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# FISCHER-TROPSCH SYNTHESIS. EVIDENCE FOR TWO CHAIN GROWTH MECHANISMS

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Fischer-Tropsch synthesis; radioisotope, tracer study; mechanism, Fischer-Tropsch synthesis; kinetics, Fischer-Tropsch synthesis; chain growth, Fisher-Tropsch synthesis, $^{14}C$, tracer studies; $^{14}C$-ethanol; $^{14}C$-1-pentanol; reactor, CSTR

The results show that n-pentanol serves to initiate Fischer-Tropsch synthesis reactions. Product accumulation in the CSTR is not adequate to explain the deviation from a constant $^{14}C$ activity/mole with increasing carbon number for alkane products. A second Fischer-Tropsch synthesis mechanism that produces only alkanes is needed to explain the deviation of the $^{14}C$ activity/mole with increasing carbon number for n-alkanes. Furthermore, the two chain growth pathways must be completely independent without the possibility of a carbon number species that is common to both mechanisms. It is suggested that the pathway that incorporates added $^{14}C$ labeled alcohol has an oxygen containing surface intermediate while the other reaction pathway involves an “oxygen-free” reaction intermediate.

## 1. Introduction

Carbon-14 isotopes were first utilized in Fischer-Tropsch studies by Emmett and coworkers [1–6]. These workers found that alcohols, and to a lesser extent alkenes, aldehydes and ketene, were incorporated into synthesis products. Ethanol and propanol were incorporated to produce results to indicate that alcohols could initiate chain growth, that the carbon skeleton of the added alcohol remained intact, and that CO was the dominant chain propagator. Emmett and coworkers were limited in their analyses since their work was carried out before gas chromatography became readily available. Schulz and coworkers [7–10] carried out a series of studies that extended the number of labeled compounds that were utilized and made extensive use of gas chromatography in the analysis of the products. These studies were in general agreement with the earlier results of Emmett and coworkers.

Recently, there has been renewed interest in the deviation of Fischer-Tropsch products from the Anderson-Schulz-Flory distribution. Anderson [11] summarized product distribution results up to about 1954. Included in this review

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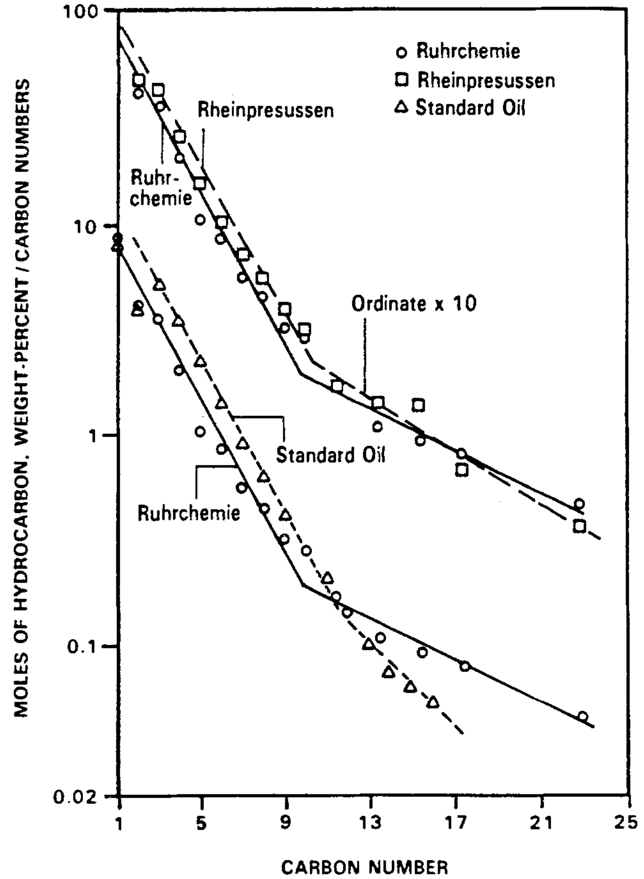

Fig. 1. Anderson-Schulz-Flory (ASF) plots for the products from Schwarzheide for catalysts for four sources and Standard Oil Company of New Jersey (reproduced from ref. [11], p. 208).

(fig. 1) were the results of the Schwarzheide tests using catalysts from Lurgi, Brabag, K.W.I., I.G. Farben, Ruhr Chemie, and Rheinpreussen [12], Standard Oil Co. of New Jersey and results using a fluidized-iron catalyst synthesis [13]. These results clearly show that two alpha values were required to account for the products and that the change to the higher alpha value occurred around carbon number 9–11. Furthermore, similar product distributions were obtained with promoted iron catalysts in fixed or fluidized bed reactors and with or without recycle. These results were obtained in larger reactors that were operated for long time periods. Other plots in Anderson's review, for example the one reproduced by Biloen and Sachtler [14] in a more recent review, appeared to follow an ASF distribution; however, careful inspection of the plot in this review shows that higher carbon number compounds deviate from the ASF line in a manner analogous to those in fig. 1.

