems for residual gas samples from a reduced fused-magnetite catalyst containing alkali are illustrated in Fig. 2. Those from cobalt are not shown as they are similar except that normal-paraffins, and not alpha-olefins, are the major hydrocarbon product at each carbon number. Moreover, little oxygenated product is formed with a cobalt catalyst. Since the Perkin-Elmer output (Fig. 2-b) is used to quantify only water, C_1 oxygenates and dimethyl ether, only these species plus carbon dioxide and C_2 and C_3 hydrocarbons (used to tie in this output with that from the Carle gas chromatograph (Fig. 2-a)) are analyzed. While all of the compounds appear in the output of the capillary column (Fig. 2-c) with the Hewlett-Packard gas chromatograph (of course, excluding hydrogen, carbon monoxide, carbon dioxide and water which do not respond to F.I.D.) only major components are identified. Hydrocarbons are classified by carbon number, and major ones such as normal-alpha-olefins, normal-beta-olefins and normal-paraffins are noted as Ole, Ole-2 and Pfn, respectively. Those peaks unidentified are mostly branched olefins and paraffins although there are a few cyclics. Normal-aldehydes, methyl-normal-ketones and normal-alcohols are represented as Ald, Ket and Alc, respectively.

Chromatograms of the aqueous-phase products from a fused-iron catalyst are shown in Fig. 3 where oxygenates are classified by carbon number. Note that normal-carboxylic acids (denoted as Acid in the figure) elute one carbon number behind the other oxygenates. The remaining major components are identified by the same notation described above. Unidentified peaks are mostly branched alcohols.

Mass spectrometry revealed that several alkenes formed in substantial amounts with the iron catalyst were also present in minor amounts in the aqueous phase. This is most likely due to the surface active properties of the higher carbon number oxygenates. Although not illustrated, gas chromatograms of the aqueous layer of product from a cobalt catalyst showed that it consisted primarily of water with only trace amounts of normal-alcohols. Organic acids can react with alcohols at room temperature to form esters. However, there was no evidence from mass spectra that this reaction had occurred to any measurable extent.

Chromatograms of the oil-phase products obtained from a fused-iron or a cobalt catalyst are depicted in Fig. 4. The chromatograms appear as a series of "peak clusters" consisting of a few major compounds and numerous minor constituents. For fused-iron (Fig. 4-a), the major peaks are n-paraffins and alpha-olefins. The satellite peaks are aldehydes, primary alcohols and methyl ketones. The remaining isomers are mostly branched hydrocarbons although there are some cyclics. Toluene (TOL) and ethylbenzene (EB) were readily identifiable from mass spectra and so are given here. For cobalt (Fig. 4-b), the major peak was the normal-paraffin and smaller peaks were branched-chain hydrocarbons. As noticed in the relative intensities of ethanol and propanol, oxygenates were produced in negligible quantities under these operating conditions.

Both chromatograms have been truncated at C_{15} as higher carbon numbers simply repeat the pattern established in Fig. 4. Likewise, chromatograms of wax trap samples are not shown as they are identical to those from the cold trap except relative concentrations at each carbon number are different. In about 90 minutes, we routinely analyze up to C_{30}.

CONCLUSIONS

The analytical method developed here allows an accurate determination of Fischer-Tropsch organic products to about C_{30}, in addition to H_2, H_2O, CO and CO_2. It was not attempted to identify each isomer formed but rather to reduce the bulk of the data typically obtained by classifying the products into industrially useful categories, i.e. oxygenates, n-olefins, n-paraffins and remaining isomers at each carbon number. We chose to depict most of the analytical scheme for products obtained over a reduced fused-magnetite catalyst containing alkali because it produced the gamut of Fischer-Tropsch products. Hence, the analytical techniques given in this paper are readily adaptable to products from other catalysts such as cobalt (as illustrated) and ruthenium, which produce mostly hydrocarbons.

ACKNOWLEDGEMENT

LITERATURE CITED

Dietz, W.A., Journal of Gas Chromatography 1967, 5, 68.

DiSanzo, F.P., Preprints of the A.C.S. Division of Fuel Chemistry
    1981, 26(2), 13.

Nijs, H.H., Jacobs, P.A., Journal of Chromatographic Science
    1981, 19, 40.

Pichler, H., Schulz, H., Chemie-Ing. Techn. 1970, 42, 1162.

