linear relation between the mole fraction of isoalkane and the carbon-number through C_9 (figure III-19).

In figure III-19 the higher carbon-number SASOL data of Pichler et al. (III-31) are plotted together with data from our run with a C-73 catalyst. The SASOL data in figure III-31 is from reference III-31 and is slightly different from that plotted in figure III-18; however, a similar trend is shown for both sets of SASOL data. The SASOL data in figure III-19 show essentially two linear regions where the percentage of isoalkane increases with increasing carbon-number. In the first, lower carbon-number region the isoalkane content increases more rapidly with carbon-number than it does in the second, higher carbon-number region. For our run with a C-73 catalyst at 260°C (figure III-19), the data represented by the closed squares (■) include a coeluting alcohol as an isoalkene; the data represented by the open squares (□) neglects the peak containing the alcohol. After correcting for the amount of alcohol, our data with C-73 is similar to data reported by Pichler et al. (III-31) for the practical catalyst and for an alkalized iron catalyst at 220°C. More importantly, the percentage of isoalkane that we obtained with the C-73 catalyst in a plug-flow reactor at 320°C and 7 atmospheres is essentially the same as we obtained at 260°C in the CSTR at 7 atmospheres. Thus, temperature alone does not appear to account for the much higher fraction of isoalkanes produced in the fluidized pilot plant synthesis.

III-E-1. Carbon-14 Tracer Studies

The conversion of syngas with carbon-14 labeled ethanol in a CSTR at 7 atmospheres produces C_2-C_4 products (figure III-20) that are consistent with the results reported earlier by Emmett and coworkers (figure III-21). In both cases the nearly constant activity/mole with increasing carbon-number is expected if the role of the added alcohol is to only initiate chain growth. However, the fraction of products produced by ethanol initiation in the 1 atmosphere work by Emmett <u>et al</u>. (30-40%) is greater than at our 7 atmosphere conditions (5-15%).

Close examination of the data in figure III-20 shows that the activity of the isobutane is only about one-half as great as the other products. A similar observation was made when the added alcohol was carbon-14 labeled 1-pentanol (figure III-22). The bottom part of figure III-22 presents the gas chromatograph and the upper curve is the output from the proportional counter that coincides with the time scale of the g.c. Consider first the C_5 compounds. G.C. peak A (and the corresponding proportional counter peak A') represents 2-methylbutane; note that even though there is a significant g.c. peak the proportional counter peak is only slightly above background. Peaks B and C, corresponding to n-pentane and 1-pentene, on the other hand, have the ^{14}C activity expected if they are derived from the labeled alcohol. A similar situation is encountered for the six carbon products. Peaks I and J, corresponding to n-hexane and 1-hexene, have significant proportional counter peaks (I' and J') indicating that a significant quantity of these are derived from the added alcohol. However, g.c. peak H, which was identified as 2-methylpentane by retention time and the g.c.-m.s. fragmentation pattern, has essentially no ^{14}C (peak H').

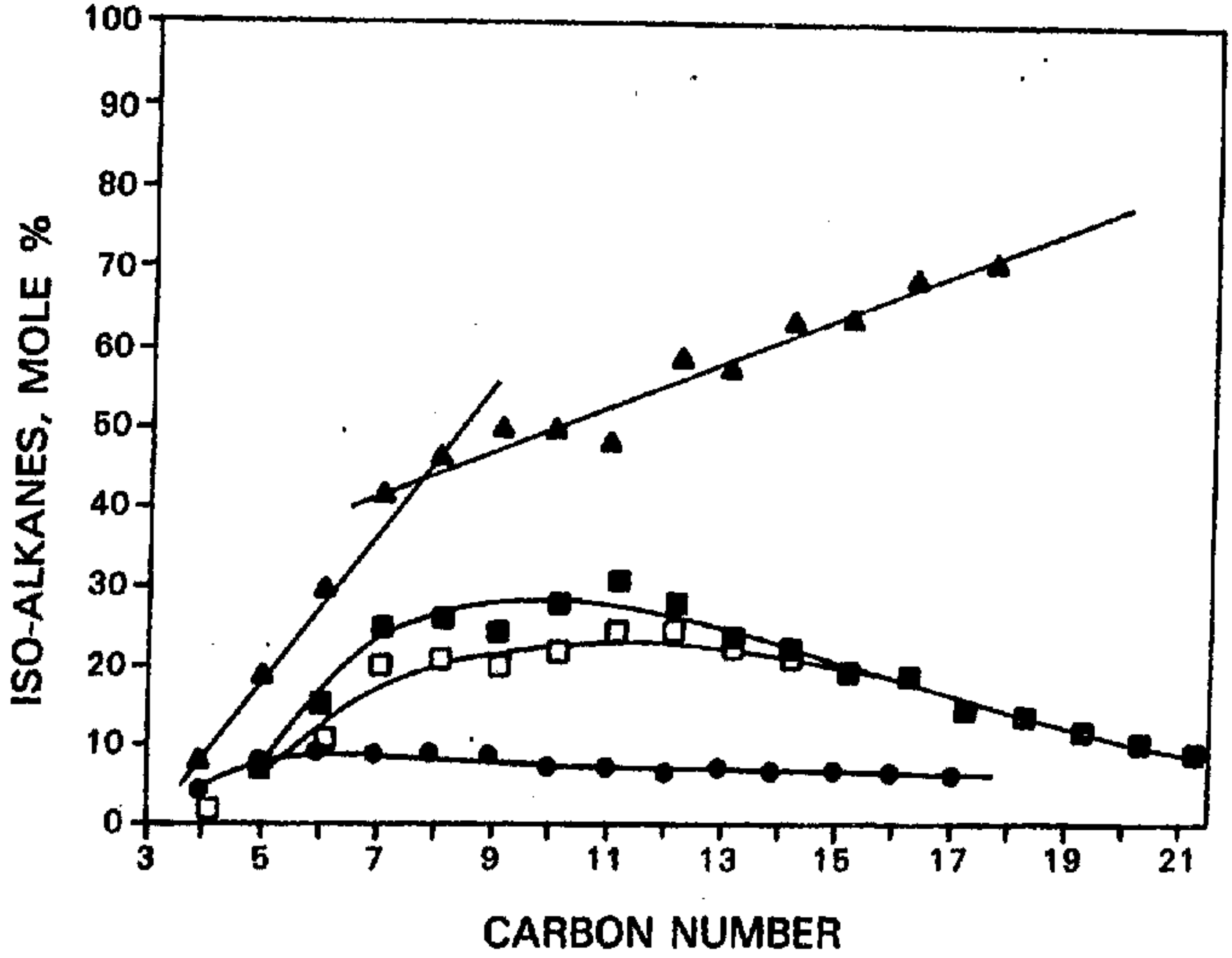


Figure III-19. Mole fraction of iso-alkene from reference III-31 for a practical catalyst (●), SASOL fluid-bed reactor (▲); this study including alcohol (■) and this study neglecting peak that includes the alcohol (□).

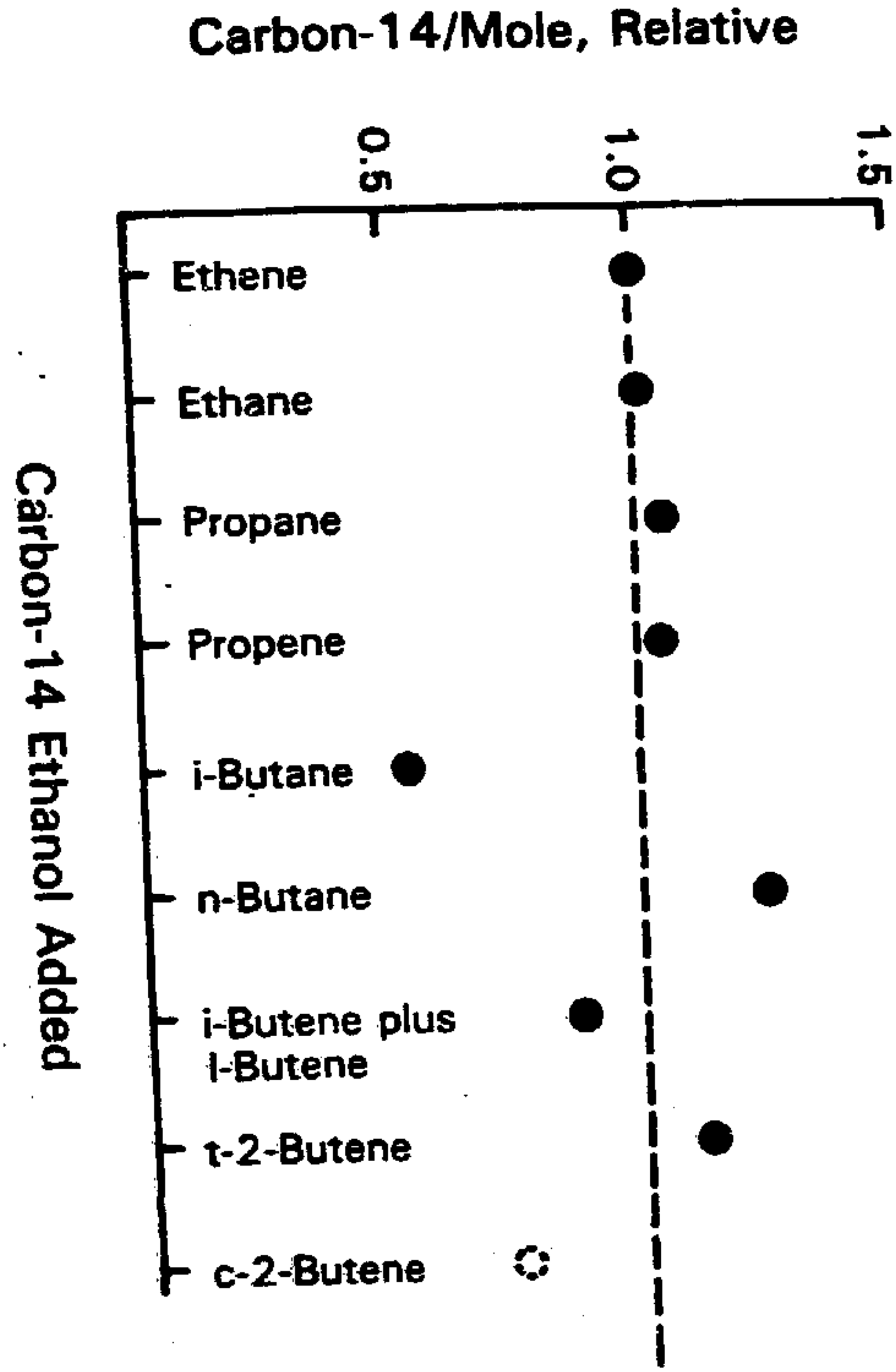


Figure III-20. Relative activity for C_2–C_4 products obtained when carbon-14 labeled ethanol was added to the synthesis gas.