Satterfield et al. [15] made detailed analysis of the products from Fischer-Tropsch Synthesis (FTS) obtained in a stirred-tank reactor utilizing a United

Catalyst, Inc. C-73 "doubly-promoted" catalyst. For the total products, these workers obtained plots that resemble the ones shown in fig. 1. However, when the products are considered on the basis of compound classes, it is apparent that fig. 1 provides an oversimplification of the situation. It appears that only the paraffins deviate from the Anderson-Schulz-Flory (ASF) plot; oxygenates and alkenes appear to follow a single ASF plot with alpha approximately 0.55. Even with a different reactor system and catalyst, the break in Satterfield's ASF plot occurs at approximately the same carbon number as was observed in the tests represented in fig. 1. Egiebor et al. [16] utilized another catalyst, iron supported on silica in a fixed-bed reactor, and obtained alkane and alkene distributions that followed the same trend as was reported by Satterfield et al. [15]. While a complete review of the question of two, or more, alpha values is beyond the scope of this introduction, additional references may be cited to support this view [17–20].

One approach to account for the two alpha values is that two sets of active sites are present on the Fischer-Tropsch catalyst. One set of sites is responsible for the products that determine one alpha value and the products produced on the other set of sites are responsible for the larger alpha value. It is difficult to believe that catalysts prepared with a variety of recipes, with different promoters, and for different active metals, would produce such similar ASF plots. Bell, for example [20], accepts the two alpha viewpoint but does not believe that any explanation had been advanced to account for the experimental observation.

The results presented in this paper utilized [1-$^{14}$C]-1-pentanol as the label. Product separation were utilized in order to evaluate the $^{14}$C distribution in alkane components over a range of carbon numbers. Results pertaining to the two alpha values are presented in this paper.

## 2. Experimental

A C-73 catalyst supplied by the United Catalysts, Inc. was utilized for this study. A portion of this catalyst was reduced for 72 hours in flowing hydrogen at 450°C. After reduction the catalyst was cooled to room temperature in hydrogen flow and the catalyst was then passivated using 1% oxygen in helium. The 1 liter stirred autoclave reactor was charged with 150 grams of the reduced, passivated catalyst, together with sufficient octacosane solvent to provide ca. 500 mL of liquid in the reactor. The catalyst-solvent mixture was heated to 300°C in flowing hydrogen and held at this temperature during a 48 hour period. An air driven agitator (ca. 600 rpm) was utilized for mixing during reduction and the synthesis run.

Mass flow regulators (Emerison, Model 5800) were utilized to control the CO and $H_2$ feed rates. The total feed rate was 180 cc STP/hr-g Fe with a gas mixture of $H_2/CO = 1.2$. The reaction temperature of 262°C ($\pm 2°$) was maintained during the approximately 150 day run period. The total pressure was maintained at 100 psig using a back pressure regulator. Labeled or unlabeled ethanol or pentanol was added to the synthesis gas mixture utilizing a Milton Roy pump. The labeled alcohol was added during a 24 hour period at a rate such that the molar ratio alcohol : CO was ca. 3 : 100. The alcohol was labeled in the carbinol position.

The reactor effluent first passed through heated transfer lines to a hot trap maintained at a nominal 65°C and then to a cold trap maintained at +10°C. The effluent from the cold trap could be passed through heated transfer lines fitted with appropriate valves to one of two gas chromatographs (GC) or through a wet-test meter to a vent. One of the GC's was a Hach gas analyzer that effected separation of $H_2$, $CH_4$, CO, $CO_2$, ethane, ethene, propane, propene, butanes and butenes. The effluent from this GC was passed to a Packard gas proportional counter where each peak that eluted was burned to $CO_2$ utilizing hot (800°C) cupric oxide; methane was added as a quench gas prior to the $CO_2$ flowing through the proportional counter. At least two, and usually five, samples were analyzed one after the other and this average value is reported; the five samples required approximately 4 to 5 hours for analysis. At least four of these multiple gas sample analyses were conducted during a 24 hour period of adding a $^{14}C$ labeled alcohol. The other GC utilized for gas analysis employed a Porpack R column to effect separation of $C_4$ through $C_9$ hydrocarbons. The effluent from this GC was passed to the proportional counter for $^{14}C$ activity determination was outlined above.

Liquid samples from the hot or cold trap were also analyzed by GC and proportional counting; columns utilized included a $1/8'' \times 30'$, 1% OV101 packed column. For quantitative $^{14}C$ analysis of liquid samples, a capillary DB-5 GC column could not be utilized since it could not provide sufficient effluent for proportional counting; the small sample size required for a capillary column would not contain sufficient $^{14}C$. Obviously, the capillary GC was utilized for chemical analyses.

