carbon number (C_4-C_{10}) alkenes did not undergo appreciable hydrogenation in secondary reactions. It therefore seems likely that alcohol and ketone or aldehyde were able to compete with CO for adsorption sites; otherwise the aldehyde, but not alkene, must be able to adsorb on sites that do not adsorb CO, and undergo hydrogenation there. If this is the case then an alcohol, once formed on the surface, must have a much higher probability for dehydrogenation or desorption than for dehydration to alkene. It therefore appears that an alcohol is not the source of the alkene products in the Fischer-Tropsch synthesis.

In summary, it appears from studies with the added alcohol that:

1) about 10-20% of the added primary alcohol incorporates into Fischer-Tropsch products but the incorporation of the 2-propanol is much less than this (1-3%),

2) hydrogenolysis of the alcohol occurs to produce an alkane with the same carbon number as the alcohol,

3) the carbon unit, added as alcohol, remains intact, apart from CO_2 elimination, during these conversions,

4) the added alcohol serves to initiate polymerization but does not serve as propogator,

5) 1- and 2-propanol form species on the surface that retain their identity and do not form a common surface species and,

6) the experimental results are inconsistent with an intermediate that has the chemical characteristics normally associated with the half-hydrogenated intermediate, and

7) n-alcohols produce normal alkanes and alkenes in a much greater yield than they produce iso-products so that the n/i hydrocarbon ratio from n-alcohol initiation is greater than the n/i ratio from the Fischer-Tropsch synthesis; for the iso-alcohol just the opposite occurs with the n/i-hydrocarbon ratio being much lower than from the Fischer-Tropsch synthesis. This latter observation supports the data obtained by Emmett and coworkers (III-17).

III-G. Role of Promoter on Product Selectivity

In order to survey the impact of a variety of promoters upon a number of catalysts, screening studies were carried out at a total pressure of 1 atmosphere. In these studies, the influence of the promoter on three different characteristics of the synthesis reaction were investigated. The three characteristics were synthesis activity as measured by CO conversion, alkane/olefin ratio in the hydrocarbon products and alpha value(s), i.e. changes of molar hydrocarbon production with carbon number.

The alkane percentages, by carbon number in the C_2 to C_{20} range, for conversions with two iron plus non-reducible metal oxide catalysts and a commercial catalyst that contains alkali (K plus Ca) are shown in figure III-36. The data clearly show a minimum in the alkane percentage at a carbon number of 4 or 5; this is true for all three catalysts. Moreover, it is

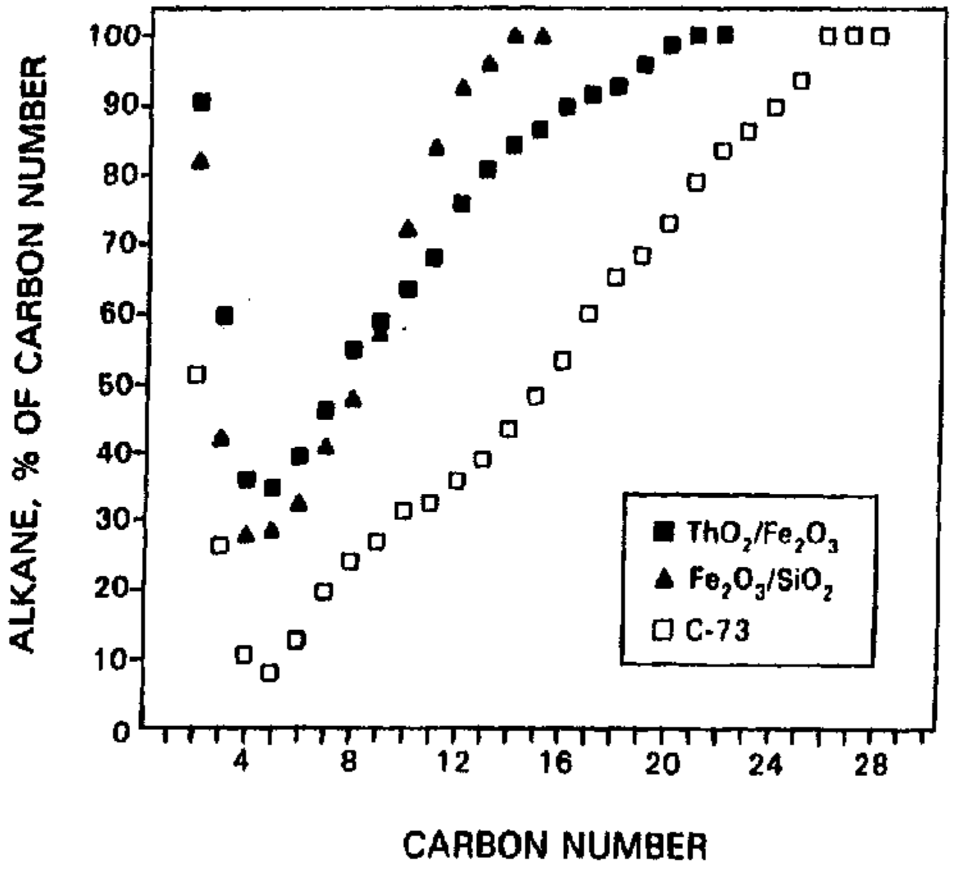


Figure III-36. The alkane percentage (n-alkane/n-alkane plus 1- and 2-alkenes) by carbon number for synthesis gas conversion with ca. 6% ThO_2/Fe_2O_3, ca. 10% Fe/SiO_2, and U.C.I. C-73 catalysts at 1 atm pressure.

apparent that the alkali-promoted catalyst produces a lower alkane percentage for all carbon numbers below about C_{20} than the other two catalysts do. The results obtained at 7 atmospheres for these three catalysts (figure III-37) are very similar in overall trend to the data generated at 1 atmosphere pressure. The similarity of the data obtained at 1 and 7 atmosphere pressure is surprising. It should be pointed out that there is some uncertainty as to whether alkanes produced from the $Fe-SiO_2$ and $Fe-ThO_2$ catalysts were primary synthesis reaction products or products of a secondary hydrogenation of olefins produced as primary products. Tracer studies show that the C_5 alkanes produced over the C-73 catalyst were virtually exclusively primary products.

The impact of alcohol addition upon the CO conversion is shown in figure III-39. This data was obtained by establishing a long term baseline activity trend (constant activity for 10 days or longer) and then adding alcohol to the syngas feed stream. The baseline activity trend for the C-73 catalyst is indicated at the left side of figure III-38 (the zero time refers to the start of an alcohol run period, not the start of a complete run period). For the C-73 promoted catalyst, the addition of alcohol, either ethanol or pentanol, did not cause the activity to change by a measurable amount; likewise, the activity remained the same following termination of alcohol addition. This was not the case with the $Fe-SiO_2$ catalyst since the activity level established with a CO/H_2 syngas feed was decreased by about 40% when either ethanol or pentanol was added to the CO/H_2 feed. In both cases with the $Fe-SiO_2$ catalyst, the activity gradually increased, following termination of alcohol addition, to finally attain an activity level approaching that obtained prior to alcohol addition. A single catalyst charge was used for the run with C-73; the run consisted of more than 150 days of continuous operation with ethanol added during day 62 and pentanol during day 95. In the case of $Fe-SiO_2$ a single catalyst charge was used but the total run length was only about 120 days. A similar decrease in activity was observed when ethanol was added to the syngas at the 1 atmosphere pressure conditions; however, in this case the activity decrease was superimposed upon a declining activity curve.

Alcohol addition influenced the alkane selectivity as well as the total activity for both of the "alkali-free" catalysts ($Fe-SiO_2$ and $Fe-ThO_2$) at both 1 and 7 atmosphere total pressure conditions (figures III-39 and III-40). While the extent of hydrogenation was slightly greater at 1 atmosphere than at 7 atmosphere pressure conditions for both the syngas and the alcohol-containing syngas feed, the pattern was the same for both pressures. Thus, the added alcohol had the same effect as the presence of alkali in the C-73 catalyst. This contrast between the two catalyst types is apparent when the data in figures III-41 and III-42 are compared to those in figures III-39 and III-40. Whereas the added alcohol had a significant impact upon the alkane selectivity of an "alkali-free" $Fe-ThO_2$ catalysts, the addition of alcohol to the syngas feed to C-73 catalyst did not have a significant impact upon alkane selectivity. Again, this was true for operation at either 1 or 7 atmospheres.

The Anderson-Schulz-Flory (ASF) plot is followed by most catalysts even though alpha, obtained from the slope, may vary depending upon the catalyst. In the case of iron catalyst, many investigators have found a break in the ASF plot at the <u>ca</u>. 9-14 carbon number range. As can be seen in figures III-43, III-44, III-45, breaks are observed at <u>ca</u>. carbon number 9 to 11 in our runs