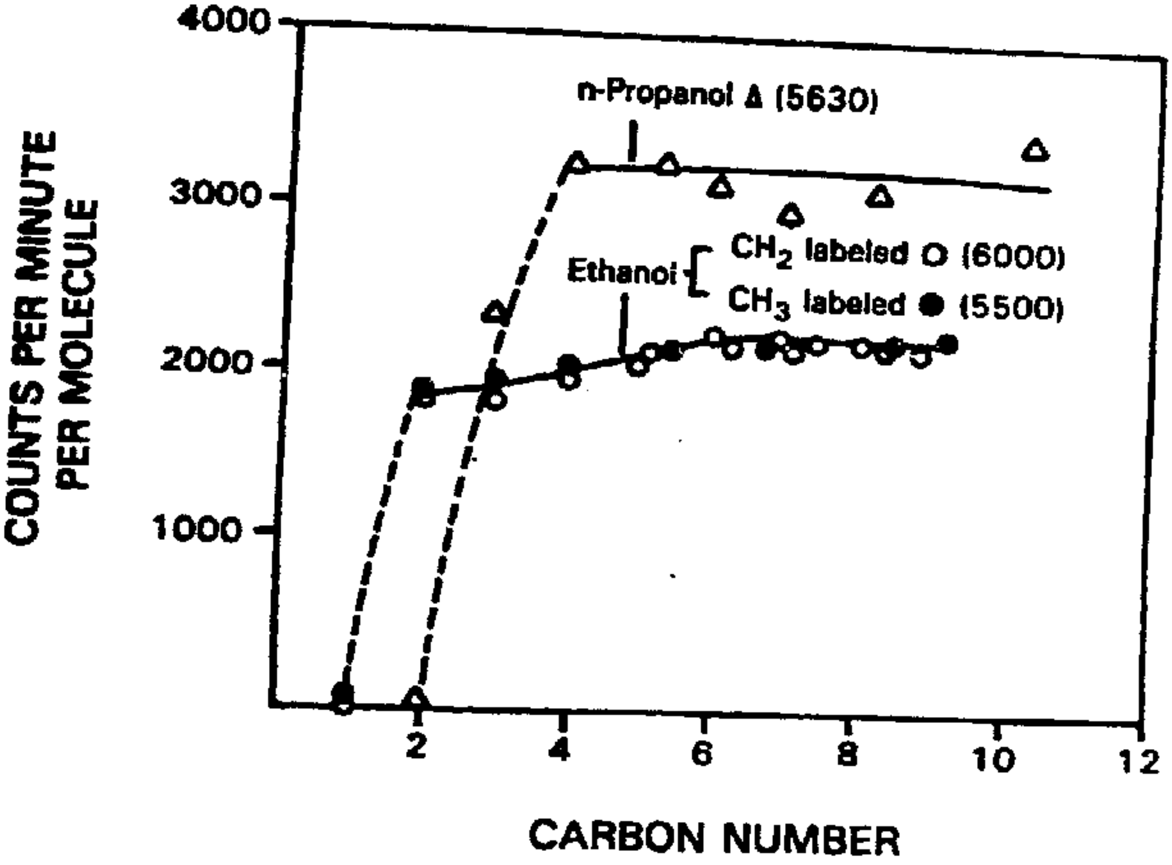


Figure III-21. Activity of products from synthesis with carbon-14 labeled ethanol or propanol (redrawn from reference III-20).

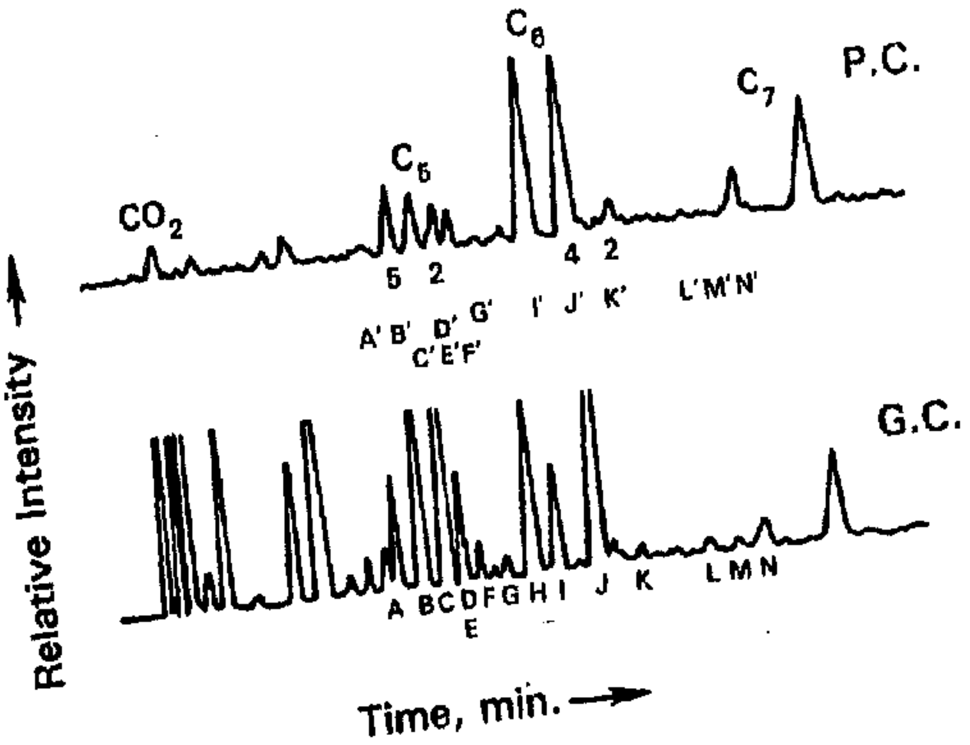
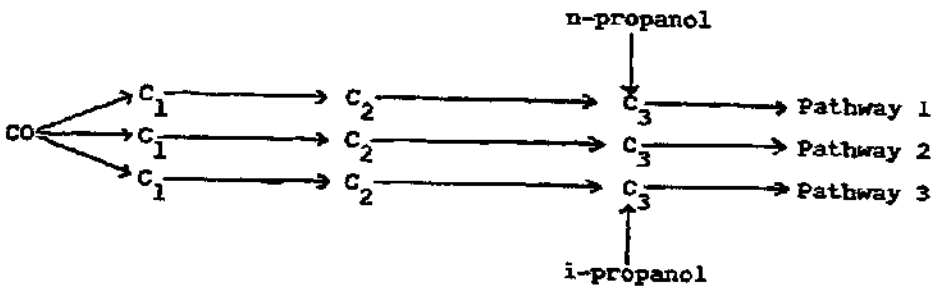


Figure III-22. Gas chromatogram (bottom) and proportional counter output (top) for the gas products when carbon-14 labeled 1-pentanol was added to the syngas (CSTR, C-73 catalyst, 7 atmosphere, 260°C).

Emmett and coworker's data (III-17, III-20, III-21) in figure III-23 correspond to the average activity of the C_4 products. When carbon-14 labeled 1-propanol was added with the syngas feed it was observed that n-butane and n-butenes had appreciable ^{14}C activity but iso-butane and iso-butene had essentially no ^{14}C activity. On other hand, the situation was reversed when ^{14}C labeled 2-propanol was added since the normal products had essentially no activity and the iso-butane and iso-butene products were very active. These activity distributions in the C_4 hydrocarbons plotted in figure III-23 show the dominance of the activity in n-butane derived from 1-propanol and in iso-butane when 2-propanol was added.

Our data, obtained by adding ^{14}C labeled propanol, agree with that of Emmett and coworkers. However, the amount of incorporation at 7 atm appears to be much lower than Emmett and coworkers observed at atmospheric pressure. The small amount of initiation with 2-propanol makes it very difficult to obtain accurate relative activities. First, the major reaction of 2-propanol was dehydrogenation to acetone; in fact, the gaseous effluent contained almost twice as much acetone as 2-propanol. This indicates that 2-propanol was adsorbed on the catalyst surface to undergo dehydrogenation and, therefore, the lack of initiation of growing chains was not due to a lack of adsorption of 2-propanol on the catalyst surface. The relative activity of propane is much higher than propene; this indicates that some fraction of the added 2-propanol underwent hydrogenolysis to directly form propane. We have observed that ethanol and 1-pentanol also undergo hydrogenolysis to form an alkane with a higher relative activity than the corresponding carbon-number alkene. However, in spite of the low ^{14}C activity in the products, an examination of the C_5 alkene data (figure III-24) clearly show that incorporation is much greater in the 2- and 3-methyl-1-butenes than in 1-pentene.

The current results, together with those reported by Emmett and coworkers, indicate that normal and iso-alcohols initiate chain growth and that different surface species are generated from these two alcohols. Furthermore, the surface species of these two growth chains do not interchange to an appreciable extent. Thus, we have two alkane synthesis pathways; one must be initiated by CO and another from alcohols. The carbon-14 labeled alcohol incorporation can therefore be depicted as in the scheme below (for ^{14}C labeled propanols):



[III-8]

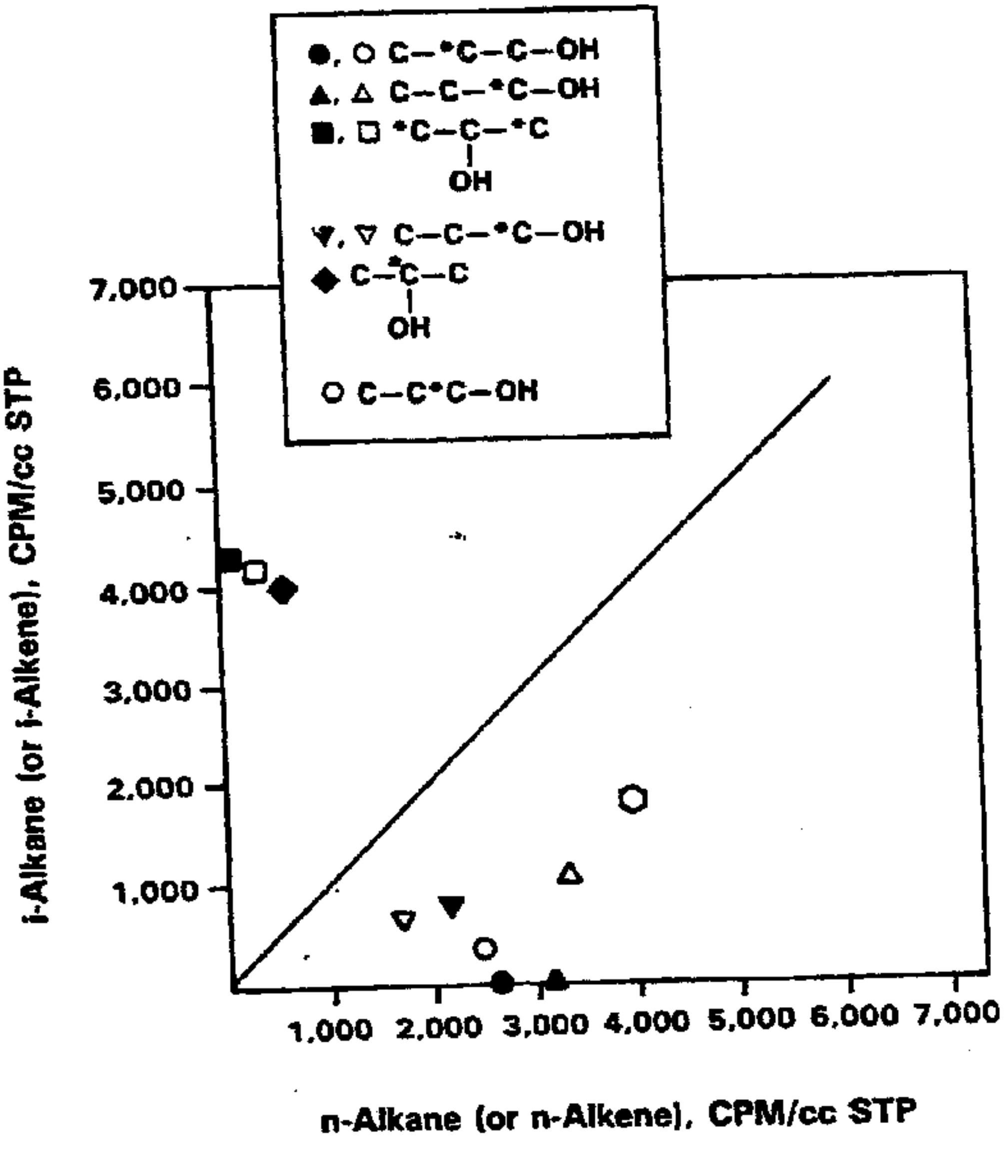


Figure III-23. Activity in the iso- and normal-alkanes (solid symbols) and alkenes (solid symbols) for synthesis products for the addition of $CH_3{*}CH_2OH$ (●,○); $CH_3CH_2{*}CH_2OH$ (▲,△; ▼,▽) and $*CH_3$-$CHOHCH_3$ (■,□) (data from references III-20 and III-22).