There were so many $C_8$ to $C_{20}$ carbon number products that alkanes and alkenes could not be separated using our packed GC columns. Consequently, a separation of the liquid products (hot and cold trap materials blended according to the mass of each produced during the run) were separated to produce an alkane and an alkene fraction. This separation was accomplished using silica gel chromatography [21]. An aliquot of the Fischer-Tropsch product was placed on top of a 4 m column filled with dry silica that had been calcined at 550°C. The amount of octacosane, present in large quantities since it was used as reactor slurry medium, was decreased by fractional crystallization prior to adding the sample to the silica column. Isopropanol was utilized to elute the sample. The initial fractions contained alkanes only.

The alkane fraction was then separated into individual components in the $C_9$ to $C_{16}$ range. Liquid chromatography separation, utilizing a mixed water-methanol water solvent, was utilized; the eluting alkane was collected and the amount of n-alkane in the fraction determined from the response of a photometer. Each alkane fraction was added to a liquid scintillation cocktail and the amount of $^{14}C$/mole determined by liquid scintillation counting. The alkane fraction was also separated by carbon number components by injecting ca. 10 $\mu$L onto a GC column and trapping each carbon number fractions at dry-ice temperature. The $^{14}C$/mole for each fraction was determined using liquid scintillation counting.

## 3. Results and discussion

An Anderson-Schulz-Flory (ASF) plot for the products produced during day 20 of the run are shown in fig. 2. Methane production was consistently lower than anticipated for an alpha value of 0.62. It is apparent that a break occurs in the plot at carbon number ca. 10. The data from about $C_{10}$ through $C_{22}$ fit an ASF plot with an alpha value of ca. 0.87. The products beyond $C_{22}$ deviate from the ASF plot showing that less of the $> C_{22}$ products were collected in the product traps than needed to fit the ASF plot. However, this deviation is likely caused by accumulation of higher weight hydrocarbons in the reactor slurry (fig. 3). Octacosane, the starting solvent, accounts for approximately 90% of the sample that was directly withdrawn from the liquid in the reactor while operating at temperature and pressure. It is apparent from the data in fig. 3 that, starting around $C_{20}$,

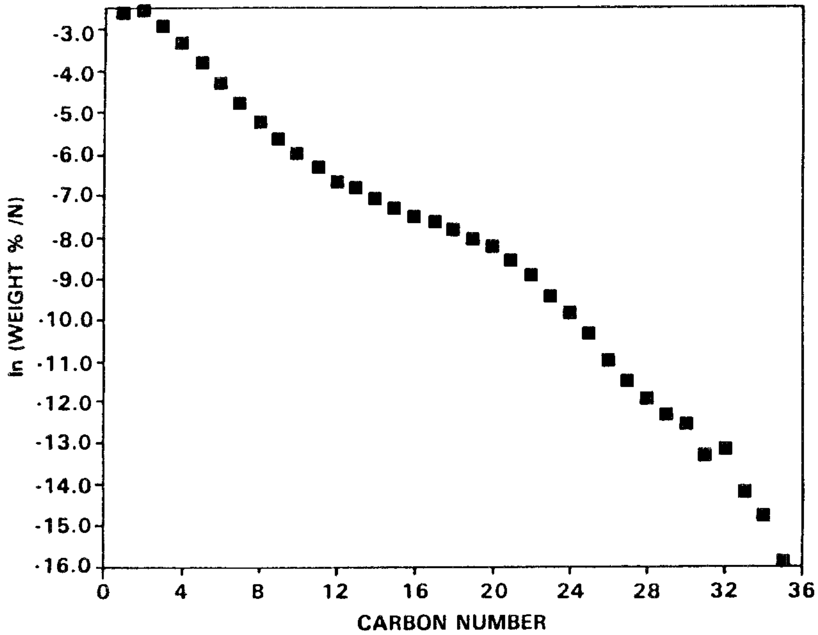

Fig. 2. ASF plot for the products produced for $(CO/H_2)$ in 0.8 at 260°C and 7 atm with a C-73 "doubly-promoted" iron catalyst.