Schulz, H., Zein El Deen, A., Fuel Processing Technology 1977, 1,
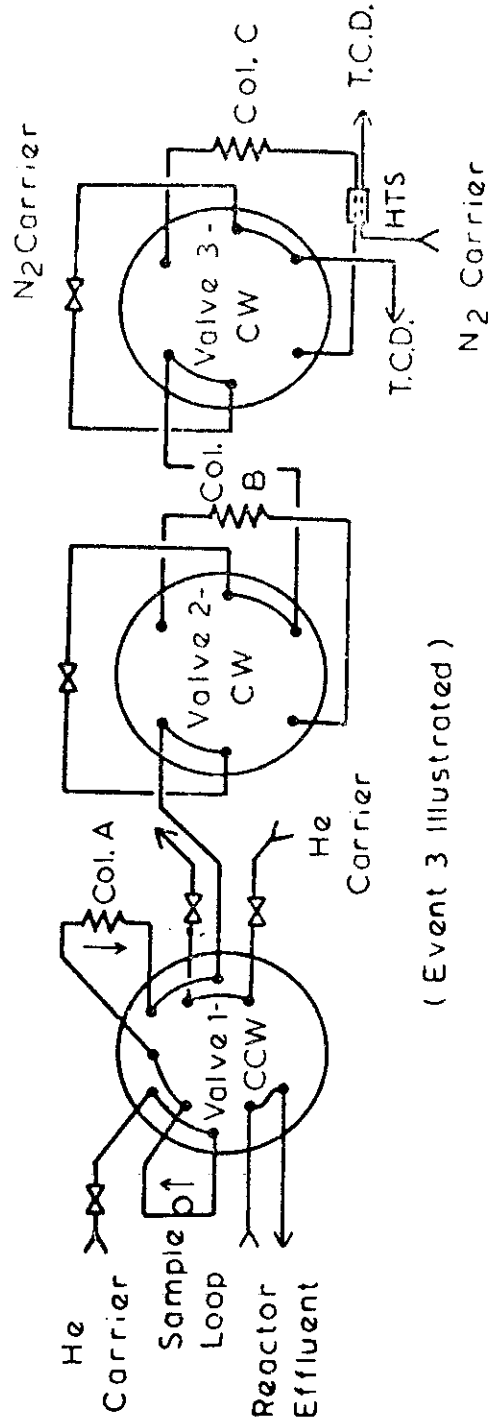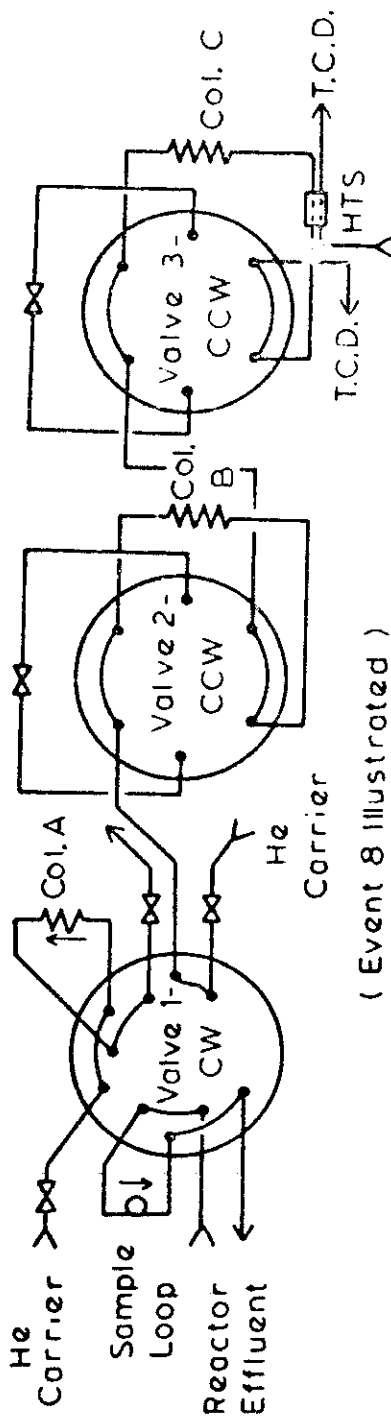   31.

Table I. Valve Sequencing Program for Carle Refinery Gas Analyzer.