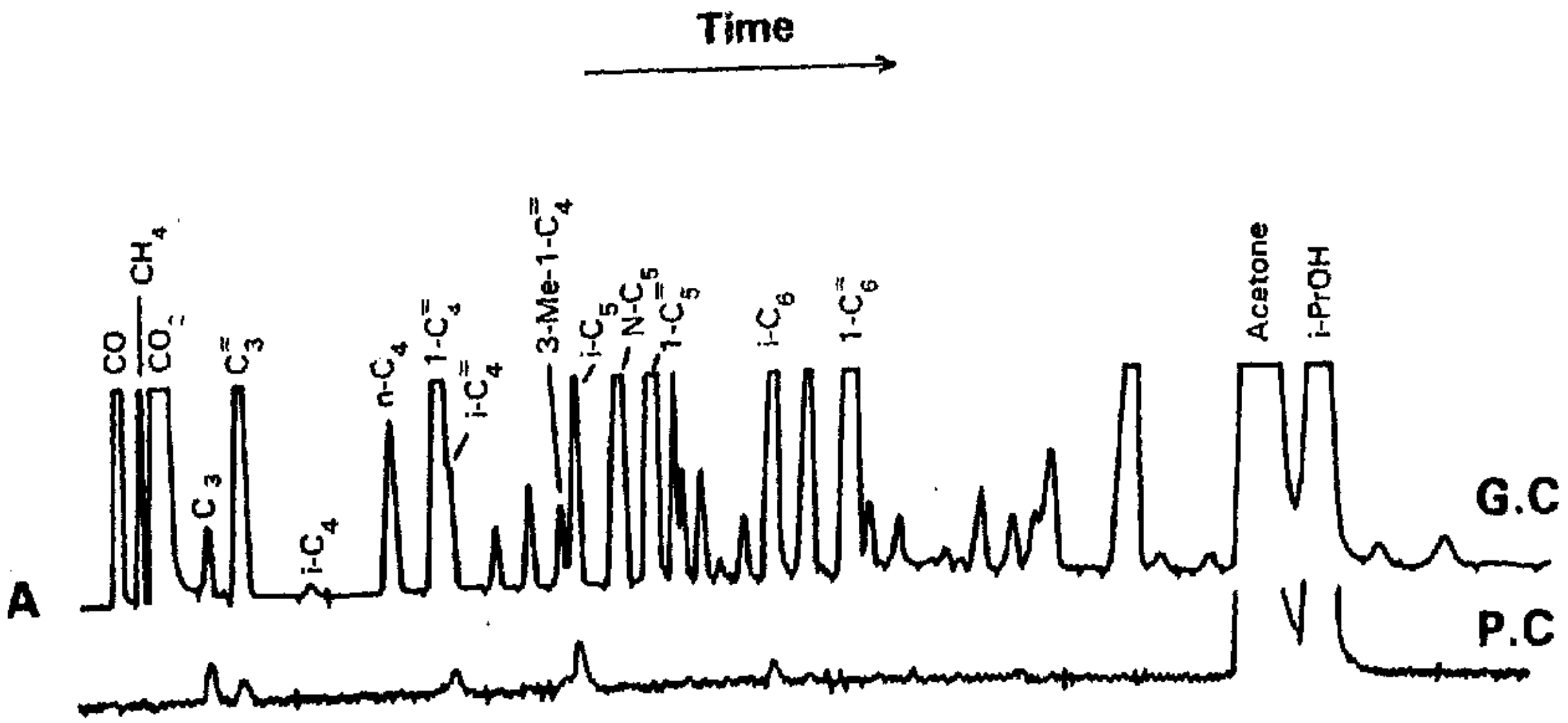


Figure III-24. Gas chromatogram (top) and proportional counter (bottom) output for the synthesis products when $CH_3{}^*CHOHCH_3$ was added to the syngas (CSTR, 80 psig, CO/H_2 = 0.6, 260°C).

The three pathways in the scheme must not interconvert to a significant degree and must have the characteristics summarized below:

Pathway	Products	^{14}C Alcohol Initiation
1	alcohols, alkanes, alkenes, etc.	n-alcohols, yes; i-alcohols, no
2	normal alkanes	no
3	isoalkanes	n-alcohols, no; i-alcohols, yes

The current data obtained at 7 atmosphere agree with the earlier data obtained by Emmett and coworkers at 1 atmosphere. Both sets of data indicate that the carbon group added as alcohol serves to initiate chain growth but the incorporation into the growing chain is small, if any. This implies that the alkyl group added as labeled alcohol remains intact during the synthesis. Furthermore, the very small amount of carbon-14 activity in carbon-number products smaller than the added alcohol support the viewpoint that the Fischer-Tropsch synthesis is essentially irreversible.

Schulz and coworkers (III-35) converted syngas mixtures containing either propene [1-^{14}C] or propene [2-^{14}C] with a cobalt catalyst and obtained essentially the same result with both labeled alkenes. The monomethylalkanes had a higher radioactivity/mole than the same carbon-number n-alkane; this was interpreted to show that propylene predominantly served to initiate chains and did not appreciably build into growing chains. With propene[1-^{14}C] addition to the syngas feed to an iron catalyst the results were less clear-cut; for example, the n-butane had approximately 10 times as much activity as the isobutane. This latter result differs from the results described above for the labeled alcohol data (III-17, III-20, III-21). It therefore appears that if the propene, formed from added propanol, undergoes secondary reactions, it does so much more slowly than the added alcohol initiates growing chains.

One can never be sure whether the added tracer compounded is converted in a parallel reaction or actually forms a species that is both common to and equivalent to a surface species in the reaction mechanism. In discriminating pathway 1 and 2, it is only necessary to show that the added alcohol actually parallels or enters into pathway 1 but not pathway 2; this has been done (III-33). It has also been shown that pathways 1 and 3, or reactions that parallel them, are completely independent. However, the data are not sufficient to prove by carbon-14 incorporation that pathways 1 and 3 are the same as those initiated by CO or a CO derived species; they do indicate that independent pathways are followed for synthesis of higher carbon-number products from n- and iso-alcohol.

A consideration of earlier chemical composition data suggested that the fraction of iso-alkane obtained with iron catalysts may be determined primarily by the reaction temperature. However, the similarity of the distribution that we obtained at 260 or 320°C with a C-73 catalyst indicate that factors other than that temperature must also be important in determining the iso- and normal-hydrocarbon distributions.

III-F. Comparison of Conversion of CO/H_2 with either i- or n-propanol

III-F-1. Chemical Compositions

The influence of added alcohol on the conversion of CO and H_2, and also on the formation of CO_2, is shown in figure III-25 for 2-propanol and in figure III-26 for 1-propanol. For 2-propanol addition, there is barely a detectable change in the conversion of CO or H_2. For 1-propanol addition, conversions appeared to be decreased, although even in this case it was less than 5%. These results indicate that the addition of alcohol to the feed to a C-73 doubly promoted iron catalyst have a very small, if any, affect on the reactant conversion during FTS. This observation agrees with those of Hall and Emmett (III-17) who reported that alcohol addition definitely decreased conversion in the FTS with singly promoted iron catalysts but not for doubly promoted catalysts. Our result also agrees with Hanlon and Satterfield's data (III-36); these workers, utilizing a C-73 catalyst, found that the addition of ethanol only slightly decreased the conversion. The small change in activity for these doubly promoted iron catalyst will be discussed later.

A detailed analysis of the C_1 to C_4 hydrocarbons showed a significant difference between the addition of 1-propanol and 2-propanol. The data in figure III-27 show that the concentration of C_1 to C_4 in the product gas stream remains almost constant with or without the addition of 2-propanol. On the other hand, the addition of 2-propanol decreased the concentration of C_1 and C_2 products in the effluent gas stream, and increased the C_3 and C_4 mole fractions in the stream, as shown in figure III-28. To obtain another view of the product distribution, Anderson-Schulz-Flory (ASF) plots for syngas only, syngas plus 1-propanol and syngas plus 2-propanol feeds are shown in figure III-29. As expected, there is no difference between the product distribution for syngas only and when 2-propanol was added; however, when 1-propanol was added, the distribution shows a small step increase in product fraction at C_3. Note that the change in C_1 and C_2 content was about 15% when 1-propanol was added; however, in the ASF plot (figure III-29), only a small difference is observed between the plot for the products with or without alcohol addition to the synthesis gas. The wide range of products, and the constraints of mass balance, limit the ability to observe the change in product distribution.

III-F-2. Radioactive Compositions

The g.c. and p.c. outputs for one of the gas phase samples from the conversion of syngas with either labeled 1-propanol or 2-propanol are shown in figure III-30 is a composite of figures III-22 and III-24. Although there is little difference in the change in the carbon number distribution for the addition of 1- or 2-propanol, there was a pronounced difference between the radioactive content of the products produced when one of these two alcohols was added. The incorporation of 1-propanol was much greater than that of 2-propanol. A more detailed analysis of the products shown in figure III-30 is presented in figure III-31, and in figure III-32. It can be seen in figure III-31 that, for the addition of 2-propanol, both iso-C_4 and iso-C_5 hydrocarbons have a higher radioactivity than n-C_4 and n-C_5 hydrocarbons. On the other hand, the incorporation of 1-propanol produces more radioactivity in the normal C_4 and C_5 hydrocarbons than those of the corresponding