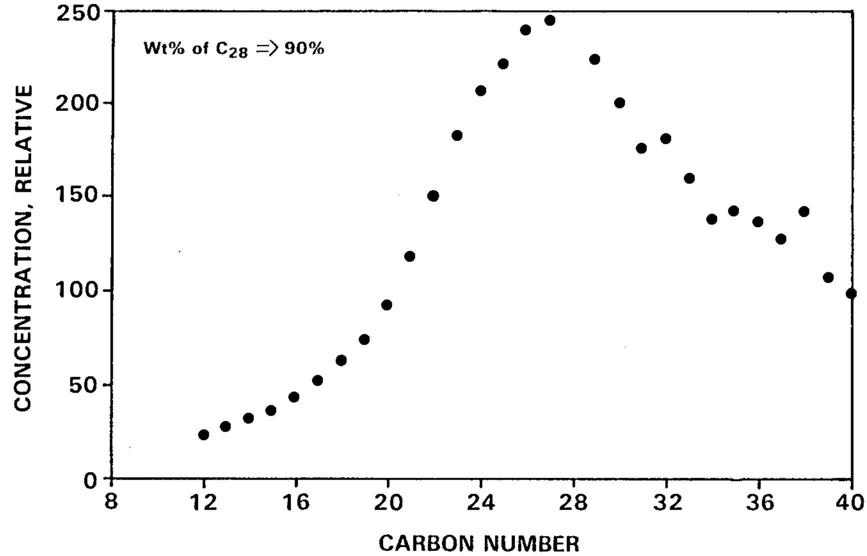

Fig. 3. Composition by carbon number for products (essentially alkanes) taken directly from the reactor following 20 days of a synthesis run (conditions as indicated in fig. 2; octacosane comprised 90% of the sample but is not plotted).

there is a rapid increase in the amount of each carbon number hydrocarbon retained in the liquid phase and that the accumulation reaches a maximum area percent (approximately equal to the weight percent) at about $C_{28}$. For clarity, $C_{28}$

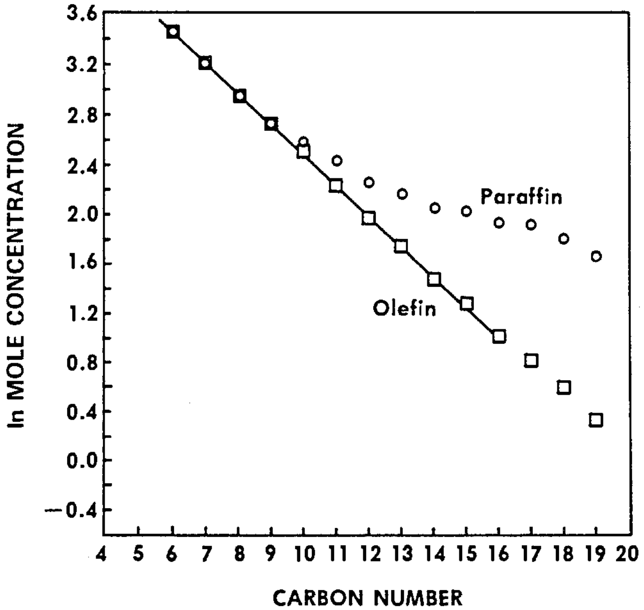

Fig. 4. Relative amounts of alkane and alkene (normalized for carbon number 6) produced during synthesis using the conditions outlined for fig. 2.

is omitted from fig 3. For carbon numbers greater than $C_{28}$ the retention continues to decline to the limit (ca. $C_{40}$) of the GC column used for the analysis. The curve in fig. 3 is very similar to one reported earlier by Huff and Satterfield [15].

The analytical data for alkanes and alkenes with carbon numbers from $C_6$ to $C_{19}$ are shown in fig. 4. The data in fig. 4 are for the n-alkane and the 1-, cis-2- and trans-2-alkanes only; however, the general trend would be the same if the small amounts (ca. 10%) of the $C_6$ to about $C_{12}$ isomeric compounds were included. For this comparison the alkene concentrations have been adjusted so that the $C_6$ alkenes and alkanes both have the same value. The alkenes fit a single ASF plot to as high a carbon number as could be accurately determined by capillary GC analysis; thus, the alkenes above $C_{20}$ are present in a much smaller concentration than the corresponding carbon number alkane [22]. The paraffins, on the other hand, begin to deviate from the ASF alkene plot at a carbon number of about $C_{10}$. These results are very similar to those reported by Huff and Satterfield [15].

Our results when $^{14}C$ labeled ethanol was added to a syngas feed at 7 atm, considering only the $C_2$ to $C_4$ gaseous products (fig. 5), are in excellent agreement with the results Emmett and coworkers [1–6] obtained at one atm operating conditions. If, as Emmett's results suggest, added $^{14}C$ ethanol serves as only a chain initiator, we could anticipate a constant $^{14}C$/mole with increasing carbon number (shown schematically in fig. 6A). If ethanol serves as a chain propagator