Event Number	Time (min)	Valve Positions			Components Eluted
		Valve 1	Valve 2	Valve 3	
1	11.0	CW → CCW	CCW	CCW	H_2
2	0.05	CCW	CCW	CCW → CW	
3	23.0	CCW	CCW → CW	CW	C_3 and C_4 hydro-
4	0.05	*CCW → CW	CW	CW	carbons
5	10.0	CW	CW	CW → CCW	CH_4 and CO
6	0.05	CW	CW	CCW → CW	
7	11.0	CW	CW → CCW	CW	CO_2 and C_2 hydro-
8	0.05	CW	CCW	CW → CCW	carbons

*Note: Column A is backflushed to vent at Event 4 and thereafter.

LIST OF FIGURE CAPTIONS

Figure 1   Valve/Column Configuration for Carle Refinery Gas Analyzer

Figure 2a   Chromatogram of Residual Gas, from Carle Refinery Gas Analyzer

Figure 2b   Chromatogram of Residual Gas, from Perkin-Elmer Gas Chromatograph

Figure 2c   Chromatogram of Residual Gas, from Hewlett-Packard Gas Chromatograph

Figure 3   Chromatogram of Aqueous-Phase Products, from Perkin-Elmer Gas Chromatograph

Figure 4a   Chromatogram of Oil-Phase Products Formed by a Reduced Fused Magnetite Catalyst Containing Alkali. Hewlett-Packard Gas Chromatograph

Figure 4b   Chromatogram of Oil-Phase Products Formed by a Cobalt/Kieselguhr Catalyst (No Additives such as ThO_2 or MgO_2 Were Present). Hewlett-Packard Gas Chromatograph

He Carrier

Col. A

Sample Loop

Reactor Effluent

Valve 1- CW

Valve 2- CCW

Col. B

Valve 3- CCW

Col. C

T.C.D.

HTS

T.C.D.

N₂ Carrier

He Carrier

(Event 8 Illustrated)

He Carrier

Col. A

Sample Loop

Reactor Effluent

Valve 1- CCW

Valve 2- CW

Col. B

Valve 3- CW

Col. C

T.C.D.

HTS

T.C.D.