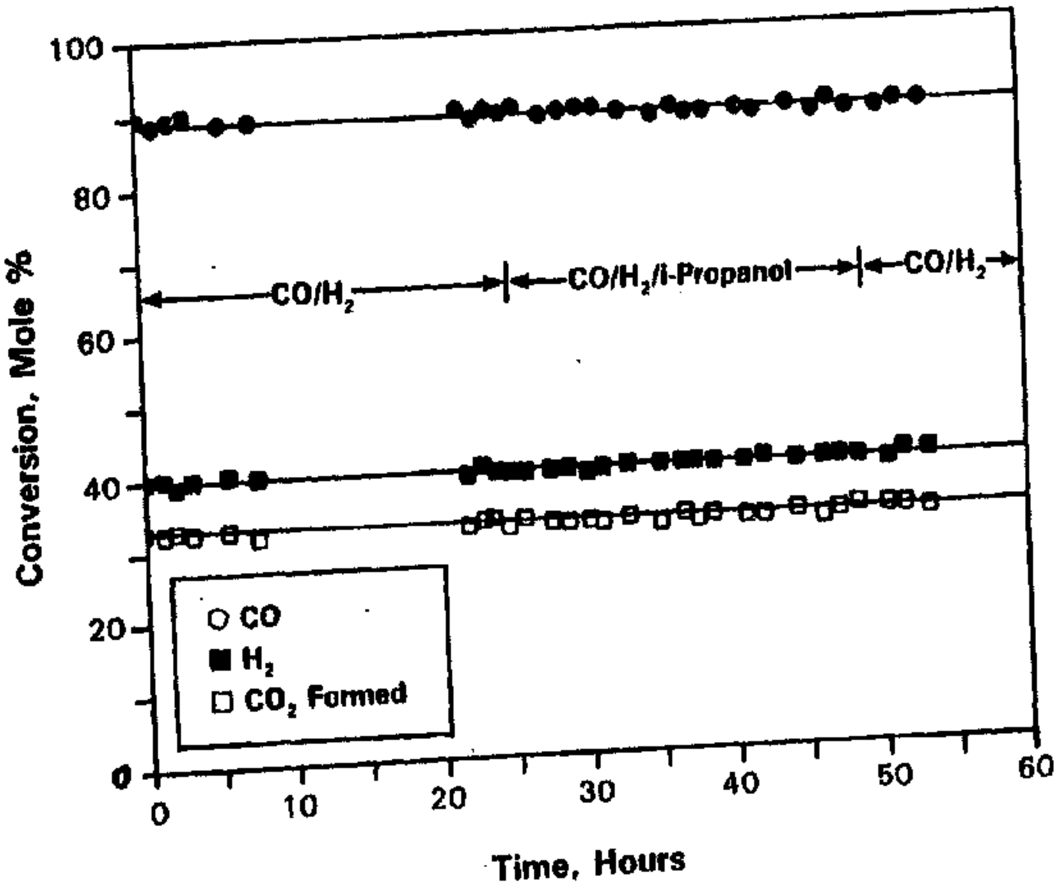


Figure III-25. Conversion of CO and H_2 at 262°C and 7 atmosphere conditions for a UCI C-73 catalyst using a CO/H_2 syngas feed and for a syngas feed containing ^{14}C labeled 2-propanol as well as the amount of CO_2 formed (based upon CO feed).

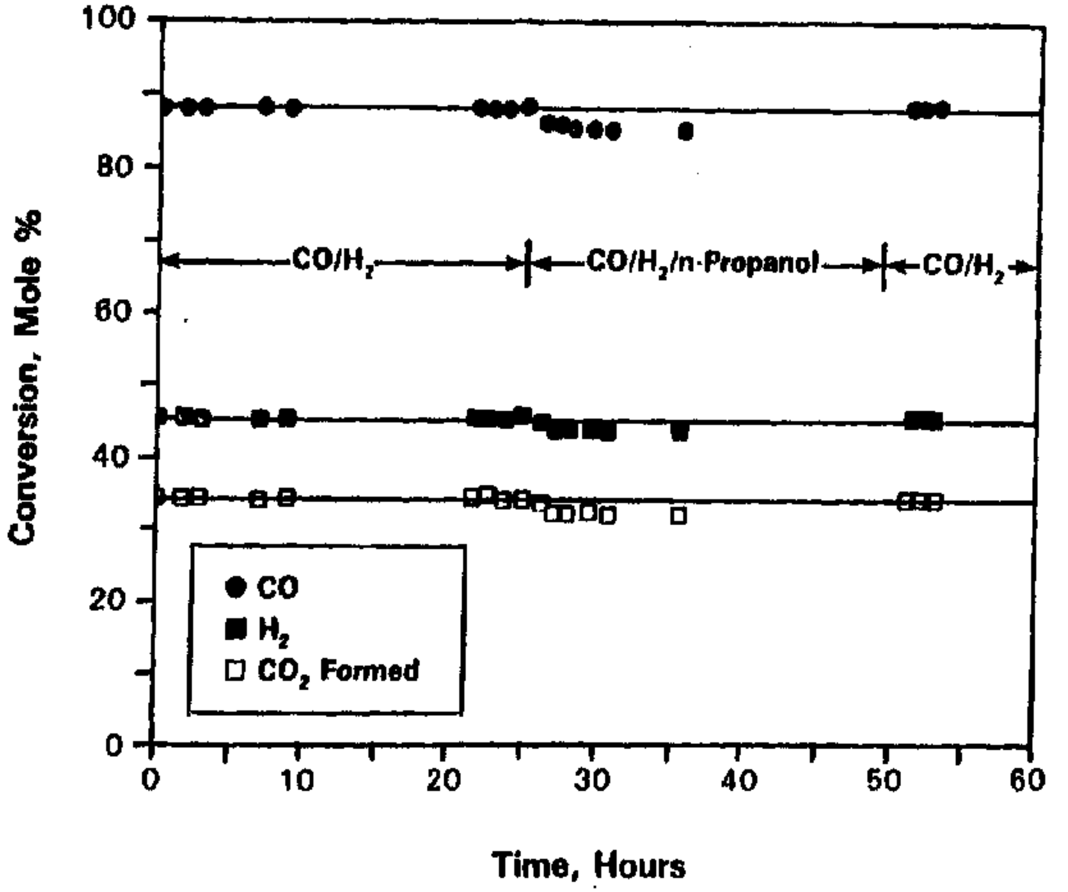


Figure III-26. Conversion of CO and H_2 at 262°C and 7 atmosphere conditions for a UCI C-73 catalyst using a CO/H_2 syngas feed and for a syngas feed containing ^{14}C labeled 1-propanol as well as the amount of CO_2 formed (based upon CO feed).

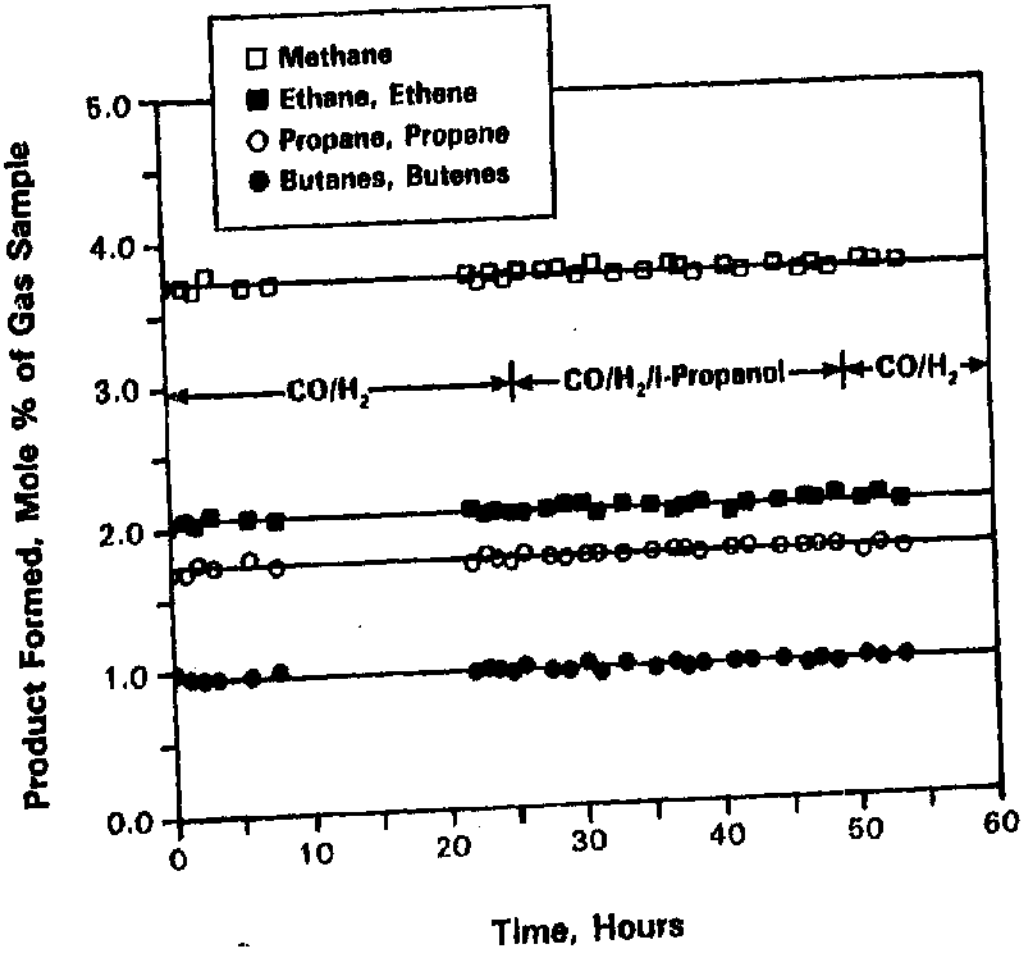


Figure III-27. Hydrocarbon product distribution of the effluent gas sample for a CO/H$_2$ = 0.8 syngas feed and the same syngas feed with <u>ca</u>. 3 mole% (based on CO) ^{14}C labeled 2-propanol.

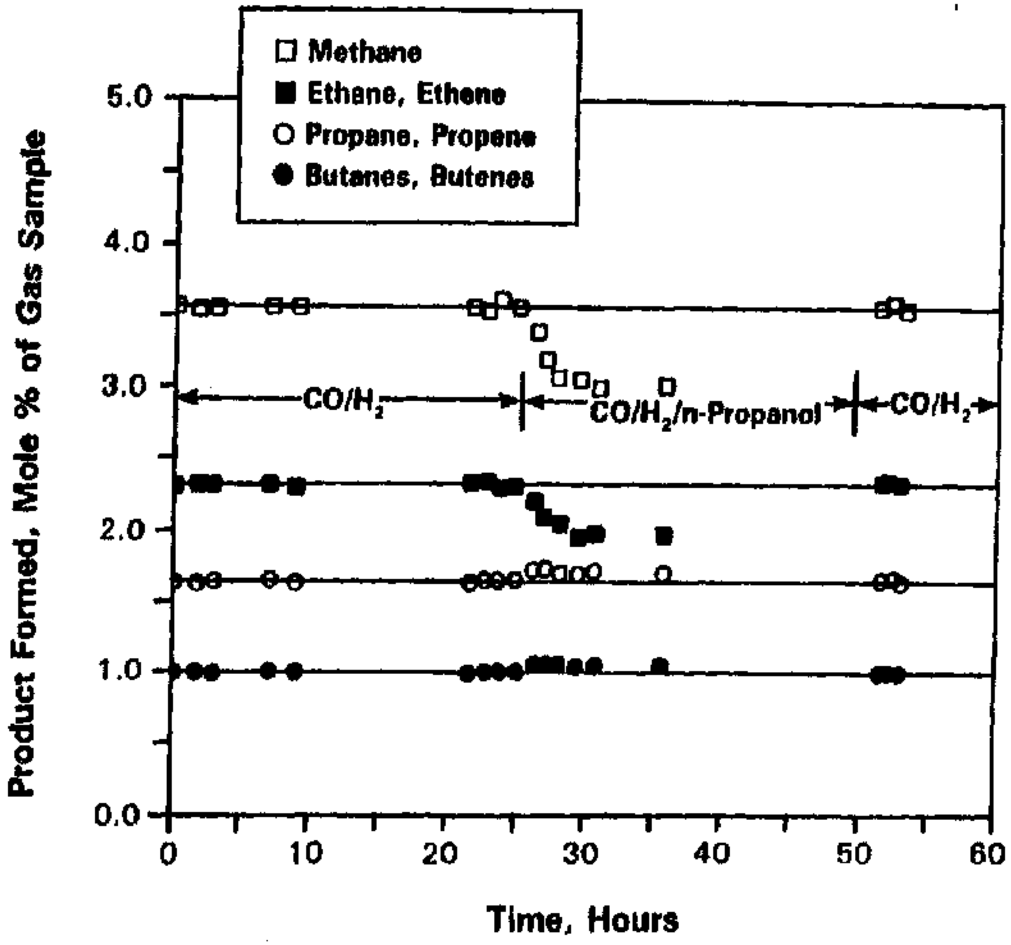


Figure III-28. Hydrocarbon product distribution of the effluent gas sample for a CO/H$_2$ = 0.8 syngas feed and the same syngas feed with _ca_. 3 mole% (based on CO) ^{14}C labeled 1-propanol.