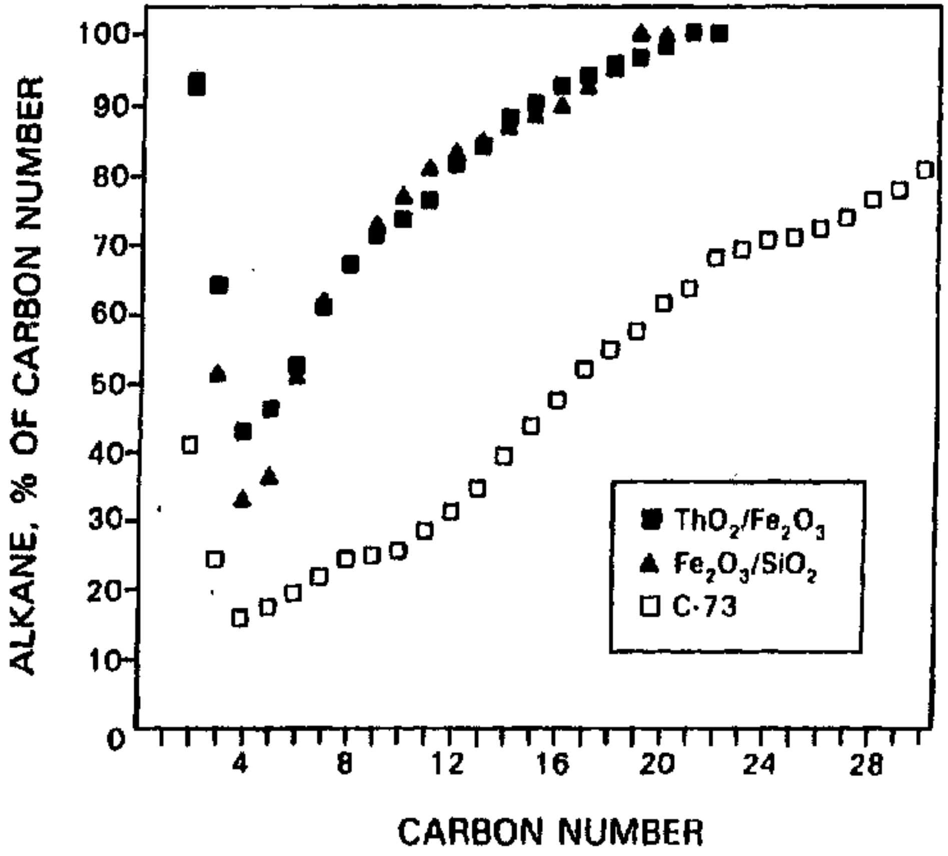


Figure III-37. The alkane percentage (n-alkane/n-alkane plus 1- and 2-alkenes) by carbon number for synthesis gas conversion with ca. 6% ThO_2/Fe_2O_3, ca. 10% Fe/SiO_2, and U.C.I. C-73 catalysts at 7 atm pressure.

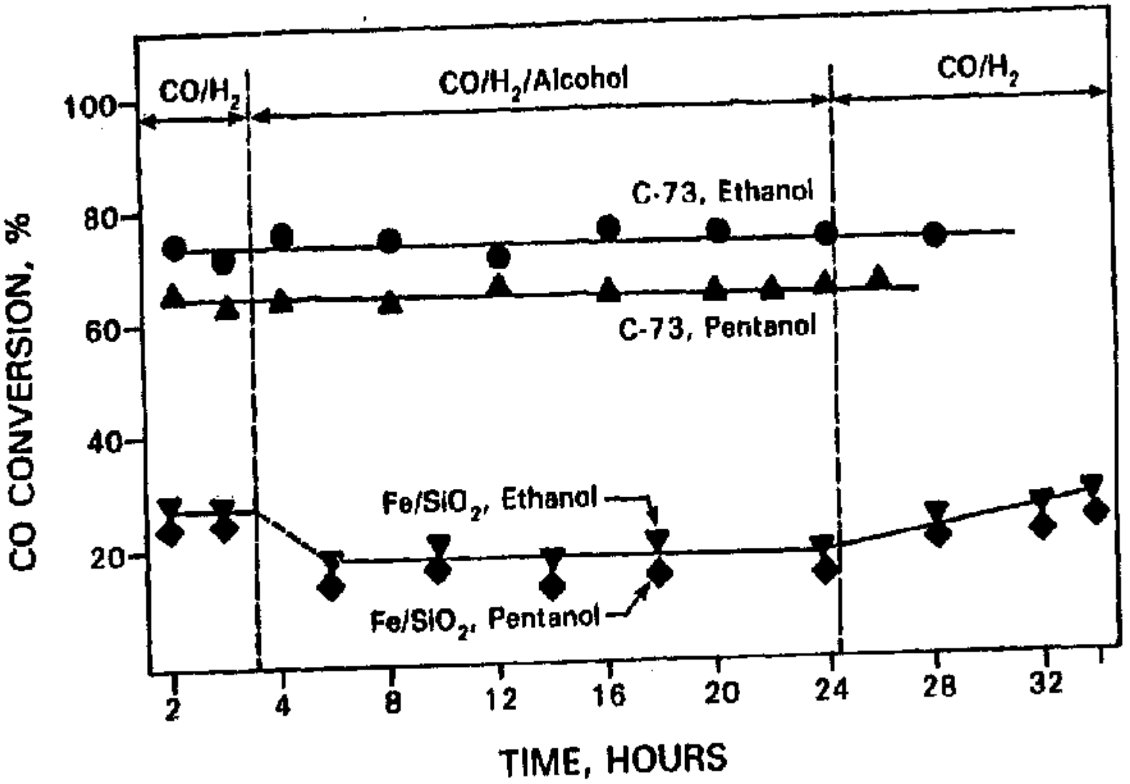


Figure III-38. The influence of added alcohol, ethanol or 1-pentanol, upon the CO conversion using an U.C.I. C-73 or *ca*. 10% Fe/SiO_2 catalyst at 7 atm pressure in a CSTR.

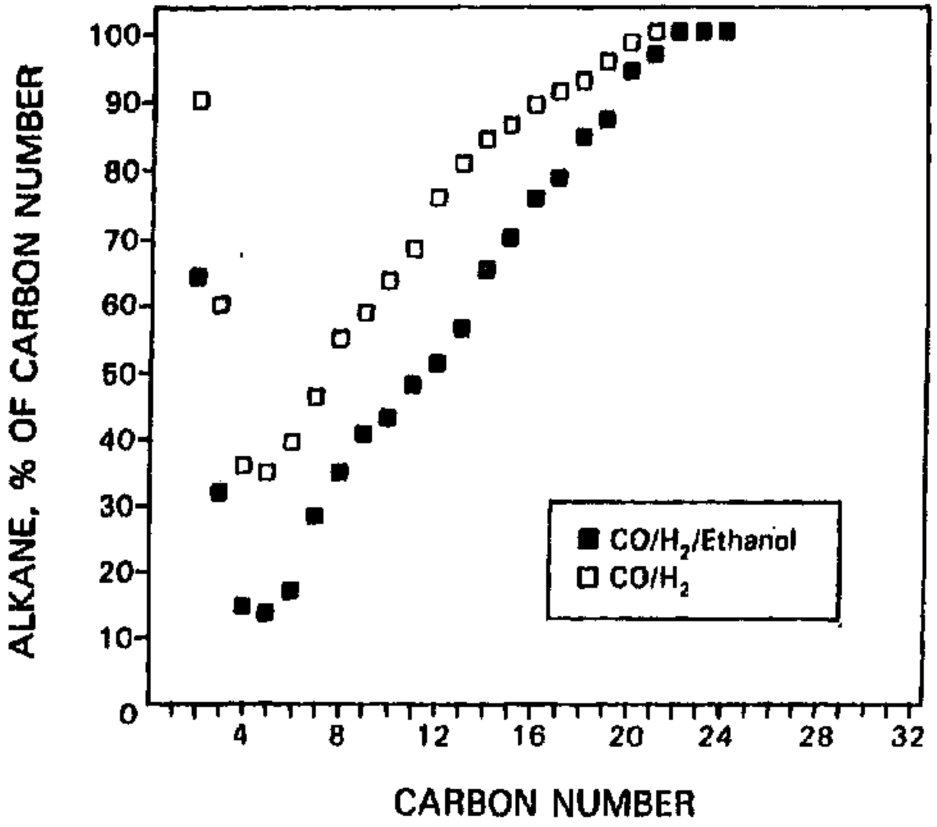


Figure III-39. The alkane percentage (*n*-alkane/*n*-alkane plus 1- and 2-alkenes) by carbon number for synthesis gas conversion with or without added ethanol for *ca*. 10% Fe/SiO_2 at 1 atm in a flow reactor.

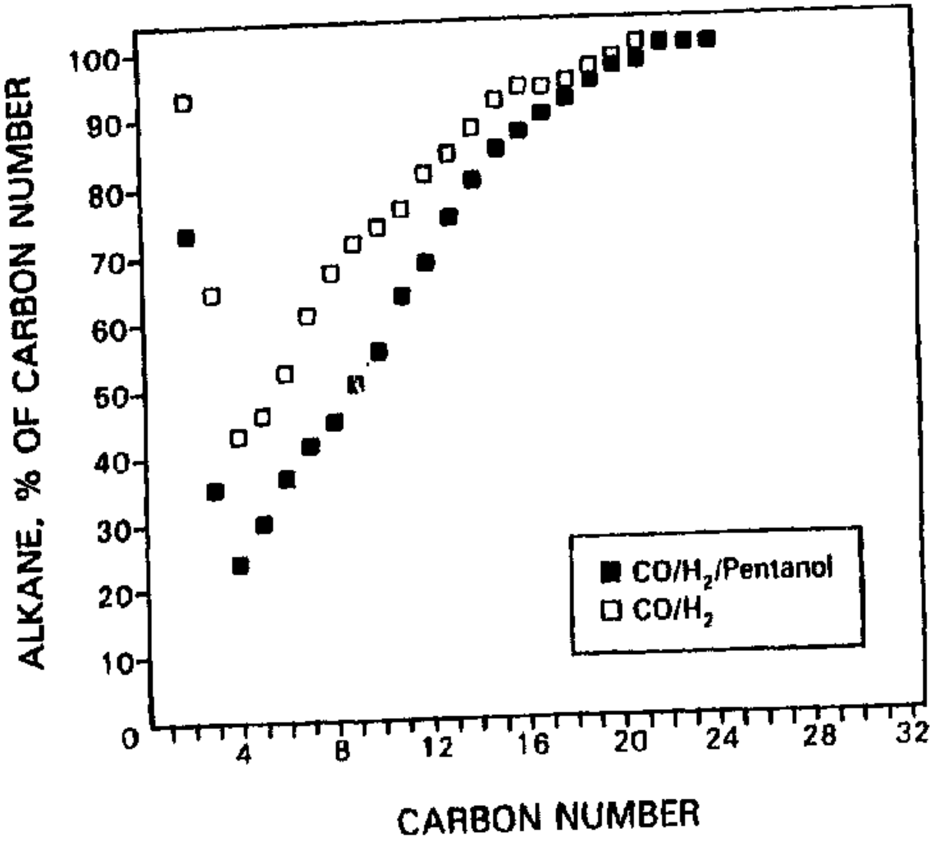


Figure III-40. The alkane percentage (n-alkane/n-alkane plus 1- and 2-alkenes) by carbon number for synthesis gas conversion with or without added ethanol for ca. 6% ThO_2/Fe_2O_3 at 1 atm in a flow reactor.