N₂ Carrier

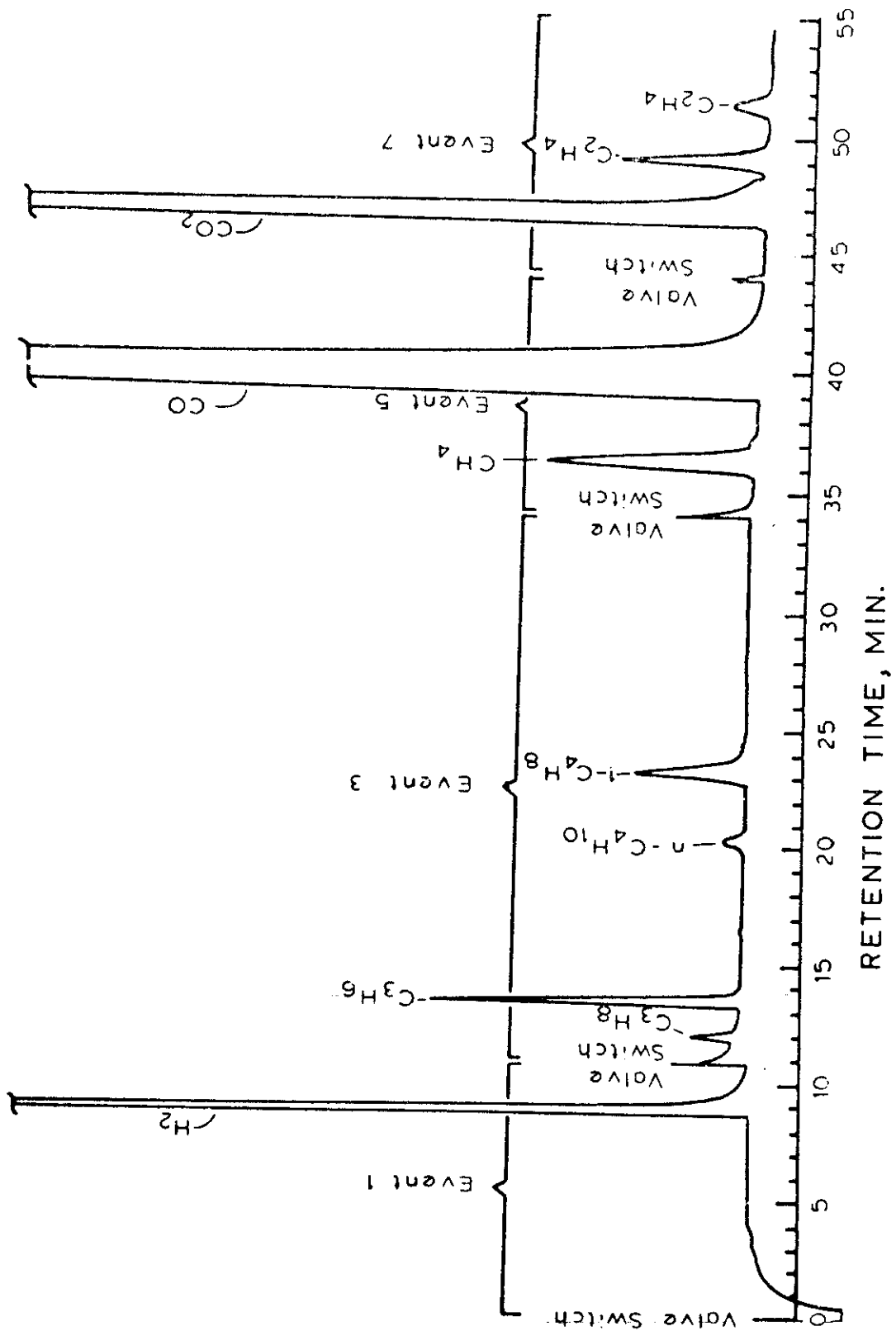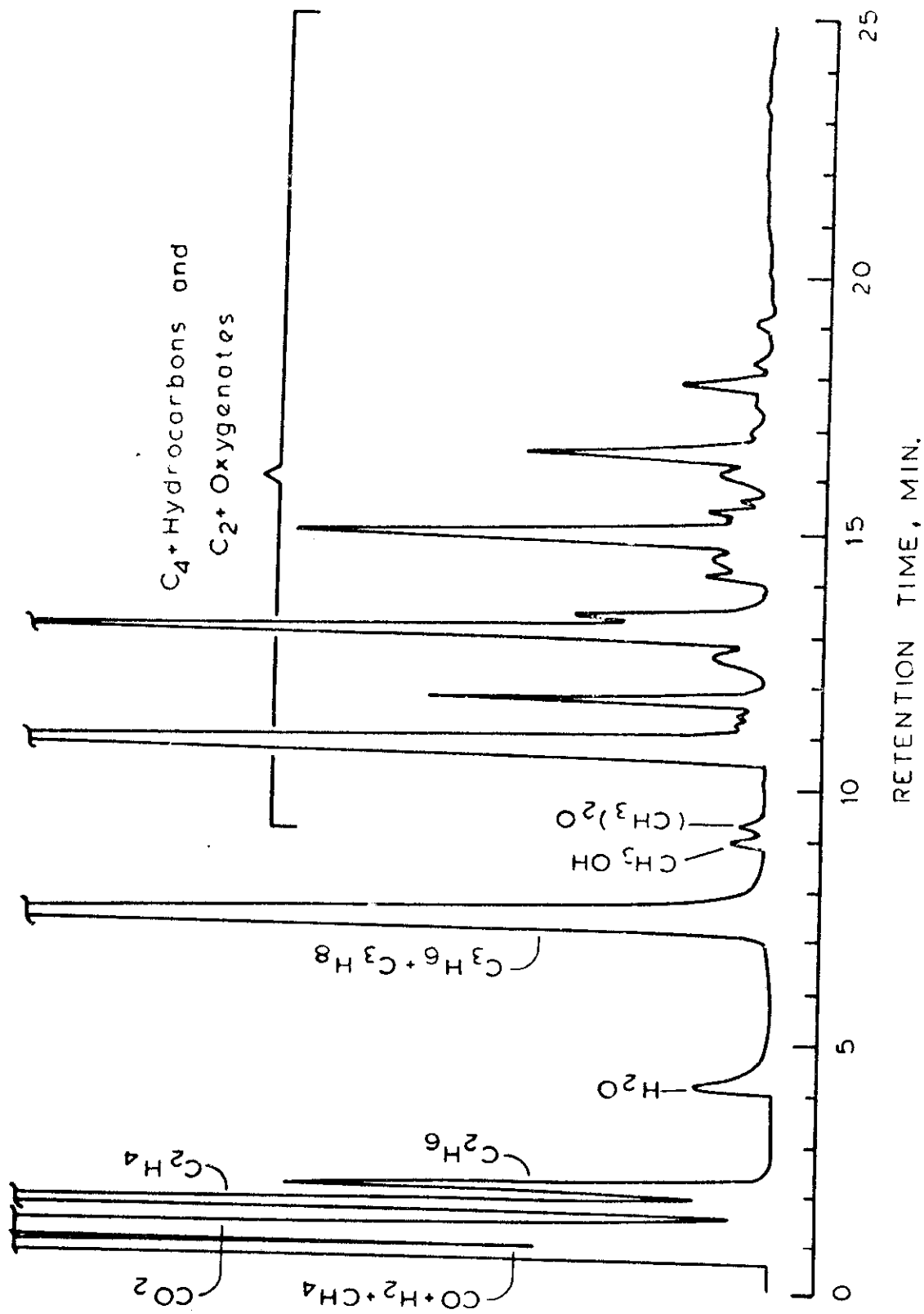He Carrier