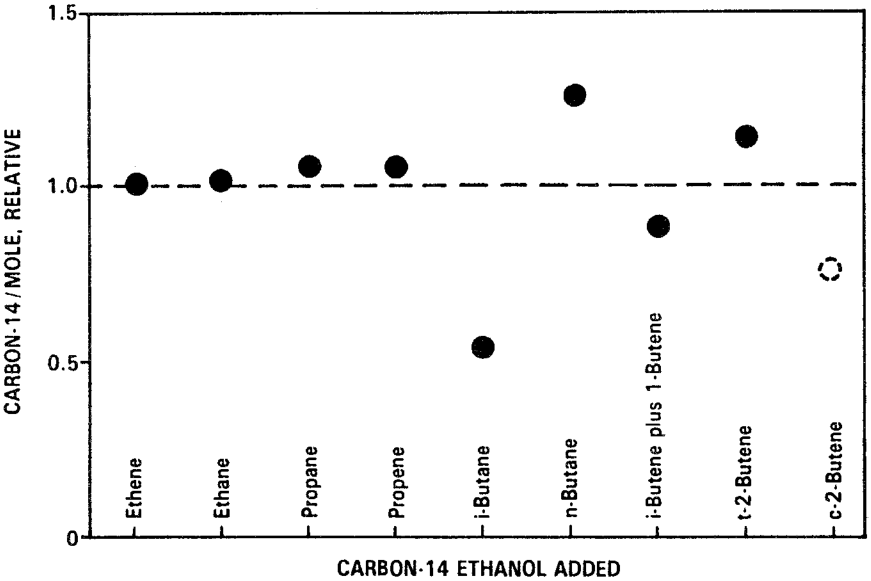

Fig. 5. Relative $^{14}C$/mole in gaseous products from the synthesis (using the same conditions as fig. 2 except 3-volume % (based on alcohol and CO) [$^{14}C$-1]-ethanol rather than [$^{14}C$-1]-pentanol was added during a 24 hour period.

we would anticipate an increasing $^{14}$C/mole with increasing carbon number (fig. 6B). Note that Emmett and coworkers obtained results that are consistent with those shown in figs. 6A and 6B (figs. 7, 8). The data in fig. 7 were obtained using labeled methanol which served as a propagator while the data in fig. 8 were obtained using ethanol or propanol and agree with the alcohol serving as an initiator. If ethanol dehydrates to ethylene which then undergoes a polymerization that is independent of the synthesis reaction, a $^{14}$C distribution shown in fig. 6C should be obtained. If the carbons of the added ethanol and CO become equivalent, the activity distribution should be as shown in fig. 6D. It is apparent that (1) our data for lower weight products when labeled ethanol is added agree with the results expected for ethanol to serve as a chain initiator, and (2) none of the four synthesis mechanisms outlined in fig. 6 account for the data for higher carbon alkanes (fig. 9). The data in fig. 9 are for products obtained when labeled pentanol was added; however, similar data are obtained for the higher carbon number alkanes when labeled ethanol is added to the syngas feed.

A stirred-tank reactor was utilized for this study; hence, there is accumulation of products in the reactor slurry during the period prior to the introduction of $^{14}$C

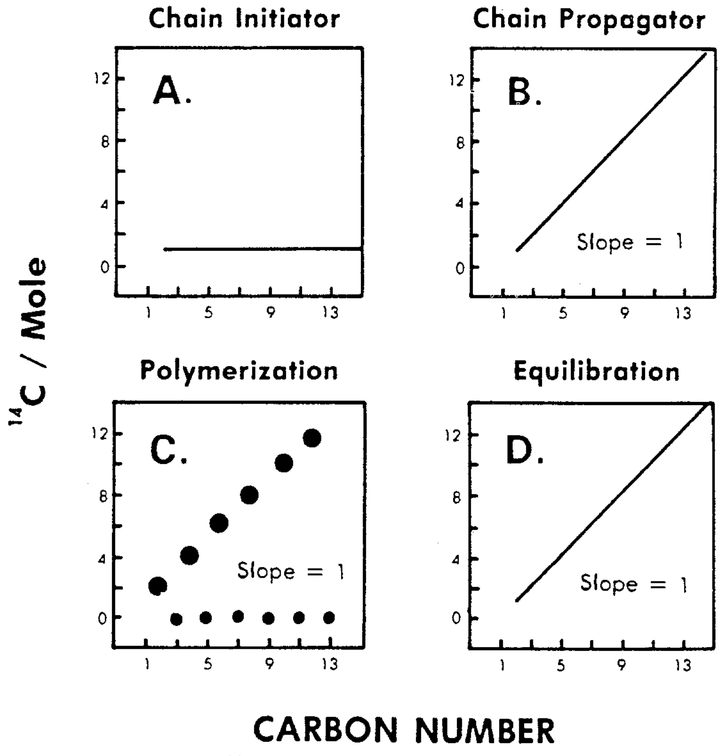

Fig. 6. Schematic representation of $^{14}$C activity by carbon number for four chain growth mechanisms (see text for mechanism details).