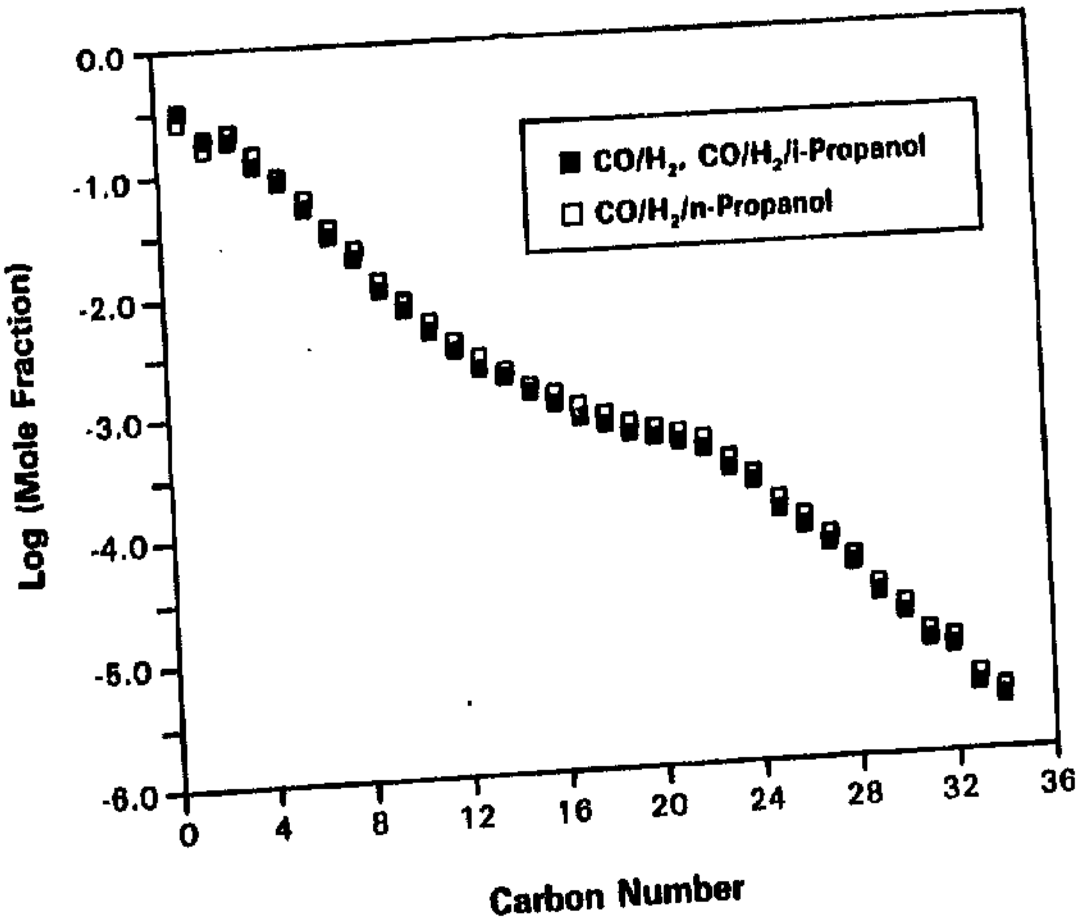


Figure III-29. Anderson-Schulz-Flory plot for the products from a syngas (CO/H_2 = 0.8) feed containing either 1-propanol (□) or 2-propanol (■) (data for syngas alone was essentially the same as for added 2-propanol case throughout the entire range of carbon numbers).

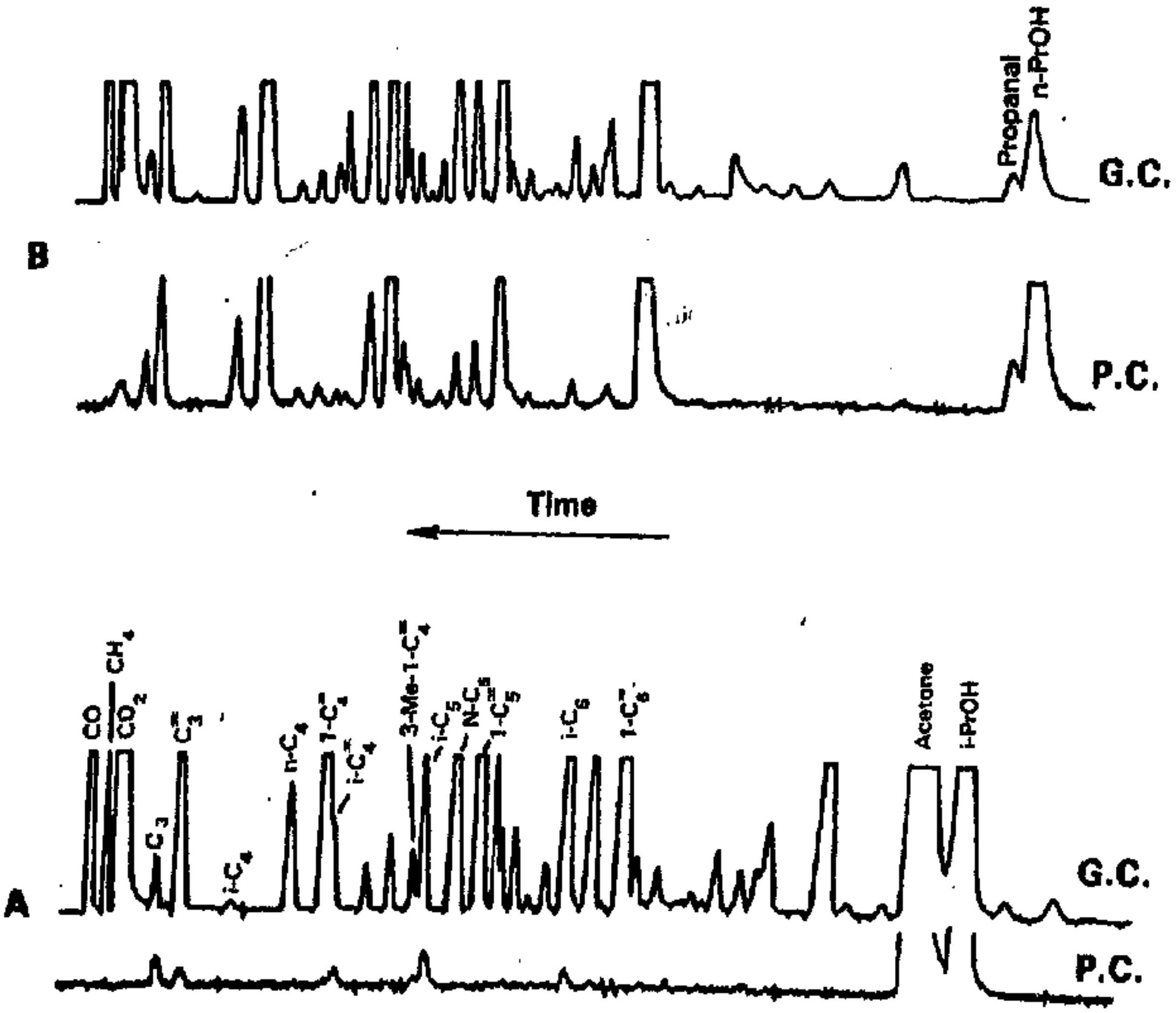


Figure III-30. Output from the gas chromatograph thermal conductivity cell (g.c.) and corresponding output from a proportional counter (p.c.) operated in series with the g.c. for:

A, synthesis gas with added ^{14}C labeled 2-propanol and
B, synthesis gas with added ^{14}C labeled 1-propanol.

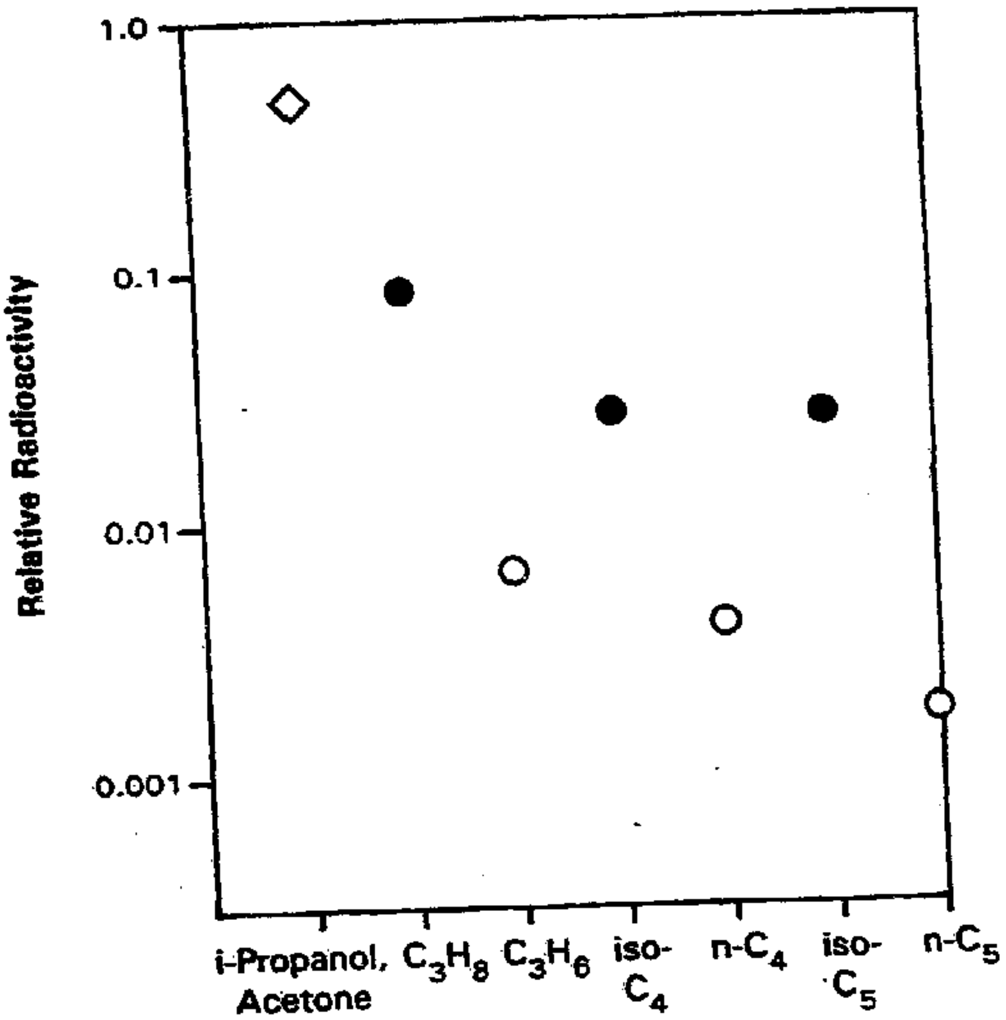


Figure III-31. Relative radioactivity for the gaseous products produced from a syngas feed that contained ^{14}C labeled 2-propanol.