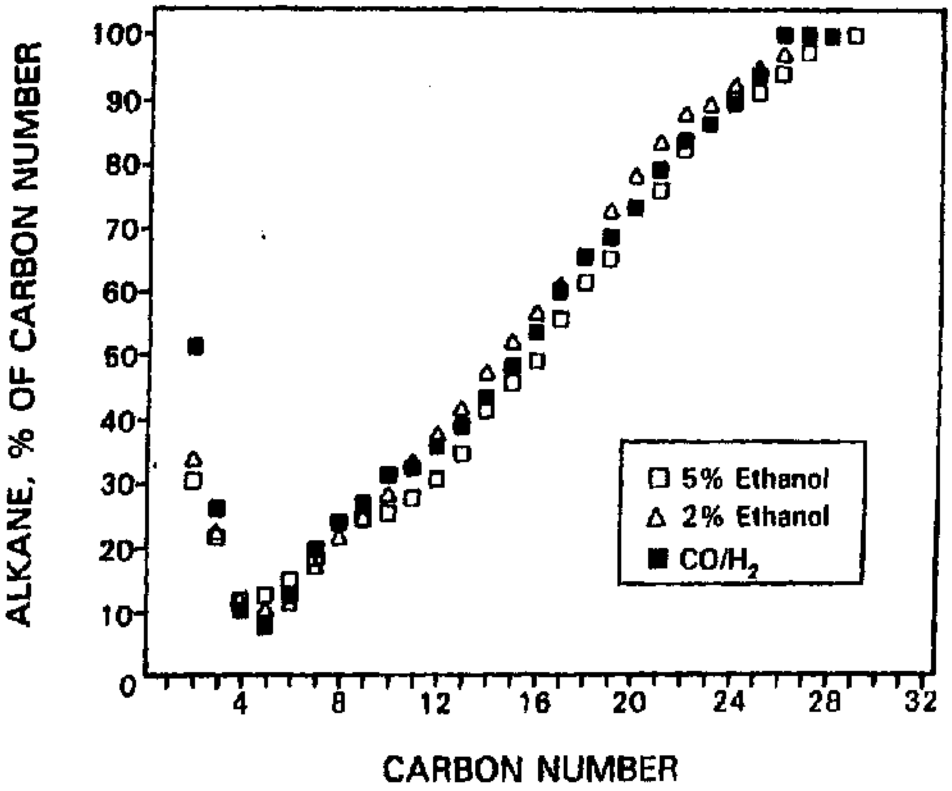


Figure III-41. The alkane percentage (n-alkane/n-alkane plus 1- and 2-alkenes) by carbon number for synthesis gas conversion with U.C.I. C-73 catalyst at 1 atm pressure for CO/H_2 alone and with either 2 or 5% added ethanol.

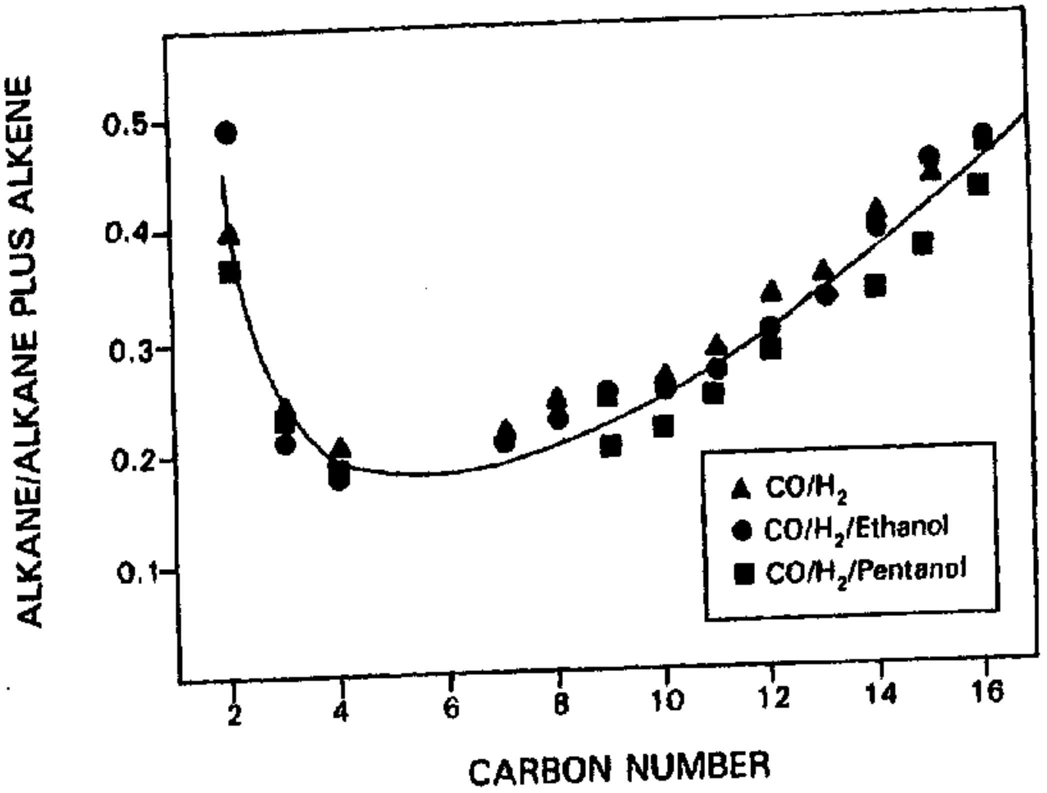


Figure III-42. The alkane percentage (n-alkane/n-alkane plus 1- and 2-alkenes) by carbon number for synthesis gas conversion with U.C.I. C-73 catalyst at 7 atm pressure in a CSTR with syngas alone or with ca. 2% added ethanol or 1-pentanol.

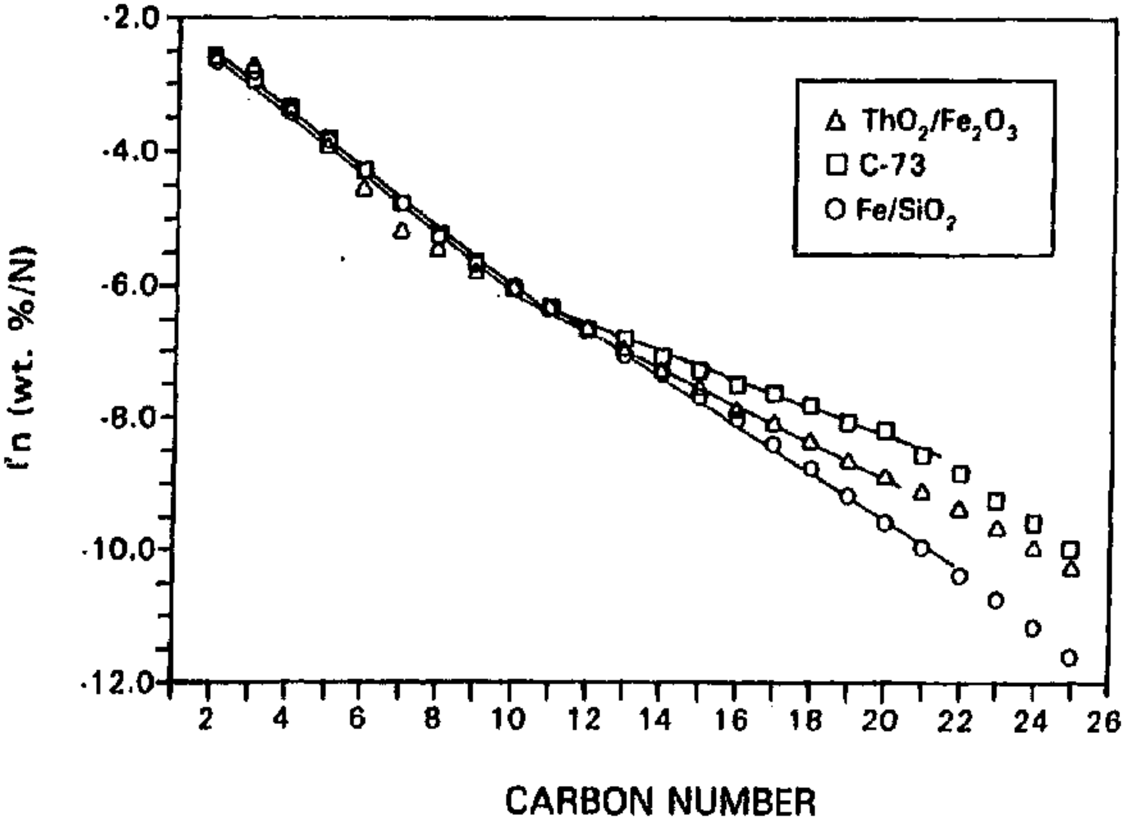


Figure III-43. Anderson-Schulz-Flory plots for the products from the conversion of a CO/H_2 = 0.8 synthesis gas at 7 atm pressure in a CSTR using a ca. 6% ThO_2/Fe_2O_3, ca. 10% Fe/SiO_2 or U.C.I. C-73 catalyst.