(Event 3 Illustrated)

Column A: 40-ft x 1/8-in stainless steel tube packed with 27% Bis (2-ethoxyethyl)
Adipate + 2.5% Silicone Dow Corning DC 200/500 on 60/80 mesh
Chromosorb PAW

Column B: 10-ft x 1/8-in stainless steel tube packed with 80/100 mesh Poropak
"QS"

Column C: 5-ft x 1/8-in stainless steel tube packed with 65/80 mesh "5A"
Molecular Sieve

RETENTION TIME, MIN.

C₄⁺ Hydrocarbons and C₂⁺ Oxygenates

(CH₃)₂O

CH₃OH

C₃H₆ + C₃H₈

H₂O

C₂H₄

C₂H₆

CO₂

CO + H₂ + CH₄

RETENTION TIME, MIN.

RETENTION TIME, MIN.

C10 Hydrocarbons
C9 Hydrocarbons
C8 Hydrocarbons
C7 Hydrocarbons
C6 Hydrocarbons
C5 Hydrocarbons
C4 Hydrocarbons

C10 Pln
C10 Ole
C9 Pln
C9 Ole
C8 Pln
C8 Ole
C7 Ole-2
C7 Pln
C7 Ole
C4 Alc
C5 Ket
C6 Ole-2
C6 Pln
C6 Ole
C5 Ket
C3 Alc
C4 Ald
C5 Ole-2
C5 Pln
C5 Ole
C2 Alc
C3 Ald + Ket
C4 Ole-2
C4 Pln
C4 Ole
C3 Ald
C3 Ole-Pln
CH4

C5 Hydrocarbons

C6 Hydrocarbons

C7 Hydrocarbons

C8 Hydrocarbons

C9 Hydrocarbons

C10 Hydrocarbons

C11 Hydrocarbons

C12 Hydrocarbons

C13 Hydrocarbons

C14 Hydrocarbons

C15 Hydrocarbons

C_{10} Pln

C_9 Pln

C_8 Pln

C_7 Pln

C_6 Pln

C_2Ald C_3 Ald-ket

C_2alc

C_6Ola C_3 Alc

C_5 ket C_2alc

C_5Alu

C_{10}Ola 2

C_7Ola

C_5Alc C_6 ket

C_6alc

C_7ket

C_{11}Ola

C_9 alc

C_{10} alc

C_{11}Pln

C_{12}Ola

C_{12}Pln

C_{13}Ola

C_{14}Ola

C_{15}Ola

tol

RETENTION TIME, MIN.

0   5   10   15   20   25   30   35   40   45   50

C$_2$ Alc

C$_5$ C10

C$_5$ Ptr

C$_5$ Hydrocarbons

C$_6$ C10-2

C$_6$ Ptr

C$_6$ Hydrocarbons

C$_6$ 2-2

C$_6$ 2-2

C$_7$ Hydrocarbons

C$_7$ Ptr

C$_7$ C10-2

C$_8$ Hydrocarbons

C$_8$ Ptr

C$_8$ C10-2

C$_9$ Hydrocarbons

C$_9$ Ptr

C$_9$ C10-2

C$_{10}$ Hydrocarbons

C$_{10}$ Ptr

Hydrocarbons

Hydrocarbons

Hydrocarbons

Hydrocarbons

Hydrocarbons

RETENTION TIME, MIN.

0 5 10 15 20 25 30 35 40 45