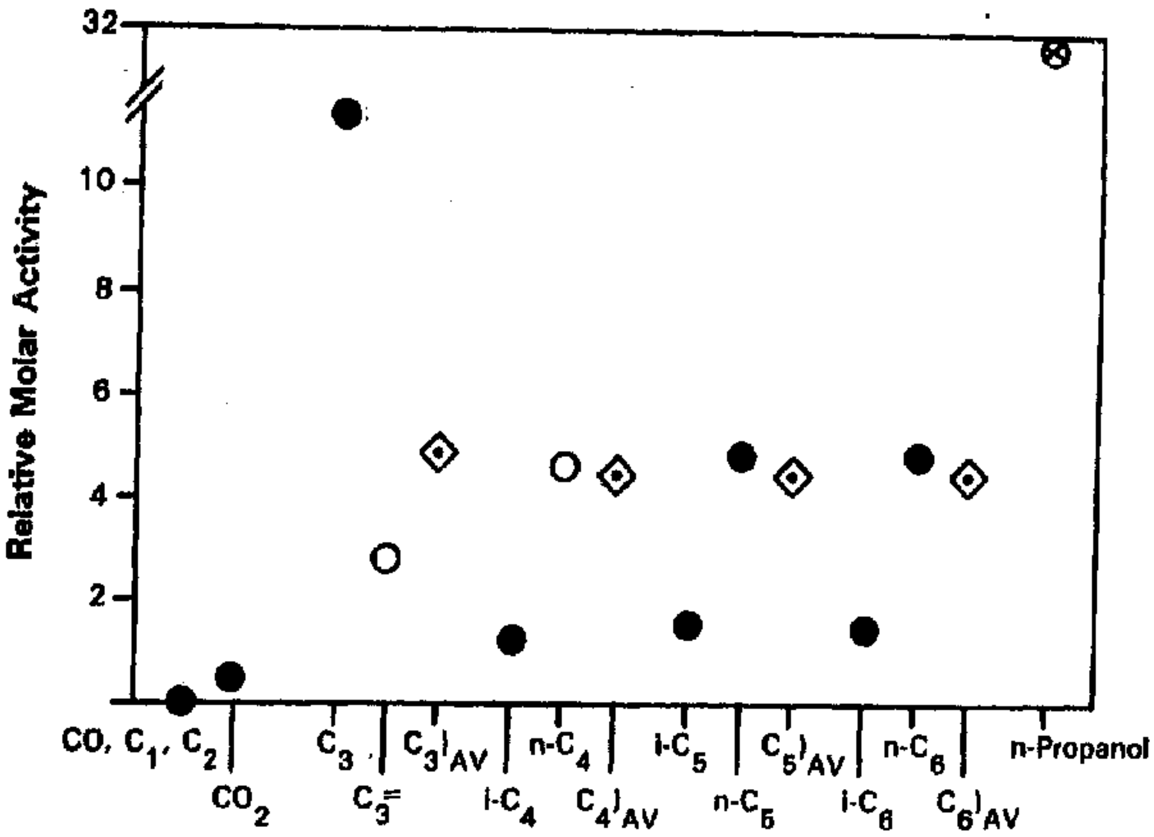


Figure III-32. Relative radioactivity for the gaseous products produced from a syngas feed that contained ^{14}C labeled 1-propanol.

iso-C_4 and iso-C_5 compounds. This agrees with earlier reports (III-17, III-20).

One of the interesting aspects of this study is that propane contains more radioactivity/mole than the other hydrocarbon products, regardless of whether 1- or 2-propanol was added. This result indicates that a portion of the propane has been formed directly from propanol; otherwise, propane should have the same molar of radioactivity as propene (assuming that the olefin is the primary product formed from alcohol conversion to C_3 hydrocarbons).

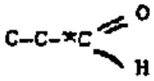
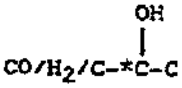
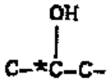
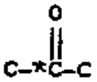
Another interesting point is that CO, CO_2, CH_4 and C_2 compounds do not have a detectable radioactivity level in the products produced when 2-propanol was added. Similar results are obtained when 1-propanol was added except that, in this case, the CO_2 does contain radioactivity. This indicates that, during the course of the synthesis, part of the added 1-propanol dissociates to form a surface intermediate that forms CO_2 directly rather than through CO as an intermediate. A similar result has been observed when ethanol was added to the syngas (III-F-16); however, the same phenomena was not found when 2-propanol was added. In addition, under the reaction conditions, 1-propanol equilibrated with propionaldehyde, while 2-propanol equilibrated with acetone as was demonstrated by both the agreement with thermodynamic calculations (Table III-3) and the equimolar ^{14}C content of the two compounds (figures III-31 and III-32). Emmett's group (III-20) obtained a similar result for the addition of 1-propanol or propionaldehyde to a syngas feed. Schulz and Achtsnit (III-38), as well as Benzinger and Madix (III-39), found that 2-propanol and acetone could equilibrate on an iron surface.

An important conclusion for the conversion of syngas containing 1-propanol was the constant radioactivity/mole for the C_3 to C_6 hydrocarbons. This indicates that 1-propanol initiates chain growth during the FTS reaction. Owing to the small extent of incorporation for 2-propanol, similar data cannot be presented in this case.

The phenomenon of direct formation of CO_2 from alcohol was investigated with other normal alcohols, and the results are summarized in figure III-33. If the loss of the carbinol carbon of the alcohol was the reverse of carbonylation, CO should be formed and it should be radioactive when a labeled alcohol was added. This was not the case. Furthermore, the higher activity of the CO_2 than of CO cannot be attributed to dilution. For example, the steady state concentration of CO_2 in the CSTR is higher than for CO; hence, the lower activity in CO cannot be due to a greater dilution by the CO. Thus, the data in figure III-33 indicate that the CO_2 was formed directly from the alcohol without first forming CO. To provide further verification of the loss of CO_2, and retention of the rest of the molecule intact, 1-hexanol was synthesized so that the ^{14}C label was located at the 2 position. Loss of the carbinol carbon should produce ^{14}C labeled pentane and unlabeled CO_2. As can be seen by the data in figure III-33, the pentane ($C_{n-1}H_{2n}$) has appreciably more activity than the CO or CO_2. In addition it is apparent that hexane also has a significant fraction of the ^{14}C label. Assuming for the moment that labeled pentane and hexane are derived only from 1-hexanol,

Table III-3

Observed Reactions of Added Propanols During the FTS Over C-73 Catalyst at 264°C and 100 psi

Reactants	Observed in Output Stream	Name of Reaction	Percentage of this Reaction
$^{a}CO/H_2/C-C-{}^{*}C-OH$	$C-C-{}^{*}C-OH$		55.2%
	 $C-C-{}^{*}C\begin{smallmatrix}\nearrow O\\ \searrow H\end{smallmatrix}$	Dehydrogenation	25%
	$C-C-{}^{*}C$	Hydrogenolysis	2.3%
	$^{*}CO_2$ and C_2	Cracking	2.0%
	$^{*}C_3$ $^{*}C_4$ $^{*}C_5\ldots$	Incorporation, Primarily normal compounds	15.3%
 $CO/H_2/C-{}^{*}\overset{OH}{\overset{\vert}{C}}-C$	 $C-{}^{*}\overset{OH}{\overset{\vert}{C}}-C-$		36.55%
	 $C-{}^{*}\overset{O}{\overset{\Vert}{C}}-C$	Dehydrogenation	59.35%
	$C-{}^{*}C-C$	Hydrogenolysis	1.56%
	$^{*}C_3$ $^{*}C_4$ $^{*}C_5\ldots$	Incorporation, Primarily iso compounds	2.49%

a There is a small amount of dimerization of normal-propanol with propionaldehyde.

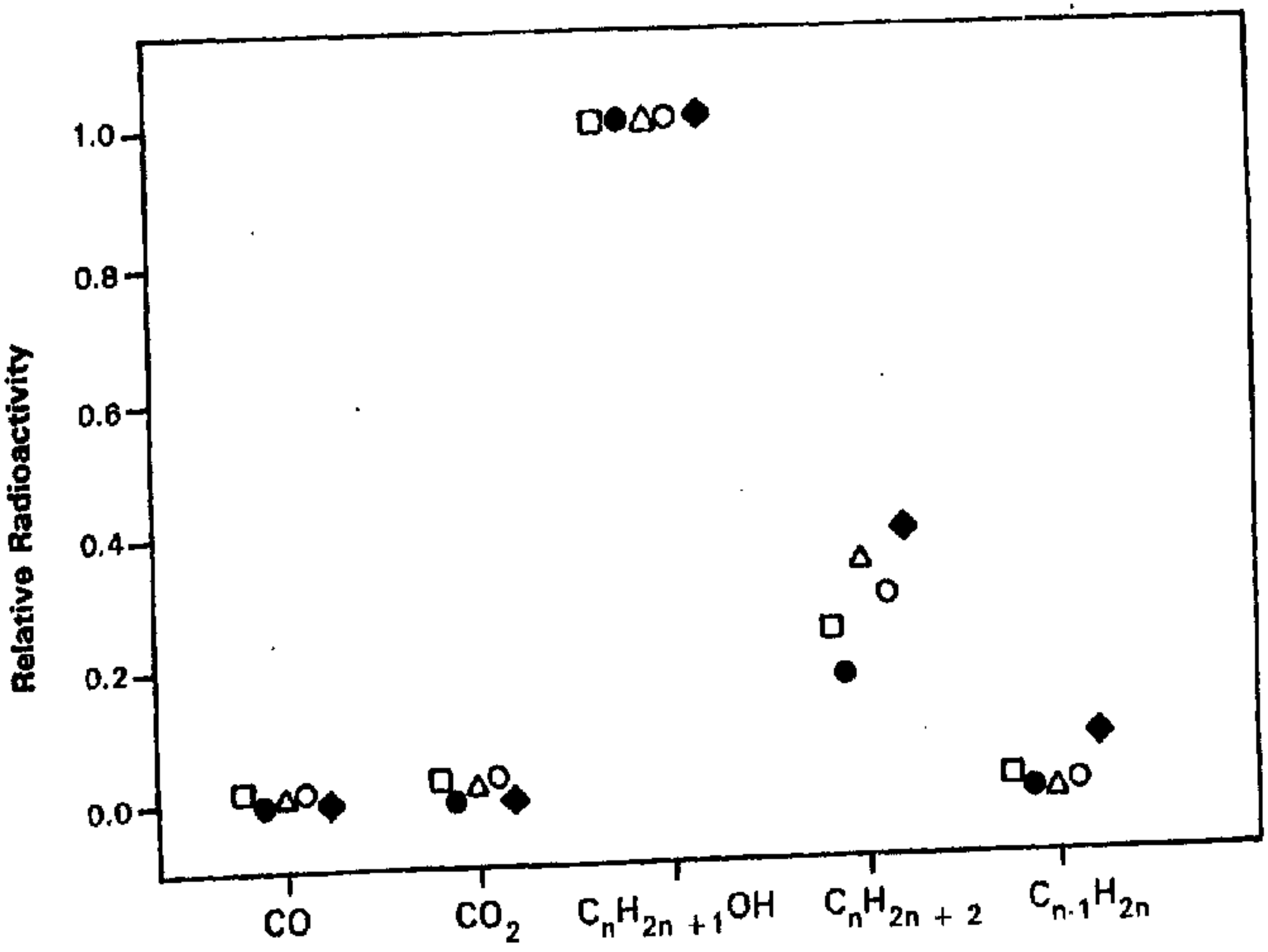
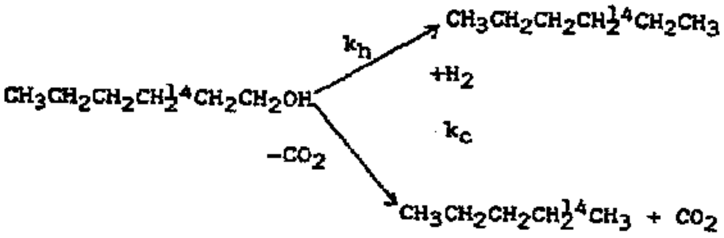