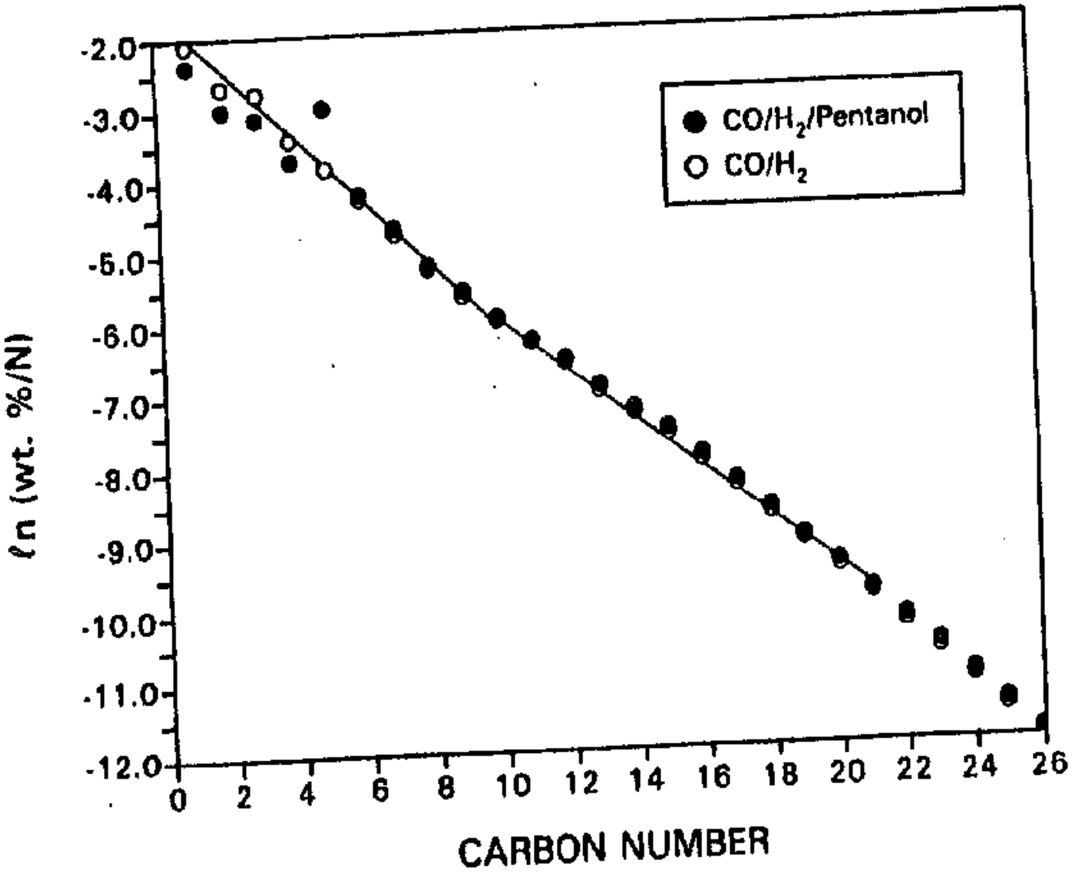


Figure III-44. Anderson-Schulz-Flory plots for the products from the conversion of a CO/H$_2$ = 0.8 synthesis gas at 7 atm pressure in a CSTR with or without ca. 2% added 1-pentanol using a ca. 10% Fe/SiO$_2$ catalyst.

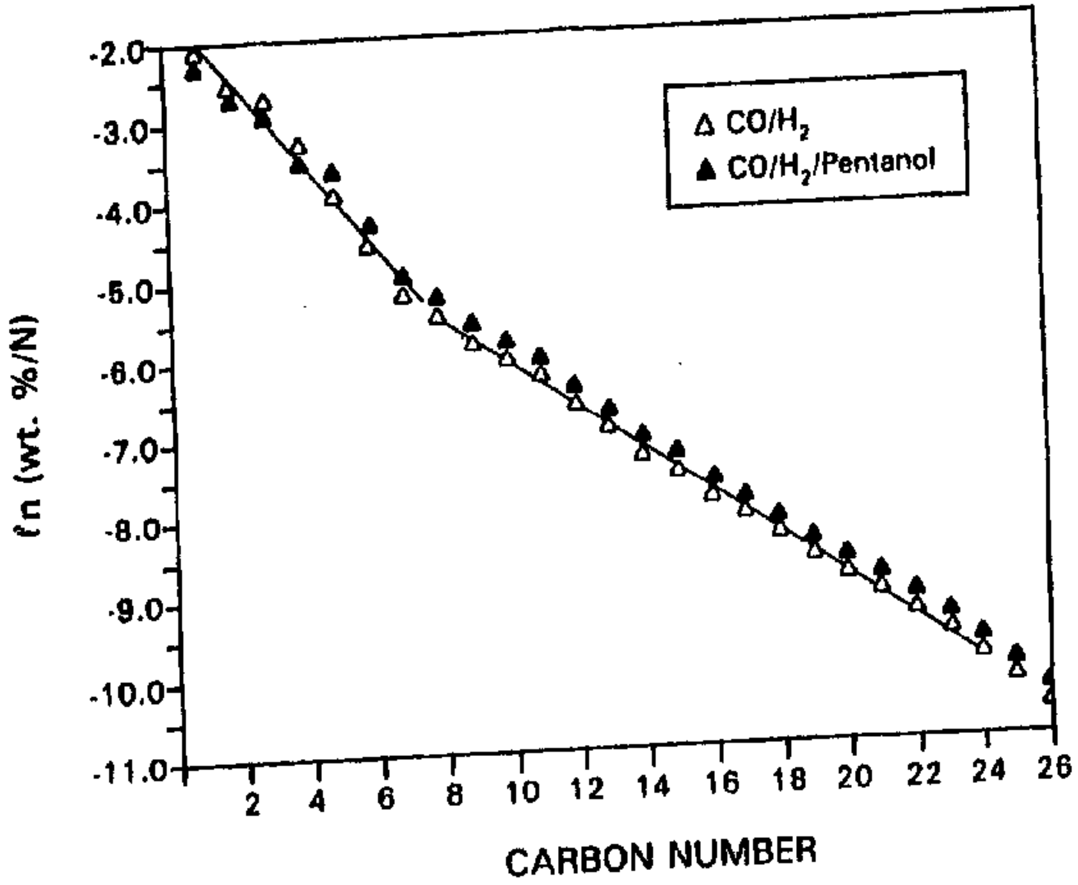


Figure III-45. Anderson-Schulz-Flory plots for the products from the conversion of a CO/H_2 = 0.8 synthesis gas at 7 atm pressure in a CSTR with or without ca. 2% added 1-pentanol using a ca. 6% ThO_2/Fe_2O_3 catalyst.

with the C-73, $Fe-SiO_2$ and $Fe-ThO_2$ catalysts. In all cases the smaller alpha value is for the lower carbon number products and is 0.61 ± 0.02 for all three catalysts. The higher alpha value is in the range of 0.8 but it may require many days of operation to determine this value, at least in part because of the low rates of production and hence equilibration of these heavier products in the reactor and product collection systems. The data for the second alpha value shown in figure III-43 does not represent the same length of time on stream and, at this time, is not considered to reflect a major difference in selectivity. The three catalysts, one with and two without alkali, all provide a two alpha ASF plot and all show a break in selectivity at essentially the same carbon number.

The ASF plots in figures III-44 and III-45 show that the addition of n-pentanol to the syngas feed does not alter the two alpha value plot, changing neither the alpha values nor the carbon number where the break occurs.

The data collected here can conveniently be discussed as falling into two categories or cases. The division is based on the effects of alcohols added to the syntheses gas feed. Case I represents the alkali-free catalysts and Case II, the alkali-containing catalysts.

The quantities of alcohol added were always less than five mole % of the total synthesis gas feed, so the changes in the partial pressures of H_2 and CO were small. These changes in partial pressures were not enough to account for the resulting changes in synthesis gas conversion or alkane content of the hydrocarbon products, according to published kinetics for iron-based catalysts (III-50). Added alcohol did, however, decrease the ratio of synthesis gas conversion and the alkane content of the hydrocarbon product from the alkali-free catalysts. It must be concluded that some chemisorption of either the alcohol or the aldehyde derived from it, occurred over these catalysts. No such changes in synthesis rate or alkane content were observed when using alkali-containing catalysts. The differences between the alkali-free and alkali-promoted catalysts were substantial in the absence of alcohol in the feed gas; and alcohol additions actually brought the results obtained in the two cases closer together. Alkali or alcohol appeared to decrease the rate of synthesis and decrease the alkane production.

The similarity in the effects of alkali and of alcohols could imply that the alcohols, on being chemisorbed, form some, presumably oxygen-containing, surface species which acts as a catalyst promoter in the same sense that alkali does. I.R. spectra permitted Blyholder and Neff (III-51) to demonstrate that alcohol absorbs on an iron surface to produce an alkoxide that is stable at lower temperatures but which decomposes when heated at 450°K. Alkoxides have also been observed on Cu, Ag and W single crystal surfaces (III-52, III-53). Thus, it is reasonable to expect the added alcohol to form, to some extent, an alkoxide according to one of the following reactions:

$$R\,OH \rightleftharpoons RO^- + H^+ \qquad [III-27]$$

or

$$R\,OH \rightleftharpoons RO + H \qquad [III-28]$$

Reaction [III-28] produces a H atom, presumably the same species that forms when molecular hydrogen is dissociatively adsorbed. The other product of reaction [III-28] is the alkoxide radical which has the potential to influence a metal much as has been observed for adsorbed S, Cl or P (III-54). In these cases, the adsorption of an atom decreases the surface coverage to a much greater extent than would be the case for physical blockage of an adsorption site. Thus, Goodman points out that the interaction of S, Cl or P with the metal is primarily electronic in nature. In these studies one promoter (or poison) atom may impact 20 to 30 adsorption sites. If the alkoxide species should behave similar to the elements used by Goodman, then it is reasonable to expect both CO and H_2 surface coverage to be lower by this electronic effect when alcohol was added than when the CO/H_2 syngas was the feed. This reduced surface coverage would be expected to reduce both the primary synthesis reaction, and thereby the CO conversion, as well as the secondary hydrogenation so that the product will be higher in alkenes.