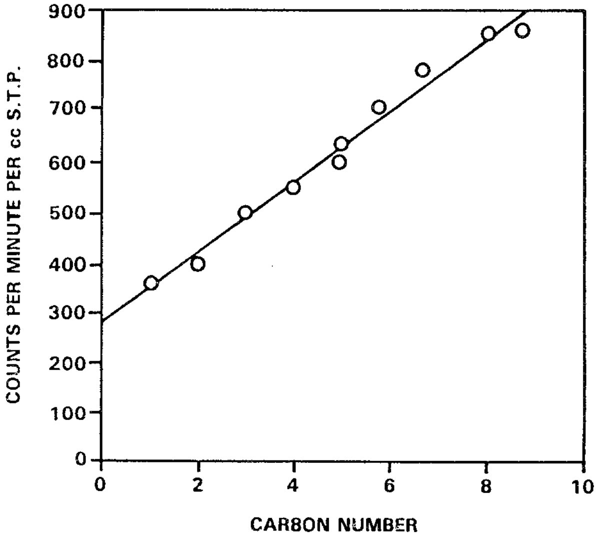

Fig. 7. Results from the addition of $^{14}C$ labeled methanol (bottom) to syngas (redrawn from ref. [11]).

labeled pentanol. This accumulation factor, $A_f$, may be obtained from the accumulation equation for this type of reactor:

$$A_f = \int (1 - e^{-t/\theta})/24$$

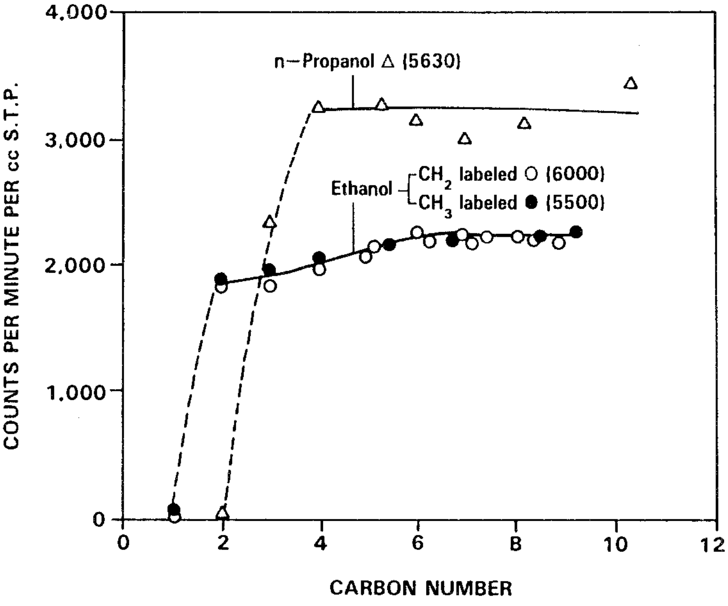

Fig. 8. Results from the addition of $^{14}C$ labeled ethanol or propanol to syngas (redrawn from ref. [11]).

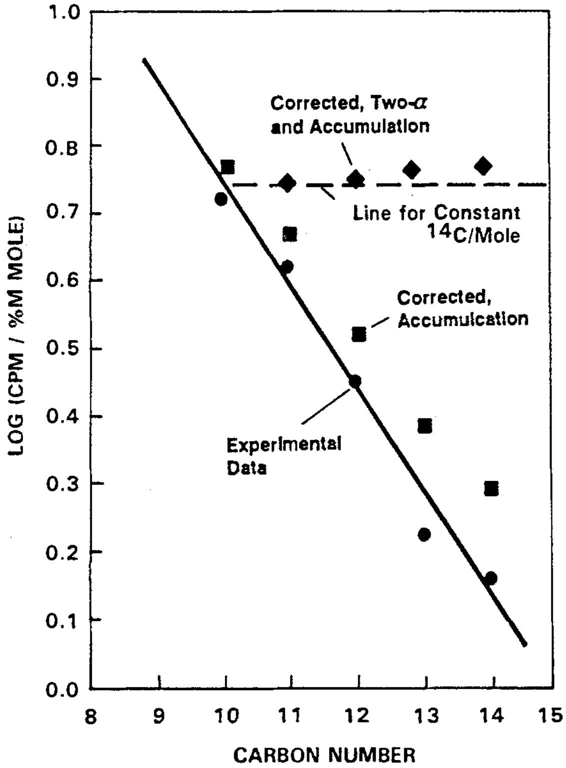

Fig. 9. Radioactivity of the: alkane products (●); experimental data corrected for accumulation using data shown in table 1 (■), and experimental data corrected for both accumulation and the two alpha mechanism (see text for details) (◆).

where $\theta$ is the residence time, $t$ is reaction time in hours, and 24 is the period during which $^{14}$C pentanol was added. $\theta$ is defined as the amount of each carbon number product in the slurry in the reactor (determined experimentally for the sample withdrawn from the reactor slurry) divided by the amount of the corresponding carbon number product produced per hour. Application of this equation permits us to adjust our data to account for the effect of product accumulation. The values in the second column of table 1 indicate the fraction of each carbon number product that would be collected over a 24 hour period of $^{14}$C addition and these permit us to calculate the impact of this accumulation upon our experimental results. To do this we have taken the radioactivity of $C_{10}$ as the basis for comparison; this was done since this is the carbon number range where product accumulation is easily determined in the material withdrawn from the reactor.