Figure III-33. The relative activity for decarbonylation (CO, CO_2 and $C_{n-1}H_{2n}$) and hydrogenolysis (C_nH_{2m+2}) products from the conversion of syngas with added normal alcohols labeled with ^{14}C at the carbinol position and ^{14}C labeled 2-propanol ($CH_3{*}CH_2OH$ (□), $CH_3{*}CHOHCH_3$ (●), $CH_3CH_2{*}CH_2OH$ (△), $CH_3(CH_2)_3{*}CH_2OH$ (○) and $CH_3(CH_2)_3{*}CH_2CH_2OH$ (◆).

then hydrogenolysis occurs about five times faster than loss of the carbinol carbon; i.e., $k_h/k_c=5$ for the following scheme:



[III-9]

The relative quantity of radioactivity in the C_5 products, n-pentane/1pentene = 3, indicate that the pentane is formed as the CO_2 is lost rather than through 1-pentene. It has been observed that ^{14}C labeled pentene, added to the syngas, does not undergo measurable isomerization to other pentenes or hydrogenation to pentane (III-40).

The water-gas shift reaction is a feature of the FTS. The higher activity in the CO_2 than in the CO suggest that, under our reaction conditions, the water-gas shift reaction is rather far removed from carbon isotope equilibration (figure III-33). Thus, the water-gas shift reaction is rather slow, compared to FTS, for the C-73 catalyst; this observation agrees with that of Bukur and Brown (III-41).

The radioactivity/mole for the oil-phase hydrocarbons is shown in figures III-34 and III-35 for products obtained when 1- and 2-propanol, respectively, were added to the syngas feed. As expected, the radioactivity of the iso-paraffins was much higher than that of the n-paraffins when 2-propanol was added to the syngas. In figure III-34 it appears that the radioactivity decreases with increasing carbon number; however, a dominant reason for this decrease is caused by hydrocarbon accumulation in the slurry reactor. After correcting for this accumulation effect, the radioactivity per mole should be constant for increasing carbon number, and this is the case as is indicated by the dotted line in figure III-34. In other words, the oil-phase results also indicate that 2-propanol initiates chain growth during FTS. The effect of accumulation is complex and merits a much more detailed study. For 1-propanol conversion, an opposite result was obtained since, in this case, the n-paraffins have a higher radioactivity than that of iso-paraffins (figure III-35).

Our data for the C_4 alkanes were shown in figure III-23 together with data reported earlier by Emmett and coworkers. This presentation emphasizes the similarity of the data generated with different catalysts and operating conditions as well as to emphasize that an iso-alcohol produces predominately branched higher carbon number compounds while normal alcohols produce predominately normal higher carbon number compounds.

III-F-3. Mechanistic Aspects of i- or n-propanol Incorporation

The Fischer-Tropsch synthesis is a complex reaction. Numerous reaction schemes have been advanced. The earliest mechanistic view was that a carbide intermediate was involved in the synthesis (III-42). The results from Emmett's pioneering ^{14}C tracer studies conclusively showed that a bulk

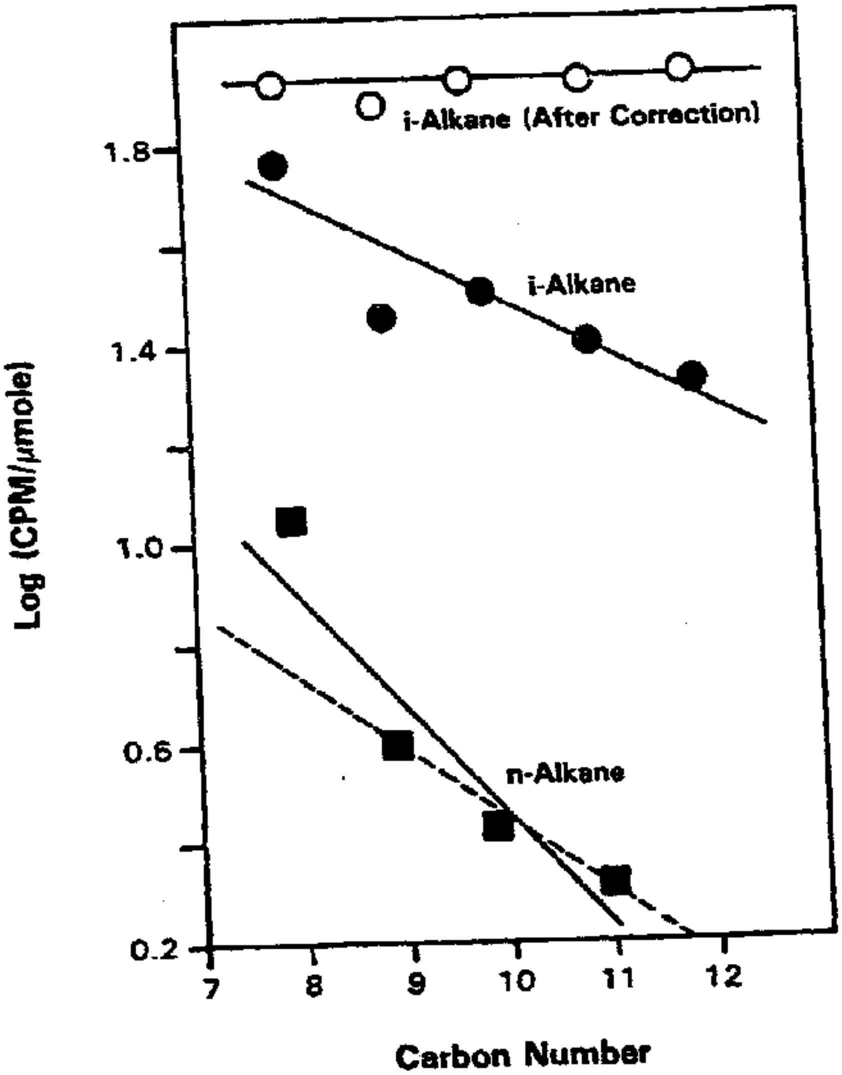


Figure III-34. The relative activity/mole for alkane and isoalkane fractions isolated by liquid chromatography from the liquid products produced during synthesis when 2-propanol was added to the syngas feed.

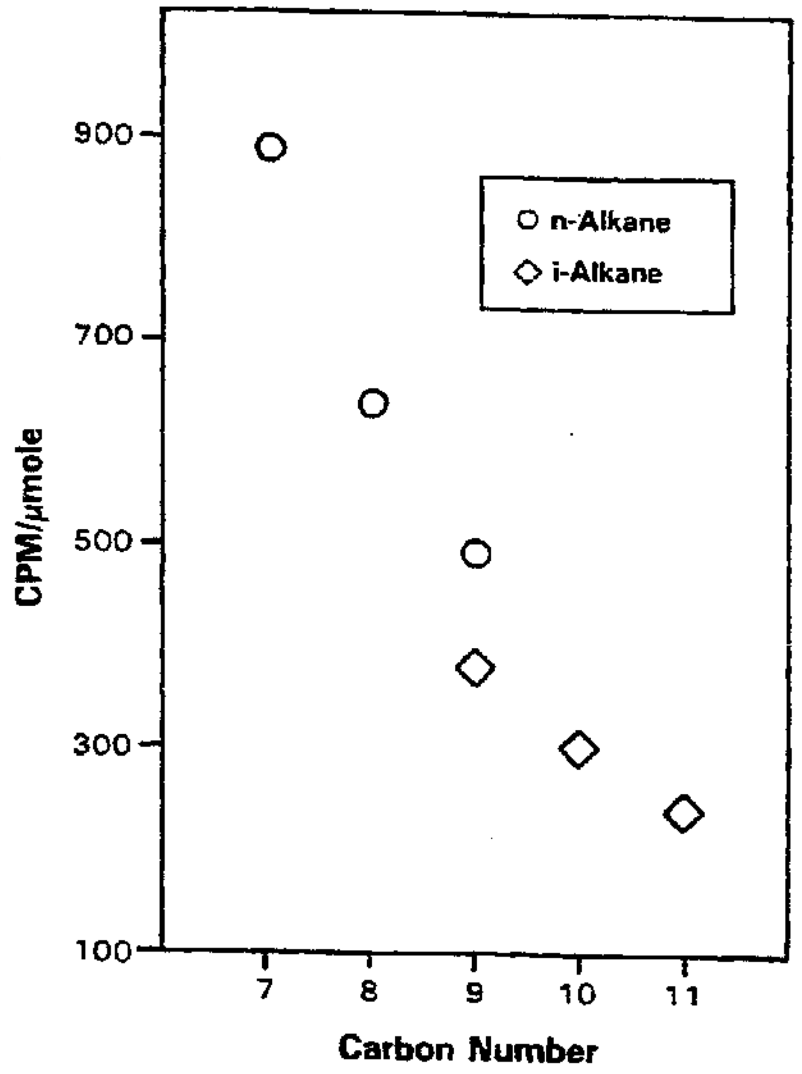


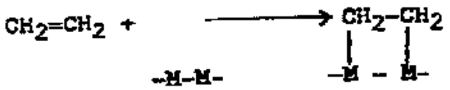
Figure III-35. The relative activity/mole for alkane and isoalkane fractions isolated by liquid chromatography from the liquid products produced during synthesis when 1-propanol was added to the syngas feed (note that a logarithmic scale was used for the activity in figure 10 but not in figure 11).

carbide could not be involved in the synthesis; furthermore, their data was consistent with only a small fraction of the products being produced through utilization of the preformed surface carbide (III-19). Emmett's tracer studies led to the proposal of a number of mechanisms that involved an oxygen containing intermediate. Sophisticated surface science instrumentation, with the capability for quantitative analysis, has become available during the past few years. Measurements with these instruments show that carbon is present on the surface in much greater concentration than oxygen. This observation led to the revival and wide acceptance of the surface carbide intermediate for Fischer-Tropsch synthesis. More recently Lee and Ponec (III-43) advanced a "hybrid" mechanism wherein a fraction of the CO was incorporated by an oxygen free species and a fraction was introduced through an oxygen-containing species.