Thus, in this interpretation of the results, the alcohol and alkali cause similar changes in K_{CO} and K_H, the adsorption constants for CO and H_2 respectively, from that of the unpromoted catalyst. The difference in the two catalysts is that the alcohol adsorbs on the unpromoted catalyst in two forms, one as a promoter and the other in a form that participates in hydrocarbon formation. When alkali is present as in the C-73 catalyst the amount of alcohol adsorbed in the promoter form is insignificant.

The lack of effect of added alcohol on the alkali-containing catalyst could be due to coverage of the iron surface with O-containing species from the alkali so that less area is available to be modified by the alcohol-derived surface species. Alternatively, since alkali promotion increases CO chemisorption (III-55 through III-58), the higher CO coverage of the surface in the alkali-promoted catalysts could reduce the formation of alcohol-derived O-containing species or speed their elimination.

Another explanation of the results, this one simply in terms of surface concentrations of reactive species, can be offered. It is based on simple Langmuir adsorption arguments. Certainly nothing more elaborate is justified. If CO, H_2 and alcohol are adsorbed competitively on a single set of sites, and the adsorption of H_2 is small relatively to that of CO and alcohol,

$$\theta_{CO} = K_{CO}P_A/(1 + K_{CO}P_{CO} + K_AP_A) \qquad [III-29]$$

$$\theta_A = K_AP_A/(1 + K_{CO}P_{CO} + K_AP_A) \qquad [III-30]$$

$$\theta_H = K_H\,P_H\,/(1 + K_{CO}P_{CO} + K_AP_A) \qquad [III-31]$$

To show that these relations can account for the observed effects of alcohol and alkali additives, illustrative values have been assigned to $K_{CO}P_{CO}$ and K_AP_A. It is assumed that there are no interactions other than an increase in $K_{CO}P_{CO}$ when alkali is present, i.e. there is no effect of adsorbed alcohol on $K_{CO}P_{CO}$, or of added alkali on K_AP_A. In Case I (alkali-free), values of $K_{CO}P_{CO}$ and of K_AP_A were chosen such that θ_A was 0.3 when alcohol was present in the feed. In that case the surface available and, in the simplest case, the rate of synthesis should be reduced by 30% from their values when no alcohol was present. In Case II (alkali-containing), the value of K_AP_A was assumed to remain constant and the value of $K_{CO}P_{CO}$ increased so that θ_A (with alcohol present) fell to 0.03. In that case the loss of rate due to added alcohol should be so small as to be virtually undetectable. The results are collected in Table I.

There is no quantitative basis for the values of $K_{CO}P_{CO}$ and K_AP_A given in Table III-4. They are simply chosen to produce the observed effects on $\theta_{H,A}/\theta_H$ and θ_A. Lack of surface saturation by CO has been proposed (III-59). Certainly that would seem reasonable from the kinetics reported in a variety of studies. The kinetics, in the form

$$\text{Rate} = k\ (P_H)^x\ (P_{CO})^y \tag{III-32}$$

generally exhibit values of x ranging from 1/2 to 1, indicating lack of surface saturation with H_2. Values of y range from 1/2 to -1, with the lower values corresponding to alkali-promoted catalysts. This suggests a higher degree of saturation of the surface with CO for alkali-containing catalysts.

The change in $K_{CO}P_{CO}$ required to go from Case I to Case II in Table I was a factor of 66. If this change were due solely to an increase in the heat of CO chemisorption on the alkali-promoted catalyst, the heat of adsorption would have to be increased by about 4500 cal/gm mole, or roughly 10%. Such an increase seems entirely plausible.

Note that according to this explanation an increase in P_{CO} by a factor of (0.25 to 0.54)/0.25 = 3.2 should have the same effect as the alcohols fed in these experiments. It would take an increase of 65-fold to reproduce the effects of alkali promotion with iron catalyst.

The other dependent variable investigated in the present work was the distribution of hydrocarbons produced, specifically the change in moles of hydrocarbon product with carbon number. In the early stages of research on this reaction it was thought that all Fischer-Tropsch product distributions could be represented by linear semilog relationships between these two variables. The origin of this relationship, probably first proposed by Herrington (III-60), was thought to be a random polymerization, actual or effective, of monomer units on the catalyst surface, together with a random termination process. More recently, the relationship has been designated the Anderson-Schulz-Flory (ASF) relationship. The first ASF plots exhibiting not one but two distinct slopes were recorded in German and U.S. pilot plants in the 1940-1950 era (III-50). Views on the existence of the two slopes (alpha values) and on the reason for the phenomenon vary widely to this day. As an example, Schlieb and Gaube (III-44) obtained a distribution of C_3-C_{40} products with an unpromoted catalyst that showed an excellent agreement with the Schulz-Flory.

In summary, it is apparent that the addition of an alcohol to a syngas feed to an unalkalized iron catalyst has an influence upon both catalytic activity and product selectivity. Furthermore, adding alkali to an iron catalyst alters activity and selectivity in the same direction as adding an alcohol to the syngas feed. It is not possible to decide whether these changes are caused by alcohol acting to physically block adsorption sites or

Table III-4

Hypothetical Surface Coverages based upon Langmuir Isotherm Calculations

	Case I ("alkali-free")	Case II ("alkali-containing")
$K_{CO}P_{CO}$	0.25[1]	16.5[2]
K_HP_H	small[1]	small[1]
K_AP_A	0.54[1]	0.54[1]
$\theta_A{}^*$	0.3[1]	0.03[1]
θ_{CO}	0.2	0.943
$\theta_{CO,A}$	0.14	0.915
$\theta_{H,A}/\theta_H$	0.7	0.97

[1] Assumed

[2] Calculated

whether the changes are effected through an electronic effect whereby one adsorbed alcohol effects the catalytic character of more than one site.

III-H. Results from Adding Labeled Alkenes to the Syngas

One of the surprising results of this study was obtained from data obtained when ^{14}C labeled pentene was added to the syngas feed to a C-73 promoted iron catalyst using a CSTR at 7 atm pressure. The surprising observation was that neither 1-pentene nor 2-pentene (a mixture of cis- plus trans-isomers) underwent significant conversion under these conditions.

First consider cis-trans-alkene isomerization; this is considered to be the most facile isomerization. As shown in figure III-46, only cis- and trans-2-pentene contain a measurable amount of radioactivity, and it was found that the cis-/trans- ratio in the radiochromatogram was the same for the product as for the reactant. This was true even though the chemical composition of the product was very different from the cis-trans- ratio of the ^{14}C labeled-2-pentene added with the syngas. Thus, cis-trans isomerization of the feed did not occur.

Positional isomerization, e.g. 1-pentene ⇌ 2-pentene, is believed to occur during the Fischer-Tropsch synthesis. However, under these reaction conditions, the interconversion of 1- and 2-pentene did not occur to a measurable extent; certainly, less than 1% of one of the isomers was converted to the other.

Many believe that alkenes are the initial products and that alkanes result from secondary hydrogenation reactions. However, as can be seen from the radiochromatohgraph in figure III-46, ^{14}C labeled pentane was not observed even though pentane comprised approximately 10% of the C_5 n-alkane-n-alkene fraction. If 10% of the alkanes present had been formed from gas phase pentenes they would have been detected easily. In fact, it is estimated that less than 2% of the alkanes represented in the gas chromatogram were formed by hydrogenation of pentenes that had equilibrated with those present in the CSTR in either the liquid or gas phase. In other words, the C_5 alkanes were formed from the surface complex(es) that represent the Fischer-Tropsch synthesis pathway(s) from CO and H_2.

The extent of 2-pentene incorporation was small. The data in figure III-47 show that the activity per mole in the C_6 – C_9 products from the synthesis when labeled 2-pentene was added to the syngas feed to a C-73 catalyst at 7 atm in a CSTR decrease with increasing carbon number. This is contrary to the result anticipated for chain initiation, where the activity/mole is the same for all carbon numbers, or for incorporation into the growing chain as a chain propogator where the activity/mole would increase linearly with carbon number. This will be discussed following consideration of the data from other alkenes and alcohols. If the straight line in figure III-47 is extrapolated to the log cpm/μmole for the C_5 activity, a value of 2.3 is obtained. Using this number, and the activity of the 2-pentene added, 3.76, one can calculate that 3.5% of the 2-pentene is incorporated to form the C_6^+ products. Similar incorporation results were obtained for the addition of 1-pentene.