Correcting the $^{14}$C/mole in the alkanes in the products for the fraction accumulated in the reactor (■, in fig. 9) does not produce agreement between experimental data and the expected constant activity with increasing carbon

Table 1
Effect of accumulation in the slurry reactor upon products of increasing carbon number

| Carbon number | $\int(1-\exp(-t/\theta))/24$ | $\theta$ [a] (hr) |
|---|---|---|
| 10 | 0.948 | 1.25 |
| 11 | 0.889 | 2.67 |
| 12 | 0.792 | 5.02 |
| 13 | 0.735 | 6.52 |
| 14 | 0.647 | 9.13 |
| 15 | 0.564 | 12.2 |
| 16 | 0.465 | 16.9 |

[a] See text for method of calculation.

number. The $^{14}C$/mole for the products are diluted to a much greater extent than can be anticipated from accumulation in a stirred-tank reactor.

Examination of figs. 2 and 4 suggested another possibility. Assume that the two alpha values in fig. 2 correspond to different product groupings. For alpha = 0.62 ($\alpha_1$), the typical Fischer-Tropsch products are formed (alkanes, alkenes, oxygenates, etc.) but for alpha = 0.87 ($\alpha_2$) the only, or only significant, products are alkanes. If the above two assumptions are valid, a second correction should be applied to the $^{14}C$/mole for the alkanes. This has been done by calculating the moles of additional alkane that is formed for each carbon number from the synthesis corresponding to $\alpha_2$. The correction for accumulation only (■, fig. 9) is not adequate but when the data are corrected for the paraffin only $\alpha_2$ synthesis and for reactor accumulation the agreement of the corrected data to the constant $^{14}C$/mole line is excellent (◆, fig. 9). Thus, the alkane data, corrected for both accumulation in the reactor and for a second alkane synthesis pathway, are consistent with a mechanism wherein the added pentanol (or ethanol) serves only as a chain initiator.

Thus, the data are consistent with the following general synthesis pathways.

$$A_1O \rightarrow A_2O \rightarrow \cdots \rightarrow A_nO \rightarrow \cdots$$
$$(A_n \text{ oxygenates, } A_n \text{ alkenes, } A_n \text{ alkanes}) \qquad [1]$$
$$B_1 \rightarrow B_2 \rightarrow \cdots \rightarrow B_n \rightarrow \cdots$$
$$B_n \text{ paraffins.} \qquad [2]$$

The incorporation of $^{14}C$ in the products illustrated for reaction [1] but not reaction [2] provides a rationale for proposing that the surface species for pathway 1 contains oxygen while a monoxygenated intermediate is involved in pathway [2]. Furthermore, pathway [1] corresponds to the ASF plot with alpha = 0.62 and pathway [2] to the ASF plot with alpha = 0.87.

In addition, the two reaction pathways ([1] and [2]) must be completely independent since the equivalence of surface species $A_n = B_n$ requires, even for completely irreversible surface synthesis reactions, that all products with carbon number *n* and greater have equal $^{14}C$/mole activity. Since this is contrary to the experimental data, none of the surface species in the two chain growth pathways may become equivalent.

Previously, the two alpha values have been attributed to two, or more, types of sites. This is one way to explain the current results provided the sites are sufficiently different so as to prohibit surface migration from one type of site to the other type. This implies that surface diffusion of adsorbed species does not occur. It appears unlikely that two sets of sites could be located on the catalyst surface so that, at a reaction temperature of 260°C, surface migration was not allowed. It also appears unlikely that catalysts prepared in various laboratories, utilizing a variety of catalyst preparation procedures as well as a range of promoter elements and concentrations, could produce two sets of sites that would produce such similar product compositions that the break in the two alpha plots consistently occur around $C_{10}$.

It is also possible to obtain the two alpha values with one set of catalytic sites if adsorbed CO is transformed in a constant ratio to two $C_1$ chain initiation species. One view of this constant ratio for initiation is shown below:

$$\begin{tikzcd}
 & (CH_xO)_a \arrow[r] & {} \arrow[r] & {} \arrow[r] & \alpha_1 \text{ products} \\
(CO)_a \arrow[ur, "x/2\,H_2", "k_1"'] \arrow[dr, "k_2"] & & & & \\
 & (O)_a + (C)_a \arrow[r, "H_2"] & {} \arrow[r] & {} \arrow[r] & \alpha_2 \text{ products}
\end{tikzcd} \tag*{[3]}$$

The ratio of $\alpha_1$ products and $\alpha_2$ products should, for reaction [3], depend upon hydrogen pressure; however, other reactions such as, for example, oxygen hydrogenation could decrease the hydrogen dependency so as to make difficult, or even impossible, to detect a hydrogen dependency. A number of proposed intermediates have been recently reviewed by Menon [22] and he incorporates the intermediates into a series of surface species that are equilibrating. The view expressed in eq. [3] differs from his proposal since the steps must be largely irreversible, including the initial pathway for CO conversion to a $C_1$ chain initiation species.