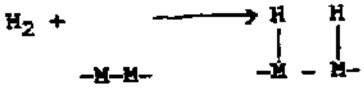
It has also been proposed that the promoted iron Fischer-Tropsch catalyst has a heterogeneous surface so that more than one type of site is available. For example, it has been proposed that an alkali promoter is responsible for the two alpha plot frequently observed (III-44); thus iron alone produces the lower alpha (*ca.* 0.6) synthesis pathway and the iron sites that are altered by the presence of alkali are responsible for the higher alpha (*ca.* 0.8) chain growth.

In syngas conversion, it is possible that the overall synthesis has a contribution that encompasses a contribution from both the variety of catalytic sites and from two or more surface intermediates. It is unlikely that any one experimental study will be able to define the complete synthesis mechanism.

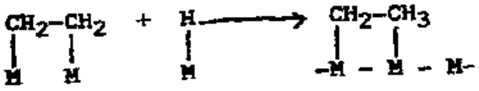
Following the discovery of deuterium, it was recognized that metal and metal oxide catalysts were very effective in catalyzing exchange between hydrogen present in alkanes or alkenes and gaseous deuterium, or vice versa. The exchange during alkene hydrogenation has been explained by a mechanism frequently referred to as the Twigg mechanism (III-45) where a half-hydrogenated state is involved in a dynamic surface equilibration as depicted below for ethylene hydrogenation (below M represents a surface site):



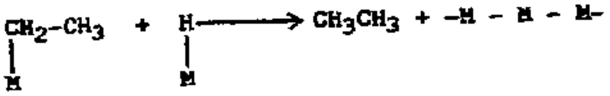
$$CH_2{=}CH_2 + \underset{-M-M-}{} \longrightarrow \underset{-M\,-\,M-}{CH_2-CH_2} \qquad [III\text{-}10]$$



$$H_2 + \underset{-M-M-}{} \longrightarrow \underset{-M\,-\,M-}{H\quad H} \qquad [III\text{-}11]$$



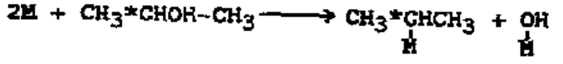
$$\underset{M\quad M}{CH_2-CH_2} + \underset{M}{H} \longrightarrow \underset{-M\,-\,M\,-\,M-}{CH_2-CH_3} \qquad [III\text{-}12]$$



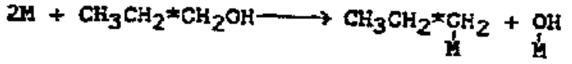
$$\underset{M}{CH_2}-CH_3 + \underset{M}{H} \longrightarrow CH_3CH_3 + -M-M-M- \qquad [III\text{-}13]$$

The product on the right hand side of equation [III-12] is the half-hydrogenated state that is formed by the addition of hydrogen to ethylene. Hydrogen-deuterium exchange could readily occur through the reversibility of reactions [III-11] and [III-12]. If D is added to ethylene to form the half-hydrogenated state, and if the small, if any, isotope effect is neglected, the reverse reaction in [III-12] would have a probability of 2 for generating a M-H entity and 1 for producing a M-D. Thus, the reversibility of reaction [III-12] readily permits the exchange of H and D. Furthermore, isomerization of higher carbon number alkenes is believed to involve a half-hydrogenated state.

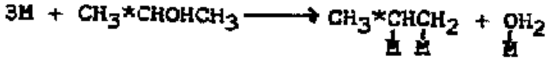
Olefins are the dominant primary products for the Fischer-Tropsch synthesis. The surface carbide mechanism involves hydrogenated surface carbon species. If 1-propanol or 2-propanol loses an OH or H_2O to form an adsorbed species, the following would apply:



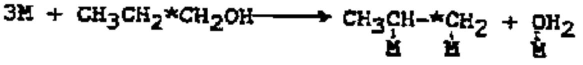
$$2M + CH_3{*}CHOH{-}CH_3 \longrightarrow CH_3{*}\underset{M}{C}HCH_3 + \underset{M}{O}H \qquad [III-14]$$



$$2M + CH_3CH_2{*}CH_2OH \longrightarrow CH_3CH_2{*}\underset{M}{C}H_2 + \underset{M}{O}H \qquad [III-15]$$

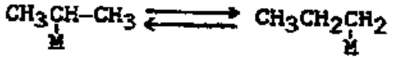


$$3M + CH_3{*}CHOHCH_3 \longrightarrow CH_3{*}\underset{M}{C}H\underset{M}{C}H_2 + \underset{M}{O}H_2 \qquad [III-16]$$



$$3M + CH_3CH_2{*}CH_2OH \longrightarrow CH_3\underset{M}{C}H{-}{*}\underset{M}{C}H_2 + \underset{M}{O}H_2 \qquad [III-17]$$

The adsorbed hydrocarbon species from dehydration according to equations [III-16] and [III-17] require that identical products be formed from 1- and 2-propanol. Since this does not happen, the contribution to the Fischer-Tropsch synthesis through these alcohols must not involve this adsorbed propene intermediate. Furthermore, if the reactions in equations [III-14] and [III-15] occur, different products can be formed from 1- and 2-propanol only if interconversion of the two adsorbed species does not occur, i.e.,



$$CH_3\underset{M}{C}H{-}CH_3 \rightleftharpoons CH_3CH_2\underset{M}{C}H_2 \qquad [III-18]$$

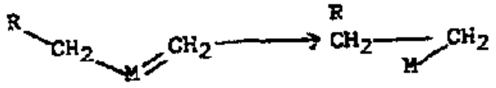
It therefore appears that the data for the conversion of the two labeled propanols require:

(1) if a common set of sites are utilized for synthesis and for alcohol incorporation, then (a) a two site adsorbed olefin is not involved and (b) a half-hydrogenated intermediate, if involved, must be a unique one that does not permit interconversion by hydrogen abstraction and addition as is normally proposed or

(2) synthesis from CO and alcohol are by parallel pathways which do not have a common surface intermediate.

Since macroscopic reversibility requires gaseous alcohol to be readsorbed and become equivalent to an adsorbed intermediate leading to the alcohol product, the assertion in (2) above would require alcohol and alkene products to be produced by a completely independent parallel pathways.

Biloen and Sachtler (III-46) considered that, for the carbide mechanism: "The totality of these data for chain growth in the Fischer-Tropsch mechanism is considered as evidence in favor of x = 2, that is, an insertion mechanism that can be visualized as cis migration, where an alkyl group forms a bond with a carbene group attached to the same metal atom"; in other words, the following equation may be written:



[III-19]

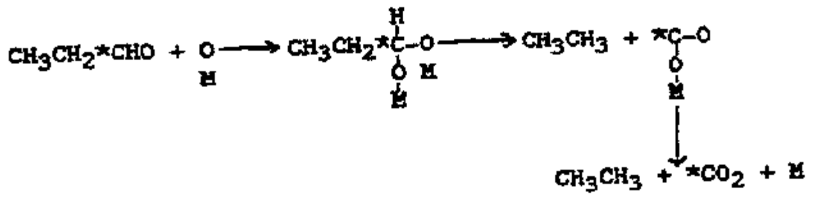
Here, again the intermediate on the right hand side (r.h.s.) of equation III-19 is one of the two singly adsorbed species involved in the half-hydrogenated mechanism. It is difficult to write an equation that converts the r.h.s. structure to an adsorbed alkene without writing structures that would permit the C_3 oxygen-free structure that is formed from each of the two propanols from becoming equivalent and, hence, to produce equivalent ^{14}C label distributions.

The retention of oxygen by the adsorbed alcohol, together with retention of oxygen during the chain growth process, permits the formation of a different ^{14}C labeled product slates from the added 1- and 2-propanol. However, one has to resort to unusual intermediates, such as dihydroxy compounds, if oxygen is to be retained.

The alcohols, both 1- and 2-propanol, did undergo extensive conversion since the equilibrium mixture of ketone or aldehyde/alcohol mixture was attained. This requires that the added alcohol be adsorbed on the surface and undergo conversion on hydrogenation/dehydrogenation sites. It seems unlikely that such catalytic sites would not be involved in Fischer-Tropsch synthesis as well.

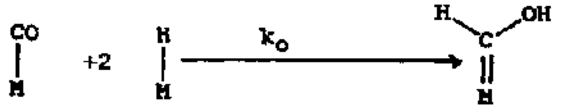
The normal alcohol undergoes a number of reactions. The data clearly document the loss of the carbinol carbon as CO_2, not CO, as well as the hydrogenolysis of the C-O bond that includes the carbinol carbon. It is inviting to propose that these two products result as follows:

$$CH_3CH_2{}^*CH_2OH \rightleftharpoons CH_3CH_2{}^*CHO + H_2 \qquad [III-20]$$



$$CH_3CH_2{}^*CHO + \underset{M}{O} \longrightarrow CH_3CH_2{}^*\overset{H}{\underset{\underset{M}{O}}{C}}-O \;\; M \longrightarrow CH_3CH_3 + {}^*\underset{\underset{M}{O}}{C}-O \;\downarrow\; CH_3CH_3 + {}^*CO_2 + M \qquad [III-21]$$

This mechanism produces CO_2 directly rather than from CO through the water gas shift reaction as the data obtained with ^{14}C labeled ethanol require; in addition, similar data was obtained for propanol, pentanol and hexanol. Because hydrocarbons are produced during the synthesis, we are unable to define whether the ratio of the alkane (with one less carbon than the labeled alcohol) to the CO_2, i.e. $[C_{n-1}H_{2n}/CO_2]$, is one as required by the stoichiometry of equation [III-21]. The above mechanism for the direct formation of CO_2 differs from one proposed earlier by Hall et al. (III-17) to explain their data as well as that of Koelbel and Engelhardt (III-47):



[III-22]

[III-23]

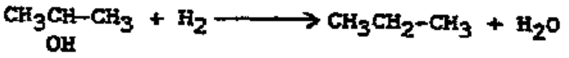
[III-24]

Our results are supported by those of Elliott and Pennella (III-48) who observed the decarbonylation of alcohols using a $Cu/ZnO/Al_2O_3$ catalyst at a slightly higher temperature (285°C) and higher pressures (<u>ca</u>. 1,000 psi) than we used in this study.

In addition to reactions [III-20] and [III-21], the alcohol underwent hydrogenolysis to produce a hydrocarbon with the same carbon number and presumably water, i.e.;

$CH_3CH_2CH_2OH + H_2 \longrightarrow CH_3CH_2{-}CH_3 + H_2O$

and



$\underset{OH}{CH_3CH{-}CH_3} + H_2 \longrightarrow CH_3CH_2{-}CH_3 + H_2O$

[III-25]

Licht and Pines have reported that this reaction readily occurs with a nickel catalyst (III-49). The result implies that the carbon, or oxygen, or both, bond to the surface so as to weaken the C-O bond; however, it is difficult to visualize rupture of this C-O bond without producing a half-hydrogenated species (the r.h.s. structure of equation [III-19]).

The inertness of alcohol toward dehydration with this catalyst is surprising, especially for 2-propanol. If alcohols are produced as the primary surface species and the α-olefins result from the dehydration of these products, then the added alcohol should readily undergo dehydration. This clearly was not the case and eliminates gas phase alcohol as a possible intermediate in the mechanism that produces α-olefins.

In this study the majority of the hydrocarbon products derived from syngas were alkenes; for example, <u>ca</u>. 80% of the C_4 hydrocarbons were alkenes. The alcohol was adsorbed and underwent dehydrogenation to a ketone or aldehyde to produce an equilibrium composition while, at the same time, the intermediate