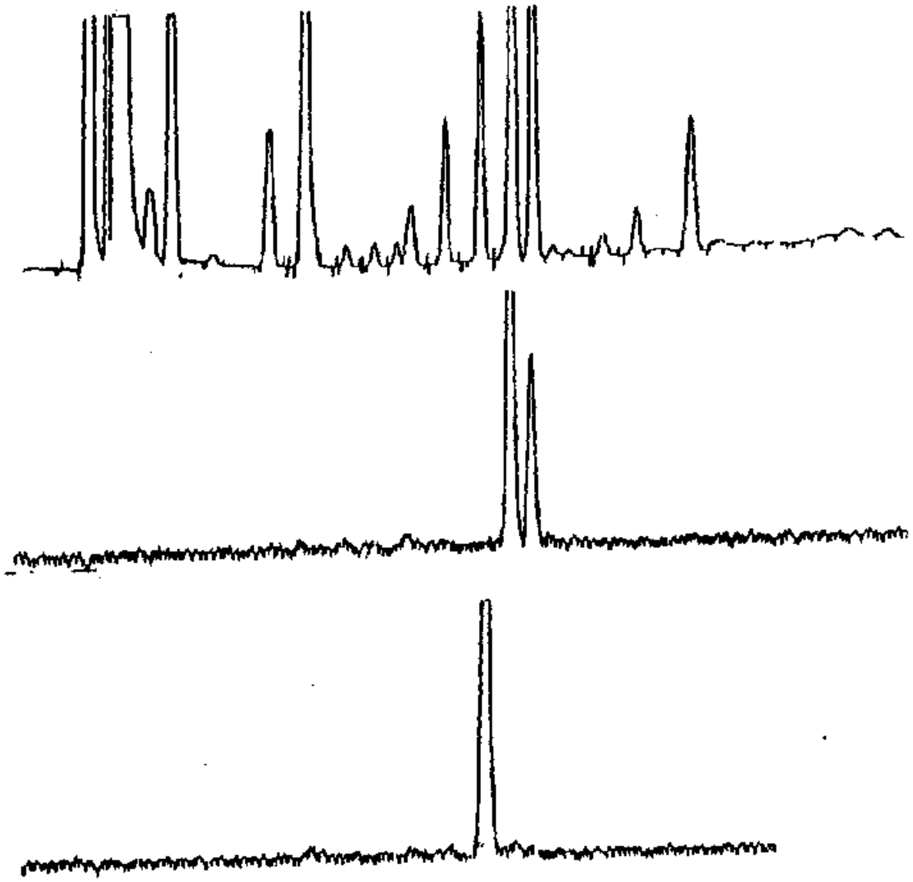
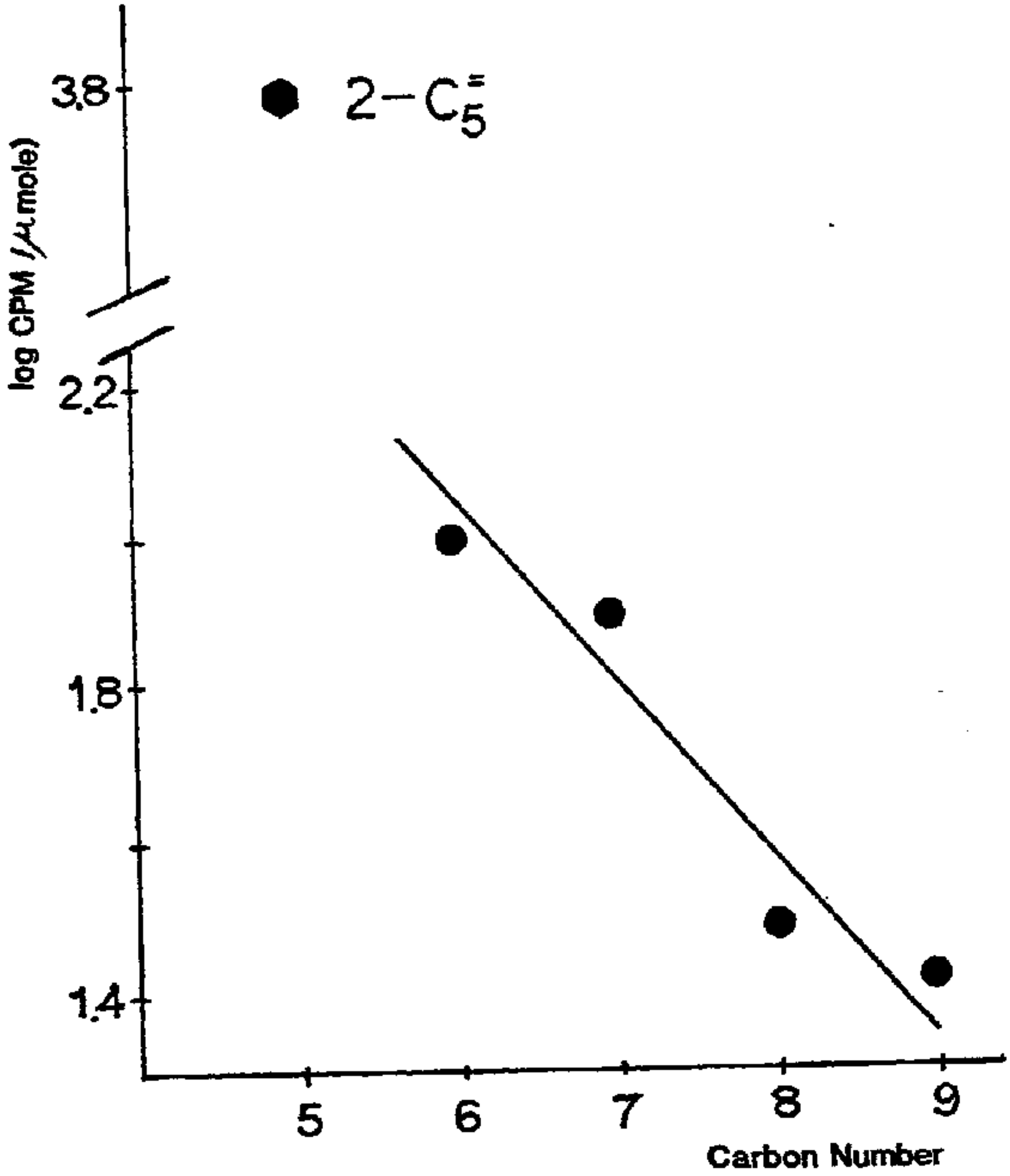


Figure III-46. Gas chromatograph (top) of the synthesis products from the conversion of syngas containing ^{14}C labeled 2-pentene with a C-73 catalyst using a CSTR at 262°C and 7 atm. The middle curve shows the corresponding output from the proportional counter showing detectable activity only in the cis- and trans-2-pentene and the bottom curve is the proportional counter output when ^{14}C labeled 1-pentene, rather than 2-pentene, was added to the syngas feed.

Figure III-47. Molar activity of the alkane products formed when cis- + trans-2-pentene was added to the synthesis gas (CSTR, 262°C, 7 atm.).



The molar activity (log cpm/μmole) of the ^{14}C labeled decene added to the syngas feed to C-73 was 5.2. Extrapolating the data in figure III-48 to C_{10} gives an activity of 4.22; hence, the incorporation of this alkene into C_{11}^+ compounds is calculated to be 10%. This is a higher value than was obtained for the addition of labeled 2-pentene where the incorporation was only 3%. It appears, as discussed below, that this larger incorporation is due to a longer hold-up of 1-decene in the CSTR than was observed for the pentenes. The addition of 1-decene or 1-decanol did not appreciably alter the chemical composition of the FTS products (figure III-49). The distribution of products (n-alkane, 1-alkene, 2-alkene and others (branched alkane and alkenes) for C_9, C_{11} and C_{12}) shown in figure II-49 were the same whether alkene or alcohol was added or not added. These two additives only impacted the C_{10} product distribution so that the amount of 1-alkene was, as expected, higher when 1-decene was added and the amount of n-decane was higher when 1-decanol was added. This latter observation is due to the hydrogenolysis of 1-decanol to n-decane.

If, as seems reasonable from the data in figure III-49, it is assumed that the C_{10} products produced directly from CO during the normal FTS is the same as when 1-decene is not added, one can calculate the distribution of 1-decene conversion products within the C_{10} fraction; these results are summarized in Table III-5. Thus, 1-decene underwent more extensive conversion to higher carbon number products as well as hydrogenation and isomerization to other C_{10} products. These results show that the extent of these secondary reactions increase with increasing molecular weight and, hence, residence time in the CSTR.

Table III-5

Distribution of Products in the C_{10} Fraction that are Formed from the ^{14}C Labeled 1-decene

Product	Amount Formed, % of the Four C_{10} Compounds
n-decane	14
trans-2-decene	10
cis-2-decene	8.8
1-decene in C_{10} fraction	66

Ethylene can be easily dehydrated by any number of oxide catalysts. There are numerous reports of very selective catalysts, especially in the patent literature (e.g. reference III-61). However, we tried a number of catalysts - HHZSM-5, alumina, phosphoric acid on silica, etc. - and were never able to attain the greater than 99% ethene selectivity. We always obtained ^{14}C labeled compounds in 2-10% yields that were not present in the original labeled ethanol. In addition, the ^{14}C labeled ethanol always contained a nonhydrocarbon ^{14}C labeled impurity that eluted with the C_3 fractions.