After realizing the possibility of two chain growth pathways in which one did not incorporate $^{14}C$, the radiochromatograms were reexamined. A radiochromatogram of a cold-trap sample is shown in fig. 10; the top curve corresponds to the proportional counter output and the bottom curve is the GC thermal conductivity cell output. Note that different attenuations were utilized for various proportional counter peaks; these changes are indicated in fig. 10. Also note that much of the $C_5$ fraction remained in the gas phase since the cold trap was maintained at ca. +10°C. Even so, it is apparent that the $C_5$ alkane (peaks A, A′) and alkenes (peaks B, B′) have significant $^{14}C$ activity; the same applies for the $C_6$ alkane (peaks H, H′) and alkenes (peaks I, I′). However, several peaks that have a large thermal conductivity area relative to n-hexane have a small, or insignificant, $^{14}C$

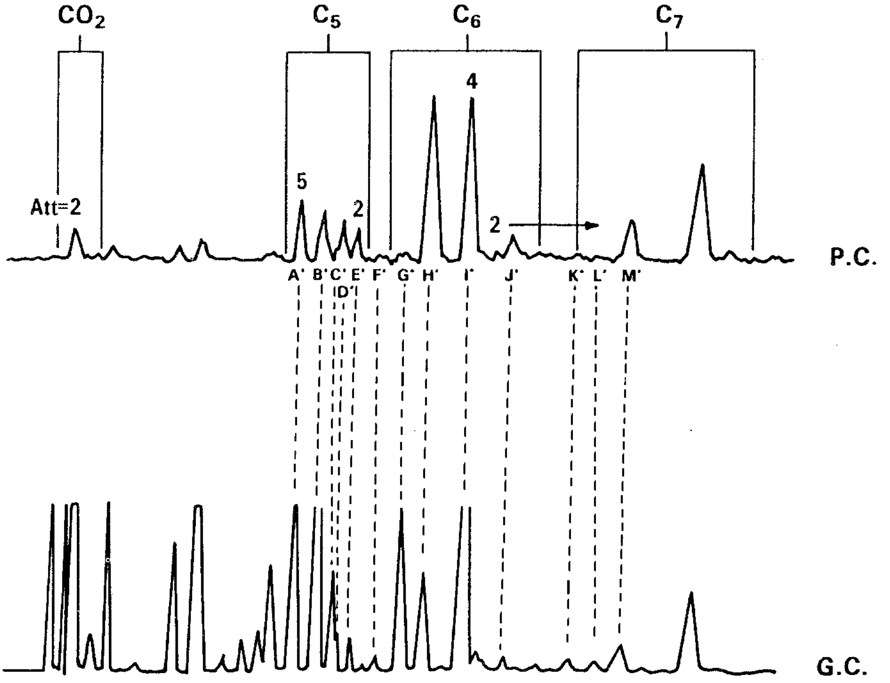

Fig. 10. Gas chromatograph (bottom) and radiochromatograph (top) for hot trap products (attenuation changes are indicated); peaks corresponding to the same compound are indicated by the same letter as, for example, A in the GC and A′ in the radiochromatogram.

proportional counter peak area relative to that for n-hexane. For a striking example, compare the relative thermal conductivity peak area of n-hexane (peak H) and a compound identified as 2-methylpentene by retention time and GC-MS analysis (peak G); clearly peak G has about twice the thermal conductivity GC area of peak H. In contrast to the thermal conductivity result; the proportional counter output for n-hexane (peak H′) is very large compared to the area of peak G′. Hence, the component represented by peaks G, G′ has essentially no $^{14}C$ activity relative to that of n-hexane. Other peaks may also be identified that have much less $^{14}C$ activity relative to n-hexane; for example, peaks C, C′; F, F′; K, K′; and L, L′. The lack of significant $^{14}C$ activity in these compounds relative to n-hexane clearly supports the view that there is a reaction pathway that does not incorporate $^{14}C$ as well as a pathway that does. Furthermore, retention times on a variety of columns indicate that these compounds that contain no, or little, $^{14}C$ are not oxygenates.

In summary, the current results show that ethanol and n-pentanol serves to initiate a FTS reaction. A second FTS mechanism that produces only alkanes is needed to explain the deviation of the $^{14}C$ activity/mole with increasing carbon number for n-alkanes. Furthermore, the two chain growth pathways must be completely independent without the possibility of a carbon number species that is common to both mechanisms. It is suggested that the pathway that incorporates added $^{14}C$ labeled alcohol has an oxygen containing surface intermediate while the other reaction pathway involves an "oxygen-free" reaction intermediate.

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