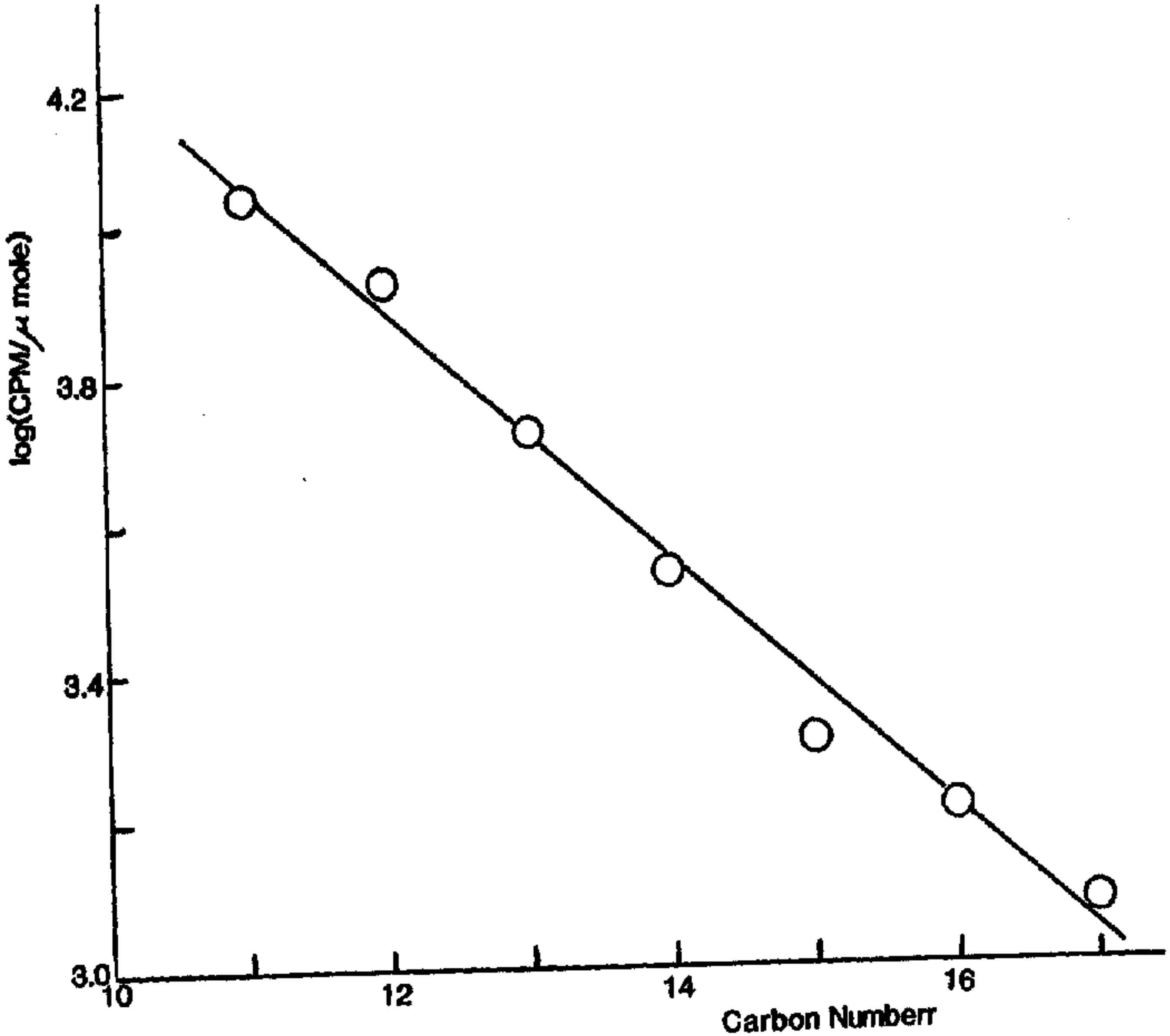


Figure III-48. Molar activity of the alkane products formed when 1-decene was added to the synthesis gas (CSTR, 262°C, 7 atm.).

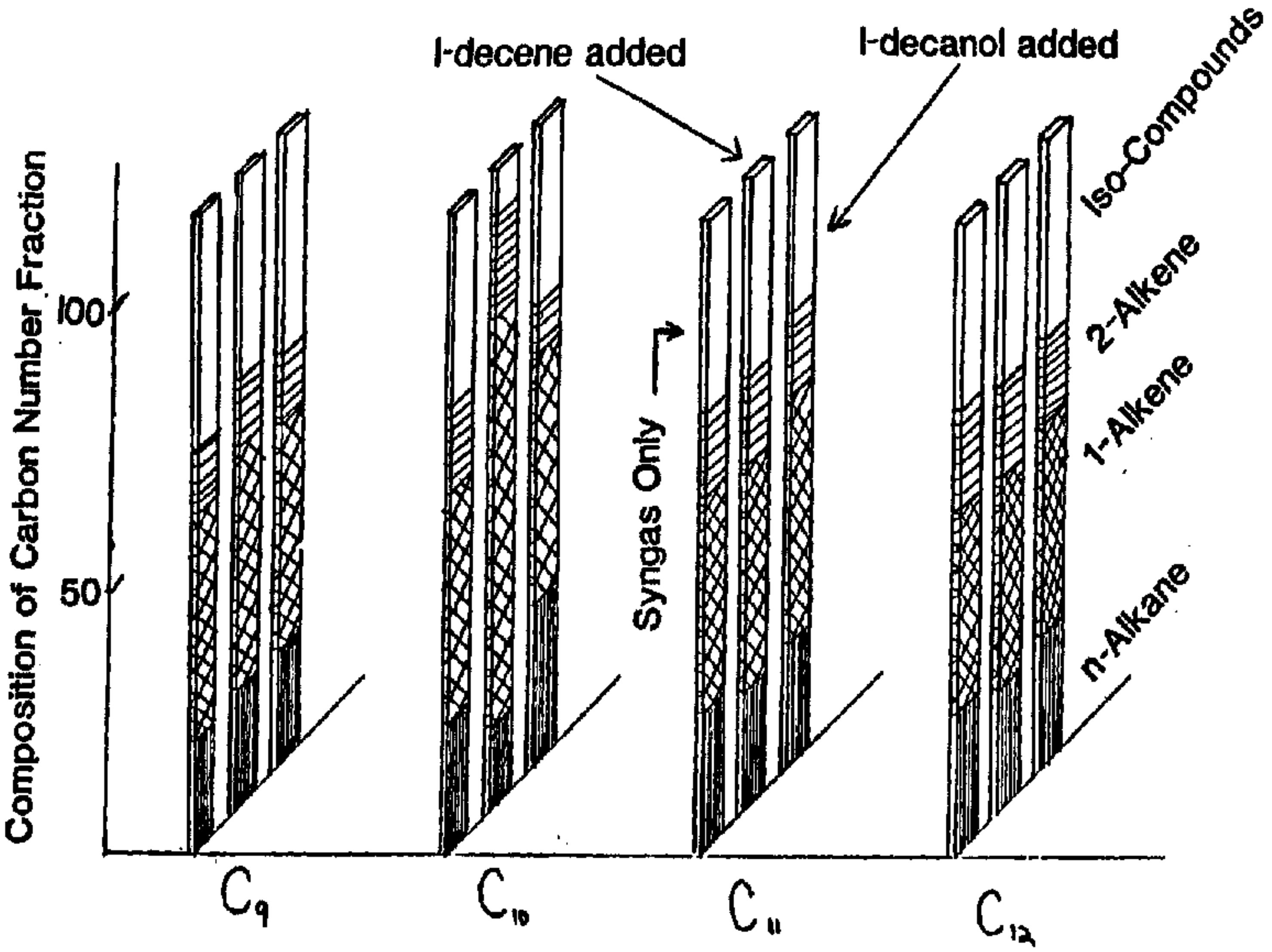


Figure III-49. Chemical composition of compound classes (n-alkane, 1-alkene, 2-alkene and iso-compounds) when the Fischer-Tropsch synthesis feed was syngas only, syngas plus 1-decene or syngas plus 1-decanol (CSTR, 262°C, 7 atm.).

It was found that HZSM-5, operated at ca. 230°C, produced some 2 to 4% of ethane as well as C_3, C_4 and higher carbon number compounds. Even so, this catalyst provided, in our judgment, the best way to generate ethylene at the slightly greater than 7 atm pressure needed for the medium pressure synthesis. Thus, a syringe pump was used to pump ^{14}C labeled ethanol to a reactor maintained at the desired temperature and pressure (ca. 7.5 atm). A dry ice trap was in-line between the reactor and the control valve used to feed the ethene product to the synthesis gas feed stream. The dry ice trap removed water and nearly all of the diethylether. Adjustment of the ethanol feed pump permitted us to provide a constant flow rate of ethene; however, the conversion ethanol had to be maintained at about 80% or less to prevent the formation of too much of the secondary products. Thus, it was not easy to obtain any desired ethene flow rate, rather a pump rate was set and the ethanol conversion was allowed to determine the exact flow rate.

Ethene underwent significant conversion and showed some unique characteristics. In contrast to pentene, ethene underwent significant hydrogenation to ethane. Thus, ethene behaves as expected for hydrogenation; it is more reactive than the higher carbon number alkenes (ref. III-67). Thus, about 40% of the added ethene was hydrogenated to ethane (Table III-6).

Table III-6

Distribution of the ^{14}C Conversion Products when ^{14}C Labeled Ethene was Added to the Synthesis Gas

Product	Amount Formed, % of ^{14}C Labeled Ethene Added
Ethane	35 to 40%
1-propanol	5 to 10%
C_5 + products	ca. 10%

In addition, it appears the ethene undergoes carbonylation to produce 1-propanol; again, ethene differs from pentene and decene (figure III-50). Considerably more incorporation occurred with ethene than with pentene.

In addition to the extent of ethene incorporation, the ^{14}C distribution is of interest. First, consider the data in figure III-51. The ^{14}C in the alkanes from C_8 to C_{16} fit a pattern that is similar to that obtained when either 1- or 2-pentene or 1-decene was added to the syngas feed. However, the slope (ca. 0.1) is smaller than obtained for either pentene or decene. When the activity is considered for a wider range of alkanes - C_{10} through C_{21} - the picture becomes more complex (figure III-52). Above a carbon number of ca. 16 the activity per mole increases as the carbon number increases. Thus, the products containing ^{14}C activity must be considered to be comprised of products that result from at least two incorporation pathways. The lower carbon number alkanes containing ^{14}C are considered to result from ethene initiating a chain with chain propogation by unlabeled CO.

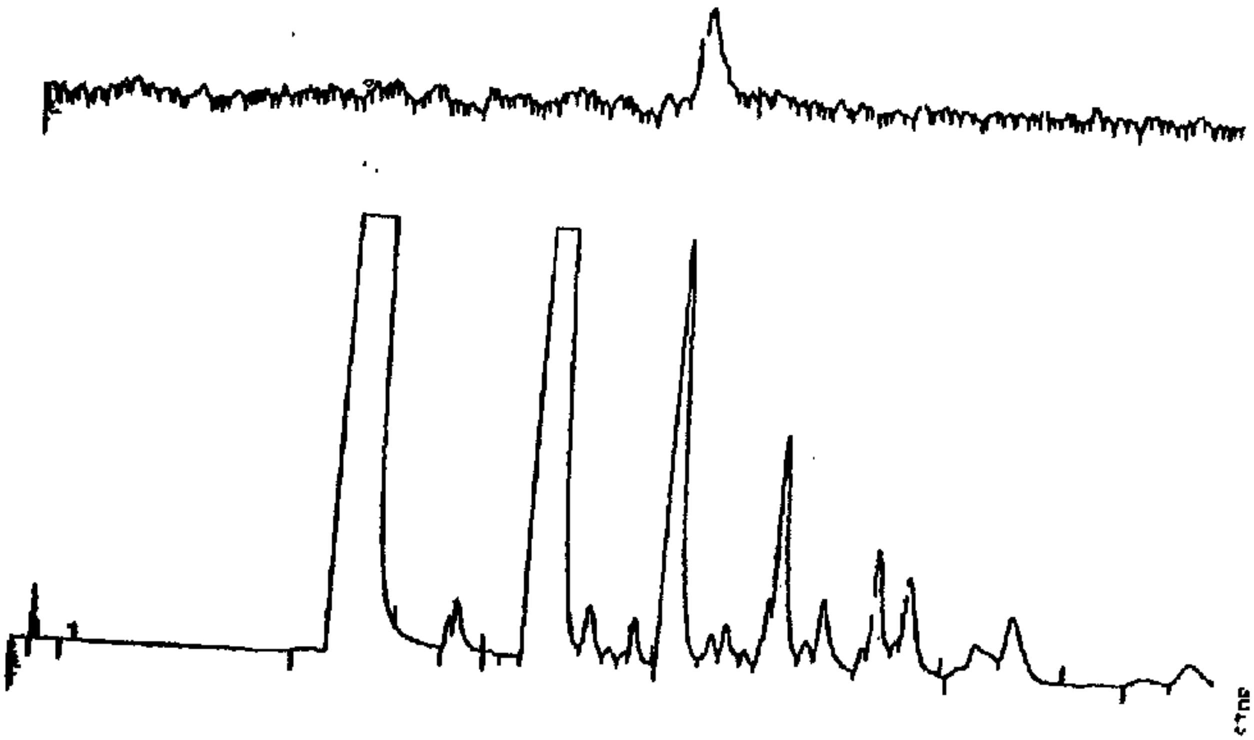


Figure III-50. Gas chromatograph (bottom) and radiogram (top) for the alcohols contained in the water phase when ^{14}C labeled ethene was added to the syngas feed to the C-73 catalyst.

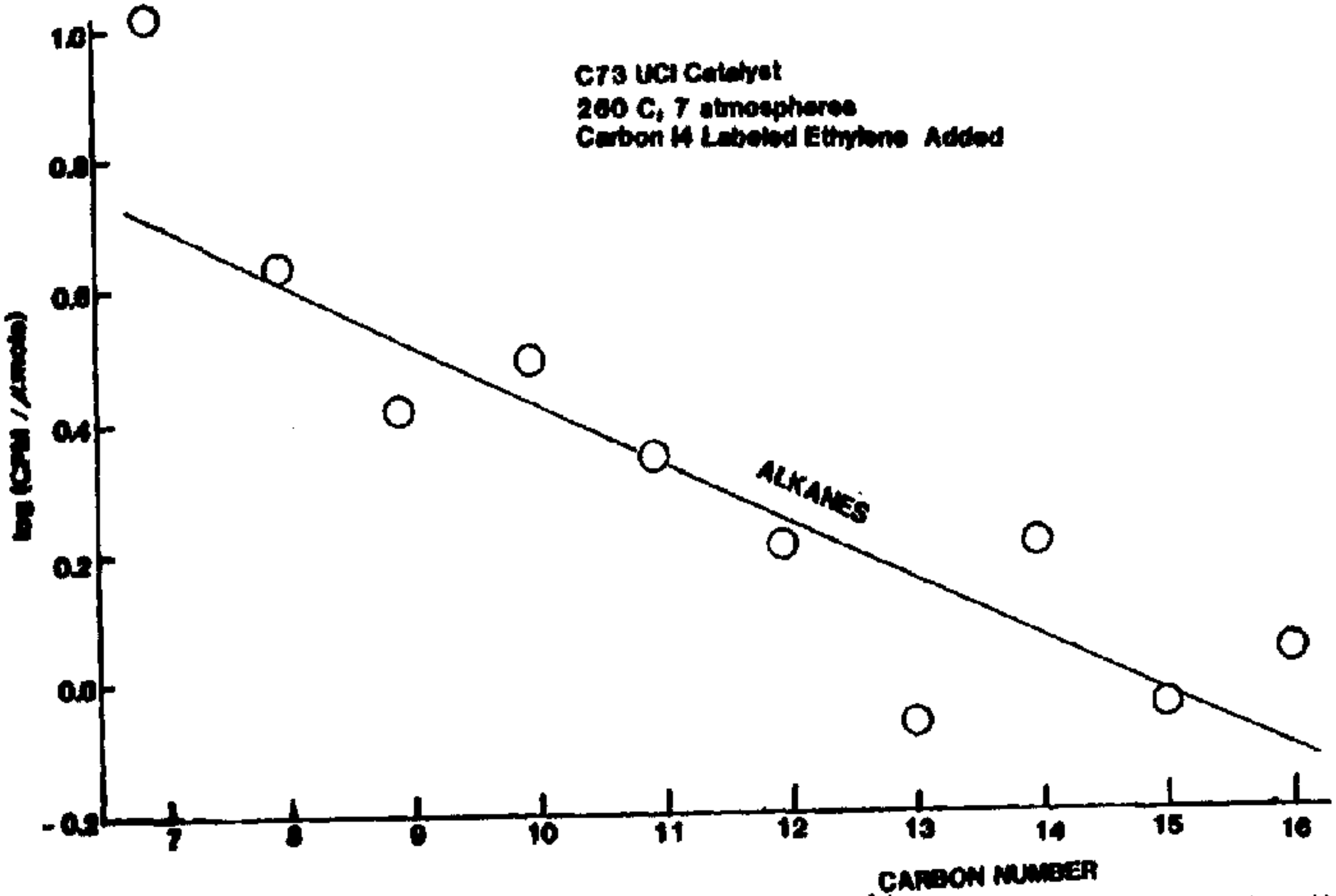


Figure III-51. ^{14}C in alkanes from the Fischer-Tropsch synthesis when ^{14}C labeled ethene was added to the feed to a C-73 catalyst (CSTR, 262°C, 7 atm.).

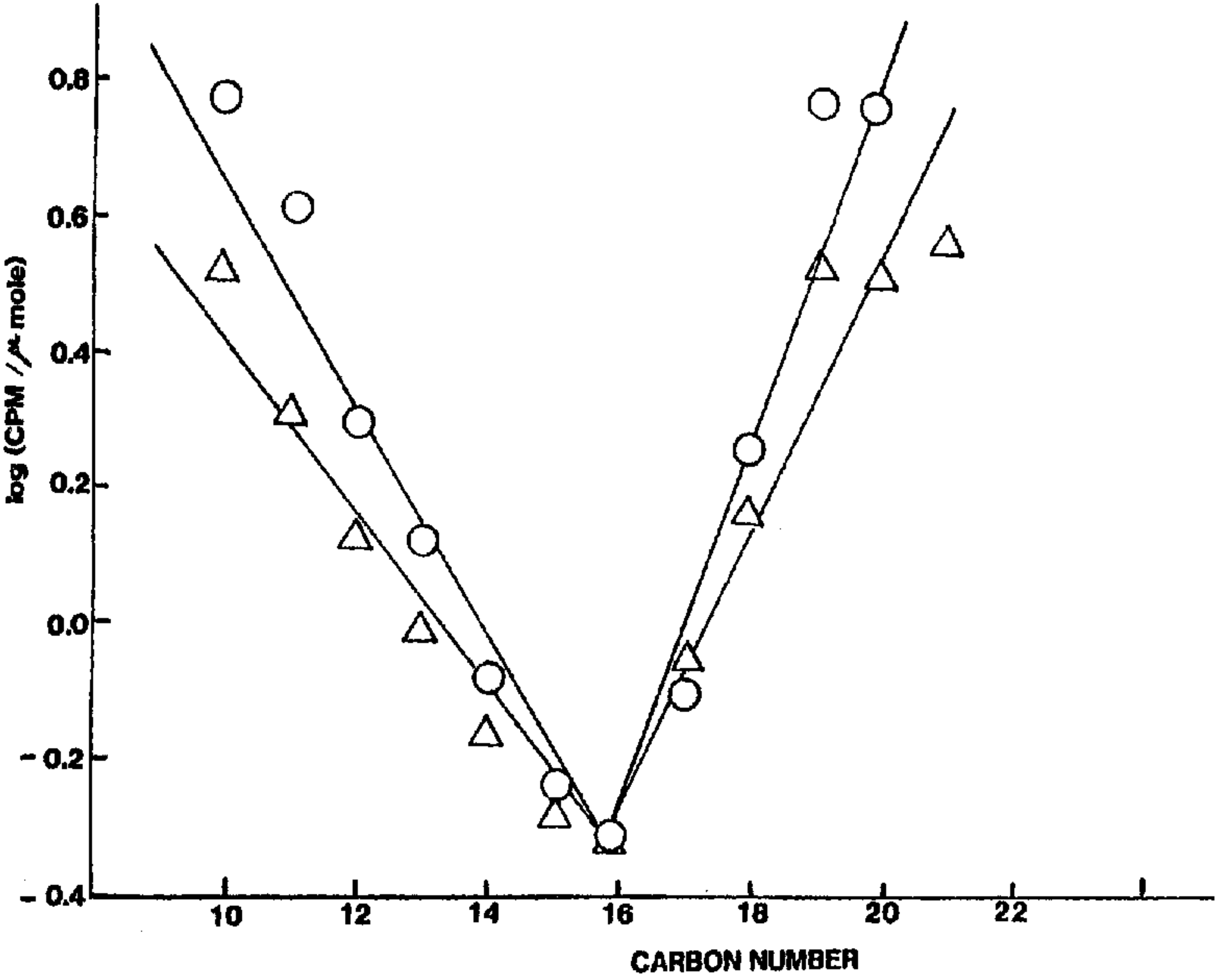


Figure III-52. ^{14}C in alkanes from the Fischer-Tropsch when ^{14}C labeled ethene was added to the feed to a C-73 catalyst (CSTR, 262°C, 7 atm.). (Alkane concentration determined by g.c. (△) or by l.c. (○)).